CHARACTERIZATION OF CURE KINETICS AND PHYSICAL PROPERTIES OF A
HIGH PERFORMANCE, GLASS FIBER-REINFORCED EPOXY PREPREG AND
A NOVEL FLUORINE-MODIFIED, AMINE-CURED COMMERCIAL EPOXY

Bryan Bilyeu, B.S., M.S.

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APPROVED:

Witold K. Brostow, Major Professor and Chair
Kevin P. Menard, Co-Major Professor
Michael R. Kozak, Committee Member
Bruce Gnade, Committee Member and Chair of the
Department of Materials Science and Engineering
Oscar N. Garcia, Dean of the College of Engineering
Sandra L. Terrell, Interim Dean of the Robert B. Toulouse
School of Graduate Studies

Kinetic equation parameters for the curing reaction of a commercial glass fiber reinforced high performance epoxy prepreg composed of the tetrafunctional epoxy tetraglycidyl 4,4-diaminodiphenyl methane (TGDDM), the tetrafunctional amine curing agent 4,4′-diaminodiphenylsulfone (DDS) and an ionic initiator/accelerator, are determined by various thermal analysis techniques and the results compared. The reaction is monitored by heat generated determined by differential scanning calorimetry (DSC) and by high speed DSC when the reaction rate is high. The changes in physical properties indicating increasing conversion are followed by shifts in glass transition temperature determined by DSC, temperature-modulated DSC (TMDSC), step scan DSC and high speed DSC, thermomechanical (TMA) and dynamic mechanical (DMA) analysis and thermally stimulated depolarization (TSD). Changes in viscosity, also indicative of degree of conversion, are monitored by DMA. Thermal stability as a function of degree of cure is monitored by thermogravimetric analysis (TGA). The parameters of the general kinetic equations, including activation energy and rate constant, are explained and used to compare results of various techniques. The utilities of the kinetic descriptions are demonstrated in the construction of a useful time-temperature-transformation (TTT) diagram and a continuous heating transformation (CHT) diagram for rapid determination of processing parameters in the processing of prepregs.
Shrinkage due to both resin consolidation and fiber rearrangement is measured as the linear expansion of the piston on a quartz dilatometry cell using TMA. The shrinkage of prepregs was determined to depend on the curing temperature, pressure applied and the fiber orientation. Chemical modification of an epoxy was done by mixing a fluorinated aromatic amine (aniline) with a standard aliphatic amine as a curing agent for a commercial Diglycidylether of Bisphenol-A (DGEBA) epoxy. The resulting cured network was tested for wear resistance using tribological techniques. Of the six anilines, 3-fluoroaniline and 4-fluoroaniline were determined to have lower wear than the unmodified epoxy, while the others showed much higher wear rates.
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CHAPTER I

EPOXIES: PROPERTIES, CHEMISTRY AND APPLICATIONS

I.1 Introduction

Epoxy resins represent an important class of polymers primarily due to their versatility. High degree of crosslinking and the nature of the interchain bonds give cured epoxies many desirable characteristics. These characteristics include excellent adhesion to many substrates, high strength (tensile, compressive and flexural), chemical resistance, fatigue resistance, corrosion resistance and electrical resistance.\(^1\) In addition, processing is simplified by the low shrinkage and lack of volatile by-products. Properties of the uncured epoxy resins, such as viscosity, which are important in processing,\(^2\) as well as final properties of cured epoxies such as mechanical strength or electrical resistance can be optimized by appropriate selection of the epoxy monomer and the curing agent or catalyst.\(^3,4\) Because of the ease of application\(^5\) and desirable properties, epoxies are widely used for coatings,\(^6,7\) corrosion protectants,\(^8\) electronic encapsulants,\(^9\) fiber optic sheathing,\(^10\) flooring and adhesives. Given so many everyday uses, every hardware store carries a wide selection of epoxy adhesives and coatings.

The properties which result in successful adhesives and coatings also made epoxies the obvious choice for matrices\(^11\) in fiber-reinforced composites.\(^12\) Man-made fiber-reinforced composites predate written history, being seen in the earliest straw-filled mud huts.\(^13\) Even glass fibers, which seem to be a modern technological achievement, date back 3,000 years to the Phoenicians.\(^14\) Commercialization and
exploitation of composites began in the Nineteenth Century\textsuperscript{15} and has steadily grown\textsuperscript{16} in both scale and range. Today glass fiber-reinforced epoxies are commonly the major components in boats,\textsuperscript{17} aircraft,\textsuperscript{18} automobiles,\textsuperscript{19} medical prostheses\textsuperscript{20} and sports equipment. Indeed, many developments were only possible using this material, including the Chevrolet Corvette\textsuperscript{21} and the Bell/Textron V-22\textsuperscript{22} tiltrotor aircraft. Epoxies and fiber-reinforced epoxy composites have influenced sports equipment,\textsuperscript{23} especially for common leisure sports such as tennis,\textsuperscript{24} golf and water sports,\textsuperscript{25} but perhaps more importantly, in high visibility sports, including Olympic cycling.\textsuperscript{26}

The market for epoxy resins has grown as new epoxies are developed and new applications are found. The worldwide consumption of epoxy resins in 1991 was over one half million tons, with the United States taking about one third.\textsuperscript{27} In 1998 the United States consumed 320,000 tons of epoxy resins, representing an overall annual increase of 3\% over the past 10 years.\textsuperscript{28}

I.2 History

Epoxies were first synthesized as early as 1891; however, commercialization did not come about for the next 50 years.\textsuperscript{3} Two independent researchers, developing separate applications, synthesized the first commercial epoxy resins. Pierre Castan of de Trey Frères in Switzerland, while developing dental restoration materials, discovered the reaction of diglycidylether of bisphenol-A (DGEBA) with phthalic anhydride. The patents were assigned to Ciba AG of Basel, Switzerland (now Ciba-Geigy) in 1942.\textsuperscript{29} At the same time, Sylvan Greenlee at DeVoe and Raynolds (later Celanese Chemical Company, and subsequently Hoechst-Celanese) in America,
while developing surface coatings, discovered another DGEBA resin, which differed only in molecular weight. Greenlee’s first of many patents was granted in 1948. These DGEBA resins and subsequent derivatives have, and continue to be, the largest product in the epoxy market, primarily in the surface coatings industry for which it was developed. The characteristics which Greenlee and Castan sought and found in DGEBA, including adhesion, hardness, inertness and thermal resistance, are responsible for its popularity.

Many other monomers and polymers have been subsequently epoxidized to increase the desirable properties of DGEBA and to develop special properties such as high electrical resistance and thermal stability.

I.3 Chemistry

Epoxies are characterized by the presence of one or more epoxide functional groups (shown in Figure 1.1) on or in the polymer chain. The epoxide group is planar, with a three-membered ring composed of one oxygen and two carbon atoms. Due to the high ring strain, similar to that in cyclopropane, the group is very reactive.

![Figure 1.1: The epoxide functional group, where R1 represents the functionalized molecule.](image)

Although DGEBA (Figure 1.2) and its derivative resins are still the most common epoxies, especially in the field of coatings, they had limited applications in the structural composites field due to their limited strength and relatively low thermal degradation.
temperature. The demands of the structural composites field spurred development of high performance epoxies.\textsuperscript{35} These requirements were met by increasing the functionality (number of epoxide groups per molecule), modifying curing agents, and replacing the thermally weak aliphatic linkages in glycidyl groups with rigid bonds.\textsuperscript{36}

![Figure 1.2: Diglycidylether of Bisphenol-A (DGEBA).](image)

The ring-opening polymerization and crosslinking in epoxy resins can be of two general types, catalyzed homopolymerization or bridging reactions which incorporate a coreactive crosslinking agent into the network. Homopolymerization, or reactions between epoxy chains, involve elimination reactions on the oxygen atom of the epoxide group using acid or base catalysts,\textsuperscript{37} often activated by radiation. The incorporation, or bridging reaction, involves nucleophilic attack on one of the epoxide carbons by an amine or an anhydride compound. A selection of common amine curing agents are shown in Figure 1.3. Reviews of curing reactions are available in the literature\textsuperscript{38,39} and terminology\textsuperscript{40} has been standardized by the International Union of Pure and Applied Chemistry (IUPAC). An obvious and important difference in the result of the two different curing methods is that in homopolymerization the network is only composed of the cross-linked epoxy monomers, whereas in the bridging reaction the network is composed of a copolymer of both epoxy monomers and a curing agent, as shown in Figure 1.4. Therefore in a bridging reaction the network properties are a
a. $\text{H}_2\text{N}-\left[\begin{array}{c} \text{C} \\ \text{H}_2 \end{array}\right]_n\text{NH}_2$

b. \[
\text{NH}_2
\]

c. $\text{H}_2\text{N}-\left[\begin{array}{c} \text{C} \\ \text{H}_2 \end{array}\right]_n\left[\begin{array}{c} \text{NH} \\ \text{C} \\ \text{H}_2 \end{array}\right]_n\text{NH}_2$

d. \[
\text{NH}_2\text{S}\\\text{O}\\\text{O}\text{NH}_2
\]

Figure 1.3: Common aliphatic (a,b) and aromatic (c,d) amines, including Polymethylene diamine (a), a polyamine (b), aniline or phenylamine (c) and 4,4'-diaminodiphenylsulfone or DDS (d)

a) $\text{R}_1\text{NH}_2 + \bigcirc \bigcirc \text{R}_2 \rightarrow \text{R}_1\text{N}-\text{CH}_2\text{CH}\text{R}_2$

b) $\text{R}_1\text{N}+\text{CH}_2\text{CH}+\text{OH} + \bigcirc \bigcirc \text{R}_2 \rightarrow \text{R}_1\text{N}-\text{CH}_2\text{CH}\text{CH}_2\text{R}_2$

c) $\text{R}_1\text{N}+\text{CH}_2\text{CH}+\text{OH} + \bigcirc \bigcirc \text{R}_2 \rightarrow \text{R}_1\text{N}-\text{C}\text{H}_2\text{CH}\text{R}_2$

Figure 1.4: Mechanism of primary amine cure of an epoxy resin, with the epoxide group under nucleophilic attack by a) a primary amine, b) a secondary amine and c) a hydroxyl group generated from reactions a and b.
function of two components, which allows modifications to be incorporated in either component. Thus, a rigid epoxy with high strength can be used with an impact resistant hardener to yield a desirable network.\textsuperscript{41}

In addition, in amine-cured epoxy reactions a side reaction between the products and reactants occurs, as shown in Figure 1.4c. Epoxy monomers may be attacked by the hydroxyl group of the product of the primary amine opened epoxy,\textsuperscript{42} if either the secondary amine is less reactive than the hydroxyl group, or by the hydroxyl group of the final product, in the case of epoxy rich systems or low functionality amines.\textsuperscript{43}

I.4 Chemical Modification – Fluorination

Epoxies and curing agents have been chemically modified for a variety of special purposes, with recent attention given to the addition of fluorine functional groups to increase electrical resistance and dielectric constant as well as for improved tribological properties, namely reduction of friction and wear. While significant work has been done in fluorinating epoxy resins or epoxidizing fluoropolymers,\textsuperscript{44,45} the costs are typically prohibitively high. Researchers are working to develop an economically viable epoxy with the friction-reducing fluoro groups bonded into a wear-resistant epoxy network. The novel approach I utilized for this work was to use a commercially available fluorinated amine curing agent.

I.5 Physical Properties

The physical properties of uncured epoxy resins vary widely. As with any polymer, the viscosity of the monomers or prepolymer depend on both the molecular weight and the molecular structure. A simple example is DGEBA, already shown in
Figure 1.2. Higher linear molecular weight monomers, i.e. those with higher values of n, exhibit higher viscosities.\textsuperscript{46} In addition, molecular structure and types of bonds will greatly affect the viscosity of the resin.\textsuperscript{47} Since epoxies are almost always used with catalysts, crosslinking agents, accelerators and various other additives, viscosity effects like plasticization must be considered.\textsuperscript{48} Many highly crosslinked epoxies exhibit low fracture toughness, so a dispersed phase\textsuperscript{49} of an elastic component, typically an elastomer or a tough thermoplastic,\textsuperscript{50-52} can be introduced into the matrix.

I.6 Curing

Epoxy curing involves two phenomena, polymerization and crosslinking. Although each phenomenon is complicated and the two are in competition during the overall curing process, generalizations and simplified models can be made. During the initial stage of curing, polymerization is favored\textsuperscript{53} because in the case of catalyzed homopolymerization, terminal epoxides are the most reactive, and in the case of coreactive agents, primary reactions are more reactive than secondary ones. Also, the terminal epoxide reactivity already mentioned plays a role. In most cases the polymerization is an addition reaction,\textsuperscript{54} and thus follows a rate equation for addition polymerization described below in Chapter 3. The molecular weight of the growing polymer increases until the molecular weight approaches infinity, so that all monomers are connected by at least one bond and a network is formed.\textsuperscript{55} At this point, called the gel point,\textsuperscript{56} the polymer possesses high molecular weight and few crosslinks, and thus behaves much like a very high molecular weight thermoplastic.\textsuperscript{57} From the gel point, crosslinking becomes the dominant phenomenon due to the lack of free monomers.
Crosslinking involves interchain bonding of intrachain reactive sites, either intrachain epoxides or secondary sites on coreactive agents.\textsuperscript{58}

Although crosslinking is a different phenomenon, the rate of chemical conversion of the epoxide groups is unaffected in most epoxy systems.\textsuperscript{59} The crosslinking reactions produce a growing network\textsuperscript{60} and reduce the mobility of the chain segments. The growth of the network results in mechanical and thermal stabilization of the structure, resulting in increasing modulus\textsuperscript{61} and glass transition and degradation temperatures.\textsuperscript{62} At a certain high degree of crosslinking, the increasing molecular weight of the structure exceeds the molecular weight which is thermodynamically stable as a rubber, and the material transforms into a glass, a process called vitrification.\textsuperscript{63} In a glassy state, the mobility of reactants is severely restricted, reducing the rate of the reaction to a diffusion-controlled reaction, which is much slower.\textsuperscript{64} Further conversion is still possible; however, the rate is much slower since the process relies on diffusion rather than mobility to bring the reactants together. When the crosslinking reaction exhausts all the reactive sites available, the resulting structure is hard (high modulus) and insoluble due to a high degree of interchain bonding.

\textbf{I.7 Prepregs}

Since epoxy resins must be mixed with various curing agents, catalysts, modifiers and additives, as well as any reinforcements, many epoxy suppliers provide premixed molding compounds (MCs) and preimpregnated fibers (prepregs). MCs and prepregs have many advantages to manufacturers since all of the careful mixing is done by and ensured by the supplier in large batches.\textsuperscript{65} The manufacturer is thus only concerned
with the actual processing of the compound. MCs are very popular in high volume industries like automotive and consumer products, whereas prepregs are very common in hand and machine layup of high fiber content laminates in aerospace and specialty markets. Prepregs are typically cured via a multiple step autoclave vacuum bag process or compression molding, depending on the part geometry and application.

1.8 Shrinkage

Shrinkage is the change in volume during processing associated with both molecular rearrangement due to curing and thermal contraction due to cooling from the processing temperature to ambient conditions. Epoxies are favored due to their low shrinkage of a few volume percent. However, in some processes, specifically closed molding, this 4 or 5 percent change can affect a product’s properties and integrity. In addition, when processing highly filled resins, the effect of fiber or particulate movement can affect the volume changes. Typically, as with thermoplastics, excess material is injected into the mold under high pressure to compensate for shrinkage. However, determining how much excess material is necessary and how much pressure is required is important for molders. The thermal contraction is relatively easy to determine, since on cooling, the material should be in a solid state, either cured or gelled. Thermal contraction is determined by measuring the volumetric change associated with the temperature change and is expressed as the Bulk Modulus. The changes due to chemical rearrangement during cure must be determined by dilatometry measurements, where the resin and curing agent are placed in a closed mold with a small piston, which measures the change in volume. The procedure has been done
with pistons of oil and of quartz, depending on the viscosity of the material being measured. In the case of a highly filled prepreg, the rearrangement of the reinforcement and the chemical shrinkage can be determined in a similar manner under processing pressures using either mercury or quartz as the piston. The results of these measurements are very important in applications where critical dimensional tolerances are required, as well as situations where internal stresses on encapsulated components and internal stresses in the epoxy itself are a concern.

I.9 Specific Systems

The two materials used in this study were a high temperature epoxy molding compound and a commercial epoxy system. The high temperature molding compound is a premixed compound of epoxy resin and amine curing agent, designated 8552 by its manufacturer Hexcel. The material consists of the tetrafunctional epoxy tetraglycidyl 4,4-diaminodiphenyl methane (TGDDM) and the tetrafunctional amine curing agent 4,4′-diaminodiphenylsulfone (DDS), along with an ionic initiator/accelerator and a thermoplastic modifier, shown in Figure 1.5. This material is common in the aerospace industry and has been the subject of many studies; however a comprehensive study of the material using different techniques is not available.

Several manufacturers produce similar prepregs with glass or carbon fiber reinforcement. Commercial TGDDM/DDS prepregs are prepared with an epoxy-rich stoichiometry. Samples were acquired in the form of both unreinforced premixed resin and 66 weight % glass fiber-reinforced prepreg tapes.
Figure 1.5: Chemical structure of TGDDM epoxy and DDS amine curing agent

The other system consists of a DGEBA epoxy, as shown in Figure 1.2, which is mixed with an aliphatic amine curing agent, as shown in Figure 1.3a. This system is similar to many of the common commercial epoxy-based adhesives in which the epoxy resin is mixed with an amine curing agent by volume. This system was characterized after mixing the two components per the manufacturer’s recommendations, but was also used in a fluorination modification experiment. Specific amounts of a fluorinated amine curing agent were substituted for part of the aliphatic amine. The chemical structures of the fluorinated amines used are provided in Figure 1.6. The fluorination study was intended to find an economically feasible method of reducing the friction on the cured epoxy surface. Most previous attempts have focused on synthetically fluorinating the epoxy chain, which is costly and complicated on industrial scale.
Figure 1.6: Chemical structures of the eight fluorinated amines used with the aliphatic amine to cure the DGEBA epoxy.

