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Cure kinetics characterization and monitoring of an epoxy resin for thick composite structures

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Cure kinetics characterization and monitoring of an epoxy resin for thick composite structures

by

Ricky Hardis

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Industrial Engineering

Program of Study Committee:
Frank E. Peters, Co-Major Professor
Michael R. Kessler, Co-Major Professor
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Iowa State University

Ames, Iowa

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Abstract

The use of fiber-reinforced polymers (FRPs) is increasing for numerous industrial applications. In-situ cure monitoring is very important to directly observe the cure process of FRPs during the manufacturing process. In this work, the possible use for in-situ cure monitoring of an epoxy resin was investigated by means of Raman spectroscopy and dielectric analysis (DEA). The cure behavior was first characterized using differential scanning calorimetry (DSC) as a baseline comparison, and the best-fit phenomenological reaction model was determined to describe the cure behavior of the epoxy resin as well as the kinetic parameters. The relationship between T_g and degree of cure was also established. The degree of cure obtained from the Raman spectroscopy and DEA under isothermal conditions was compared to the one obtained from the DSC. A good agreement was observed among the three methods, supporting in-situ cure monitoring during manufacturing. An implementation plan for in-plant monitoring was also discussed.

Chapter 1: Introduction

1.1 Background

Fiber-reinforced polymers (FRPs) are one category of composites that utilize fiber materials to mechanically increase the strength and elasticity. These fiber materials are interlocked with a weaker matrix (a thermoset resin) and allowed to cure through a polymerization process. There are several factors that need to be taken into account when it comes to producing FRPs that exhibit excellent strength and elasticity. Some of which include mechanical properties of both fiber and resin, orientation and length of the fiber, volume fraction ratio of both fiber and resin, void content and the degree of resin cure [1].

Typically, thermosets consist of a mixture of resin and hardener, and catalysts are usually present in the hardener to accelerate cure. Clearly, the cure phenomenon in thermosets is an exothermic process, which means that heat is generated during cure. Unlike thermoplastics, thermosets such as epoxy, unsaturated polyester, polyurethane, vinyl ester and many others undergo chemical reactions during their use. Because of these reactions, the viscosity of the thermosets increases, and ultimately crosslinking occurs. Therefore, they lose their capability to flow or dissolve. The cure phenomenon, which is the crosslinking process, normally starts with the growth and branching of chains. With the reaction taking place, the increase in molecular mass also becomes faster, causing a decrease in the total number of molecules and an increase in viscosity. Numerous chains are ultimately connected together into a network formation of infinite molecular mass, and therefore the mobility of individual polymer chains consequently diminishes [2, 3]. Once the materials are crosslinked, they turn into an insoluble and infusible rigid part.

The use of FRPs is increasing for numerous industrial applications. For structural and engineering applications, for instance, where both the strength and elasticity are critical, FRPs are commonly used to produce large and complicated structures due to their excellent physical and mechanical properties. A key property is the relatively high strength-to-weight ratio [4-7]. Manufacturing processes of FRPs

have continuously been developed, and some of the industries that use FRPs include aerospace, automotive, marine and construction [7-9]. Building FRPs involves a process in which fiber materials with high strength and high modulus are bonded together with low modulus resin during or after the molding process. As previously mentioned, the fiber materials are often orientated to provide the greatest properties in the desired direction.

There are various molding techniques when it comes to producing FRPs: autoclave/vacuum bag, wet layup, pultrusion, Resin Transfer Molding (RTM), Vacuum Assisted Resin Transfer Molding (VARTM) and others. Although these molding techniques are fairly different from one another, their development process requires a proper mold design, a successful injection strategy and a well-defined cure cycle of the materials [10]. Optimization of these process parameters through trial and error is not preferred due to expensive costs and large time consumption. Therefore, computer simulation models should be employed to design the molding process and optimize the process parameters.

Characterization of the cure kinetics of the resin is one of the prerequisites for designing the molding process and optimizing the process parameters. It has been shown that the cure process is the most crucial stage in the manufacturing of composite parts. Manufacturers of the resin often provide recommendations on its cure cycle, but generally the recommendations cannot be accurately followed in the industry due to differing component and mold geometry. Hence, it is essential to study the curing characterization of the resin first. Characterization, design and optimization of the cure process will help control the exotherm and predict the cure cycle of the materials. Issues such as the time and temperature to reach full cure and the optimum temperature to decrease the cycle time can be addressed. Acceptable cure temperatures can also be proposed to avoid vitrification (glass formation) and high temperatures at which undesirable side reactions or degradation may occur [2].

FRPs are commonly used to manufacture much of the wind turbine blade structure. Subcomponents of the blade include the root, the shear web, the spar cap, the skin and the core, which can be seen in Figure 1. One common blade fabrication

method is to produce the spar cap and root sections separately, and then infuse them into the blade assembly.

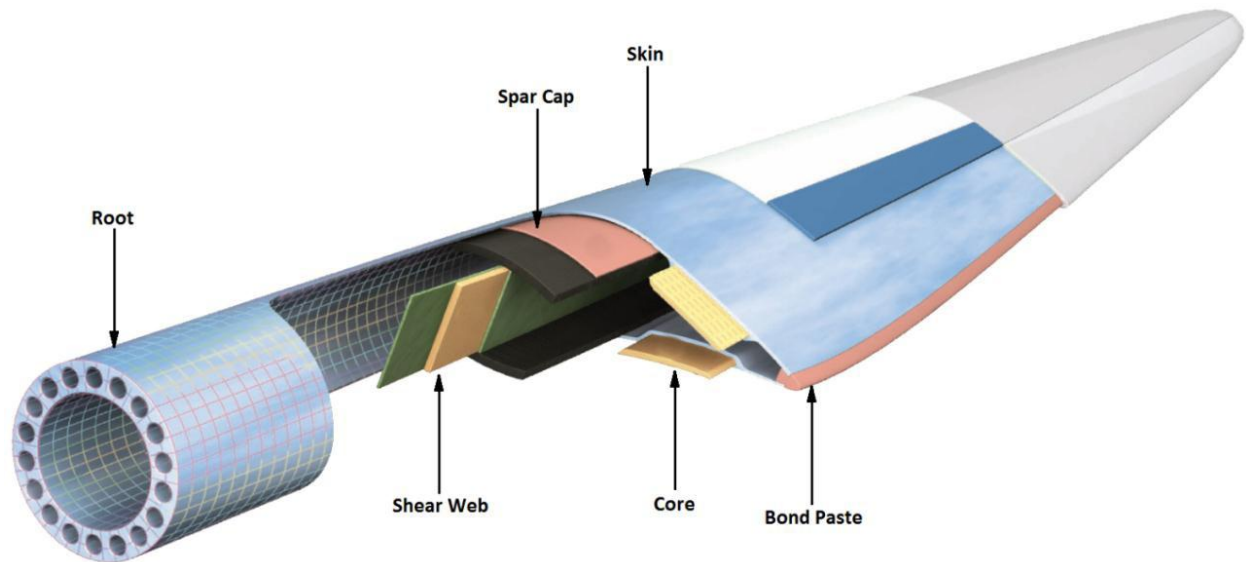


Figure 1: Components of wind turbine blade [11]

The spar cap is the main load carrying member within the blade. For a megawatt scale 40 m turbine blade, the spar cap is approximately 60 mm thick, 500 mm wide and made of unidirectional fabric. The thickness tapers towards the tip end to approximately 15 mm via dropping plies of fabric. The exotherm during cure of the spar cap undergoes different reaction rates at different areas of the spar cap leading to non-uniform curing. This causes heat to develop, and some of the fabric gets restricted when it tries to expand due to varying heat of reaction, creating waves in the fabric. The waves that develop may be internal to the spar cap or could erupt to the surface, as shown in Figure 2. In any case, the waves are critical quality characteristics because they have a significant negative impact on the fatigue life of the blades. These problems are often associated with ineffective curing process parameters.

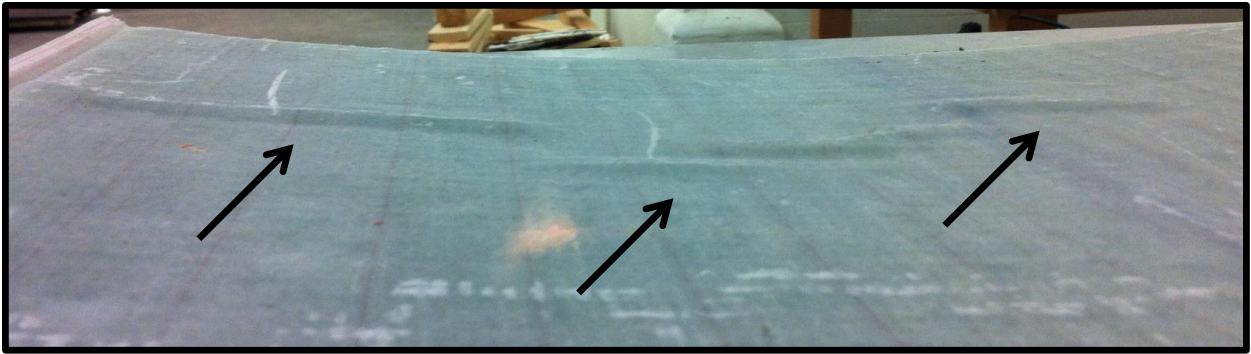


Figure 2: Fabric wave on surface finish

There is a need to precisely monitor and control the cure process to improve the quality of the turbine blades. Without a method to directly measure the cure process, the manufacturers need to determine an adequate cure time to prevent the worst case scenarios that might happen to the parts, such as under-curing and premature demolding. Although an adequate cure time has been established to ensure that the cure reaction is finished, conservative estimates increase the manufacturing cycle times, leading to over-curing which results in poor properties of the part. The goal is to control the cure process during manufacturing via in-situ cure monitoring to ultimately achieve a better quality product.

Many different analytical methods have been studied to characterize the cure reaction and monitor the cure process of thermosets, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) [1, 6, 8, 10, 12-19]. These methods, however, typically are not practiced for in-situ cure monitoring because they are only performed in laboratories under ideal conditions. Previous studies have shown that there are several other useful methods that can be utilized to monitor the cure process in real time including dielectric analysis (DEA), Raman spectroscopy, infrared spectroscopy (IR), and ultrasonic methods [3, 7-9, 12, 20, 21]. It is important that any in-situ cure monitoring method is non-invasive and non-destructive so that the manufacturing process is not influenced or even disturbed.

In this study, the cure behavior of a commercially available epoxy resin system obtained from Momentive Specialty Chemicals (Columbus, OH) was characterized. The epoxy system was based on standard diglycidyl ether of bisphenol A (DGEBA) epoxy

resin and a modified aliphatic amine as a curing agent. The blend system was chosen based on its use in manufacturing wind blades. The cure kinetics of the epoxy system was characterized by means of differential scanning calorimetry (DSC) in both dynamic and isothermal methods. Several phenomenological reaction models were fitted with the dynamic experimental results, and the model that best fit the data was presented to predict the degree of cure at any isothermal temperature. Isothermal measurements of the epoxy resin cure were also conducted using Raman spectroscopy and dielectric analysis (DEA). This study will compare the results on the degree of cure obtained from DSC, Raman spectroscopy and DEA to investigate the possible use for in-situ cure monitoring of thick section composites such as spar caps.

1.2 Differential Scanning Calorimetry (DSC) Overview

Differential Scanning Calorimetry or DSC is a thermal analysis technique used to measure the difference in the amount of heat flow rate necessary to increase the temperature of a sample and a reference as a function of temperature [22]. DSC is a widely used experimental technique to obtain a thorough understanding of the cure process. As a sample is heated, cooled and/or held isothermally, DSC measures the heat flow from or into the sample. The fundamental key in this technique is that when the sample goes through a physical change due to chemical reactions, it will take more or less heat to keep temperature of the sample increasing at the same rate as the reference. This trend will determine whether the process is exothermic or endothermic. Particularly for thermosets, DSC can provide excellent information about glass transition temperature (T_g), onset of cure, heat of cure, maximum rate of cure, completion of cure and degree of cure.

Isothermal measurements and dynamic measurements are the two different approaches that can be utilized to examine the cure kinetics of a resin. Isothermal measurements involve maintaining the sample at a fixed temperature for various time intervals, whereas dynamic measurements involve heating the sample at a constant

rate over a desired temperature range. In the DSC measurements, the degree of cure (α) ranges from 0 (completely uncured) to 1 (fully cured) and is defined as follows:

$$\alpha(t) = \frac{H(t)}{H_T} \quad (1)$$

where $H(t)$ is the heat of the reaction up to time t and H_T refers to the total heat of the reaction. Common DSC measurements involve measurements of the heat flow as a function of time, and the enthalpy can be obtained by integrating the area of exothermic peak, which is the integration of the heat flow.

Once the cure behavior of the resin has been examined with the DSC, it is important to find a kinetics model that can describe the cure behavior. A variety of kinetics models have been developed to relate the rate of cure and degree of cure. Phenomenological reaction models are the most common models to describe thermoset cure reactions [6, 10]. The kinetic parameters of the cure reaction can be obtained by fitting the data obtained from the DSC measurements to the phenomenological reaction models.

In kinetics analysis by DSC, the rate of reaction is assumed to be proportional to the rate of heat generation and can be expressed as:

$$\frac{d\alpha}{dt} = \frac{1}{H_T} \frac{dH(t)}{dt} \quad (2)$$

It is also assumed that the rate of reaction can be defined by two separable functions, $K(T)$ and $f(\alpha)$:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (3)$$

where $d\alpha/dt$ is the rate of reaction, $K(T)$ is the temperature dependent rate constant, and $f(\alpha)$ corresponds to the reaction model. The temperature dependence of the reaction rate is generally defined through an Arrhenius expression:

$$K(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where E_a is the activation energy, A is the pre-exponential factor, R refers to the universal gas constant, and T corresponds to the absolute temperature. Combining the

two equations together and also substituting $\beta = dT/dt$ (the heating rate), the rate of reaction can be defined as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (5)$$

Therefore, if the reaction model which describes the data is known, the conversion obtained at a given temperature or heating rate can be predicted using the above equations. Several kinetics models have previously been proposed to adequately describe the cure behavior of thermosets. In general, the cure behavior of thermosets is usually described by n^{th} order or autocatalytic models, which can be seen in Table 1.

Table 1: Phenomenological reaction models used in this study

Model	Designation	$f(\alpha)$	Parameters
n^{th} Order	Fn	$(1 - \alpha)^n$	A, E_a, n
n^{th} Order Autocatalytic	FnA	$(1 - \alpha)^n(1 + K_{cat}\alpha)$	A, E_a, n, K_{cat}
Prout-Tompkins Autocatalytic	PT	$(1 - \alpha)^n\alpha^m$	A, E_a, n, m

For the isothermal cure measurements, it is important that the degree of cure can be estimated as the reaction progresses. In order to calculate the degree of cure, the first formula can be modified as:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad (6)$$

where ΔH_T equals the total enthalpy of reaction measured at a certain heating rate for an unreacted sample, and ΔH_R is the residual heat of the reaction for the isothermally cured sample for a certain period of time. With this formula, the degree of cure can be calculated as the cure progresses. It is also essential to develop a relationship between α and T_g (glass transition temperature) since T_g provides a better value for monitoring the cure process.

1.2.1 Kissinger Method

From the dynamic DSC measurements, the kinetic parameters can also be determined by using the Kissinger method in which the activation energy and pre-exponential factor are assumed to be constant [23]. The Kissinger method assumes a

first order equation by only looking at one data point for each heating rate, which is the peak temperature. The equation for the Kissinger method can be defined as:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (7)$$

where T_p is the peak temperature. By plotting $\ln(\beta/T_p^2)$ versus $1/T_p$, the values of activation energy and pre-exponential factor can be estimated by calculating the slope of the linear fit and the y-intercept. At peak temperature, it can be assumed that the maximum reaction rate, $d\alpha/dt$, occurs at this point, and therefore $d^2\alpha/dt^2$ is equal to zero.

1.2.2 Model-Free Isoconversional Method: Ozawa-Flynn-Wall Analysis

Several other methods have been developed to calculate the activation energy and pre-exponential factor including the model-free isoconversional methods. These methods are different from the previous one because they assume that both the activation energy and pre-exponential factor are functions of the degree of cure, which means that they are not constant throughout the reaction.

One of the model-free isoconversional methods, the Ozawa-Flynn-Wall analysis, provides a simple relationship between the conversion dependent activation energy, E_α , heating rate and isoconversion temperature [24-26]:

$$\log \beta = -\frac{0.4567E_\alpha}{RT_i} + A' \quad (8)$$

For each degree of conversion, A' is a constant that can be defined as:

$$A' = \log \left[\frac{AE_\alpha}{g(\alpha)R} \right] - 2.315 \quad (9)$$

where $g(\alpha)$ is a conversion dependent function. To determine the corresponding activation energy and pre-exponential factor at each degree of cure, a plot of $\log \beta$ vs. $1/T_i$ should be drawn at each degree of cure. The resulting slope is proportional to the activation energy, E_α , and the intercept is proportional to the pre-exponential factor, A' . By doing this analysis, the relationship between the activation energy and degree of

cure can be quantified to provide extra information about the change in kinetics throughout the reaction.

1.3 Raman Spectroscopy Overview

Raman spectroscopy has proven to be one of the most popular in-situ monitoring techniques for reaction progression. It is a spectroscopic technique that measures rotational and vibrational transitions in molecules and specifically used to detect chemical bonds and their changes during reaction [27]. Some of the advantages of Raman spectroscopy over other spectroscopy methods include its ability to produce well-resolved spectra that can be easily quantified. The measurement time is also very short allowing easy collection of data. Raman spectroscopy is both qualitative and quantitative, which means that the relative intensity of Raman peaks is associated with certain components in a sample. This relative intensity is also directly proportional to the relative concentration of the components. Hence, with Raman spectroscopy, qualitative and quantitative information can be easily extracted from the spectra.

Raman spectroscopy relies on inelastic monochromatic light scattering which is usually obtained from a laser. As soon as the laser interacts with a sample, the frequency of photon in the laser beam will change. This photon is absorbed by the sample and then reemitted. The resulting energy from the reemitted photon will shift the frequency up or down compared to the original laser light frequency, which is called the Raman effect.

In Raman spectroscopy, a sample is typically illuminated with a laser beam. The laser light travels through the sample and interacts with the electron cloud and molecule's bonds. A photon, which can be defined as a quantum energy of electromagnetic radiation, stimulates the molecule moving it from the ground state to a virtual energy state. Afterwards, the molecule returns to a different rotational or vibrational state. The energy difference between the original state and new state results in a frequency shift of the emitted photon with respect to the original monochromatic frequency.