I.10 Abbreviations and Acronyms

- **DDS**: 4,4′-diaminodiphenylsulfone
- **DGEBA**: diglycidylether of bisphenol-A
- **IUPAC**: International Union of Pure and Applied Chemistry
- **MC**: molding compound
- **TGDDM**: tetraglycidyl 4,4-diaminodiphenyl methane

I.11 References


29 P. Caston, European Patents CH 211116 (1938), DRP 749512 (1938), GB 518057 (1938).


In the most basic sense, thermal analysis is the study of the state or changes of state of a material in terms of thermal energy. A qualitative understanding of changes of properties of materials with temperature has existed since the first pottery and bricks were fired and the first bread was baked, with evidence depicted graphically in numerous carvings and drawings, including well preserved Egyptian excavations\textsuperscript{1} depicting a balance and fire. In 1789 Josiah Wedgewood of pottery fame studied the effect of heat on the shrinkage of clays.\textsuperscript{2} However, quantitative thermal analysis required measurable quantities. The first and most important of these being thermometry which was introduced in 17th century Florence.\textsuperscript{3} With temperature, properties like heat capacity could shed light onto the intrinsic properties of materials. Differential thermal analysis was introduced in the late 1800’s by Le Chatelier.\textsuperscript{4} Nernst\textsuperscript{5} introduced the thermobalance in 1903, and other techniques, as well as improvements in existing techniques followed quickly.\textsuperscript{6} Extensive reviews of the history of thermal analysis are available in the literature.\textsuperscript{7-9}

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defined thermal analysis as “a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.”\textsuperscript{10} This definition was adopted by the International Union of Pure and Applied Chemistry (IUPAC) and the American Society
for Testing and Materials (ASTM). Although thermal analysis of polymers is a relatively young field, compared for instance to metallurgy and analytical chemistry, the great variety and number of reviews of techniques, instrumentation, properties and terminology demonstrates the importance of the subject. It is clear that thermal analysis of polymers is a field which is multidisciplinary, incorporating chemistry, physics, biology, engineering and other diverse disciplines.

II.2 Heat of Reaction

Due to the high potential energy of the ring-strained epoxide groups in the uncured resin, there is a large Gibbs function difference associated with the ring-opening reaction. Since the Gibbs function change ($\Delta G$) is expressed in the form of both enthalpic ($\Delta H$) and entropic ($\Delta S$) changes, the reaction is called exergenic. Although structural changes will result in a significant entropy change, the enthalpy change is the dominant product. The change in enthalpy results in the evolution of thermal energy or heat, making this an exothermic reaction. Since the opening of the epoxide rings have much higher energy (and enthalpy) differences than the other reactions, the amount of heat evolved and the rate of evolution will correspond to the number of epoxide groups reacting and the rate of the reaction.

Reactions which generate heat are studied by calorimetry. Many types of calorimeters exist, although only a few are appropriate for polymerization reactions. Early studies of epoxy polymerization used differential thermal analysis (DTA), which monitors temperature differences between the sample and a reference, and adiabatic calorimetry, which monitors the temperature of a thermally isolated system.
However, these techniques have low sensitivities and many limitations. The current standard technique for quantitative evaluation is the measurement of the change in enthalpy using Differential Scanning Calorimetry (DSC), since the heat flow during a constant pressure reaction is defined as the change in enthalpy of the system.

Two types of DSCs are available, a heat-flux DSC (based on the Boersma DTA design) and a power-compensation DSC. The heat-flux DSC, shown in Figure 2.1, measures the difference in temperature between a sample and reference heated at a programmed rate in a common oven using thermocouples attached to the bottom of the sample holders. The power-compensation DSC, shown in Figure 2.2, employs separate heating elements and thermocouples for sample and reference, applying separate currents to the heaters to maintain a null difference in the temperature.
Both types of DSC instruments generate plots of heat flow as a function of the programmed temperature. However, due to the difference in measurement techniques, the heat flow ordinate value is calculated differently. Since the heat-flux DSC measures the temperature difference between the sample and reference cells, calculation of the heat flow requires an accurate temperature and sample dependent thermal resistance value of the system as a proportionality factor.\textsuperscript{72,73} The power-compensation DSC also requires a thermal resistance value; however, that value represents the heating elements, not the entire system, and is constant\textsuperscript{74} over a wide operating temperature range.\textsuperscript{75-77} The power-compensation DSC maintains the programmed temperature ramp in both sample and reference, ensuring greater temperature control in the sample.\textsuperscript{78-80} This is important in temperature sensitive reactions, including thermoset curing. The sensitivity and limits of detection,\textsuperscript{81,82} as well as the linearity of the signals\textsuperscript{83,84} of both types of DSC have been evaluated. Schawe and Höhne have thoroughly described the linearity,\textsuperscript{85} signal\textsuperscript{86} and influence of materials properties\textsuperscript{87,88} of power-compensation DSC measurements. The influence of changes of heat capacity of a sample during a measurement has been established\textsuperscript{89} and evaluation techniques\textsuperscript{90} have been proposed to account for it. To determine the extent of a curing reaction or the degree of cure, $\alpha$, the change in enthalpy is compared to the total change in enthalpy of the complete reaction, as represented by Equation 2.1 and illustrated in Figure 2.3. This technique is common in research.\textsuperscript{91-111}

\[
\alpha = \frac{\Delta H}{\Delta H_{\text{total}}} \tag{2.1}
\]
Figure 2.3: An example of a DSC thermogram showing the portion of the total reaction, as measured by the enthalpic exotherm, reacted at time $t$.

Figure 2.4: An example of a DSC thermogram showing the total $\Delta H$ from a slow temperature scan.
Alternatively, the difference between the total and any residual enthalpy changes can be compared to the total, where $\Delta H$ in Formula 2.1 would be replaced by $(\Delta H_{\text{total}} - \Delta H_{\text{resid}})$. Generally the total change in enthalpy is determined using a slow temperature ramp from a low temperature to a temperature just below the onset of thermal degradation, as shown in Figure 2.4. The reaction enthalpic changes are measured during isothermal measurements, as shown in Figure 2.5. Or, if residual enthalpies are used, then an isotherm is followed by a similar ramp as the total enthalpy measurement, as shown in the chronogram in Figure 2.6 and the thermogram in Figure 2.7. Although the value is reported as the degree of cure, it should be understood that the actual degree of cure is not necessarily equal to this value since an assumption has been made that the total enthalpy represents complete or 100% conversion.

Figure 2.5: An example of a DSC thermogram, showing a series of isothermal measurements at 120°C, 140°C and 160°C.
Figure 2.6: Temperature program and measured heat flow for a residual enthalpy measurement using DSC.

Figure 2.7: A series of residual enthalpy measurements for different curing times. The reaction rate, \(\frac{d\alpha}{dt}\), is related to the heat flow, \(\frac{dH}{dt}\), by the
The rate of the curing reaction can be determined from the isothermal data used to determine the degree of cure. Since the enthalpy change is plotted as a function of time, the rate of change in time, $dH/dt$ will represent the rate of the reaction.\textsuperscript{118,119}

Nonisothermal methods,\textsuperscript{120-122} utilizing a single temperature scan run to monitor reaction enthalpic change,\textsuperscript{123-125} as in Figure 2.8, or using a series of scans with different rates,\textsuperscript{126-137} as shown in Figure 2.9 are advantageous due to the shorter time to run the experiments and avoidance of estimation of the lost area at the beginning of the isotherms. However, nonisothermal experiments are generally less accurate than isothermal ones.\textsuperscript{138,139}

Figure 2.8: An example of a DSC thermogram of a $\Delta H$ scan (at 5 K/min) from which the rate of the reaction can be calculated using a single scan model.
Figure 2.9: A Series of DSC thermograms at different scanning rates (5, 10 and 20 K/min), from which a time dependant rate can be calculated.

II.3 Molecular Weight, Segment Mobility and Crosslink Density

Epoxy curing involves an increase in both linear molecular weight and crosslink density, both of which result in reduced chain segment mobility. Increasing the linear molecular weight or crosslink density of a polymer chain increases the position of the glass transition temperature, $T_g$, as shown in Figure 2.10. Many thermosetting polymer systems exhibit a relationship between the $T_g$ and the degree of chemical conversion. Most epoxy-amine systems exhibit a linear relationship, which implies that the change in molecular structure with conversion is independent of the cure temperature. Such a $T_g$ shift, in many circumstances, gives better resolution of cure state than enthalpy changes, especially at high and low degrees of cure.

Descriptions of the shift as a function of chemical structure, as well as
extensive theoretical models based on either free volume\textsuperscript{173-180} or time-dependent relaxation\textsuperscript{181-191} are abundant in the literature, including a review.\textsuperscript{192} Evidence for free volume models comes primarily from the pressure dependence of $T_g$ in both Thermomechanical Analysis (TMA)\textsuperscript{193-199} and DSC\textsuperscript{200-208} measurements, whereas relaxation effects can be seen in the frequency dependence of Dynamic Mechanical Analysis (DMA) measurements,\textsuperscript{209-218} as well as the effect of scanning rate in most thermal analysis techniques.\textsuperscript{219-227} The $T_g$ can be measured by a variety of techniques, each with certain advantages and disadvantages depending on the material and conditions. Comparisons of techniques show that while sensitivity to transitions vary,\textsuperscript{228-231} the value of the $T_g$ is similar given appropriate conditions.\textsuperscript{232}

![Figure 2.10: A DSC thermogram showing a series of $T_g$ measurements of samples cured for different times at specific temperatures.](image)
II.3.1 Differential Scanning Calorimetry

The most convenient, and generally most accurate, method for determining the \(T_g\) of polymers is Differential Scanning Calorimetry (DSC).\textsuperscript{233,234} The \(T_g\) is taken as the temperature at the inflection point (peak of derivative curve)\textsuperscript{235,236} of the baseline shift in heat flow, or as the temperature at the half height shift in baseline heat flow. In situations where the \(T_g\) is distorted or masked by other events, like curing exotherms or enthalpic relaxations, the \(T_g\) may be determined by the onset, but results should be noted as onset values to avoid confusion. For consistency in reporting, an ASTM standard has been established.\textsuperscript{237}

The shift in baseline heat flow associated with the glass transition is a result of the difference in heat capacity between the rubber and the glass.\textsuperscript{238-240} Since this shift is an effect of the heat capacity change,\textsuperscript{241} resolution of the glass transition can be increased by calculating and plotting the constant pressure heat capacity, \(C_p\).\textsuperscript{242} The \(C_p\) curve is calculated by comparing the heat flow (or differential power supplied), a baseline, and a reference material,\textsuperscript{243-246} usually sapphire, as described in an ASTM standard.\textsuperscript{247} A power-compensation DSC has a long term energy calibration stability, hence the sapphire measurement is unnecessary if the curve is available in the software or has been run before, provided that the DSC has been properly calibrated using a high purity heat of fusion standard such as indium\textsuperscript{248,249} or a liquid crystalline polymer standard\textsuperscript{250,251} reference material. The \(C_p\) curve can be used to calculate the constant volume heat capacity \(C_v\);\textsuperscript{252-254} however, the validity of the conversion is not absolute and the benefit is not clear. Wunderlich has compiled a database of \(C_p\) values for many...
different polymers from the literature and compared them with molecular structures.\textsuperscript{255}

The versatility of DSC to measure both exotherms and $T_g$s is also a limitation, because when measuring an uncured or a partially cured thermoset, a residual exotherm follows the $T_g$ being measured, sometimes even overlapping it as shown in Figure 2.11.

![DSC Thermogram with Curing Exotherm](image)

**Figure 2.11:** An example of a DSC thermogram with the curing exotherm occurring right after the $T_g$, distorting both measurements.

**Accurate $T_g$ calculations require stable baselines before and after the transition, and the curing exotherm interferes with the upper baseline. In these cases, the $T_g$ can only be determined as the onset.**
II.3.2 Temperature-Modulated DSC

An alternative to the measurement of $C_p$ is Temperature-Modulated DSC (TMDSC). TMDSC utilizes a modulated temperature ramp, much like dynamic mechanical analysis uses a dynamic force, and dielectric relaxation analysis uses an alternating current. TMDSC is a derivative of an earlier technique, Alternating Current (AC) Calorimetry. AC Calorimetry utilizes an oscillating heating ramp, accomplished by the use of an auxiliary pulsed heat source (usually a chopped laser) over the linear programmed heating ramp, to measure the $C_p$ during the single run experiment. Analogous to Dynamic Mechanical Analysis (DMA) and Dielectric Analysis (DEA), TMDSC mathematically deconvolutes the response into two types of signals, an in-phase and an out-of-phase response to the modulations, as well as producing an average heat flow, which is analogous to the DSC signal using a linear heating ramp. There are two primary methods of performing TMDSC, sinusoidal and square wave modulation.

The first method, introduced and patented by Reading and developed by Reading and Wunderlich utilizes a sinusoidal modulation superimposed over the traditional linear heating ramp or isotherm, shown in Figure 2.12. The other method, introduced, patented and developed by Schawe, utilizes square wave modulations, shown in Figure 2.13. The two methods can be described by a single temperature function

$$T(t) = T_0 + \beta_0 t + \left(\frac{4}{\pi}\right) T s \left[ \frac{1}{2} \left( \sin(\omega_0 t) / 1^2 \right) - \frac{1}{3^2} \left( \sin(3\omega_0 t) / 3^2 \right) + \frac{1}{5^2} \left( \sin(5\omega_0 t) / 5^2 \right) - \ldots \right] \quad (2.3)$$
where $T_0$ is the initial temperature, $\beta_0$ is the underlying heating rate, $T_a$ is the amplitude of the temperature modulation and $\omega_0$ is the angular frequency. In the special case of sinusoidal modulation, the first harmonic would dominate the series.

![Figure 2.12: Sine wave temperature modulations (Reading).](image1)

![Figure 2.13: Square wave temperature modulations (Schawe).](image2)

Although the modulations are related and can be described by a single function (Equation 2.3), the methods of evaluation of the signal developed by Reading and Schawe are quite different. Both methods use a Fourier transform to produce an average heating rate ($q_{av}$), an average heat flow ($h_{av}$), an amplitude of heating rate ($A_q$), an amplitude of heat flow ($A_h$) and a phase angle between the heating rate and heat flow ($\phi$). However, Reading and Schawe use these values in different ways to calculate the values of the components.

Reading’s technique produces three values. The total heat flow ($H_T = h_{av}/q_{av}$) is usually expressed as the total heat capacity ($C_p^T$) representing the response to the
overall average heating ramp, which is similar to what would be observed in linear DSC heat capacity measurements. The “reversing” component \( (C_p^{\text{rev}} = A_h/A_q) \) represents the ratio of the amplitude of the heat flow to the amplitude of the heating rate. These two signals are subtracted to yield the “non-reversing” component \( (C_p^{\text{nr}} = C_p^T - C_p^{\text{rev}}) \). The reversing component represents thermally reversible events, such as \( T_g \)s and meltings, whereas the non-reversing component will represent thermally irreversible events, including relaxations, crystallizations and curing exotherms.

Schawe’s technique\(^{282-284}\) uses a linear response approach, which includes a dependence on the phase lag between the signal and response. His approach also begins with the total heat capacity \( (C_p^T = h_{av}/q_{av}) \) and includes a \( C_p \) value calculated as the ratio of the heat flow amplitude to the heating rate amplitude, however his value is called the complex heat capacity \( (C_p^* = A_h/A_q) \). The reason for the difference is that from this value, he proposes a separation of the complex heat capacity \( (C_p^*) \) into two components, real and imaginary:

\[
C_p^* = C_p' + i C_p''
\] (2.4)

with \( C_p' \) representing the real, in-phase component, termed storage heat capacity, and \( C_p'' \) representing the imaginary, out-of-phase component, termed loss heat capacity. The two values are calculated using the phase angle, \( \phi \), between the signal and response:
\[ C_p' = C_p^* \cos \phi \]  
\[ C_p'' = C_p^* \sin \phi \]  

Hutchinson\textsuperscript{285} has evaluated the various types of modulations based on sine and square waves and the methods of evaluation and constructed a single parameter model to explain and predict the signals generated in TMDSC. Other models have also been proposed and evaluated\textsuperscript{286-289} although the basis for the modulation signals and evaluation, including the phase lag, is derived\textsuperscript{290,291} from electrical signal modulation\textsuperscript{292} in the electronics and telecommunications field. The frequency dependence of the measurement is a parameter which has drawn considerable attention\textsuperscript{293-298} Corrections to the phase angle to compensate for various sample and instrument effects have been proposed\textsuperscript{299-306}.

As in DMA and DEA measurements, the storage signal will include the elastic, or in-phase response of the material, which in this case will be the molecular level responses, including glass transitions and meltings. The loss signal represents viscous, or out-of-phase events, which are the kinetic effects, such as stress relaxations, crystallizations and curing. The total heat capacity is the non-separated average signal, which is equivalent to the heat capacity signal produced by traditional DSC.

TMDSC has been used for separation of \(T_g\)\textsuperscript{307-312} enthalpic relaxations\textsuperscript{313-317} and curing exotherms\textsuperscript{318-332} It also has the advantage of measuring heat capacities in one scan\textsuperscript{333-341} as opposed to the two or more scans required in traditional DSC, giving insight into the thermodynamic properties of the polymer\textsuperscript{342-348}.
TMDSC is also well-suited to measure thermal conductivity of polymers and composites, which gives valuable insight into the molecular structures. It has also been used to evaluate physical aging in both thermoplastics and thermosets as well as materials in other industries. Phase separation can also be monitored during the cure of a thermoset system.

II.3.3 Step Scan DSC

Step Scan DSC is a calorimetric technique involving applying a short heating step followed by an isotherm, which can separate quick intrinsic transitions like glass transitions from time dependent kinetic processes. A representation of a typical Step Scan DSC heating program is shown in Figure 2.14. Similar to AC Calorimetry, Step Scan separates events which occur during a quick change in temperature from

Figure 2.14: Step Scan DSC temperature program and resulting heat flow signal.
those which occur after the temperature change, during the isotherm.\textsuperscript{364} Events which occur during the heating portions are plotted in the Thermodynamic $C_p$ line, while those occurring during the isotherms are plotted in the Iso K line, as shown in Figure 2.15.

For the thermodynamic events to be separated from the kinetic ones, the rate and duration of the temperature jumps, as well as the length of the isotherms are important – if the ramp is too slow or the jump too great, some kinetic events may occur during the ramp. The parameters for the temperature step, heating rate and isothermal time depend on the material and the events to be separated. Typically for

![StepScan Curves](image)

**Figure 2.15:** The heat flow generated by the Step Scan heating program is separated into a Thermodynamic $C_p$ signal including events occurring during the heating and an Iso K signal for events which happen during the isotherm.
polymers, a temperature jump of 1 to 5 °C with a heating rate between 2 and 20 °C/min provides the time necessary for the thermodynamic molecular rearrangements, while happening faster than the kinetic effects. Kinetic effects typically occur within about 30 to 60 seconds of the temperature jump. Typically, a small temperature jump of a few degrees over the course of 10 to 30 seconds, followed by a 30 to 60 second isotherm allows separation of events in many polymers.\textsuperscript{365}

II.3.4 High Heating Rate DSC

A recent method to separate thermodynamic events from kinetically controlled ones is high heating rate DSC, commercialized by Perkin Elmer as Hyper DSC. The high heating rate DSC technique exploits the time dependence of kinetic events to push them to higher than usual temperatures. Intrinsic thermodynamic events are rate independent, so the event will occur at the same temperature, regardless of what rate is used,\textsuperscript{366} as shown in Figure 2.16. Somewhat analogous to the temperature jump method\textsuperscript{367} of measuring kinetic reaction rates, high heating rate DSC allows the measurement of glass transitions so fast that the kinetic reaction doesn’t have time to begin before the material is quenched, thus glass transitions of a reacting system can be measured without the typical simultaneous reaction. This technique is only possible due to recent advances in instrument design, which allow controlled heating and cooling rates up to 500 °C/min. To separate an overlapping epoxy cure from the glass transition, rates on the order of 100 °C/min are usually sufficient, as shown in Figure 2.17. However, to complete the $T_g$ scan without affecting the cure state requires rates of 200 to 500 °C/min, as shown in Figure 2.18.\textsuperscript{368}
Figure 2.16: Verification that the $T_g$ and onset are rate independent for rates from 5 to 200 °C/min.

Figure 2.17: Six consecutive scans on one sample at 100 °C/min with the curing exotherm shifted away from the $T_g$, but not eliminated.
Figure 2.18: Six consecutive scans on one sample at 200 °C/min with the curing exotherm pushed beyond the range of the scans as shown by the constant $T_g$.

One very practical application to come from high heating rate DSC is the measurement of $T_g$ as a function of time with a single sample. Typically each time the $T_g$ of a thermoset is measured for a given time and temperature, a new sample must be used. With high heating rate DSC, one sample can be cured for a certain amount of time at a specified temperature, then the $T_g$ can be determined at such a high rate that the sample’s cure state is not affected, then the same sample is quenched, ramped to the cure temperature for another certain amount of time and the process repeated until the reaction is complete at that temperature, as shown in Figure 2.19. A series of $T_g$ values are produced for curing times at a specific temperature, as shown in Figure 2.20.
Figure 2.19: The heating program in high heating rate DSC which cures a sample for a specific amount of time at a certain temperature, then scans for the $T_g$ without affecting the cure state, so the process can be repeated.

Figure 2.20: Series of $T_g$ values generated by a single sample using high heating rate DSC. Cure temperature is 140 °C and the times are given in minutes.
II.3.5 Thermomechanical Analysis

The $T_g$ can also be measured accurately using thermomechanical analysis (TMA). TMA is the measurement of changes in linear or volumetric dimension as a function of temperature or time. The $T_g$ appears as an abrupt increase in slope in the linear thermal expansion curve, shown in Figure 2.21, with the $T_g$ indicated as the calculated onset of the change in slope, as described in an ASTM standard. In addition to the sensitivity of the technique to the $T_g$, the linear or volumetric change in dimension with temperature gives insight into molecular structure. The slope of the dimensional change as a function of temperature is the thermal expansivity or the ASTM defined "linear coefficient of thermal expansion" (LCTE).

Figure 2.21: An example of a TMA thermogram showing the change in slope of the expansion, or linear displacement with temperature, with the onset of change in slope representing the $T_g$. 
Modern TMA instruments employ a low voltage differential transducer (LVDT) to measure dimensional changes against the probe tip, producing resolution of linear changes in micro- to nanometer scale. A TMA instrument must be calibrated for both height, using dimensionally precise quartz standards, and temperature from the melting (collapse) of a high purity standard like indium, as described by ASTM 1363.\textsuperscript{379}

II.3.6 Dynamic Mechanical Analysis

Epoxies undergo changes in mechanical behavior as a function of cure.\textsuperscript{380-388} In addition to the shift in $T_g$, there are changes in the viscoelastic behavior\textsuperscript{389,390} due to both polymerization\textsuperscript{391} and crosslinking.\textsuperscript{392,393} Dynamic Mechanical Analysis (DMA) instruments\textsuperscript{394-397} allow the application of a dynamic force in addition to the static force of TMA, just as TMDSC allows a modulated temperature signal over the linear temperature ramp of DSC. As shown in Figure 2.22, the phase lag between the applied dynamic force and the response yields a complex modulus, which can be mathematically separated into storage or in-phase, elastic response and loss or out-of-phase, viscous response, as shown in Equation 2.7.

Dynamic Mechanical Analysis

![Figure 2.22: Signal – Response for DMA measurements](image)
\[ E^* = E' + iE'' = \sigma^* /\varepsilon^*. \quad (2.7) \]
\[ \tan \delta = E''/E' \quad (2.8) \]

The \( T_g \) can be measured accurately using dynamic mechanical analysis (DMA), which can in the case of highly filled\(^{398-403}\) or highly crosslinked polymers\(^{404-407}\) give better resolution and more information than DSC,\(^{408-415}\) and better reproducibility\(^{416}\) than older techniques, such as Vicat softening\(^{417}\) and deflection\(^{418}\) temperature standards.\(^{419}\) The \( T_g \) in DMA measurement is generally taken as the peak in \( \tan \delta \).\(^{420-422}\) ASTM\(^ {423-425}\) recommends the peak in the loss modulus.\(^{426,427}\) Other methods include the inflection point or the half height value of the drop in storage modulus (M'), the onset of the drop in storage modulus, the onset of increase in loss modulus and the onset of the increase in \( \tan \delta \). A DMA thermogram is shown in Figure 2.23 with storage and loss moduli and \( \tan \delta \) shown. There is also a frequency dependence to the DMA signals, as shown in Figure 2.24. This frequency dependence is due to the viscoelastic nature of the polymer and can be used to determine the activation energy of the transition, namely how much energy is required to make the transition. A plot of the \( \tan \delta \) values as a function of frequency, from which the activation energy is calculated, is shown in Figure 2.25.

DMA (and TMA) measure dimensional changes and force responses using a variety of fixtures, each with specific applications and benefits.\(^{428}\) Applications include tensile, compression or expansion (linear and volumetric), flexural and shear.\(^{429,430}\) Specialized techniques for shear measurements include torsional pendulum,\(^{431-435}\) torsional braid analysis (TBA)\(^ {436}\) and torsional impregnated cloth analysis (TICA).\(^ {437-439}\)
A DMA instrument must be calibrated for temperature, height and force. The temperature calibration is described by ASTM using the melting temperature of a high purity standard. Height is done using a quartz height standard. Force motor calibration is performed by balancing standard weights.

Figure 2.23: A DMA thermogram using 3 point bending fixtures, showing all the signals used to calculate the $T_g$. 
Figure 2.24: A series of DMA scans through the glass transition of a fluorinated epoxy at various frequencies.

Figure 2.25: The frequencies plotted as a function of temperature of peak tangent delta, from which the activation energy of the transition is calculated.
II.3.7 Thermally Stimulated Depolarization

Another method to measure the change in \( T_g \) and chain segment mobility during the curing process is thermally stimulated currents (TSC).\(^{441}\) TSC is basically a very low frequency (\( 10^{-2} \) to \( 10^{-4} \) Hz) dielectric relaxation study.\(^{442-448}\) TSC can be performed in either polarization (TSP)\(^{449-451}\) or depolarization (TSD)\(^{452-460}\) mode. TSC involves the polarization of electrets,\(^ {461-470}\) or polar chemical bonds within the polymer chain, making it very sensitive, even in copolymers,\(^{471-484}\) highly crosslinked thermosets and filled composites.\(^{485,486}\) The sensitivity of TSC, specifically TSD, to molecular motion\(^{487-490}\) and chain segment mobility yields well resolved \( T_g \) measurements,\(^{491-504}\) in many cases, better resolved than DSC.\(^{505-518}\) Also, TSC experiments are not affected by mechanical effects like gelation as in DMA. TSC, especially TSD, measurements exhibit a time dependence, which can be measured as the characteristic Debye\(^{519}\) relaxation time, which is analogous to the DMA retardation or phase lag time.\(^{520-527}\) A series of relaxation times\(^ {528,529}\) can be used to calculate the compensation point,\(^{530-533}\) which is the convergence of the frequency dependent relaxation times, much like extrapolation to zero heating rate in DSC or zero shear in DMA. TSP measures the polarization or absorption of charge, reflected in a change in the current supplied to maintain the electric field, by the polymer as a function of time or temperature, whereas TSD studies the current induced by depolarization or release of stored charge in a polarized sample. TSD is more useful in curing studies than TSP, so emphasis is on TSD.\(^ {534}\) Shifts in \( T_g \) as a function of conversion are performed in a similar fashion as shifts by DSC; samples are cured at a certain temperature for a certain time, then quenched and the \( T_g \)
determined during a controlled heating ramp, with \( T_g \) values plotted as a function of curing conditions (time and temperature).\(^{535-551}\)

In TSD a sample is quickly heated to a poling temperature where an electric field of predetermined strength is applied through parallel plates for a specific time. Alternatively, the sample can be polarized by corona\(^{552-556}\) or electron beam\(^{557-561}\) charging.\(^{562}\) For thermosets, the poling temperature will be at the curing temperature and the poling time will be a part of the curing time. After poling, the sample is quenched to a relatively low temperature maintaining the electric field. At the selected low temperature, the electric field is discontinued and the circuit is shorted to dissipate any residual static charges on the surface or in voids caused by the electric field. The sample is heated from this low temperature to a temperature higher than the poling temperature at a slow, controlled rate and any current discharged is measured using a sensitive picoammeter (sensitive to \( 10^{-15} \) Amperes or \( 10^7 \) electrons per second), and plotted against temperature. The TSD temperature program is depicted graphically in Figure 2.26. A typical TSD current thermogram is shown in Figure 2.27.

![Figure 2.26: Temperature program in TSD, with applied electric field shaded.](image-url)
Figure 2.27: TSD plot of discharge current as a function of temperature.

II.4 Chemoviscosity

The conversion induced change in viscosity, known as chemoviscosity, can be used to monitor conversion (analogous to $T_g$ shift) and the change of physical state.\textsuperscript{563-570} Since viscosity describes a material’s resistance to flow, it is defined as the ratio of shear stress to shear strain,

$$\eta = \frac{\tau}{(d\gamma/dt)} \quad (2.9)$$

where $\eta$ is the viscosity, $\tau$ is the stress and $d\gamma/dt$ is the rate of strain. Viscosity
measurements are performed routinely on liquids using a variety of methods, including capillary, concentric cylinder, cone and plate and many other viscometers. These techniques are well suited to measurements of liquids from low viscosity fluids, such as water \((10^3 \text{ Pascal seconds})\) to higher viscosity ones, such as syrup \((10^2 \text{ Ps})\), and even some polymer melts \((10^2 \text{ to } 10^7 \text{ Ps})\). However, measurement of very high viscosity materials from heavy pitch \((10^9 \text{ Ps})\) to window glass \((10^{21} \text{ Ps})\) is beyond the range of most shear measurements. These high viscosity materials can be measured using DMA. However, DMA measures mechanical or Young’s modulus \((E)\), rather than the shear modulus required for viscosity computation. Young’s modulus \((E)\) is related to shear modulus \((G_s)\) by either the Poisson ratio \((\nu)\) or the bulk modulus \((K_B)\), given by

\[
E = 2G_s(1 + \nu) = 3K_B(1 - 2\nu) \quad (2.10)
\]

The Poisson ratio, also called the lateral strain contraction ratio, relates the change in lateral strain to the longitudinal strain. DMA measurements record the complex modulus, \(E^*\), which is the ratio of complex stress, \(\sigma^*\), to complex strain, \(\varepsilon^*\), and deconvolute that signal into a storage \((E')\) and a loss \((E'')\) signal and a phase dependent \(\tan \delta\):

\[
E^* = \frac{\sigma^*}{\varepsilon^*} = E' + iE'' \quad (2.11)
\]

\[
\tan \delta = \frac{E''}{E'} \quad (2.12)
\]

From the moduli and the frequency \((\omega)\) of the measurements, the complex viscosity,
\( \eta^* \), can be calculated, which can be separated into storage and loss components.

\[
\eta^* = \eta' - i\eta'' = \frac{E^*/\omega}{(E')^2 + (E'')^2}^{1/2}
\]

(2.13)

\[
\eta' = \frac{E''}{\omega}
\]

(2.14)

\[
\eta'' = \frac{E'}{\omega}
\]

(2.15)

The frequency of the dynamic signal has a large effect on the response, as depicted in Figure 2.28.

A single frequency series of isothermal DMA measurements of complex viscosity as a function of time, shown in Figure 2.29, exhibits the characteristic changes happening during a curing cycle. The epoxy prepreg is heated quickly to the...
isothermal temperature resulting in a temperature-dependent drop in viscosity. The minimum viscosity will generally be a function of the isothermal temperature, provided that no significant reaction has occurred, provided that the heating rate is faster than the time scale of the reaction onset. Of course, the value of the minimum viscosity will be determined by the molecular structure of the components of the prepreg and the effect of the overall mixture.\textsuperscript{577} However, usually the relative viscosities (relative to other isotherms) are used, so that the absolute value is not important in kinetics calculations. After the minimum viscosity, the reaction will proceed, increasing the molecular weight and the relative viscosity.\textsuperscript{578,579} This increase in viscosity, analogous to the rise in $T_g$ used in previous models, is proportional to the increase in molecular weight, and thus the kinetics of the reaction.\textsuperscript{580-588}
II.5 Gelation

Gelation refers to the point during the curing reaction where the molecular weight approaches the maximum, usually assumed to be infinite, meaning that all monomers are connected to the network by at least one chemical bond. While gelation is a microscopic effect, it produces macroscopic effects. Microscopic gelation refers to the definition of the gelation phenomenon, i.e. all monomers connected by at least one bond to the network. Since it occurs at a defined point in polymerization, it will occur at a specific degree of conversion.

Microscopic gelation is difficult to measure since the measurable properties would be solubility and molecular weight. However, the consequence of exceeding the microscopic gel point, is macroscopic gelation, which is much easier to measure. The macroscopic gel point is a mechanical property and can be identified by common thermal analysis techniques, including in-situ testing. Beyond gelation, there is no increase in molecular weight, only an increase in crosslink density and a decrease in free chain segment length.

Gelation does not significantly affect the chemical conversion or curing reaction, so it does not appear in DSC measurements. However, it does have a large influence on the mechanical properties of the polymer. Gelation affects the stiffness (modulus), adhesion and general processability of thermosets and composite prepregs, so it is important from an industrial processing standpoint. Gelation appears in the complex modulus, tan δ and complex viscosity of DMA measurements; however, as with many thermal events, there is no unequivocal definition at which point
the gelation occurs. Gillham,\textsuperscript{598-602} who first plotted gelation curves as part of overall time-temperature-transformation (TTT) diagrams\textsuperscript{603} developed with Enns,\textsuperscript{604-606} defines it as the a peak in the tan $\delta$ of a DMA isotherm, which was also adopted as an ASTM standard.\textsuperscript{607} This definition is common in scientific literature.\textsuperscript{608-614} Others define it as the peak in loss modulus.\textsuperscript{615} Some define it by the onset or inflection point of the increase in the storage modulus, whereas others define it as the onset of the plateau of the maximum of the storage modulus. A common method has been to use the crossover point,\textsuperscript{616-620} which is where the storage and loss moduli cross, or are equal, and the tan $\delta$ is equal to unity,\textsuperscript{621} however it has been shown to be inaccurate in many cases\textsuperscript{622-624} and can only be used as a quantitative measure or as a reference conversion value for one particular system. This discrepancy lies primarily in the application for which the data is being used, i.e. someone concerned with laminate adhesion would identify a different point than someone concerned with ensuring dimensional stability, and different than a researcher interested in characterizing the physical state of the material. The DMA isothermal plot in Figure 2.30, identifies the gel point using Gillham’s terminology, i.e. the peak in tan $\delta$.