If the final vibrational state's energy is higher than the original state's, the emitted photon will move to a lower frequency in order to balance the total energy. This phenomenon is known as a Stokes shift. On the other hand, if the final vibrational state's energy is lower than the original state's, the emitted photon will move to a higher frequency, and this shift is defined as an Anti-Stokes shift.

Raman effects are expressed in wavenumbers, and this formula can be used to convert between the wavelength and wavenumbers of shift in the Raman spectra:

$$\Delta w = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \quad (10)$$

where Δw is the Raman shift in wavenumber, λ_0 is the excitation wavelength and λ_1 is the Raman spectrum wavelength.

1.4 Dielectric Analysis (DEA) Overview

Dielectric materials are materials that can store and use energy under an applied electric field [12]. The ions and dipoles that are present in these materials induce conductive and capacitive characteristics. Before an electric field is applied to a sample, the ions and dipoles initially undergo random orientation. When applying an electric field to the sample, the ions, defined as small, polarized yet insignificant amount of impurities, start to move towards an electrode of opposite polarity while the dipoles try to align with the electric field.

In dielectric analysis (DEA), parallel plate electrodes are typically used to study dielectric properties in the laboratory settings. A sample is placed between two electrodes, and a sinusoidal AC voltage at a certain frequency is applied across the electrodes to create an electric field. The resulting signal is obtained during the process by measuring the change in amplitude and phase shift in regards to the mobility of the ions and the alignment of the dipoles. From the amplitude change and phase shift, the dielectric properties of permittivity, ϵ' , and loss factor, ϵ'' , can be obtained. The complex permittivity, ϵ^* , can be defined as [28]:

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (11)$$

In dielectric cure monitoring, the conductive nature of materials is the most important aspect of all the properties. As previously mentioned, an applied electric field causes the ions in the materials to migrate from one electrode to the other. As ions flow through a medium, their mobility greatly depends on the nature of the medium. Ions flowing through a very fluid material have high conductivity and mobility, which results in low resistivity corresponding to low viscosity. On the contrary, ions flowing through an elastic material have low conductivity and mobility, resulting in high resistivity, which is related to high viscosity. In the case of polymers, the materials start off as liquids, and as the cure reaction progresses, they become solids. Hence, during the cure process, the mobility of ions and rotation of dipoles become more and more limited. Since ion conductivity is related to the ion mobility which is related to the material's viscosity, ion conductivity is a good indicator of the viscosity change during the cure process. It should be noted that at low frequencies, the change in the loss factor is mainly contributed by the ion conductivity [12]. In general, the degree of cure of materials can be calculated using the dielectric properties of permittivity and loss factor arisen from ionic current and dipole rotation in the sample.

For in-plant monitoring, parallel plate electrodes can be incorporated to monitor

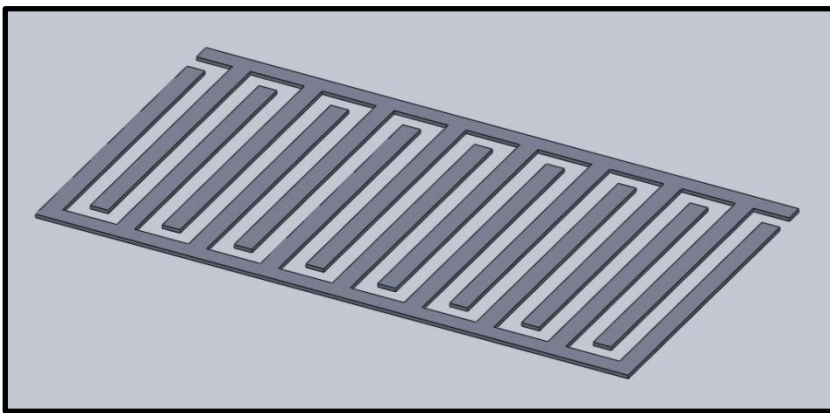


Figure 3: An example of interdigitated sensors

the curing process if the surface of the part is flat and its thickness is small compared to the plate size. This becomes an issue when producing complex-shaped and/or thick parts. Utilizing parallel plate electrodes

is also not possible when producing parts with an open mold because the top plate will be unusable. Therefore, interdigitated sensors have been reported to be an alternative to parallel plate electrodes [1, 7, 8, 29]. These sensors, as shown in Figure 3, can be embedded on the surface of the molds' structures without interrupting the process

being monitored. In the wind blade manufacturing industry, the interdigitated sensors could be placed on or near the mold surface before laying down the fiberglass.

1.5 Thesis Organization

The layout of the thesis is described as follows. Chapter 2 presents a literature review of past researches which have studied the cure kinetics characterization using Differential Scanning Calorimetry (DSC), Raman spectroscopy and Dielectric Analysis (DEA). Chapter 3 presents the main chapter of the thesis which explains detailed understanding of the cure monitoring using Differential Scanning Calorimetry (DSC), Raman spectroscopy and Dielectric Analysis (DEA) as well as the possibility of in-situ cure monitoring, and is presented as a manuscript. Then, finally the general conclusion from the research will be discussed in Chapter 4 along with an implementation plan for future research.

Chapter 2: Literature Review

In the manufacture of wind blades, the ability to monitor and control the cure process proves to be highly important to prevent under-curing or over-curing of the parts. Without a way to directly measure the cure process, it is difficult to understand the problems with the exothermic reaction. Unfortunately, there have not been many studies that report the possibilities of in-situ cure monitoring in the wind blade manufacturing process. Therefore, it is important to first examine the potential of monitoring the cure of materials by performing tests in the laboratory environment. Performing small-scale laboratory experiments will provide a strong indication of the potential for in-situ cure monitoring in the wind blade manufacturing industry.

Understanding the fundamental science of the curing process allows for reassurance before developing in-site cure monitoring methods. Many different analytical methods have been utilized to characterize the cure reaction and monitor the cure process of thermosets, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) [1, 6, 8, 10, 12-19]. These methods are typically used in laboratories under ideal conditions. Although these methods cannot be used in practical applications, they offer a very good insight of how the reaction progresses and can be used as a reference of characterizing the cure process.

Dielectric analysis (DEA), Raman spectroscopy, infrared spectroscopy (IR) and ultrasonic methods have been shown to be useful for in-situ cure monitoring [3, 7-9, 12, 20, 21]. Any in-situ cure monitoring should not be invasive nor destructive, nor should it have any influence in the reaction process. In recent studies, dielectric analysis and Raman spectroscopy have been reported to be a few of those promising non-invasive in-situ cure monitoring methods.

2.1 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) has been used extensively to characterize the cure kinetics of various materials. Sbirrazzuoli et al. utilized DSC to investigate the cure kinetics of isothermal and dynamic measurements of diglycidyl

ether of bisphenol A (DGEBA) with m-phenylenediamine (m-PDA) [30, 31]. The experimental data were then analyzed using an advanced isoconversional method to determine a variation in the activation energy with increasing degree of cure. It was found that as the degree of cure increased, the activation energy of curing decreased.

Flammersheim and Opfermann also examined the cure kinetics of isothermal and dynamic measurements of the same materials used by Sbirrazzuoli et al [32]. Contrary to the results obtained by Sbirrazzuoli et al., Flammersheim and Opfermann argued that the activation energy was almost constant regardless of the degree of cure. Based on the experimental results, the phenomenological modeling is a useful tool to adequately describe the experimental cure kinetics data. The model parameters, based on the dynamic measurements, can be used to predict the isothermal cure model. In particular, for the dynamic measurements, at least three heating rates should be used to get a good model, and the difference between the maximum and minimum heating rates should be at least one order of magnitude. Heating rates between 0.5 and 20 K/min are considered acceptable, allowing reliable DSC measurements. For the isothermal measurements, the cure temperatures are generally selected as desired depending on the application of the materials.

Kessler and White observed the cure kinetics of polydicyclopentadiene prepared by ring-opening metathesis polymerization using DSC [15]. The dynamic experimental data were fitted with different phenomenological kinetic models: first order, second order, n^{th} order, n^{th} order with autocatalysis and Prout-Tompkins autocatalytic model. The isoconversional method was also used in the study to calculate the cure-dependent activation energy and pre-exponential factor since the isoconversional method can be used to evaluate both simple and complex chemical reactions.

The cure kinetics of thermosetting bisphenol E cynate ester was studied by Sheng et al. [16]. Two different methods for isothermal cure were used to measure the degree of cure vs. time. The first method involved partially curing the sample poured into silicon rubber molds in an oven at certain cure temperatures for various curing times. A small piece of the sample was subsequently used for the dynamic DSC scan to obtain the residual heat of reaction and glass transition temperature. The second

method involved putting the uncured sample in the DSC cell and heating it at the desired cure temperatures for various curing times. A subsequent dynamic scan was then performed to measure the heat of reaction. The results from the two methods were compared, and they matched very closely.

Badrinarayanan et al. examined the cure characterization of Soybean Oil-Styrene-Divinylbenzene Thermosetting Copolymers, a type of bio-based resins [6]. The dynamic and isothermal measurements were performed using the DSC. The phenomenological reaction models used to describe the dynamic DSC measurements were presented. For the isothermal DSC measurements, the cure temperatures were determined considering the resin's application in the production of FRPs through pultrusion. The sample was partially cured for various curing times, and following this was the dynamic DSC scan. From these isothermal measurements, the kinetic equations to predict the degree of cure at any cure temperature were proposed.

2.2 Raman Spectroscopy

As mentioned before, differential scanning calorimetry (DSC) is typically used in laboratories under ideal conditions. Although DSC typically is not used in practical applications, it provides excellent information about the reaction kinetics of materials. With the on-going research about the use of in-situ cure monitoring methods, Raman spectroscopy has been thought to have a good potential in the real world since Raman spectroscopy is a non-destructive monitoring method [3, 9].

A study by Vaskova and Kresalek reported a Raman spectroscopy analysis on the cure kinetics of an epoxy resin [3]. The diglycidyl ether of bisphenol A (DGEBA) and N'-(3-aminopropyl)-N,N-dimethylpropan-1,3-diamin were mixed together, and the Raman spectrum of the reaction was obtained over time. The epoxide ring vibration was spotted at 1252 cm^{-1} , and its intensity decreased with time corresponding to the opening of the epoxide ring during the reaction. Other Raman peaks at 1112 cm^{-1} , 1186 cm^{-1} and 1608 cm^{-1} corresponding to resin backbone vibrations remained constant during the course of the reaction, and thus could be used as a reference when observing the degree of cure.

Merad et al. also presented an analysis on in-situ cure monitoring of the epoxy resin curing by Raman spectroscopy and compared the results to the ones obtained by DSC [9]. The materials used in the study were a commercially available grade of diglycidyl ether of bisphenol A (DGEBA) mixed with 4,4'-diamino diphenyl sulfone (DDS). In this system, the 1275 cm^{-1} peak corresponded to the epoxide ring being consumed by the reaction while the 1160 cm^{-1} peak corresponded to the phenyl ring which remained unaffected and consistent throughout the reaction. The intensity of the 1275 cm^{-1} peak was normalized by dividing it by the intensity of the 1160 cm^{-1} peak and observed throughout the cure reaction. A close comparison of the degree of cure vs. time between Raman spectroscopy and DSC was observed.

A Raman spectroscopic method for polymerization monitoring was proposed by B&W Tek, Inc. [33]. Similar observations were obtained using a different type of epoxy, Tra-bond 2116 epoxy. The epoxy band at 1260 cm^{-1} clearly decreased with time, which was explained by the opening of the epoxide ring by the cure reaction. While the intensity the 1260 cm^{-1} peak decreased with time, the phenyl ring stretch at 1610 cm^{-1} remained unaffected, and therefore could be used a reference.

2.3 Dielectric Analysis (DEA)

Many studies have been performed to develop a dielectric system for the purpose of in-situ cure monitoring. Most of the experiments in these studies, however, were carried out under non-isothermal conditions. When it comes to the resin transfer molding (RTM) process, it is very important that any in-situ cure monitoring method be non-destructive. It has been stated that in order to observe the cure through the thickness of composite materials, sensors for the dielectric system must be implanted within the fabric. This effort, however, has been reported to adversely affect the mechanical performance of the parts [1, 7]. McIlhagger et al. attempted to develop a dielectric system for the in-situ cure monitoring of the resin transfer molding process using parallel plate electrodes holding four layers of carbon fiber interlocked with a two part system of epoxy and hardener [7]. The transitions in the resin such as minimum viscosity, gelation, vitrification and full cure were identified by performing a non-

isothermal cure schedule similar to the RTM process. Nevertheless, the limit on the thickness of composite materials was not mentioned at all when measuring the sample with parallel plate electrodes. This becomes an issue when measuring very thick composites, particular in the wind blade manufacturing industry where the parts are typically very thick. The parts are typically cured under near isothermal conditions, but there has been little study about determining the end of cure under isothermal conditions.

Kim and Lee demonstrated a new method of cure monitoring for glass/polyester and glass epoxy composites at a constant heating rate [8]. A thermocouple and interdigitated sensors were placed between the composite sheets. The degree of cure was calculated from the dissipation factor, and when comparing it to the one obtained by the DSC, an agreement up to 70% degree of cure was observed.

Hussain et al. investigated the cure monitoring and characterization of epoxy-silicate nanocomposites using an online dielectric cure monitoring technique [12]. In the study, an aluminum pan was used to hold the samples, and a sensor was placed under an aluminum pan. The samples were cured under non-isothermal cure cycles to observe the onset point, minimum viscosity, gelation point, end of cure and glass transition temperature of the nanocomposites.

A study by Kim and Char explored the dielectric changes during the curing of diglycidyl ether of bisphenol A (DGEBA) with diaminodiphenylmethane (DDM) as a curing agent [21]. Some of the dielectric experiments were conducted at several isothermal temperatures with varying frequency. It was observed that the loss factor was inversely proportional to the applied frequency meaning that the contribution from ionic conductivity was dominant, but as the cure reaction progressed, the contribution from dipole relaxation started appearing because the mobility of the ions was diminishing. In the study, the degree of cure was not calculated from the dielectric properties, but instead estimated from the kinetics equation obtained by DSC experiments.

One interesting study by Sernek and Kamke observed the dielectric analysis for continuous online monitoring of a PF adhesive cure in a hot press [20]. The PF adhesive

was placed in between two sheets of veneer held by the hot press. An interdigitated sensor was placed in between the sheets of veneer, and the cure process of the PF adhesive was performed at several isothermal temperatures. The degree of cure of the adhesive was calculated using two different methods: dielectric loss factor and conductivity, and both methods led to similar results.

Chapter 3: Cure Kinetics Characterization and Monitoring of an Epoxy Resin for Thick Composite Structures

3.1 Introduction

Fiber-reinforced polymers (FRPs) are one category of composites that utilize fiber materials to mechanically increase the strength and elasticity. These fiber materials are interlocked with a weaker matrix (a thermoset resin) and allowed to cure through a polymerization process. The use of FRPs is increasing for numerous industrial applications. For structural and engineering applications, for instance, where both the strength and elasticity are critical, FRPs are commonly used to produce large and complicated structures due to their excellent physical and mechanical properties. A key property is the relatively high strength-to-weight ratio [4-7]. FRPs are also commonly used to manufacture much of the wind turbine blade structure. Subcomponents of the blade include the root, the shear web, the spar cap, the skin and the core. One common blade fabrication method is to produce the spar cap and root sections separately, and then infuse them into the blade assembly.

The spar cap is the main load carrying member within the blade. For a megawatt scale 40 m turbine blade, the spar cap is approximately 60 mm thick, 500 mm wide and made of unidirectional fabric. The thickness tapers towards the tip end to approximately 15 mm via dropping plies of fabric. The exotherm during cure of the spar cap undergoes different reaction rates at different areas of the spar cap leading to non-uniform curing. This causes heat to develop, and some of the fabric gets restricted when it tries to expand due to varying heat of reaction, creating waves in the fabric. The waves that develop may be internal to the spar cap or could erupt to the surface. In any case, the waves are critical quality characteristics because they have a significant negative impact on the fatigue life of the blades. These problems are often associated with ineffective curing process parameters.

There is a need to precisely monitor and control the cure process to improve the quality of the turbine blades. Without a method to directly measure the cure process,

the manufacturers need to determine an adequate cure time to prevent the worst case scenarios that might happen to the parts, such as under-curing and premature demolding. Although an adequate cure time has been established to ensure that the cure reaction is finished, conservative estimates increase the manufacturing cycle times, leading to over-curing which results in poor properties of the part. The goal is to control the cure process during manufacturing via in-situ cure monitoring to ultimately achieve a better quality product. In-situ monitoring will provide information about the cure process in real time. Characterization, design and optimization of the cure process will help control the exotherm and predict the cure cycle of the materials. Issues such as the time and temperature to reach full cure and the optimum temperature to decrease the cycle time can be addressed. Acceptable cure temperatures can also be proposed to avoid vitrification (glass formation) and high temperatures at which undesirable side reactions or degradation may occur [2].

Many different analytical methods have been studied to characterize the cure reaction and monitor the cure process of thermosets, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) [1, 6, 8, 10, 12-19]. These methods, however, typically are not practiced for in-situ cure monitoring because they are only performed in laboratories under ideal conditions. Nevertheless, these methods can provide excellent information about glass transition temperature (T_g), onset of cure, heat of cure, maximum rate of cure, completion of cure and degree of cure. Sbirrazzuoli et al. utilized DSC to investigate the cure kinetics of isothermal and dynamic measurements of diglycidyl ether of bisphenol A (DGEBA) with m-phenylenediamine (m-PDA) using an advanced isoconversional method [30, 31]. Flammersheim and Opfermann also examined the cure kinetics of isothermal and dynamic measurements of the same materials used by Sbirrazzuoli et al. and determined that the phenomenological modeling would be a useful tool to adequately describe the experimental cure kinetics data [32]. Kessler and White observed the cure kinetics of polydicyclopentadiene prepared by ring-opening metathesis polymerization using DSC by fitting different phenomenological kinetic models [15]. Sheng et al. studied the degree of cure vs. time of thermosetting bisphenol E cynate ester by performing

isothermal cure [16]. Badrinarayanan et al. examined the cure characterization of Soybean Oil-Styrene-Divinylbenzene Thermosetting Copolymers and developed a model to determine the degree of cure at any temperature and time [6].

Previous studies have shown that there are several other useful methods that can be utilized to monitor the cure process in real time including dielectric analysis (DEA), Raman spectroscopy, infrared spectroscopy (IR), and ultrasonic methods [3, 7-9, 12, 20, 21]. It is important that any in-situ cure monitoring method is non-invasive and non-destructive so that the manufacturing process is not influenced or even disturbed. It is also important that the method offers real time information about the cure reaction. In recent studies, dielectric analysis and Raman spectroscopy prove to be a few of those promising non-invasive in-situ cure monitoring methods.