As described earlier, DMA transitions exhibit a frequency dependance. However, since gelation is an isoconversion event, it is frequency independent. The gel point is defined as the point where the tan $\delta$ becomes frequency independant.\textsuperscript{625-628} However, this method requires many measurements at different frequencies. The gel point can be defined in terms of viscosity since it represents the maximum viscosity.\textsuperscript{629-631}
II.6 Vitrification

Vitrification is defined as the point at which the molecular weight or cross-link density of the curing polymer exceeds that which is thermodynamically stable as a rubber, and the material undergoes a transition from a rubber to a glass at which point the reaction dramatically slows due to the reduced mobility of the reactants. The vitrification point can be measured using DSC, TMDSC and DMA.
Although vitrification is a thermal transition from a rubber to a glass and does appear in DSC measurements, the determination of the point and quantification of the shift in baseline heat flow or $C_p$ usually occurs around the end of the curing (since it is a decrease in the reaction rate) and as such is usually masked by the curing reaction exotherm. This is one of the clearest applications of TMDSC, since the curing exotherm appears in the loss $C_p$ and the vitrification appears in the storage $C_p$. A series of isothermal TMDSC plots identifying the vitrification point are shown in Figure 2.31.

DMA has been used extensively to investigate the vitrification point, and continues to be the most common method. The first epoxy TTT diagram, proposed by Gillham and Enns, was constructed primarily from torsional braid analysis (TBA), a specialized torsional DMA measurement. Gillham defines the vitrification in TBA and

![Graph showing TMDSC isotherms with temperature and specific heat as variables.](image)

Figure 2.31: TMDSC isotherms showing vitrification as half height drop in storage $C_p$. 

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DMA measurements as the highest tan δ peak below the melt, which usually corresponds to the maximum value of the storage modulus during an isothermal experiment. Measurement of vitrification in isothermal DMA and TBA studies are common. DMA isotherms showing vitrification points from parallel plate and 3-point bending modes are shown in Figures 2.32 and 2.33. Vitrification generally occurs when the increasing \( T_g \) equals the cure temperature. Although the reaction dramatically slows, it is still significant until the \( T_g \) exceeds the cure temperature by 20 to 40 °C.

Figure 2.32: A parallel plate DMA isotherm (160 °C), with vitrification defined by the second peak in tangent delta in time.
Figure 2.33: A 3-point bending DMA isotherm (160 °C), with vitrification defined by the second peak in tan δ in time.

II.7 Thermal Stability

Thermogravimetric Analysis (TGA) is the measurement of weight loss as a function of temperature or time. A TGA instrument consists of a sensitive (typically ±0.1 µg) microbalance monitoring the weight of a sample enclosed in a programmable oven. Many reviews of TGA instrumentation are available in the literature. TGA is used extensively to study decomposition, especially of multicomponent systems, including polymer blends, polymers with additives and reinforced and filled polymer composites. The offgassing of absorbed moisture or residual solvent can indicate the viscosity and gas permittivity of a sample in an indirect manner. Thermal stability, or resistance to thermal degradation, is related to the degree of cure, since the bond energies of aliphatic linkages tend to be higher than those of unsaturated structures. This relationship can be used to relate the kinetics of thermal
decomposition to the curing reaction. TGA can be used to study the kinetics of either decomposition or chemical reactions involving the release of volatile by-products, i.e. condensation reactions. Kinetics can be evaluated using isoconversion data plots, activation energy calculated from the slope of initial reaction, varied heating rate analysis or a "model-free" method and comparisons of techniques have been evaluated. A modulated TGA technique exists and some separation of weight losses have been described, however, since most weight losses are non-reversible events, only weight losses with different time dependancies may be separated. TGA experiments can be performed in either oxidizing (O₂ or air) or non-oxidizing (N₂ or Ar) environments, depending on the reaction or decomposition being examined. A series of TGA decomposition thermograms are shown in Figure 2.34.

![TGA decomposition thermograms](image)

**Figure 2.34:** A series of TGA decomposition thermograms at different scanning rates.
TGA instruments must be calibrated for both temperature and weight. Weight calibrations are performed with standards which have been weighed to the desired accuracy (usually \( \pm 0.1 \, \mu g \)) and will not react with moisture or oxygen in the air, as such platinum is a common standard. Temperature can be calibrated by two methods – fusible link or magnetic Curie temperature. The fusible link technique uses a small weight attached to the balance by a link made of a high purity standard which will result in a sudden weight loss at the melting point of the standard.\(^{685,686}\) The magnetic Curie temperature method uses the well known temperature-dependant magnetic properties of some metals and alloys. These materials exhibit a change in magnetism at a specific temperature, called the Curie point.\(^ {687}\) The calibration is performed by placing a magnet above or below the standard in the TGA sample pan, where it will display an exceptionally high or low weight due to the magnetic field, until the temperature is raised to the Curie temperature.\(^ {688}\) Materials and procedures have been recommended by the National Institute of Standards and Technology (NIST).\(^ {689}\)

II.8 Shrinkage

Shrinkage during processing of epoxies is due to the chemical rearrangement of the molecular components, the rearrangement of any fibers or fillers in reinforced materials, and the thermal contraction in epoxies cured above ambient temperatures. The thermal contraction is the easiest component to measure, since the dimensional change in the solid state will correspond to the Bulk Modulus times the difference in temperature between processing and ambient conditions. The shrinkage due to chemical rearrangement during the cure is also straightforward, except when pressure
is applied. Since the most important measurements are for injection and compression molders, pressure usually is a very important factor. The rearrangement of fibers and fillers depend on many factors including the nature of the reinforcement, temperature and viscosity of resin and the cure state of the matrix, as well as what pressure is applied. Measurement of volume changes is called dilatometry. Dilatometry allows the measurement of volumetric changes associated with thermal contraction and expansion in amorphous\textsuperscript{690, 691} and semicrystalline\textsuperscript{692} thermoplastics, rubbers,\textsuperscript{693-695} epoxies\textsuperscript{696} and even inorganic crystals,\textsuperscript{697-699} as well as a means to describe bulk, aging\textsuperscript{700} and composite\textsuperscript{701-703} and pressure\textsuperscript{704} effects on phase transitions.

Thermal shrinkage due to the difference in temperature between processing and ambient conditions depends solely on the Bulk Modulus\textsuperscript{705-707} of the material, which is simplified due to the fact that the product will be in the solid state and it usually does not undergo a phase change during the cooling process. For isotropic materials, the Bulk Modulus can be estimated from the Linear Coefficient of Thermal Expansion (LCTE) determined from linear TMA measurements. However, the preferred method is to confine the sample in a closed cell with a confining fluid to measure the dimensional change of the fluid. Unlike the linear TMA measurements, the sample can be any shape and homogeneity and isotropism is not required. The confining fluid which surrounds the sample may be any inert liquid which does not undergo a phase change over the temperature interval, including silicone oils,\textsuperscript{708, 709} mercury\textsuperscript{710-712} and even powdered alumina. The closed cell can be of any material, but low expansivity materials like quartz or invar are preferred. Obviously, the thermal volume change due to the cell
and the fluid must be subtracted from the results. Typically minimal pressure is used, since during the cooling stage after a part is ejected from the mold, the part is not under pressure. A sample dilatometry cell is shown in Figure 2.35.

Figure 2.35: A quartz dilatometry cell using alumina powder as the confining fluid which measures volumetric changes via linear measurement.

During the curing reaction, there will be a small amount of shrinkage due to the chemical rearrangement of the molecules themselves. This is typically between a fraction of one and a few volume percent. This measurement is done in a dilatometer like the one used for thermal shrinkage for nonpressured processing like casting or potting. However, in many applications like injection and compression molding, pressure is an important factor. Measurements should be made under similar pressures.
as those used in the processing, since pressure will affect the molecular rearrangement. For this reason, the dilatometer must employ a piston, the cell must maintain structural integrity at that pressure, and the fluid must not undergo any pressure-induced changes.

In processing fiber-reinforced compression molded prepregs, fiber wound injection molded epoxy or highly filled parts, the movement of the reinforcement under pressure can change the volume of the parts. The shape and orientation of the reinforcement, as well as the nature of the material (glass or carbon), will affect this change, but the temperature, viscosity and degree of cure of the matrix and the pressure applied will have a large influence on how much the reinforcement can move. This measurement must be done in situ, in that processing conditions must be simulated in the instrument. The dilatometer must be brought to the processing temperature and pressure applied as quickly as possible, since curing will be occurring simultaneously and will drastically affect any movement of the reinforcement, as shown in Figure 2.36.

II.9 Tribology

Tribology, the study of frictional properties, is typically studied using materials in contact moved in a shear direction. Obviously, static friction would be force without motion and dynamic friction would be force producing motion. Tribological instruments typically consist of a monitored surface in the form of a skid or plate in contact with a stationary surface or object. Depending on the application, a skid in contact with a surface or a pin in contact with a movable disk may be used. A skid of the same or
Figure 2.36: The TMA measurement of a dilatometry cell showing both void elimination and fiber rearrangement and shrinkage due to curing.
different material as the stationary surface may be pulled, and either the force necessary to produce initial movement or the force necessary to maintain motion is recorded. A pin on disk study typically uses a disk of the investigated material subject to rotational force while in contact with a pin of a certain geometry and material, which yields data on both friction and also wear or abrasion. Both skid and plate and pin on disk are common in tribological studies.

Wear, another tribological property, is measured by depth of penetration caused by abrasion of a material by a standard material. One system uses a diamond indenter to measure the scratch depth as a function of force applied.

II.10 Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CHT</td>
<td>Continuous Heating Transformation</td>
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<tr>
<td>DEA</td>
<td>Dielectric (Relaxation) Analysis</td>
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<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>ICTAC</td>
<td>International Confederation for Thermal Analysis and Calorimetry</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LCTE</td>
<td>Linear Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>LVDT</td>
<td>Low Voltage Differential Transducer</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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TBA  Torsional Braid Analysis
TGA  Thermogravimetric Analysis
TICA  Torsional Impregnated Cloth Analysis
TMA  Thermomechanical Analysis
TMDSC  Temperature-Modulated Differential Scanning Calorimetry
TSC  Thermally Stimulated Currents
TSD  Thermally Stimulated Depolarization
TSP  Thermally Stimulated Polarization
TTT  Time-Temperature-Transformation

VCTE  Volumetric Coefficient of Thermal Expansion

II.11  Symbols

A  Amplitude

$C_p$  Specific Heat Capacity at Constant Pressure

$C_p^*$  Complex Specific Heat Capacity at Constant Pressure

$C_p'$  Storage Specific Heat Capacity at Constant Pressure (Elastic Component)

$C_p''$  Loss Specific Heat Capacity at Constant Pressure (Viscous Component)

$C_v$  Specific Heat Capacity at Constant Volume

E  Young’s (Mechanical) Modulus

E*  Complex Young’s Modulus

E’  Storage Young’s Modulus (Elastic Component)

E''  Loss Young’s Modulus (Viscous Component)

g  gram
G  Gibb’s Function
G_s  Shear Modulus
H  Enthalpy
dH/dt  Rate of Change of Enthalpy in Time
Hz  Hertz (cycles per second)
K_s  Bulk Modulus
P  Pascal (pressure unit)
q  Heat Quantity
s  Second (time unit)
S  Entropy
T  Temperature
T_g  Glass Transition Temperature
α  Degree of Conversion
δ  phase angle (usually given as tan δ)
ε  Mechanical Strain
γ  Shear Strain
η  Viscosity
η*  Complex Viscosity
η’  Storage Viscosity (Elastic Component)
η”  Loss Viscosity (Viscous Component)
ν  Poisson’s Ratio
φ  Phase Angle

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σ  Mechanical Stress
τ  Shear Stress
ω  Angular Frequency

II.12 References


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CHAPTER III  
KINETIC MODELS AND EQUATIONS  

III.1 Introduction  

Chemical kinetics is the description of conversion of reactants to products. In the case of cure kinetics of an epoxy+amine system, the rate of conversion will be described by the consumption of epoxide and amine functional groups and the production of aliphatic bonds, as described in Chapter 1. The traditional chemical method for kinetic rate determination is mechanistic - the concentrations of products or reactants are monitored throughout the reaction and the rates of change in concentrations are fitted to an equation. Once the mechanism is determined and modeled, then the reaction can be described by reactant or product concentrations in time as a function of a temperature-dependant rate constant.¹

However, many curing reactions are quite complex, involving multiple competing reactions with several kinetic equations superimposed at different degrees during the overall reaction, producing very complicated models.²⁻⁵ In addition, in many instances the exact chemistry or concentrations of reactants may not be known, especially in industrial applications where premixed compounds or prepreg composites are supplied by an outside source. For these situations, phenomenological models are attractive and have demonstrated value and validity.⁶⁻⁸

Phenomenological models use properties which are related to the reaction, for example the change in viscosity or shift in glass transition temperature of a growing polymer. These models describe the degree of conversion or per cent of cure from
uncured to fully cured as a function of time and temperature. Phenomenological models are advantageous because they do not require knowledge of the reaction mechanism, only the changes in properties.

Due to the complexity of the 4,4’-diaminodiphenylsulfone (DDS) cured tetruglycidyl 4,4-diaminodiphenyl methane (TGDDM) system and the application of curing commercial prepregs in this work, emphasis is on phenomenological modeling, with references to mechanistic models where applicable.

III.2 Kinetic Equations

As any chemical reaction, the curing reaction will be described by a rate equation, which will relate the rate of the reaction to the rate constant and the consumption of reactants or production of products. In the case of thermoset curing, a generalized rate function utilizing the degree of cure, \( \alpha \), which is the disappearance of epoxide functional groups or appearance of chemical bonds, with \( (1 - \alpha) \) representing the epoxide group concentration.

\[
d\alpha/dt = k (1 - \alpha)^n
\]  

(3.1)

This equation describes an nth order equation, so that the reaction rate is dependant only on the concentration of epoxide (and curing agent). However, many thermosetting materials are autocatalytic, so that the product of the reaction serves as an additional catalyst in the reaction, as in the catalyzation of the epoxy+amine system by generated hydroxyl groups.
Kinetic modeling of autocatalytic reactions requires an additional term to account for this effect, namely

\[
d\alpha/dt = k \alpha^m (1 - \alpha)^n \tag{3.2}
\]

where \( \alpha^m \) represents the catalytic effect of the products of the reaction with an order of \( m \). It is also apparent, that an \( n \)th order reaction is a special case of the autocatalytic reaction where \( m = 0 \).

Most epoxies exhibit either \( n \)th order or autocatalytic curing reactions, although it is not always apparent which type an epoxy will follow. However, the two types are readily differentiated by experimental data. As can be easily predicted from Equation 3.1, an \( n \)th order reaction will exhibit its maximum rate at the beginning of the reaction, whereas the autocatalytic reaction, predicted from Equation 3.2, will exhibit its maximum rate at some later time during the reaction, typically 20 to 40 \% of the reaction.\(^9\) The order is generally determined by plotting the degree of conversion as a function of time and fitting the curve. This is usually accomplished using a log-log plot and fitting using the Least Squares\(^{10}\) method. In addition to the time dependence of the rate of conversion, the rate constant, \( k \), is temperature dependent, usually assumed to follow an Arrhenius relation of the form:

\[
k = Ae^{-E_a/RT} \tag{3.3}
\]
where $k$ is the reaction rate constant, $A$ is the pre-exponential function, and $E_a$ is the activation energy. Thus, Equations 3.1 and 3.2 can be written as

$$\frac{d\alpha}{dt} = (Ae^{-E_a/RT}) (1 - \alpha)^n$$  \hspace{1cm} (3.4) \\
$$\frac{d\alpha}{dt} = (Ae^{-E_a/RT})\alpha^m (1 - \alpha)^n$$  \hspace{1cm} (3.5)

with the incorporation of the Arrhenius temperature dependence. The initial rate of an autocatalytic reaction is not necessarily zero since the reaction can proceed via alternative paths, especially in the presence of impurities like water and catalyzing ions. Taking this into account, the autocatalytic equation is given as

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n$$  \hspace{1cm} (3.6)

where $k_1$ is the reaction rate constant at zero time and $k_2$ is the rate constant of the reaction by traditional pathways. The initial rate constant, $k_1$, is easily calculated from the experimental data since it equals the rate at zero conversion.

The activation energy, represented by $E_a$ in the Arrhenius temperature dependence of the rate constant $k$, can be calculated for both mechanistic and phenomenological models, and as such allows a comparison between the results. As with other chemical reactions, the activation energy can be conceptually thought of as the energy, in this case thermal energy, necessary for the reaction to proceed.

In mechanistic models, the activation energy is the slope of the $\ln k$ vs. $1/T$ (or
1000/T) curve since \( \ln k = \ln A - E_a(1/RT) \). The natural logarithm of the pre-
exponential factor, \( A \), is the \( y \) (or \( \ln k \)) intercept. The activation energies of
phenomenological models are usually calculated from a time-temperature relationship
computed with a shift factor, or via the temperature dependence of the time to reach a
certain conversion.