A study by Vaskova and Kresalek reported a Raman spectroscopy analysis on the cure kinetics of an epoxy resin [3]. The epoxide ring vibration was spotted at 1252 cm^{-1} , and its intensity decreased with time corresponding to the opening of the epoxide ring during the reaction. Other Raman peaks at 1112 cm^{-1} , 1186 cm^{-1} and 1608 cm^{-1} , corresponding to resin backbone vibrations, remained constant during the course of the reaction, and thus could be used as a reference when observing the degree of cure. Merad et al. presented an analysis on in-situ cure monitoring of the epoxy resin curing by Raman spectroscopy and compared the results to the ones obtained by DSC [9]. It was reported that a close comparison of the degree of cure vs. time between Raman spectroscopy and DSC was observed.

Many studies have also been performed to develop a dielectric system for the purpose of in-situ cure monitoring. Most of the experiments in these studies, however, were carried out under non-isothermal conditions. Kim and Lee demonstrated a new method of cure monitoring for glass/polyester and glass epoxy composites at a constant heating rate by placing a thermocouple and interdigitated sensors between composite sheets [8]. The degree of cure was compared to the one by the DSC, and an agreement up to 70% degree of cure was observed. Hussain et al. investigated the cure monitoring and characterization of epoxy-silicate nanocomposites using an online dielectric cure monitoring technique by curing the samples non-isothermally [12]. A study by Kim and

Char explored the dielectric changes during the curing of diglycidyl ether of bisphenol A (DGEBA) with diaminodiphenylmethane (DDM) as a curing agent [21]. One interesting study by Sernek and Kamke observed the dielectric analysis for continuous online monitoring of PF adhesive cure in a hot press by putting sensors in between the two hot presses [20].

It has been stated that in order to observe the cure through the thickness of composite materials, sensors for the dielectric system must be implanted within the fabrics. This effort, however, has been reported to adversely affect the mechanical performance of the parts [1, 7]. McIlhagger et al. attempted to develop a dielectric system for the online cure monitoring of the resin transfer molding process using parallel plate electrodes holding four layers of carbon fiber interlocked with a two part system of epoxy and hardener [7]. This becomes an issue in the wind blade manufacturing industry when producing complex-shaped and/or thick parts or when producing parts with an open mold because the top plate will be unusable. The parts are typically cured under near isothermal conditions, but there has been little study about determining the end of cure under isothermal conditions.

In this study, the epoxy system was based on standard diglycidyl ether of bisphenol A (DGEBA) epoxy resin and a modified aliphatic amine as a curing agent. The blend system was chosen based on its use in manufacturing wind blades. The cure kinetics of the epoxy system was characterized by means of differential scanning calorimetry (DSC) in both dynamic and isothermal methods. Several phenomenological reaction models were fitted with the dynamic experimental results, and the model that best fit the data was presented to predict the degree of cure at any isothermal temperature. Isothermal measurements of the epoxy resin cure were also conducted using Raman spectroscopy and dielectric analysis (DEA). This study will compare the results on the degree of cure obtained from DSC, Raman spectroscopy and DEA to investigate the possible use for in-situ cure monitoring of thick section composites such as spar caps.

3.2 Experimental

3.2.1 Materials

The materials used in this study were purchased from Momentive Specialty Chemicals (Columbus, OH) and stored at room temperature. The EPIKOTE™ Resin RIMR 135 is based on standard diglycidyl ether of bisphenol A (DGEBA) epoxy resin, and the EPIKURE™ Curing Agent MGS RIMH 1366 is a modified aliphatic amine type. The mass ratio between the resin and curing agent was set at 100:30 to replicate industrial practice for thick section fiber reinforced polymer composites as used in wind blade spar caps.

3.2.2 Sample Preparation

To prepare the sample, the desired amount of resin and hardener was added to a vial and mixed using a magnetic stirring bar to ensure a homogeneous mixture. The sample was then immediately flash frozen using liquid nitrogen to avoid premature curing reactions.

3.2.3 DSC Measurements

The DSC measurements were performed with a TA Instruments Q20 DSC (New Castle, DE). The experiments were carried out under a constant flow of nitrogen of 50 mL/min. Prior to each DSC run, a small amount of uncured sample (7-10 mg) was sealed into a Tzero Aluminum Hermetic DSC. The sample pan was then put in the DSC cell which was pre-cooled to -50 °C. For the dynamic DSC measurements, the DSC cell was subsequently heated at a constant rate of 2, 5, 10, 15 and 20 °C/min over a temperature range of -50 to 275 °C.

Isothermal measurements were performed using a TA Instruments Q2000 DSC (New Castle, DE) to investigate the relationship between the degree of cure and glass transition temperature (T_g). The isothermal measurements were performed under a constant flow of helium of 25 mL/min used as purge gas. Three isothermal cure temperatures ($T_c = 60, 80$ and 100 °C) between the onset of the reaction and the peak

heat flow from the dynamic scan were selected. A small amount of uncured sample (7-10 mg) was transferred into a Tzero Aluminum Hermetic DSC pan and placed in the DSC cell previously maintained at room temperature. The DSC cell was quickly heated up to the desired cure temperature and then isothermally kept at that temperature for various times ranging from 2 minutes to 2 hours. Following this scan, the DSC cell was immediately cooled down to -50 °C and then heated to 275 °C at 10 °C/min to measure the residual heat of the reaction (ΔH_R). The glass transition temperature was evaluated at the inflexion point of the stepwise transition. The area under the exothermic peak was largely the heat of reaction. The residual heat of the reaction and the total heat of reaction of the uncured sample at 10 °C/min were simultaneously used to determine the final conversion at various isothermal cure temperatures. Finally, all the DSC data were analyzed using the Netzch Thermokinetics program.

3.2.4 Raman Spectroscopy Measurements

Real-time Raman spectra were collected using a Mark II holographic fiber-coupled stretch probehead from Kaiser Optical Systems, Inc. (Ann Arbor, MI) attached to a HoloLab 5000R modular research Raman spectrograph. A 785-nm laser was emitted to the sample with a 200 mW laser power to induce the Raman scattering effect. The exposure time for each spectrum was 5 seconds whereas the time interval between each acquisition was approximately one second. The measurements were conducted at three isothermal temperatures ($T_c = 60, 80$ and 100 °C). For each cure temperature, the sample was inserted into a 1-mm ID quartz capillary tube. The filled sample tube was placed inside the probehead and allowed to cure as the Raman spectra were collected.

3.2.5 DEA Measurements

The dielectric analysis measurements were conducted using a Novocontrol Technologies (Hundsangen, Germany). The two parallel plate electrodes used were brass circles, 19.28 mm and 31.92 mm in diameter. The sample was placed on the larger plate and covered with the smaller one. The gap between the electrodes was

maintained at 0.5 mm using a small piece of Teflon tape as a spacer. The experiments were conducted at three isothermal cure temperatures ($T_c = 60, 80$ and 100 °C) under a nitrogen purge. A sinusoidal AC voltage of 1 V at a frequency of 1 Hz was applied between the electrodes to create an electric field. The permittivity and loss factor data were collected as a function of time.

3.3 Results and Discussion

3.3.1 DSC Cure Characterization

3.3.1.1 Dynamic Scanning Method

In the DSC measurements, the degree of cure (α) ranges from 0 (completely uncured) to 1 (fully cured) and is defined as follows:

$$\alpha(t) = \frac{H(t)}{H_T} \quad (1)$$

where $H(t)$ is the heat of the reaction up to time t and H_T refers to the total heat of the reaction. Common DSC measurements involve measurements of the heat flow as a function of time, and the enthalpy can be obtained by integrating the area of exothermic peak, which is the integration of the heat flow.

The dynamic DSC curves for the epoxy resin system examined in the study at different heating rates ranging from 2 to 20 K/min are shown in Figure 4. The different symbols illustrate the experimental data at different heating rates, whereas the lines are drawn from the model fits, which will be discussed later. As

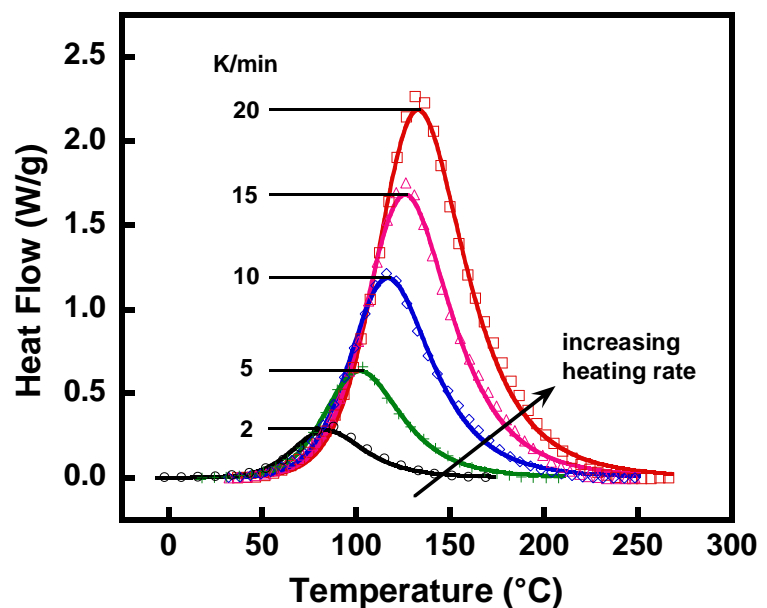


Figure 4: Dynamic DSC cure behavior of the resin. The experimental data are shown as symbols, and the lines represent the best model fits.

expected, the DSC cure of epoxy resin is characterized by a broad exothermic peak, and with increasing heating rate, the magnitude of the exotherm increases as well.