A mechanistic model has been developed for autocatalytic, amine-cured epoxies.
To fully account for the autocatalysis by hydroxyl groups generated, the multifunctional
nature of the amine curing agent, and the presence of ionic catalysts, including
impurities like water and other hydroxyl containing species, Horie\textsuperscript{11} has proposed a rate
equation which considers all reactions possible including

\[
\begin{align*}
A_1 + E + (HX)_E & \xrightarrow{k_1} A_2 + (HX)_E \\
A_1 + E + (HX)_0 & \xrightarrow{k_1'} A_2 + (HX)_0 \\
A_2 + E + (HX)_E & \xrightarrow{k_2} A_3 + (HX)_E \\
A_2 + E + (HX)_0 & \xrightarrow{k_2'} A_2 + (HX)_0
\end{align*}
\]

where \( A_1, A_2 \) and \( A_3 \) are primary, secondary and tertiary amines, \( E \) is epoxide, \( (HX)_0 \) are
hydroxyl groups and catalysts present in the system initially, and \( (HX)_E \) are hydroxyl
groups generated by epoxy reactions. These reactions can be assembled into the
overall kinetic equation\textsuperscript{12}

\[
\frac{dx}{dt} = k_1 a_1 e_0 x + k_1' a_1 e_0 c_0 + k_2 a_2 e_0 x + k_2' a_2 e_0 c_0
\]
where $x$ is the epoxide consumed, $c_0$ and $e_0$ are the initial concentrations of $(HX)_0$ and epoxide, $a_1$ and $a_2$ are the concentrations of primary and secondary amines. When the primary and secondary amines are approximately equal in reactivity, the reaction rate may be simplified to

$$\frac{dx}{dt} = (k_1 x + k_1' c_0)(e_0 - x)(\alpha_0 - x/2) \quad (3.12)$$

Converting the concentration of epoxide loss, $x$, to fractional conversion, $\alpha$, transforms Equation 3.12 to:

$$\frac{d\alpha}{dt} = (k_1 \alpha + k_1')(1 - \alpha)(B - \alpha) \quad (3.13)$$

where $k_1 = k_1(e_0)^2 / 2$, $k_1' = k_1'e_0c_0 / 2$ and $B = 2a_0 / e_0$. $B$, the stoichiometric ratio of amine hydrogen equivalents to epoxide equivalents, is unity in balanced mixtures. This model has been used successfully for some systems following the required assumptions.\textsuperscript{13-17} However, commercial TGDDM/DDS systems can not be adequately modelled with this equation.\textsuperscript{18,19} In addition, extensive knowledge of the chemistry and stoichiometry of the mixture is essential. In the specific case where $B = 1$, Equation 3.13 reduces to Equation 3.6 with $m = 1$ and $n = 2$, as expected.

Epoxy curing reactions are further complicated by the diffusion controlled\textsuperscript{20} reaction occurring at the onset of vitrification when the kinetic reaction ends. The overall reaction is actually
where $k_a$ is the overall reaction rate constant, $k_T$ is the Arrhenius rate constant for the kinetically controlled reaction and $k_d$ is the diffusion rate constant.

### III.3 Kinetic Methods

#### III.3.1 Isothermal Differential Scanning Calorimetry

Fitting isothermal DSC data to the autocatalytic phenomenological Equation 3.6 is difficult due to the number of variables, including two different exponents. Several numerical methods, including rate analysis and linear regression, have been used. However, many methods rely on a combined order which limits the generality. A differential method has been proposed which does not rely on a combined order.

Several methods assume a combined, or overall, reaction order where the sum of exponents $m$ and $n$ is assumed to be constant. In the simplest method, the overall reaction order assumption allows the calculation of the rate constant, $k_2$, which can be substituted back into Equation 3.6 and the values of $m$ and $n$ calculated. This method is based on several assumptions - the primary and secondary amines are of similar reactivities and the hydroxyl groups function only as catalysts for the amine reactions, i.e. reaction 1.3c is insignificant. This has been verified for some amine catalyzed epoxy systems, especially in amine-rich systems. However, Dušek found that the assumption of equal reactivities of amines is only true for aliphatic amines, not for aromatic amines. The combined reaction order has been shown to be invalid for multifunctional aromatic amines and epoxy-rich systems, specifically for the
epoxy-rich commercial TGDDM/DDS systems.$^{34-38}$

A method, proposed by Ryan and Dutta,$^{39}$ uses the time at maximum rate. It was successfully used to model an epoxy-amine system. However, this model also relies on the combined order assumption, limiting its applications. A nonlinear regression analysis method was used by Moroni et al.$^{40}$ for an epoxy; however, this method also relies on the combined order assumption, limiting its use.

One method which does not rely on a combined order was proposed by Kenny.$^{41}$ The method involves taking the natural logarithm of both sides of Equation (3.6), which yields

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k_1 + k_2\alpha^m) + n \ln(1 - \alpha)$$  \hspace{1cm} (3.15)

A plot of $\ln(d\alpha/dt)$ as a function of $\ln(1 - \alpha)$ generates a line with slope $n$. Rearranging Equation 3.6 in a different form yields

$$\ln\{[(d\alpha/dt)/(1 - \alpha)^n] - k_1\} = \ln k_2 + m \ln \alpha$$  \hspace{1cm} (3.16)

Substituting $n$ and $k_1$, $m$ can be calculated by the slope and $k_2$ from the intercept.

III.3.2 Single Scan Differential Scanning Calorimetry

Although isothermal DSC evaluation produces accurate quantitative results, it is very time-consuming, stimulating a desire for a fast method to characterize cure kinetics, even at the cost of accuracy. The desire for a method to quickly characterize a
curing reaction in a single DSC scan led to several methods.

The first single scan DSC method was proposed by Borchardt and Daniels. The method is similar to the isothermal method in that the degree of conversion throughout the scan is a function of the fractional enthalpy change in time. The same equation is

\[
\ln \left( \frac{d\alpha}{dt} / (1 - \alpha)^n \right) = \ln k = \ln A - E/RT \quad (3.17)
\]

with the temperature \( T \), as a function of time. Using Equation 3.17, the variables \( \ln A \), \( E \) and \( n \) can be calculated from a single DSC scan. Such an nth order equation, as well as the autocatalytic equation are generally written as

\[
k_n = \frac{d\alpha}{dt} / (1 - \alpha)^n \quad (3.18)
\]

\[
k_a = \frac{d\alpha}{dt} / \alpha(1 - \alpha)(B - \alpha) \quad (3.19)
\]

For the nth order equation, Barrett proposed plotting \( \ln \left( (d\alpha/dt) / (1 - \alpha)^n \right) \) as a function of \( T^{-1} \) gives \( \ln A \) and \( E \) from the slope and intercept provided that \( n \) is chosen to produce a linear plot. Alternative evaluation techniques have proposed using the incremental form and second derivative of Equation 3.15. While this technique has given adequate approximations for some nth order reactions, it generally gives much higher activation energy values, in some cases completely invalid results.

III.3.3 Multiple Scanning Rate DSC

Multiple heating rate dynamic DSC scans are isoconversion measurements,
meaning that the time-dependant temperature to reach a certain degree of conversion
as a function of heating rate is measured. Several models have been proposed to
relate the isoconversion temperatures to scanning rate. Most models use the peak in
the curing exotherm in the scan as an isoconversion point.

One of the first successful models to relate the temperature of the exotherm
peak to the scanning rate was proposed by Kissinger.\textsuperscript{58,59} His model, based on
Differential Thermal Analysis (DTA) studies, provides

\[
\frac{d[\ln(\varphi/T_p^2)]}{d[1/T_p]} = \frac{-E}{R} \tag{3.20}
\]

where \( \varphi = dT/dt \) is the heating rate and \( T_p \) is the peak temperature. Equation 3.20
may also be written as

\[
A = \frac{\varphi \exp[E/RT_p]}{RT_p^2[n(1 - \alpha_p)^{n-1}]} \approx \frac{\varphi \exp[E/RT_p]}{RT_p^2} \tag{3.21}
\]

where \( \alpha_p \) is the conversion at the peak and the approximation is based on Kissinger’s
assumption that \([n(1 - \alpha_p)^{n-1}] = 1\). This is the model for an nth order reaction.
However, an autocatalytic equation based on this relationship has been developed,\textsuperscript{60} as
follows:

\[
A \approx \frac{\varphi E \exp[E/RT]}{RT_p^2[2\alpha_p + 2B\alpha_p - 3\alpha_p^2 - B]} \tag{3.22}
\]
The most common method is based on work by Ozawa\textsuperscript{61,62} and Flynn and Wall.\textsuperscript{63,64} Integration of the general rate equation and rearrangement produces

\[ \int_{0}^{\alpha_i} \frac{d\alpha}{dt} \approx \frac{AE}{\varphi R} p(E/RT) \] (3.23)

where \( \alpha_i \) is a specified conversion and \( T_i \) is the temperature to reach that conversion, \( \varphi \) is the scanning rate and \( p(E/RT) \) is an approximate solution to the exponential integral. Using values tabulated by Doyle,\textsuperscript{65} the exponential can be approximated as

\[ \log p(E/RT_i) \approx -2.315 - 0.4567 E/RT_i \] (3.24)

Using this value, the equation can be rewritten as:

\[ E \approx \frac{-R \Delta(\log \varphi)}{0.4567 \Delta(1/T_i)} = \frac{-R \Delta(\ln \varphi)}{1.052 \Delta(1/T_i)} \] (3.25)

A similar model proposed by Fava,\textsuperscript{66} employs a rigorous approach based on Ozawa’s model. Values for \( (d\alpha/dt)_p \) at various scanning rates are plotted against \( 1/T_p \) and parameters calculated.

Barton\textsuperscript{67} used a model relating conversion and conversion rate to activation energy:
\[
\ln \frac{(d\alpha/dt)_i}{(1 - \alpha)^n} = -\frac{E}{RT_i} + \ln A \quad (3.26)
\]

where \(i = 1, 2\), representing the two different scanning rate values. Setting \(\alpha_1 = \alpha_2\) for the isoconversion peak temperatures, \(T_1\) and \(T_2\), and combining the equations yields

\[
\ln \frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} = -\frac{E}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.27)
\]

This model allows calculation of the activation energy from two different rate scans, independent of rates. However, this equation gives no indication of reaction order or pre-exponential factor (A). Hernández-Sánchez and Vera-Graziano\(^68\) set \((d\alpha/dt)_1 = (d\alpha/dt)_2\), yielding

\[
\ln \frac{1 - \alpha_1}{1 - \alpha_2} = -\frac{E}{nR} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.28)
\]

Equation 3.25 can also be solved for a nonisoconversion situation where \(T_1 = T_2\),

\[
\ln \frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} = n \ln \frac{1 - \alpha_1}{1 - \alpha_2}. \quad (3.29)
\]

These equations, particularly Ozawa’s and Barton’s, have been used successfully for both simple\(^69-72\) and complex\(^73-75\) thermosetting systems, including the TGDDM/DDS\(^76\) system, which was not able to be modeled by the single rate method. In addition, in
situations where multiple curing reactions\textsuperscript{77-80} can be resolved separately, e.g. primary and secondary amine reactions, the parameters can be calculated for each reaction.\textsuperscript{81}

III.3.4 Time-Temperature Superposition

The viscoelastic nature of polymers is the basis for the principle of time-temperature superposition\textsuperscript{82} - the time of an event is related to the temperature at which it takes place. This is apparent in polymers which have large viscous and elastic characteristics, although it can be detected in viscous liquids and elastic solids also. The principle is well accepted in the field of polymers, as demonstrated by predicted ambient temperature lifetime studies conducted in short times at elevated temperatures,\textsuperscript{83} and the velocity dependence of impact tests,\textsuperscript{84} which can lead to low velocity predictions of ballistic impact property predictions conducted at low temperatures. The relationship has been demonstrated for many characteristics by Ferry\textsuperscript{85} and Goldman.\textsuperscript{86} While a qualitative understanding of the relationship between time and temperature has been known for a long time, creating a quantitative formula which would describe the behavior has proven difficult.

The most common relationship for polymers above the glass transition is the Williams-Landel-Ferry\textsuperscript{87} (WLF) model given as

\[
\log a_T = - \frac{[C_1 (T - T_i)]}{[C_2 + (T - T_i)]} \quad (3.30)
\]

where \(a_T\) is defined as the shift factor, or the degree to which the property curve will be shifted vertically or horizontally in relation to the reference curve by the temperature
difference, and $C_1$ and $C_2$ are constants. However, this model only works for temperatures greater than the glass transition temperature. For temperatures below the glass transition temperature, i.e. in the glassy state, the most common model is based on an Arrhenius relationship given as $^{88}$

$$\ln a_T = \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right).$$  \hspace{1cm} (3.31)

A model based on free volume derived by Brostow, $^{89,90}$ which works for all temperatures is

$$\ln a_T = A + \frac{B}{(\nu - 1)}$$  \hspace{1cm} (3.32)

where $A$ and $B$ are constants and $\nu$ is the reduced volume, defined as the ratio of volume to incompressible or hard-core volume. The WLF equation is a special case of Equation 3.29 which relies on linear proportionality of reduced volume and temperature, which is only a good approximation from the $T_g$ to around 50K above. However, the simplicity of the formula and the lack of complex intrinsic material behavior combined with the fact that most studies are performed within the limited range of reliability provide the popularity of the equation.

These models have been applied to thermosets usually in the form of time to reach a specific conversion as a function of temperature. $^{91,92}$ Prime $^{93}$ proposed an isoconversion Arrhenius relationship between the times ($t_1$ and $t_2$) to reach a certain
conversion at two temperatures ($T_1$ and $T_2$),

$$
\ln a_T = \frac{E}{R \left(\frac{1}{T_1} - \frac{1}{T_2}\right)}
$$

(3.33)

Wisanrakkit and Gillham$^{94,95}$ proposed a similar isoconversion relationship,

$$
\ln a_T = \ln (t_2) - \ln (t_1)
$$

(3.34)

where $t_1$ and $t_2$ are the times to reach a specified conversion.

III.4 Physical Models

III.4.1 Glass Transition Temperature Shift

During the polymerization part of the reaction, before gelation and crosslinking, the increase in $T_g$ associated with the linear chain growth is proportional to the concentration of monomers, using the decrease in concentration $\alpha$ in the form

$$
\frac{1}{T_g} = \frac{1}{T_{g0}} + k\alpha
$$

(3.35)

where $T_{g0}$ is the glass transition temperature at zero conversion, $k$ is the rate constant and $\alpha$ is the conversion, which is only valid for values up to gelation. This equation assumes that no crosslinking takes place, which is a good approximation at low conversion.

In the region between gelation and vitrification where crosslinking is the dominant reaction, two primary models have been used. Fox and Loshaek$^{96}$ proposed a
model which predicts a linear increase in $T_g$ with crosslink density, whereas DiMarzio proposed a model which predicts linearity of $1/T_g$ with crosslink density. Later modeling approaches combined both effects, polymerization and crosslinking, into one model. The first of these, $T_g$ as a function of conversion models was proposed by DiBenedetto. DiBenedetto established a relationship to predict the shift in $T_g$ based on lattice energies and segmental mobilities of the cured and uncured materials,

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(\varepsilon / \varepsilon_0 - \frac{C_v}{C_0}) \times x}{1 - (1 - \frac{C}{C_0}) \times x} \quad (3.36)$$

where $x$ is the crosslink density or fraction of segments crosslinked, $\varepsilon$ is the lattice energy, and $c$ is the segmental mobility. This equation has been used successfully for many cross-linking systems, except in cases of very high cross-linking. This equation was modified by Couchman to combine the lattice energy and segmental mobility into the heat capacity value,

$$\frac{T_g - T_{g0}}{T_{g0} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (3.37)$$

where $\lambda$ is a structural dependent parameter defined as $\Delta C_p/\Delta C_{p0}$. This equation was found to model some systems with $\lambda$ values ranging from 0.43 to between 0.46 and 0.58. However, the equation does not adequately model epoxy-rich systems, due to the complexity of the reactions. Venditti and Gillham further modified the equation to the following form:
\[
\ln (T_g) = \frac{(1 - \alpha) \ln(T_{g0}) (\Delta C_p/\Delta C_{p0}) \alpha \ln(T_{g\infty})}{(1 - \alpha) + (\Delta C_p/\Delta C_{p0}) \alpha}. \tag{3.38}
\]

This equation was found to model the epoxy-rich systems, which the previous models could not, in addition to the systems which were modeled by the other equations.

The diffusion controlled part of the reaction after vitrification has been evaluated by phenomenological models, and Wisanrakkit and Gillham proposed a separate conversion-T\(_g\) model to cover this part of the overall reaction

\[
\ln [k_d(T)] = \ln [k_d(T_g)] + \frac{2.303 C_1 (T - T_g)}{C_2 + |T - T_g|}. \tag{3.39}
\]

where \(C_1\) and \(C_2\) are WLF parameters. Assuming \(k_d(T_g)\) is constant and setting \(r = 2.303C_1\), Equation 3.25 becomes

\[
\ln (k_d) = \ln (k_{d0}) + \frac{r (T - T_g)}{C_2 + |T - T_g|}. \tag{3.40}
\]

which may be used to calculate the activation energy and preexponential factor.