The peak temperature, T_p , shifts to a higher temperature range with increasing heating rate, β . Hence, the Kissinger method can be employed to calculate the activation energy and the pre-exponential factor of the cure of epoxy resin examined in this study. The equation for the Kissinger method can be defined as [24]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (2)$$

where R is the universal gas constant. By plotting $\ln(\beta/T_p^2)$ versus $1/T_p$, the values of activation energy, A , and pre-exponential factor, E_a , can be estimated by calculating the

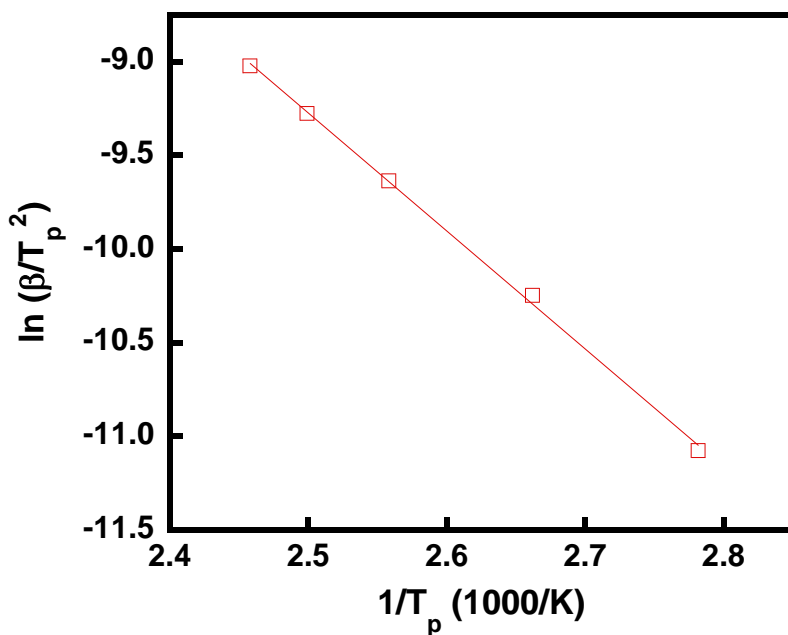


Figure 5: Kissinger's plot to determine activation energy (E_a). The slope of the linear fit represents E_a .

log A as 15.22 s^{-1} .

Once the cure behavior of the resin has been examined with the DSC, it is important to find a kinetics model that can describe the cure behavior. A variety of kinetics models have been developed to relate the rate of cure and degree of cure. Phenomenological reaction models are the most common models to describe thermoset cure reactions [6, 10]. The kinetic parameters of the cure reaction can be obtained by

slope of the linear fit and the y-intercept, as shown in Figure 5. At peak temperature, it can be assumed that the maximum reaction rate, $d\alpha/dt$, occurs at this point, and therefore $d^2\alpha/dt^2$ is equal to zero. The Kissinger method provides the value of activation energy as 52.37 kJ/mol and the value of

fitting the data obtained from the DSC measurements to the phenomenological reaction models.

In kinetics analysis by DSC, the rate of reaction is assumed to be proportional to the rate of heat generation and can be expressed as:

$$\frac{d\alpha}{dt} = \frac{1}{H_T} \frac{dH(t)}{dt} \quad (3)$$

It is also assumed that the rate of reaction can be defined by two separable functions, $K(T)$ and $f(\alpha)$:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (4)$$

where $d\alpha/dt$ is the rate of reaction, $K(T)$ is the temperature dependent rate constant, and $f(\alpha)$ corresponds to the reaction model. The temperature dependence of the reaction rate is generally defined through an Arrhenius expression:

$$K(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where E_a is the activation energy, A is the pre-exponential factor, R refers to the universal gas constant, and T corresponds to the absolute temperature. Combining the two equations together and also substituting $\beta = dT/dt$ (the heating rate), the rate of reaction can be defined as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (6)$$

Therefore, if the reaction model which describes the data is known, the conversion obtained at a given temperature or heating rate can be predicted using the above equations. Several kinetics models have previously been proposed to adequately describe the cure behavior of thermosets. In general, the cure behavior of thermosets is usually described by n^{th} order or autocatalytic models, which can be seen in Table 2.

Table 2: Phenomenological reaction models used in this study

Model	Designation	$f(\alpha)$	Parameters
n^{th} Order	Fn	$(1 - \alpha)^n$	A, E_a, n
n^{th} Order Autocatalytic	FnA	$(1 - \alpha)^n (1 + K_{cat}\alpha)$	A, E_a, n, K_{cat}
Prout-Tompkins Autocatalytic	PT	$(1 - \alpha)^n \alpha^m$	A, E_a, n, m

The dynamic DSC measurements in this study were fitted with the reaction models displayed in Table 2 by using multivariate least squares regression. All the parameters and the F-values were calculated based on the respective reaction models and can be seen in Table 3. The F-values, which were computed using a statistical F-test method, are normally used as an indication of the reaction model that best fits the experimental data. The F-test method compares the models' variances against each other. Specifically, the model with an F-value of one has the least deviation out of all the models compared. Moreover, if the F-value of the second best-fit model is higher than the critical F-value at 95% confidence interval, then the model with an F-value of one is determined as the best-fit model.

Table 3: Kinetic parameters determined by fitting dynamic DSC measurements with phenomenological reaction models

Model	E_a (kJ/mol)	$\log A$ (s^{-1})	n	$\log K_{cat}$	m	F-value*
Fn	73.59	7.70	1.92			5.34
FnA	52.02	4.39	2.26	0.81		1.82
PT	50.58	4.82	1.89		0.39	1.00

*The critical F-value at 95% confidence interval is 1.09.

In this instance, the Prout-Tompkins autocatalytic model provides the best description of the cure behavior of the epoxy resin studied in this work, as shown in Figure 4, where $\log A = 4.82 s^{-1}$, $E_a = 50.58$ kJ/mol, $n = 1.89$ and $m = 0.39$. Some minor deviations are present between the experimental data and the model fit due to the fact that the phenomenological models are unable to sufficiently describe the complicated cure behavior of epoxy resin in the dynamic DSC measurements. The difference could also be attributed to experimental uncertainties in the measured data.

When comparing the values of activation energy and pre-exponential factor obtained from the Prout-Tompkins autocatalytic model and the Kissinger method, the numbers are similar. Therefore, the two methods are a good approximation to determine the constant values of activation energy and pre-exponential factor.

3.3.1.2 Model-Free Isoconversional Method: Ozawa-Flynn-Wall Analysis

If the activation energy is assumed to be changing throughout the reaction as a function of the degree of cure, then the model-free isoconversional methods can be used to observe how the activation energy changes throughout the entire reaction. One of the model-free isoconversional methods, the Ozawa-Flynn-Wall analysis, provides a simple relationship between the conversion dependent activation energy, E_α , heating rate and isoconversion temperature [24-26]:

$$\log \beta = -\frac{0.4567E_\alpha}{RT_i} + A' \quad (7)$$

For each degree of conversion, A' is a constant that can be defined as:

$$A' = \log \left[\frac{AE_\alpha}{g(\alpha)R} \right] - 2.315 \quad (8)$$

where $g(\alpha)$ is a conversion dependent function. To determine the corresponding activation energy and pre-exponential factor at each degree of cure, a plot of $\log \beta$ vs. $1/T_i$ should be drawn at each degree of cure, which can be seen in Figure 6. The resulting slope is proportional to the activation energy, E_α , and the intercept is proportional to the pre-exponential factor, A' .

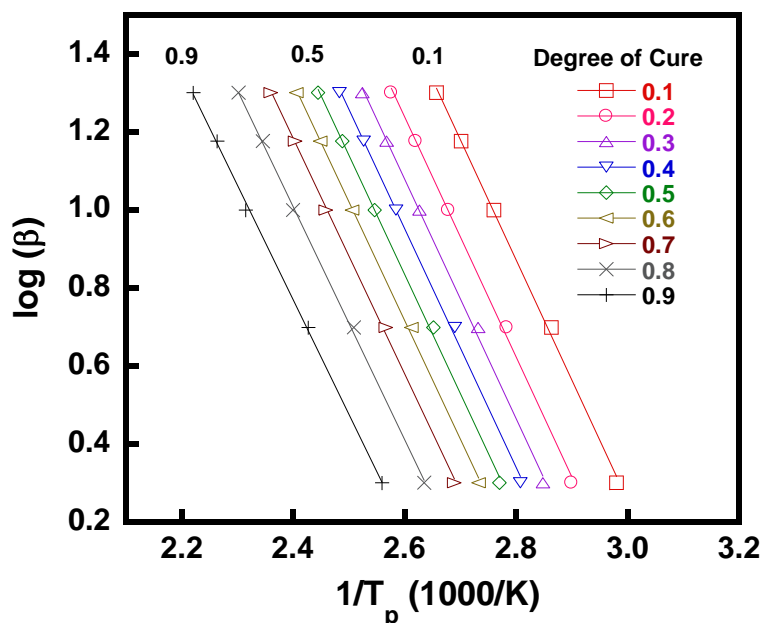
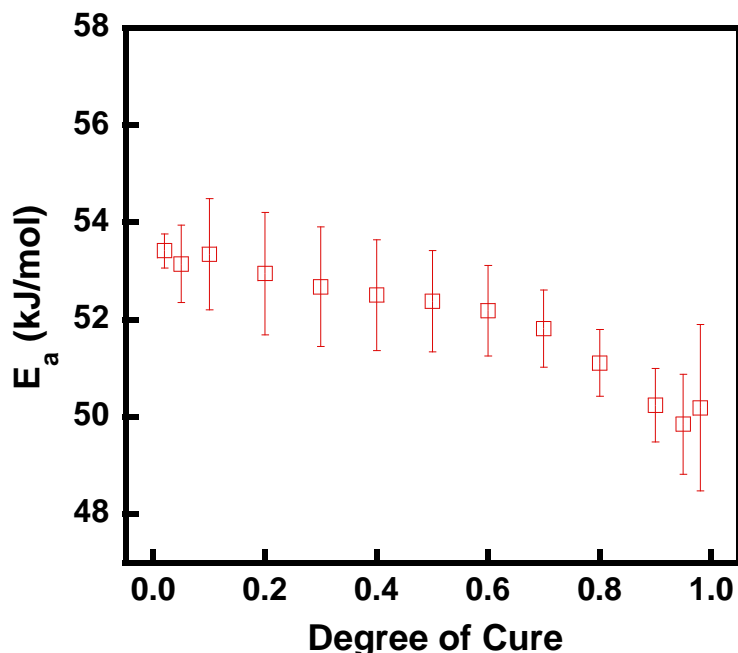