**III.4.2 Viscoelastic Relaxation Time Shift**

The glass transition temperature shift described above can also be described using viscoelastic theory. The \(T_g\) shift is described as resulting from changes in the frequency-dependent relaxation time, \(\tau(\omega)\), due to the change in mobility of the growing chains and network.\(^{113}\)

The relaxation time is taken to be a thermally activated process, so it can be
modeled by an Arrhenius relationship

\[ \tau (T, \alpha) = \tau_\alpha \exp \left( \frac{E_a}{RT} \right) = \frac{1}{\omega} \tag{3.41} \]

where \( E_a \) is the activation energy of the glass transition, \( \tau \) is the relaxation time, \( \tau_\alpha \) is the relaxation time at the conversion at the transition and \( \omega \) is the frequency of the stimulus. The \( T_g \) can be defined as

\[ T_g = -\frac{E_a}{R \ln(\omega \tau_\alpha)}. \tag{3.42} \]

Substituting viscoelastic relationship equations, this can be written as

\[ T_g = \frac{E_a}{R \ln[C_1 (1 - \alpha)^\Phi + C_2]} \tag{3.43} \]

where

\[ C_1 = \exp(E_a/RT_g0) - \exp(E_a/RT_{g\infty}) \tag{3.44} \]
\[ C_2 = \exp(E_a/RT_{g\infty}) \tag{3.45} \]

and \( \Phi \) is a parameter accounting for chain entanglement. The activation energy of the transition may be determined by multiple frequency experiments using the relationship\(^{114,115}\)

\[ E_a = \frac{d(\ln \omega)}{d(1/T_{\text{max}})} \tag{3.46} \]
This viscoelastic relaxation model has been used to successfully model a multifunctional epoxy through the complete curing reaction.\textsuperscript{116}

III.4.3 Gelation

The degree of conversion at the microscopic gel point can be calculated if the chemistry of the reactants is known. The first formula for calculating the microscopic gel point, proposed by Flory\textsuperscript{117} in 1941, is

\[
(\alpha_1 \alpha_2)_{gel} = \frac{1}{(f_1 - 1)(f_2 - 1)}
\] (3.47)

where \(\alpha_1\) is the conversion of reactant 1, \(\alpha_2\) is the conversion of reactant 2, \(f_1\) is the functionality of reactant 1, \(f_2\) is the functionality of reactant 2, and

\[
\alpha_2 = B \alpha_1
\] (3.48)

where \(B\) is the stoichiometric ratio. For an epoxy-amine reaction, where the amine is reactant 1 and the epoxy is reactant 2, \(B\) is the ratio of amino hydrogens to epoxide groups, so Equation 3.16 reduces to

\[
\alpha_{2gel} = \left( \frac{B}{(f_1 - 1)(f_2 - 1)} \right)^{1/2}
\] (3.49)

III.4.4 Chemoviscosity

The molecular weight dependant viscosity change during the reaction has been
modeled using the semi-empirical model\textsuperscript{118-120}

\begin{equation}
\eta(t) = \eta_0 \exp(kt)
\end{equation} \hspace{1cm} (3.50)

where $\eta_0$ represents the minimum viscosity at very low conversion and $k$ is the reaction rate constant. An Arrhenius temperature dependence for both $\eta_0$ and $k$ was introduced by Roller\textsuperscript{121,122} in the form

\begin{equation}
\ln \eta(t) = \ln \eta_{\infty} + \frac{\Delta E_\eta}{RT} + tk_{\infty} \exp \left( \frac{\Delta E_k}{RT} \right)
\end{equation} \hspace{1cm} (3.51)

where $\eta_{\infty}$ is the viscosity at infinite temperature or $T_{\infty}$, $\Delta E_\eta$ is the activation energy for viscosity, $k_{\infty}$ is the rate constant at infinite temperature and $\Delta E_k$ is the activation energy for the reaction kinetics. In the early stage of cure, the viscosity is assumed to be Newtonian. Analogous to models using other techniques, this isothermal model can be modified to a dynamic model by integration of the kinetic term\textsuperscript{123}

\begin{equation}
\ln \eta(t,T) = \ln \eta_{\infty} + \frac{E_\eta}{RT} + \int_0^t k_{\infty} \exp \left( \frac{\Delta E_k}{RT} \right) dt
\end{equation} \hspace{1cm} (3.52)

The change in viscosity during the curing reaction has also been modeled\textsuperscript{124} using a Williams-Landel-Ferry (WLF) equation of the form

\begin{equation}
\log \eta(T) = \log \eta(T_s) + \frac{a(T - T_s)}{b + (T - T_s)}
\end{equation} \hspace{1cm} (3.53)
where $T_S$ is a reference temperature which will depend on the degree of cure and $a$ and $b$ are constants. The shift factor, $a_T$, between the isothermal viscosity functions is defined by

$$a_T = \frac{\eta(T)}{\eta(T_S)}. \quad (3.54)$$

Tajima and Crozier\textsuperscript{125} found $T_S$ to be a linear function of $\alpha^2$ and $\log \eta(T_S)$ to be a linear function of $\alpha$ by regression analysis of epoxy viscosity data. Lee and Han\textsuperscript{126} modified Equation 3.35 to

$$\log \eta(T, \alpha) = (a_1 + b_1 \alpha) - \frac{a_2(b_2 + T - c_2\alpha)}{a_3 + T - c_2\alpha} \quad (3.55)$$

where $a_1$, $a_2$, $a_3$, $b_1$, $b_2$ and $c_2$ are parameters. A simple equation, which is used often, was developed by Castro\textsuperscript{127} and Wang et al.\textsuperscript{128}

$$\frac{\eta}{\eta_0} = \left(\frac{\alpha_g}{\alpha - \alpha_g}\right)^{f(\alpha, T)} \quad (3.56)$$

where $\alpha_g$ is the conversion at the gel point and $\eta_0$ is the initial viscosity at zero conversion at the isothermal temperature, which is described by the Arrhenius equation

$$\eta_0 = A_\eta \exp \left(\frac{E_\eta}{RT}\right) \quad (3.57)$$

where $A_\eta$ and $E_\eta$ are the viscosity dependent pre-exponential factor and activation
energy. This equation has been used successfully for fast curing resins.\textsuperscript{129}

A similar relationship introduced by Stolin et al.\textsuperscript{130} relates $\eta$ to degree of cure with the equation

$$\eta = \eta_\infty \exp(\frac{E_\eta}{RT}) - K\alpha$$ (3.58)

where $\eta_\infty$ is the viscosity at maximum cure, a constant, $E_\eta$ is the activation energy of the viscosity change, and $K$ is a constant. Using this data, good estimations of $\eta$ in time have been found for a TGDDM/DDS system.\textsuperscript{131}

III.5 Decomposition Kinetics

Thermal degradative stability has been related to the degree of cure.\textsuperscript{132} Activation energy of the degradation process increases with increasing cure temperature, implying that increasing crosslink density, raises the amount of thermal energy required to degrade the chemical structure. Prime\textsuperscript{133} has verified this for a cross-linking magnetic tape coating. The degree of cure of many thermosets have been investigated by TGA thermal stability.\textsuperscript{134-136}

Degradation of cured epoxies is a multistep process, which includes chain scission, char formation or carbonization, and char stabilization.\textsuperscript{137} Since both TGDDM and DDS contain aromatic ring structures and the network contains cyclic structures, degradation begins at these points.\textsuperscript{138-140}

TGA degradation kinetics may be performed by either isothermal or by varied heating rate methods. The derivation of the equations from differentiation and
integration of formulas relating the degree of cure to activation energy and temperature are described elsewhere by Dickens and Flynn, Flynn and Wall, and in the ASTM standard. Although a series of isotherms of different samples at different temperatures can be performed, and the curves analyzed by classical curve fitting and the parameters determined, the technique is very time consuming and tedious, and other techniques give similar results. A technique called “factor-jump” simulates the series of isotherms by using temperature jumps between isotherms with one sample. This is similar to the temperature-jump and pressure-jump methods common in chemical rate measurements. In the factor-jump method, the sample is subjected to a series of isotherms, with rapid jumps between the isotherms, while the weight and temperature are monitored. The activation energy is estimated from the relationship:

\[
E_a = \frac{RT_2 T_2}{T_2 - T_1} \ln \frac{r_2}{r_1}
\]

(3.59)

where \(r\) and \(T\) are the rates and temperatures of the two isotherms. These isotherms are assumed to occur at the same degree of conversion, thus this is not a variable. A common method in TGA degradation stability is the use of multiple scanning rates. The scanning rate and temperature of degradation are related by

\[
\ln \beta = 1.05\left(\frac{E_a}{RT}\right)
\]

(3.60)
where $\beta$ is the scanning rate and $E_a$ is the activation energy associated with the degradation process occurring at temperature $T$.\textsuperscript{148-150} The activation energy can be calculated by plotting $\ln \beta$ versus $1/T$ for a series of different heating rate scans.

### III.6 TTT and CHT Diagrams

Adjusting parameters during thermoset curing was difficult in industry until the introduction of the TTT diagram since a 10% decrease in temperature didn’t usually correspond to a 10% increase in curing time. In fact, a 10% decrease in temperature might produce uncured parts regardless of the time given. The TTT diagrams have been used extensively to describe time and temperature dependent transformations in metals\textsuperscript{151} for many years, especially in nonequilibrium states. The adaptation of the TTT diagram to thermosetting polymers by Gillham and Enns\textsuperscript{152} gave a fast easy to read understanding of the relationship between processing parameters and an understanding of the physical state of the material in response to the conditions it had been exposed to. The TTT diagram tells processors what temperature to store their materials to ensure no precuring, how much they can precure material and still ensure adhesion between components, how much they have to precure to ensure dimensional stability, what the optimum processing conditions should be, the lowest temperature that ensures full cure or a certain degree of cure and the maximum cure temperature to avoid degradation. A TTT diagram is usually presented with $T_g$ plotted as as a function of the natural logarithm of curing time in isoconversion curves.\textsuperscript{153,154} The primary curves shown are gelation and vitrification as a function of time and temperature.
Figure 3.1: A typical Time-Temperature-Transformation (TTT) diagram, showing the various physical states caused by time and temperature-dependent curing.

One limitation with a TTT diagram is that many isotherms and $T_g$ scans must be done. While special DSC’s capable of high heating rates, described in Chapter 2, can perform multiple scans on a single sample, traditional DSC and other $T_g$ measurements like DMA and TMA require many measurements on multiple samples to determine the individual points used to construct each line. One alternative to the many measurements required for a TTT diagram is to construct a similar Continuous Heating Transformation (CHT) diagram from a series of single scans at different rates,
dramatically reducing the number of experiments required.

The CHT diagram is constructed from single scans at different rates as shown in Figure 3.2. Each scan is plotted on a temperature vs. natural log time graph with the key transitions indicated by points. The points representing initial $T_g$, gelation (from DMA scans) and vitrification from all of the scans can be connected to form a transformation diagram which gives the same information as a TTT diagram.

![Figure 3.2](image)

Figure 3.2 A typical Continuous Heating Transformation (CHT) diagram, with the scans represented by lines and the resulting transformations connected by a dashed line.
III.7 Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CHT</td>
<td>Continuous Heating Transformation</td>
</tr>
<tr>
<td>DDS</td>
<td>4,4’-diaminodiphenylsulfone</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<tr>
<td>TGDDM</td>
<td>tetracyclic 4,4-diaminodiphenyl methane</td>
</tr>
<tr>
<td>TTT</td>
<td>Time-Temperature-Transformation</td>
</tr>
<tr>
<td>WLF</td>
<td>Williams-Landel-Ferry</td>
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III.8 Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>amine concentration.</td>
</tr>
<tr>
<td>$a_T$</td>
<td>shift factor in time-temperature superposition.</td>
</tr>
<tr>
<td>A</td>
<td>preexponential term or frequency factor.</td>
</tr>
<tr>
<td>B</td>
<td>stoichiometric ratio of amine hydrogen to epoxide equivalents.</td>
</tr>
<tr>
<td>c</td>
<td>segment mobility</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat capacity at constant pressure.</td>
</tr>
<tr>
<td>e</td>
<td>epoxide concentration.</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy of reaction or transformation.</td>
</tr>
<tr>
<td>f</td>
<td>functionality of components, i.e. number of functional groups on reactant.</td>
</tr>
<tr>
<td>HX</td>
<td>abbreviation for hydroxyl groups</td>
</tr>
<tr>
<td>k</td>
<td>rate constant.</td>
</tr>
<tr>
<td>K</td>
<td>constant</td>
</tr>
</tbody>
</table>
m order of catalytic term in autocatalytic reaction.

n order (power function) of non-autocatalytic or nth order reaction.

r rate

R gas constant.

t time.

t_{i,g,p} time to reach specific point i, gel point or peak rate.

T temperature.

T_{0,i,g,p} temperature at beginning of reaction, point i, gel point or peak rate.

α degree of conversion or cure representing the % aliphatic bonds formed.

α_{i,p,g} degree of conversion at a specific value i, peak rate or gel point.

dα/dt rate of conversion in time.

β heating rate.

δ phase angle (usually expressed as tan delta or phase lag)

ε lattice energy

φ heating rate.

Φ chain entanglement factor.

η viscosity

η_{0,∞} viscosity at beginning of reaction or end of reaction.

λ structural parameter

τ relaxation time

ω angular frequency
III.9 References


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CHAPTER IV

EXPERIMENTAL CONDITIONS

The two materials used in this study were a high temperature epoxy molding compound and a commercial epoxy system. The high temperature molding compound is a premixed compound of the tetrafunctional epoxy tetruglycidyl 4,4-diaminodiphenyl methane (TGDDM) and the tetrafunctional amine curing agent 4,4′-diaminodiphenyl-sulfone (DDS), along with an ionic initiator/accelerator and a thermoplastic, designated 8552 by its manufacturer Hexcel. The compound was provided as neat resin and as 66 weight percent glass fiber reinforced preregs, both as uniaxial and biaxial fibers.

The commercial epoxy system is a DGEBA epoxy resin and a separate aliphatic amine, manufactured by System3. The System3 epoxy resin was mixed with the curing agent and in the fluorination studies was also mixed with a mixture of aliphatic amine and various fluorinated amines, including 2-fluoroaniline, 3-fluoroaniline, 4-fluoroaniline, 3,5-difluoroaniline, 3,4-difluoroaniline, 2,6-difluoroaniline, 3-aminobenzotrifluoride and 3,5-bis(trifluoromethyl)aniline obtained from Fluorochem USA (West Columbia, SC).

Differential Scanning Calorimetry (DSC) experiments were performed on a Perkin-Elmer DSC-7 (power compensation type) operating on a UNIX platform using ice coolant and nitrogen (30 ml/min) purge gas on resin and composite samples of 5 to 10 mg, weighed on an analytical balance to ±.05 mg enclosed in crimped aluminum pans. Isothermal measurements were performed at 10 K intervals between 100 and 180°C scanning from ambient to the isothermal temperature at 40 K/min and holding at the isotherm for an appropriate time (100 - 1000 minutes). Temperature scans for total
enthalpy changes and glass transition temperatures were performed using the same conditions with a scanning rate of 5 K/min from ambient to 350°C. The DSC-7 was burned out and calibrated for temperature with indium and zinc. It was also calibrated for enthalpy using the heat of fusion of indium at the beginning of this project and on a monthly basis during the project. The sensitivity of the DSC-7 is 35 µW with calorimetric precision of 0.1 %. The temperature accuracy and precision is 0.1 °C.

TMDSC experiments were performed on a Perkin-Elmer Pyris-1 operating on a Windows NT platform using liquid nitrogen as the coolant and helium (20 ml/min) as the purge gas on resin and composite samples of 5 to 10 mg in crimped aluminum pans. Isothermal measurements were performed at 10 K intervals between 120 and 180°C holding for an appropriate time (100 to 500 minutes). Temperature scans were performed from subambient (-100°C) to 300°C at 10 K/min. The Pyris-1 was burned out and calibrated for temperature with both indium and zinc standards and for enthalpy with the heat of fusion of indium at the beginning and monthly during the project. The sensitivity of the Pyris-1 is 35 µW with calorimetric precision of 0.1 %. The temperature accuracy and precision is 0.1°C.

Step Scan experiments were performed on a Perkin-Elmer Pyris-1 operating on a Windows NT platform using liquid nitrogen as the coolant and nitrogen (20 ml/min) as the purge gas on resin and composite samples of 5 to 10 mg in crimped aluminum pans. Temperature scans were performed from subambient (-100°C) to 300°C at 10 K/min. The Pyris-1 was burned out and calibrated for temperature with both indium and zinc standards and for enthalpy with the heat of fusion of indium at the beginning
and monthly during the project. The sensitivity of the Pyris-1 is 35 $\mu$W with calorimetric precision of 0.1 %. The temperature accuracy and precision is 0.1°C.

Hyper DSC (high heating rate) experiments were performed on a Perkin-Elmer Diamond DSC operating on a Windows 2000 platform using liquid nitrogen as the coolant and helium (20 ml/min) as the purge gas on resin samples of 5 to 10 mg in crimped aluminum pans. Temperature scans were performed from subambient (-100°C) to 300°C at rates up to 500 K/min. The Diamond DSC was burned out and calibrated for temperature with both indium and zinc standards and for enthalpy with the heat of fusion of indium at the beginning and monthly during the project. The sensitivity of the Diamond DSC is 35 $\mu$W with calorimetric precision of 0.1 %. The temperature accuracy and precision is 0.1°C.

Thermomechanical Analysis (TMA) experiments were performed on a Perkin-Elmer TMA-7 operating on a UNIX platform using ice coolant without a purge gas on composite prepregs cubes of 5 mm per side. A quartz linear expansion probe was used on both the surface of the cube and on the movable piston of a quartz dilatometry cup. Temperature scans were performed from ambient to 300°C at 10 K/min, using a probe force of 5 mN except in the pressure dependence studies where the force was varied from 5 to 20 mN. The temperature was calibrated using indium under the compression probe tip. The linear sensivity of the TMA-7 is 0.4 mm. The temperature accuracy is $\pm$ 2°C.