Figure 6: Ozawa-Flynn-Wall analysis to determine E_α and A'

When plotting the activation energy separately as a function of cure, as shown in Figure 7, one can observe that the activation energy slowly decreases as the degree of cure increases. The decrease in the activation energy might have occurred because of the autocatalytic effect in the curing process. Nevertheless, the difference between the maximum E_α (53.42 kJ/mol) and minimum E_α (49.85 kJ/mol) is quite small, which shows a good



agreement with the values obtained from the phenomenological models and the Kissinger method.

Figure 7: Ozawa-Flynn-Wall's activation energy as a function of degree of cure

3.3.1.3 Isothermal Curing Method

For the isothermal cure measurements, it is important that the degree of cure can be estimated as the reaction progresses. In order to calculate the degree of cure, the first formula can be modified as:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad (9)$$

where ΔH_T equals the total enthalpy of reaction measured at a certain heating rate for an unreacted sample, and ΔH_R is the residual heat of reaction for the isothermally cured sample for a certain period of time. With this formula, the degree of cure can be calculated as the cure progresses. It is essential to develop a relationship between α and T_g (glass transition temperature) since T_g provides a better value for monitoring the cure process.

Figure 8 displays the dynamic DSC scans of the samples that had been cured isothermally for various times at 80 °C. The glass transition temperature (T_g) is noted by the sudden decrease in the heat flow, and the broad exothermic peak area after the T_g corresponds to the residual heat of reaction, ΔH_R . As expected, the residual heat of

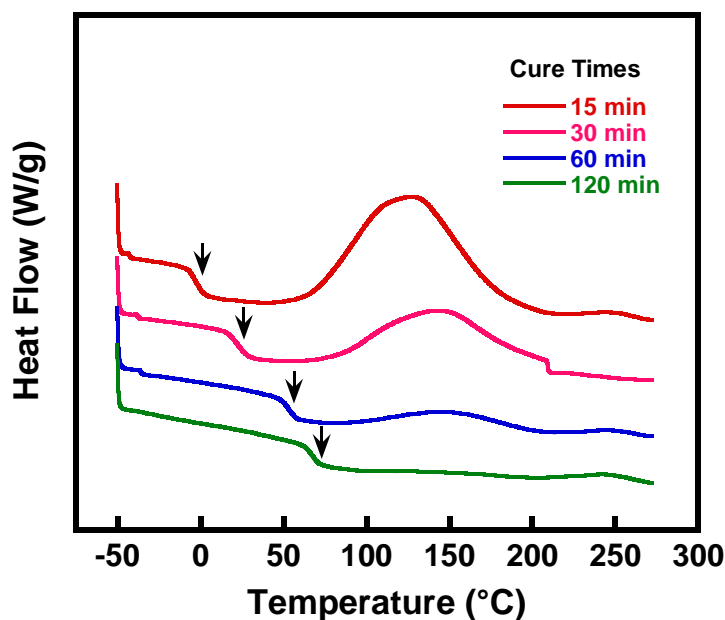


Figure 8: A series of DSC curves for partially cured samples at 80 °C for various times

reaction decreases with an increase in isothermal cure time. The decrease in residual heat of reaction and increase in T_g shows the progress of cure reaction with time.

The degree of cure can be obtained by using equation 9. The total heat of reaction, ΔH_T , is calculated to be 425.33 J/g by performing a dynamic DSC scan of an uncured sample at 10 °C/min. The degree of

cure obtained at three different isothermal temperatures for several time periods can be seen in Figure 9. As expected, conversion increases with increasing cure temperature and cure time.

In terms of predicting the degree of cure of the epoxy system, the Prout-Tompkins autocatalytic model parameters obtained from the dynamic DSC scans can be used to predict the cure behavior under isothermal conditions. In Figure 10, the predicted values of degree of cure at three isothermal cure temperatures ($T_c = 60, 80$ and 100 °C) are compared to the experimental data. The model prediction, which is represented by the line, fits the experimental data quite well, which indicates that the

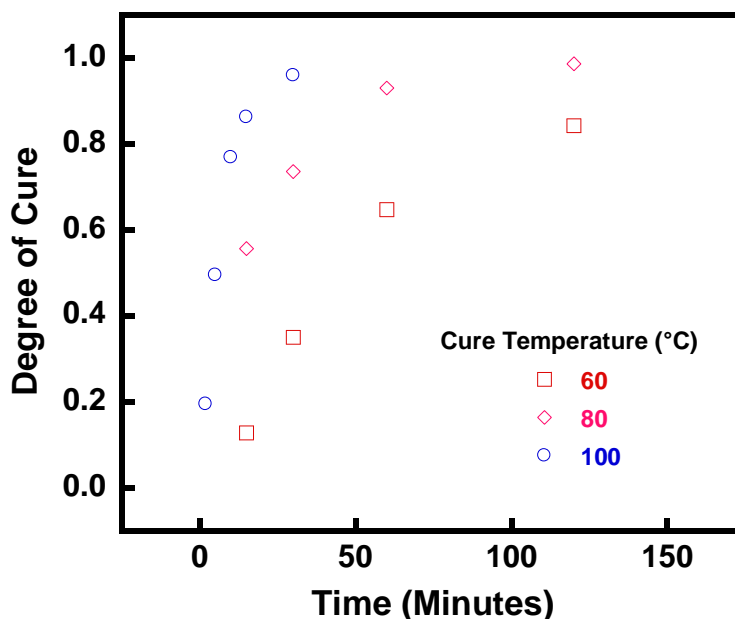


Figure 9: DSC degree of cure as a function of time at three isothermal cure temperatures

Prout-Tompkins autocatalytic model is a good model fit for the epoxy system studied in this work.

The glass transition temperature has been said to provide a better monitoring output of the cure process. At a high degree of cure, measuring the residual heat of reaction tends to be more difficult. Therefore, T_g is considered to be a better tool to observe the degree of cure.

There is a one-to-one non-linear relationship between T_g and degree of cure, α , and the

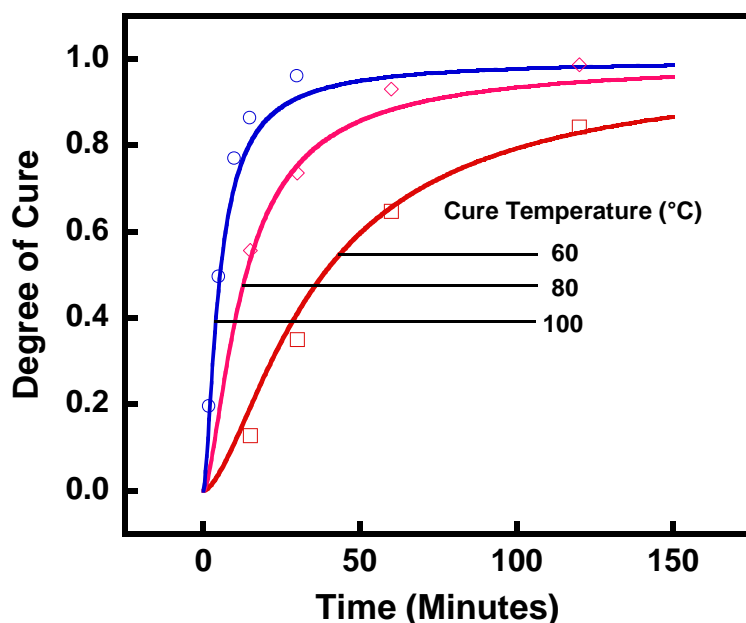


Figure 10: DSC degree of cure as a function of time at three isothermal cure temperatures. The symbols represent the experimental data, and the lines correspond to the model prediction.