Dynamic Mechanical Analysis (DMA) experiments were performed on a Perkin-Elmer DMA-7e operating on a Windows NT platform using either ice or liquid nitrogen
coolants depending on the experiment and nitrogen (30 ml/min) purge gas on composite prepreg tape (2 mm X 10 mm X 10 mm). Temperature scans were performed from either ambient or subambient (-100°C) to 300°C. Isotherms were performed from ambient to the isotherm at 20 K/min and held for an appropriate time with isothermal temperatures at 10 K increments between 120 and 180°C. DMA experiments were performed using steel three point bending and parallel plate fixtures. The DMA instrument was calibrated for temperature with indium and for force with a 500 mg weight, as well as for position, deflection and furnace control. The linear sensitivity of the DMA-7e is 0.4 mm. The temperature accuracy is ± 5°C.

Dynamic Mechanical Analysis (DMA) frequency scans were performed on a Perkin-Elmer Diamond DMA operating on a Windows 2000 platform using liquid nitrogen coolant and nitrogen (30 ml/min) purge gas on cured resin samples (2 mm X 10 mm X 10 mm). Temperature scans were performed from ambient to 300°C. These experiments were performed using steel flexural fixtures. The linear sensitivity of the Diamond DMA is 0.4 mm. The temperature accuracy is ± 5°C.

Thermally Stimulated Depolarization (TSD) experiments were performed on a Thermold TSC/RMA using liquid nitrogen coolant and ultra-high purity helium as the purge gas and chamber atmosphere. Steel screw-down 5 mm diameter disc fixtures were used on tape prepregs. The poling temperature was the same as the isothermal curing temperature - between 120 and 180°C. The poling time was 5 minutes with a 500 V/m electric field. The total curing time was the sum of the poling time and prepoling time at the curing temperature. The cooling ramp was 5 K/min, and the
depolarization heating ramp was 2 K/min. The current sensitivity of the Thermold TSC/RMA is 1 femtoampere. The temperature accuracy is ± 5°C.

Thermogravimetric Analysis (TGA) experiments were performed on a Perkin-Elmer TGA-7 operating on a UNIX platform using air cooling and dry air (30 ml/min) as the purge gas and as the pneumatic control source on prepreg tape samples of about 50 mg. Temperature scans were performed from ambient to 500°C at rates of 5, 10, 20 and 40 K/min. The TGA was calibrated for temperature with a two standard calibration using the magnetic Curie temperatures \( T_c \) of Perkalloy \( T_c = 596°C \) and Alumel \( T_c = 163°C \). The microbalance was calibrated for weight with a 100 mg standard. The weight sensitivity of the TGA-7 is 0.1 µg, with accuracy of 0.1 % and precision of 10 ppm. Temperature accuracy is ± 5°C.

Tribological scratch testing was performed on a CSEM microscratch tester using CSEM software version 2.3. The indenter was a 200 micron radius diamond tipped Rockwell indenter.
CHAPTER V

RESULTS

V.1 Heat of Reaction

Isothermal Differential Scanning Calorimetry (DSC) scans were performed to characterize the time and temperature-dependent rates and degrees of conversion. The isothermal scans are presented in Figure 5.1. The results of integration and fitting the data to the autocatalytic model, given in Chapter 3 as Equations 3.2 and 3.5, are: the activation energy is $54.9 \pm 7.0$ kJ/mol, the natural logarithm of the preexponential term is $8.38 \pm 0.02$ s$^{-1}$ and the combined reaction order equal to one with $n = 0.7$ and $m = 0.3$. The total enthalpy change is $557 \pm 1$ J/g obtained from a separate DSC temperature scan. The plot using DSC results of degree of conversion as a function of time for the isothermal temperatures studied is presented in Figure 5.2. Figures 5.3 presents the calculated isochronal time curves on a conversion vs. curing temperature plot. Figure 5.4 illustrates the temperature dependence of the combined rate constant, $k = k_1 + k_2$, in a plot of natural logarithm of $k$ vs. inverse temperature $(1000/T)$ from which the activation energy is calculated. Figure 5.6 is a plot of natural logarithm of rate $(\ln d\alpha/dt)$ as a function of natural logarithm of conversion $(\ln \alpha^n(1-\alpha)^m)$. Figure 5.7 depicts the calculated isoconversion curves demonstrating the relationship between time and temperature.
Figure 5.1: Series of isothermal DSC heat flow measurements showing the changes in enthalpy in time for three temperatures: 120, 140 and 160 °C, which are proportional to the number of constituents reacting in time.

Figure 5.2: Calculated conversion vs. time for curing temperatures given in °C using data from isothermal autocatalytic measurements.
Figure 5.3: Calculated conversion vs. curing temperature for several isochronal times, given in minutes from isothermal autocatalytic DSC results.

Figure 5.4: Calculated temperature dependent function k from isothermal autocatalytic DSC results.
Figure 5.5: Calculated natural logarithm of $k$ as an inverse function of temperature for each isothermal temperature with isoconversion lines.

Figure 5.6: Calculated natural logarithm $k$ as a function of natural logarithm conversion, given by the order parameters $m$ and $n$ with isothermal lines drawn from isothermal autocatalytic DSC results.
Figure 5.7: Calculated conversion as a function of time and temperature, shown are isoconversion curves from isothermal autocatalytic results.

V.2 Dynamic Differential Scanning Calorimetry

Dynamic kinetics were determined with both single scan and with varied scanning rate methods. These were done to compare with the isothermal results and determine the reliability of scanning kinetics.

The single scan method, shown in figure 5.8, was applied with the scanning rate of 5 K/min. The results of integration of this curve are that the activation energy is $81.9 \pm 3.1 \text{ kJ/mol}$ and the natural logarithm of the preexponential factor is $15.3 \pm 0.9 \text{ s}^{-1}$ with the reaction order estimated as one. Figures 5.9 and 5.10 are plots of the calculated degree of conversion as a function of time and temperature. Figure 5.11 is a plot of natural logarithm of the rate constant as a function of inverse temperature $(1000/T)$. Figure 5.12 is a plot of calculated isoconversion curves as a function of time and temperature. An additional single scan experiment was performed with the rate of
10 K/min providing similar results: the activation energy is $81.0 \pm 1.5$ kJ/mol and the natural logarithm of the preexponential factor is $14.7 \pm 0.4 \text{ s}^{-1}$.

![Figure 5.8: DSC single scan at 5 K/min for use in kinetic calculations.](image)

![Figure 5.9: Results of calculated conversion vs. time at specified curing temperatures given in °C, from single scan kinetic equation.](image)
Figure 5.10: Results of calculated conversion vs. temperature at specified curing times given in minutes, calculated from single scan kinetic equation. Note: curves shift to shorter times at higher temperatures.

Figure 5.11: Calculated temperature dependent function $k$ from single scan kinetics.
Figure 5.12: Calculated conversion as a function of time and temperature, shown are isoconversion curves. Note: shape of curves demonstrates Arrhenius relationship and high conversion curves have higher time and temperature values.

Scanning DSC measurements were also done using the multiple scanning rate method. The scanning rates were 5, 10 and 20 K/min, as shown in Figure 5.13. The values of peak conversion and scanning rates were fitted to Equation 3.25, shown in Figure 5.14. The resulting activation energy is $61.8 \pm 4.3$ kJ/mol.

Figure 5.13: DSC scanning exotherms for three scanning rates, 5, 10 and 20 K/min with peak conversion rates identified and total integrated change in enthalpy given.
Figure 5.14: Curve fit of the natural logarithm of scanning rates as a function of inverse temperature from which activation energy and preexponential factor can be calculated. High value of coefficient (R) indicates precision of equation fit to data.

V.3  Glass Transition Temperature Shift

The glass transition temperature shift as a function of time and temperature was performed by DSC and Thermally Stimulated Depolarization (TSD). The DSC studies were performed by curing at a certain time and temperature in isothermal mode, quenching and performing a temperature scan. The $T_g$ was calculated as the onset of the shift in baseline heat flow since the half difference in heat flow shift could not be accurately determined due to the residual exotherm overlap with the later part of the $T_g$ shift. The $T_g$ values of various time and temperature values are displayed graphically in Figure 5.15. Plotting the $T_g$ shift as a function of time on a logarithmic time scale, shown in Figure 5.16, allows calculation of the shift factor by Equations 3.33 and 3.34, shown in Figure 5.17. Since the slopes are approximately equal, the shift factor is
Figure 5.15: $T_g$ shift as a function of time at curing temperatures as measured from DSC with the ultimate $T_g$ for each temperature shown as a line from TSD.

Figure 5.16: $T_g$ shift as a function of time at various curing temperatures, plotted on logarithmic scale so shift factor can be calculated.
Figure 5.17: Natural logarithm of the shift factors as a function of inverse temperature, from which activation energy and preexponential factor are calculated.

determined by the difference in time-intercepts (x-intercept) from curve fitting. The activation energy is calculated as the slope of the plot of shift factors as a function of inverse temperature. The activation energy by this method is $65.9 \pm 1.2$ kJ/mol.

The TSD measurements of chain mobility and $T_g$ were performed similarly by curing at an isothermal temperature for a certain time (including the poling time), quenching, and subsequently scanning as a function of temperature. The $T_g$ (increase in mobility) is taken as the peak in discharge current. The $T_g$'s of the maximum isothermally cured samples were well resolved using TSD; however, the partially cured samples showing the $T_g$ shift with curing time were unreliable. The TSD apparatus manufacturer recommends and the controlling software requires a slow quench rate (5 to 20 K/min) which is not fast enough to quench the reaction in the partially cured state. For comparison, the other techniques for quenching the reaction use a 50 to 200 K/minute
cooling ramp. The quality of the fully cured $T_g$s justifies further work with TSD which was not possible in this study.

A series of $T_g$'s for the DGEBA epoxy taken at different times during an isothermal experiment is shown in Figure 5.18. Note that unlike the previous series, this series was done with one sample on one program using high speed DSC which drastically reduced the time necessary to generate the series of points.

Figure 5.18: A series of $T_g$'s for DGEBA at 140 °C at various times generated with a single sample on a single high speed DSC program.
V.4 Viscosity

The viscosity as a function of time during a series of isothermal Dynamic Mechanical Analysis (DMA) 3-point bending experiments is presented in Figure 5.19. The area of interest on log scale is shown in Figure 5.20.

![Figure 5.19: Plots of viscosity as a function of time during a series of isothermal DMA 3-point bending measurements.](image1)

![Figure 5.20: Area of viscosity as a function of time curve from which the shift factors are determined.](image2)
Fitting the shift factors shown in Figure 5.20 to a linear relationship between the natural logarithm of shift factor and inverse temperature yields the line shown in Figure 5.21. The Equation of this line was used to calculate the activation energy to be $33.8 \pm 1.8 \text{ kJ/mol}$ and the preexponential factor to be $1.5 \pm 0.5 \text{ s}^{-1}$.

Figure 5.21: Curve fit of shift factors from superposition of viscosity curves from which activation energy and preexponential factor can be calculated.

The viscosity change during curing at various isothermal temperatures is shown in Figure 5.22. The curves are DMA parallel plate measurements providing better resolution at low viscosity values. The values of the minimum viscosities are plotted as a function of inverse temperature in Figure 5.23. Substituting the slope and intercept into the Arrhenius equation, Equation 3.57, the viscosity activation energy is calculated to be $17.5 \pm 2.5 \text{ kJ/mol}$ and the logarithm of the preexponential factor is $10.7 \pm 0.7 \text{ s}^{-1}$.
Figure 5.22: A series of isothermal parallel plate viscosity plots in time.

Figure 5.23: Curve fit of time to minimum complex viscosity for various isothermal temperatures plotted as natural logarithm vs. inverse time.
V.5 Thermal Stability

The rate of thermal decomposition was determined by variable scanning rate TGA studies. The kinetic rate was calculated using Equation 3.60 with linear regression. The activation energy of decomposition is $131.9 \pm 12.0 \text{ kJ/mol}$ and the natural logarithm of the preexponential factor is $15.1 \pm 2.0 \text{ s}^{-1}$ with a first order decomposition reaction. Similar work in the literature\(^1\) found a much lower value, around $50 \text{ – } 80 \text{ kJ/mol}$. The series from which this calculation was performed is presented in Figure 5.24.

![Figure 5.24: The series of different scanning rate thermal decomposition curves, plotted as weight loss as a function of temperature, from which the activation energy and preexponential factor are calculated.](image)
V.6 Comparison of Kinetic Results

A compilation of the results of activation energy and natural logarithm of the preexponential factor calculations of the techniques used is presented in Table 5.1.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_a$(kJ/mol)</th>
<th>$\ln A$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC Isothermal</td>
<td>54.9 ± 7.0</td>
<td>8.38 ± 0.02</td>
</tr>
<tr>
<td>DSC Single scan</td>
<td>81.9 ± 3.1</td>
<td>15.3 ± 0.9</td>
</tr>
<tr>
<td>DSC Multiple scan</td>
<td>61.8 ± 4.3</td>
<td>14.2 ± 1.1</td>
</tr>
<tr>
<td>DSC $T_g$ Shift Factor</td>
<td>65.9 ± 1.2</td>
<td>11.0 ± 0.4</td>
</tr>
<tr>
<td>DMA Viscosity Shift Factor</td>
<td>33.8 ± 1.8</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>DMA Viscosity Minima</td>
<td>17.5 ± 2.5</td>
<td>10.7 ± 0.7</td>
</tr>
<tr>
<td>TGA degradation</td>
<td>131.9 ± 12.0</td>
<td>15.1 ± 2.0</td>
</tr>
</tbody>
</table>

Table 5.1: Results of calculation of activation energy and preexponential factor.

Values for activation energy in the literature for similar prepregs are 50,$^2$ 71,$^3$, 73$^4$ and 70$^5$ kJ/mol. From these results, an average literature value of 66.0 kJ/mol can be used for comparison. One study in the literature on a similar prepreg using single scan DSC determined the activation energy to be 109$^6$ kJ/mol which is expectedly higher than for other techniques.

The results given in Table 5.1 cover a large range of activation energy values; however, three of the seven techniques are in the range reported in the literature. The three results which agree with literary values are from isothermal, multiscan and $T_g$ shift by DSC. The $T_g$ shift result is the closest to the average reported in the literature. The single scan DSC is somewhat higher in activation energy value, likely due to the effect observed and explained in literature comparisons of isothermal and single scan DSC studies.$^7$-$^11$ The viscosity shift factor result is less than the literary average by about 50 %, which implies that it is useful but within limitations. The viscosity minima calculations produce a very low value of activation energy; however, this is the viscosity...
activation energy not the kinetic activation energy produced in the other methods. The result from TGA degradation is higher than the rest of the techniques, as well as higher than the literature values. This implies that this value does not follow the same model as the rest. This is reasonable since thermal stability, while related to degree of cure, is not necessarily a simple one-to-one linear relationship.

V.7 Transformations

V.7.1 Gelation

The gel point was identified as the lower of the two peaks in the tan δ of parallel plate DMA isotherms, shown in Figure 5.25. This feature is also evident in three-point bending DMA isotherms as a small peak or shoulder, shown with the corresponding parallel plate isotherm in Figure 5.26. Gelation occurs at a certain degree of conversion, so it appears as an isoconversion line on the TTT diagram.

V.7.2 Vitrification

Vitrification was determined by TMDSC and DMA isotherms and Step Scan DSC ramps. TMDSC isotherms showing the characteristic downward shift in baseline storage \( C_p \) are shown in Figure 5.27. Vitrification appears in DMA measurements as the higher of two peaks in the tan δ, as shown in Figure 5.28. Vitrification also appears in parallel plate DMA isotherms, shown in Figure 5.25. Due to the extremely high modulus of the glass fiber reinforced prepreg, the vitrification point is not well resolved in parallel plate measurements.

Vitrification points during scanning experiments were performed using Step Scan DSC at various rates. The curing exotherm was separated from the rubber to glass
transition and the time of half height change was recorded. The curing exotherm was used to determine the time/temperature of full cure or the point of flat baseline.

Figure 5.25: DMA parallel plate isotherm (160°C) showing the gel point as the lower temperature peak of two in tan δ and the vitrification point as the higher temperature transition. Note that gelation is evident in tan δ and storage and loss moduli. Also, vitrification is poorly resolved.
Figure 5.26: A plot of $\tan \delta s$ from both parallel plate and three-point bending DMA isotherms (120°C), with gelation visible in both as the lower temperature peak.

Figure 5.27: TMDSC isotherms showing vitrification as the half height drop in $C_p'$. Note: vitrification occurs at higher times for lower curing temperatures.
Figure 5.28: A tan δ plot in time from a DMA three-point bending isotherm (at 120°C) with the gelation and vitrification points identified. Note: vitrification is well resolved while gelation appears as a shoulder.

Figure 5.29: Plots of tan δs from both parallel plate and three-point bending DMA isotherms (at 160°C) showing difference in sensitivity to vitrification.
V.7.3 Time-Temperature-Transformation Diagram

A time-temperature-transformation (TTT) diagram, Figure 5.30, was constructed from the best resolved gelation and vitrification data. The initial $T_g$ was determined by both TMDSC and DMA three-point bending, with TMDSC having greater temperature accuracy. The final $T_g$ was measured by TMDSC, TMA and DMA three-point bending with DMA being the best resolved. The increase in $T_g$ with time at various temperatures was measured by DSC, gelation was measured by DMA parallel plate and vitrification was measured by TMDSC and DMA three-point bending. The regions and transitions identified follow conventions proposed by Gillham. Notable curing temperature effects can be seen in the TTT diagram. At temperatures below the $T_{g0}$ ($6^\circ C$) there is no reaction, so this is the safe storage temperature. Between $T_{g0}$ and $T_{g-gel}$ ($6$ to $86^\circ C$) the material will react, albeit very slowly, and will eventually vitrify before it gels. Between $T_{g-gel}$ and $T_{g-vit}$ ($86$ to $248^\circ C$) the material will first gel, then vitrify. Above $T_{g-vit}$ ($248^\circ C$) the material will gel, but will not vitrify. This diagram provides an easy to read description of the transformations taking place in processing of composite prepregs, and allows manipulation of processing conditions to modify physical properties. This TTT diagram is consistent with a similar diagram\textsuperscript{12} for DDS cured TGDDM found in the literature.
Figure 5.30: Time temperature transformation diagram for the TGDDM/DDS system in this study with gelation and vitrification curves identified. The initial $T_g$ used for the curve was determined by DSC; however, the value from DMA three-point bending is included as points for comparison. The gelation points were determined by DMA parallel plate measurements. The points used to construct the vitrification curve were determined by TMDSC; however, values from DMA three-point bending were included as experimental points for comparison. The final $T_g$ values were determined by DMA three-point bending, TMDSC and TMA, with DMA three-point bending values used to construct the curve since it was the highest, ensuring that this is the maximum.
V.7.4 Continuous Heating Transformation (CHT) Diagram

The glass to rubber and rubber to glass transitions determined from Step Scan DSC temperature scans were used to construct the CHT diagram shown in Figure 5.31. Three lines connecting the glass to rubber transition points, the rubber to glass transition points (vitrification points) and the points of final cure at the end of exotherms, indicate the physical states of the reacting epoxy.

Figure 5.31: The CHT diagram constructed from Step Scan DSC scanning measurements. Average heating rates, including both heating and isotherm, are plotted on a temperature vs. Log time. The initial $T_g$ and vitrification points are indicated on each scan line. The points are connected to indicate a transformation.
V.8 Shrinkage

The results of prepreg shrinkage during the curing process in the mold from dilatometry for different pressures and fiber orientations after separating the void elimination and fiber rearrangement from the resin shrinkage are presented in Figures 5.32 and 5.33.

The shrinkage due to fiber rearrangement shows a strong dependence on the cure temperature, the pressure applied and the fiber orientation. Higher pressure (10 psi vs. 5 psi) results in larger shrinkage. Higher cure temperatures (160°C vs. 120 and 100°C) typically result in lower shrinkage, due to the faster reaction rate which means less time for rearrangement before gelation and the faster increase in viscosity. At the lowest cure temperature (100°C), when there is sufficient time for rearrangement, biaxially oriented fibers exhibit higher bulk shrinkage than uniaxial ones, likely due to the higher void content between the layers. At higher cure temperatures (120 and 160°C), the orientation has less effect.

As expected, the resin shrinkage is a constant 0.5 % regardless of orientation, cure temperature or pressure. Since the resin shrinkage is due to chemical bonding and network structure, it should be a constant value, and epoxies in general have very low values of shrinkage. In addition to providing the shrinkage value, the consistency verifies that the separation of chemical and macroscopic changes are correct.
Figure 5.32: The change in volume due to void elimination and fiber rearrangement measured by dilatometry at cure temperatures of 100, 120 and 160 °C and pressures of 5 and 10 psi for both uniaxial and biaxial fibers.
Figure 5.33: The change in volume due to resin shrinkage during cure measured by dilatometry at cure temperatures of 100, 120 and 160 °C and pressures of 5 and 10 psi for both uniaxial and biaxial fibers. The scaling chosen is appropriate for the precision of the measurement.
V.9 Fluorinated Amine Curing Agents

The eight fluoroanilines described in Chapter 1 were used in conjunction with the aliphatic amine to cure the DGEBA epoxy and were evaluated for wear resistance and physical properties, as well as verification of cure state. The results of wear testing, shown in Figure 5.34, imply that the formulations with 2- and 3-fluoroamine and 3,5 difluoroaniline reduce the wear rate of the epoxy, namely the depth of the probe as a function of the number of passes was less than that of the unmodified epoxy.

Figure 5.34: Results of tribological wear testing for various fluorinated amines. The probe depth as a function of distance across the 100 mm test area (0 – 100 mm is first pass, 101 – 200 is second pass on same area) is shown for each compound.
Since physical properties unrelated to the presence of fluorine groups, such as degree of cure and hardness, may also affect the wear properties, the storage moduli and frequency dependence of the tan δs of the formulations were measured and activation energies calculated to compare to the unmodified cured epoxy. The storage modulus of the unmodified epoxy at 1 Hz is 4.7E7 Pa, with the peak in tan δ occurring at 52°C, as shown in Figure 5.35. The corresponding frequency dependent activation energy is 317.8 kJ/mol, as shown in Figure 5.36.

The storage modulus of the 2-fluoroaniline-cured epoxy at 1 Hz is 8.0E7 Pa, with the peak in tan δ occurring at 38°C, as shown in Figure 5.37. The corresponding frequency dependent activation energy is 224.2 kJ/mol, as shown in Figure 5.38.

The storage modulus of the 3-fluoroaniline-cured epoxy at 1 Hz is 5.0E8 Pa, with the peak in tan δ occurring at 46°C, as shown in Figure 5.39. The corresponding frequency dependent activation energy is 370.1 kJ/mol, as shown in Figure 5.40.

The storage modulus of the 3,5 difluoroaniline-cured epoxy at 1 Hz is 6.0E8 Pa, with the peak in tan δ occurring at 48°C, as shown in Figure 5.41. The corresponding frequency dependent activation energy is 381.6 kJ/mol, as shown in Figure 5.42.

In the three formulations, the storage moduli increased, the Tgs indicated by peak in tan δ decreased and the activation energies of the transitions changed. The storage modulus for the 2-fluoroaniline formulation increased by a small amount, while the other two increased by an order of magnitude. This is expected, since the incorporation of aromatic rings will make the network more rigid. The decrease in Tgs
and lower activation energies are likely due to the lower amine functionality, resulting in lower degree of crosslinking.

Figure 5.35: DMA frequency scan of unmodified epoxy showing storage and loss moduli for various frequencies, as well as the corresponding tan δs.

Figure 5.36: Activation energy of unmodified epoxy calculated from frequency dependence of tan δ.
Figure 5.37: DMA frequency scan of 2-fluoroaniline-cured epoxy showing storage and loss moduli for various frequencies, as well as the corresponding tan δs.

Figure 5.38: Activation energy of 2-fluoroaniline-cured epoxy calculated from frequency dependence of tan δ.
Figure 5.39: DMA frequency scan of 3-fluoroaniline-cured epoxy showing storage and loss moduli for various frequencies, as well as the corresponding tan δs.

Figure 5.40: Activation energy of 3-fluoroaniline-cured epoxy calculated from frequency dependence of tan δ.
Figure 5.41: DMA frequency scan of 3,5 difluoroaniline-cured epoxy showing storage and loss moduli for various frequencies, as well as the corresponding tan δs.

Figure 5.42: Activation energy of 3,5 difluoroaniline-cured epoxy calculated from frequency dependence of tan δ.
Fluorinated compounds tend to phase separate in mixtures, many times migrating to the surface of the mixture due to Gibbs function considerations. This can be advantageous in the case of self-stratifying coatings, i.e. a small amount of fluorinated compound migrates to the surface of the bulk compound to form a coating. However, it can be a disadvantage if the goal of fluorination is to modify bulk properties, as in attempts to increase bulk electrical resistance or dielectric strength.

The fluorinated aniline-cured epoxy systems were all tested by infrared scans across a cross sectional sample to test for phase separation. The distribution of fluorine groups was determined to be equivalent across the entire cross section, which means that there was no phase separation or migration of the fluorine functional groups. The most likely explanation for the lack of phase separation is that the viscosity increases and the network forms faster than the fluorinated anilines can migrate. Also, since the fluoroanilines are aromatic amines, with a highly electronegative fluorine group, the amine group will be much more reactive than the nonfluorinated aliphatic amine. The fluoroaniline should react quickly with the epoxy monomers, thus rapidly increase in molecular weight and quickly bond to the growing network through crosslinking.
### V.10 Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>CHT</td>
<td>Continuous Heating Transformation</td>
</tr>
<tr>
<td>DDS</td>
<td>4,4’-diaminodiphenylsulfone</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TGDDM</td>
<td>tetraglycidyl 4,4-diaminodiphenyl methane</td>
</tr>
<tr>
<td>TMDSC</td>
<td>Temperature-Modulated Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>TSD</td>
<td>Thermally Stimulated Depolarization</td>
</tr>
<tr>
<td>TTT</td>
<td>Time-Temperature-Transformation</td>
</tr>
</tbody>
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### V.11 Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Celsius (degrees Celsius)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific Heat Capacity</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>J</td>
<td>Joules</td>
</tr>
<tr>
<td>k</td>
<td>rate constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>mm</td>
<td>milimeters</td>
</tr>
<tr>
<td>mol</td>
<td>mole (6.02 X 10^{23} molecules)</td>
</tr>
<tr>
<td>nm</td>
<td>nanometers</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
</tbody>
</table>
\( T \) \hspace{1cm} \text{temperature} \\
\( T_g \) \hspace{1cm} \text{glass transition temperature} \\
\( \alpha \) \hspace{1cm} \text{degree of conversion} \\

V.12 References


CHAPTER VI

CONCLUSIONS

VI.1 Summary

Mechanistic models are not applicable to most industrial prepregs, especially complex systems like the ion-initiated 4,4’-diaminodiphenylsulfone (DDS)-cured tetragnicodyl 4,4-diaminodiphenyl methane (TGDDM) studied here. These models require knowledge of the initial concentrations of all components including impurities and of all steps in the reaction. The simplified mechanistic model for TGDDM/DDS proposed by Horie considers four reaction steps, which have four different rate constants and eight variables. Obviously, fitting an experimental curve to a four term, eight variable equation is meaningless unless each step can be modeled separately.

Phenomenological models monitor property changes during the overall curing reaction and have the advantage of not requiring detailed knowledge of concentrations or reaction mechanisms. The property changes as a function of curing studied were the heat of reaction, shift in glass transition temperature ($T_g$), viscosity and thermal stability. These changes were related to the rate and degree of the curing reaction.

The heat of reaction was studied as the change in enthalpy using differential scanning calorimetry (DSC) in both isothermal and dynamic measurements. Both isothermal and multiscan measurements produce similar values of activation energy consistent with values reported in the literature. Single scan experiments produced higher values of activation energy; however, this result is expected and is consistent with both theory of the technique and with similar studies in the literature. While
Isothermal and multiscan DSC results are both consistent, the multiscan technique is more attractive for industrial applications due to the much shorter time to complete the series of experiments.

The $T_g$ change during the reaction was studied by DSC with the final $T_g$ of each curing temperature determined by thermally stimulated depolarization (TSD) due to limited resolution of DSC at very high crosslink densities. The ultimate $T_g$ at full or maximum cure was determined by thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA). DSC is advantageous due to the small sample size and temperature accuracy; however, it has low sensitivity at high degrees of crosslinking and high filler levels due to heat capacity effects. Although they have lower temperature accuracy due to the furnace size, TSD, TMA and DMA are more sensitive to the $T_g$ at high degrees of crosslinking. In addition, the pressure dependence of TMA and frequency dependence of DMA must be considered. Standard values for pressure in TMA and DMA, frequency in DMA and scanning rate in DSC have been established by organizations like the American Society of Testing and Materials (ASTM) to ensure consistency in reported values. The $T_g$ shift was modeled using the shift factor based on the time-temperature superposition principle. The value of activation energy was slightly higher than the heat of reaction values, but within the range of values in the literature. This could be due to the use of $T_g$ by onset rather than the standard half height shift in baseline heat flow. The use of high heating rate DSC solves these problems by allowing the half height shift $T_g$ to be calculated without the usual
interference from the overlapping curing exotherm, in addition to offering much faster 
$T_g$ series measurements from a single sample on a single program.

The cure-dependent viscosity, chemoviscosity, was monitored by DMA. Two 
methods were used – shift factor and time to minimum viscosity. The shift factor was
determined by comparing a series of isothermal 3-point bending experiments. The 
calculated activation energy was lower than expected, possibly due to the limitations of 
using a bulk phenomenological property to monitor molecular changes. The time to 
minimum viscosity was determined for a series of temperatures using isothermal 
parallel plate experiments. This comparison produces a viscosity activation energy 
which is related to but not equal to the kinetic activation energy - the value calculated 
in the other techniques. Although this value is representative of the changes occurring 
during curing, it can not be easily compared to the results of other methods. The result 
of the minimum viscosity measurements is also limited by the resolution of low 
viscosities in DMA.

Thermal stability of the prepreg was determined by thermogravimetric analysis 
(TGA) using the variable scanning rate technique. The calculated value of activation 
energy is much higher than obtained by other techniques and than the literature values, 
implying that the thermal stability is not directly proportional to the degree of cure.

Cure kinetics is described accurately using isothermal and multiscan heat of 
reaction by DSC and glass transition shift by DSC. Chemoviscosity shift factor produces 
acceptable results while single scan DSC should only be used as an estimation 
technique with expected high results. Thermal stability results are exceptionally high
and should not be used with this epoxy system, unless an appropriate relationship can be established. Likewise, the minimum viscosity results require an appropriate relationship to curing to be useful in models.

While the cure kinetics are important, other effects not described by the models are important in processing, namely gelation and vitrification. These effects, along with cure kinetic information are effectively presented in a time-temperature-transformation (TTT) diagram or a continuous heating transformation (CHT) diagram. Gelation is determined by DMA with parallel plate exhibiting greater sensitivity than 3-point bending. Vitrification is both a thermodynamic transition and a mechanical effect and appears in temperature-modulated DSC (TMDSC) and Step Scan DSC as well as DMA 3-point bending isotherms.

In a processing environment, shrinkage is also an important consideration. The shrinkage due to curing as well as that due to pressure induced void elimination and fiber rearrangement was characterized. While curing causes some shrinkage, the largest dimensional change is due to voids and fiber rearrangement. The void elimination, and especially the fiber rearrangement was dependent on the curing temperature and the pressure applied, while the shrinkage due to curing was not. The quartz dilatometer cell with alumina as a confining fluid produced consistent and reliable data.

Attempts to produce an economical wear-resistant coating material from commercial DGEBA and fluorinated amines produced promising results. Wear resistance was increased in three of the seven formulations, while the goal of
commercially available, economical additives was maintained – each fluoroaniline was added to the epoxy as a curing agent, just like any other amine, so no added complications in processing. The three promising formulations were 2-fluoroaniline, 3-fluoroaniline and 3,5 difluoroaniline.

VI.2 Recommendations

- Multiscan DSC is attractive in industrial settings due to the accuracy of results and the short time to complete the series of experiments.
- Isothermal DSC and $T_g$ shift methods provide accurate results; however, both are time consuming and the isothermal method is limited to low curing temperatures due to lost data during the heating step. These limitations can be compensated for by recent advances. Isothermal DSC should be performed using high heating rate DSC (500 °C/min) to avoid reactions during the ramp to isothermal temperature. The $T_g$ shift measurements should be done with high heating rate DSC, so that one sample can be rapidly scanned for $T_g$, then quenched before any curing takes place, then ramped to the isotherm, cured for a predetermined amount of time, quenched, then rescanned for $T_g$, and so on. This way, one sample and one program series determines all the points for one isothermal curing line.
- DSC is an efficient method for determining the $T_g$ values during the multiple experiments required for the shift model due to the small sample size (5 – 10 mg) and accuracy ($\pm 0.01$ °C); however, resolution decreases with increasing crosslink density. High heating rate DSC increases efficiency of data generation.
• Ultimate \( T_g \) is well resolved using TSD and DMA, extending the range from DSC alone.

• The viscosity shift factor models the reaction; however, the minimum viscosity model is limited by the simplicity of the model (and assumptions) and the limitations of measuring low viscosities using parallel plate DMA.

• Gelation and vitrification are well resolved in DMA with a strong fixture dependence: parallel plate is more sensitive to gelation with three-point bending sensitive to vitrification.

• The time-temperature-transformation (TTT) and continuous heating transformation (CHT) diagrams provide useful processing information in a graphical format making it well-suited in industrial applications.

• Shrinkage due to chemical curing as well as that due to pressure dependent void elimination and fiber rearrangement can be easily determined from a quartz dilatometer measured with a TMA.

• Wear resistance of an epoxy can be economically increased by using a fluorinated aniline curing agent.

VI.3 Suggestions for Future Work

• Residual enthalpy DSC or high heating rate DSC measurements would eliminate the error in the lost area approximation in isothermal measurements and provide \( T_g \) values in the same scan, thus allowing construction of both enthalpy and \( T_g \) models in the same experiment.
• TMDSC and Step Scan DSC would also allow measurement of both residual enthalpy and $T_g$ simultaneously with the added benefit of separation of the signals for improved resolution.

• Minimum viscosity measurements could be improved through the use of a technique sensitive to low viscosity like shear rheometry.

• Shrinkage measurements could be improved by using a higher force TMA and a steel or invar dilatometer cell to simulate pressures closer to those used in compression molding.

• The preliminary attempts to fluorinate a commercial DGEBA epoxy resin with fluorinated amine curing agents should be explored further – the cure state, modulus and tribological properties should all be coordinated to ensure that the effects seen in tribological experiments are actually due to the fluorination and not the physical state.
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