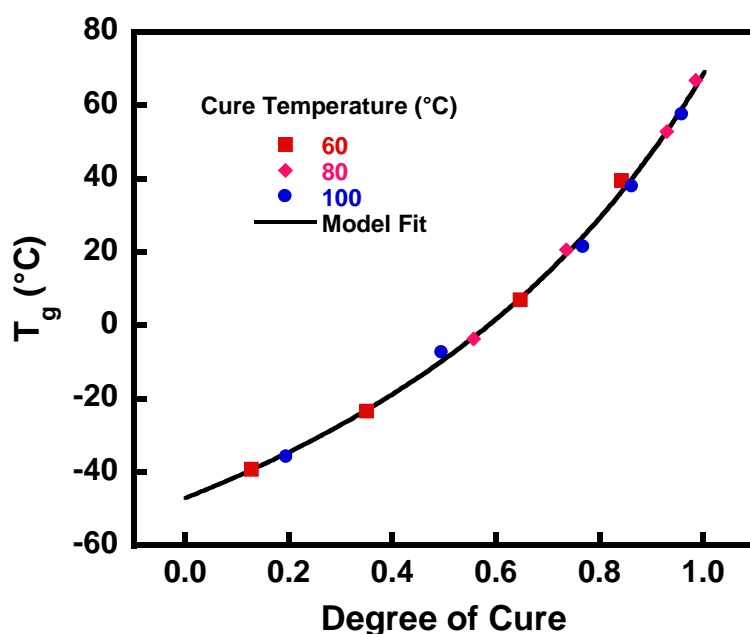


Figure 11: T_g vs. degree of cure α plot with DiBenedetto equation fitting

relationship between T_g and α can be mathematically developed using the empirical DiBenedetto equation, which is defined as [34]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (10)$$

where T_{g0} corresponds to the T_g of the uncured monomer, and $T_{g\infty}$ is the maximum T_g of the fully cured sample. The parameter λ is equal to $\Delta C_{p\infty}/\Delta C_{p0}$ where $\Delta C_{p\infty}$ and ΔC_{p0} represent the differences in heat capacity between the glass and rubbery states at T_g for the fully cured sample and uncured sample, respectively.

From the isothermal DSC measurements, the values of T_g and α can be determined experimentally. A plot of T_g vs. α is shown in Figure 11 with T_g increasing non-linearly with degree of cure. The different symbols represent the experimental data at different isothermal temperatures, whereas the line is drawn from the DiBenedetto equation. Using the equation, T_{g0} , $T_{g\infty}$ and λ values were calculated by least squares regression as 47.07 °C, 68.35 °C and 0.49.

3.3.2 Raman Spectroscopy Cure Characterization

Raman spectroscopy measures rotational and vibrational transitions in molecules and specifically used to detect chemical bonds and their changes during reaction [27]. The rotational and vibrational information is very specific to the chemical bonds in the sample, and the peaks in the spectrum correspond to certain chemical bonds allowing simple identifications. The relative intensity of Raman peaks is also directly proportional to the relative concentration of the components in a sample.

Figure 12 shows the Raman

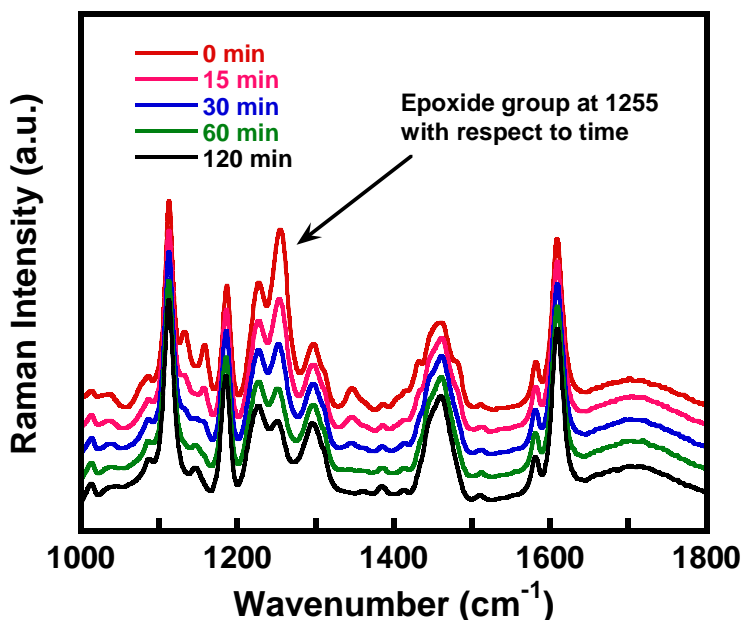


Figure 12: Real-time Raman spectra featuring the reactive and reference peaks during cure at 80 °C

spectra obtained at 80 °C at various cure times with the last four curves being shifted down for better illustration of the reaction progress. The peak at 1255 cm⁻¹ corresponds to the epoxide group, and the intensity is observed to be decreasing over time during the cure reaction. The decrease in intensity can be explained by the opening of the epoxide group during the cure reaction. Raman peaks at 1112 cm⁻¹ and 1186 cm⁻¹ corresponding to the C-C stretch remain unchanged throughout the cure reaction. Another peak at 1609 cm⁻¹ assigned to the stretching of phenyl ring also remains constant throughout. All these peaks are consistent with what has been reported in the literature [3, 9, 33]. As a result, these three constant peaks can be used as a reference to observe the degree of cure of the epoxy resin, which is indicated by the change in intensity of the epoxide group.

To calculate the degree of cure, it is important to normalize the peak intensity at 1255 cm⁻¹ by dividing it by that of one of the reference peaks. The degree of cure can be calculated using the equation below:

$$\alpha(t) = 1 - \frac{I_{1255}(t)/I_{ref}(t)}{I_{1255}(0)/I_{ref}(0)} \quad (11)$$

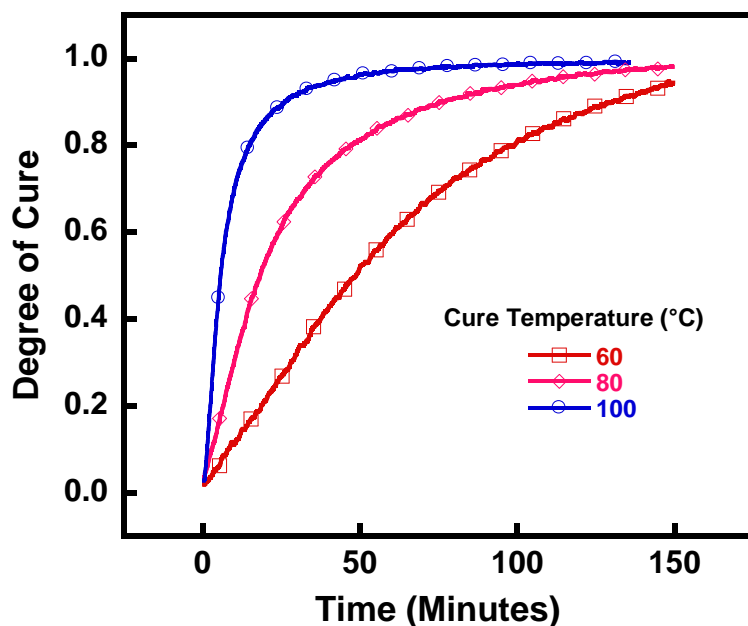


Figure 13: Raman spectroscopy degree of cure as a function of time at three isothermal cure temperatures

where $I(t)$ and $I(0)$ correspond to the intensity at time t and the beginning, respectively. The subscripts 1255 and ref represent the values at 1255 cm⁻¹ and the reference wavenumbers (1112 cm⁻¹, 1186 cm⁻¹ or 1609 cm⁻¹). In this case, the 1609 cm⁻¹ wavenumber was used as a reference. Figure 13 shows the degree of cure obtained by Raman

spectroscopy at 60, 80 and 100 °C. Similar to the DSC results, the degree of cure increases with increasing cure temperature and cure time.

3.3.3 DEA Cure Characterization

In dielectric analysis (DEA), the ions and dipoles that are present in the materials induce conductive and capacitive characteristics. Before an electric field is applied to a sample, the ions and dipoles initially undergo random orientation. When applying an electric field to the sample, the ions, defined as small, polarized yet insignificant amount of impurities, start to move towards an electrode of opposite polarity while the dipoles try to align with the electric field.

The resulting signal is obtained during the process by measuring the change in amplitude and phase shift in regards to the mobility of the ions and the alignment of the dipoles. From the amplitude change and phase shift, the dielectric properties of permittivity, ϵ' , and loss factor, ϵ'' , can be obtained. The complex permittivity, ϵ^* , can be defined as [28]:

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (12)$$

In dielectric cure monitoring, the conductive nature of materials is the most important aspect of all the properties. In the case of polymers, the materials start off as liquids, and as the cure reaction progresses, they become solids. Hence, during the cure process, the mobility of ions and rotation of dipoles become more and more limited. Since ion conductivity is related to the ion mobility which is related to the material's viscosity, ion conductivity is a good indicator of the viscosity change during the cure process. By measuring the change in the dielectric loss factor, which is mainly contributed by the ion conductivity at low frequencies, the degree of cure of materials can be calculated [12].

The loss factor is shown to be decreasing with cure time in Figure 14. It is observed that the decrease is more rapid at higher cure temperatures, which is in relation with DSC results. In the presence of an electric field, the changes in transitional mobility of ions and the rotational mobility of dipoles become more apparent with increasing cure time. The decrease in loss factor is due to the ion and dipole mobility

becoming more restricted as the sample turns into solids. The loss factor, in particular, is dominantly characterized by the ion mobility migrating from one electrode to the other with opposite polarity.

The measurement of loss factor as a function of cure temperature and time allows for the calculation of degree of cure. A new formula is proposed for the degree of cure calculation, which is defined as:

$$\alpha(t) = \frac{\log(\varepsilon''_0) - \log(\varepsilon''_t)}{\log(\varepsilon''_0) - \log(\varepsilon''_\infty)} \quad (13)$$

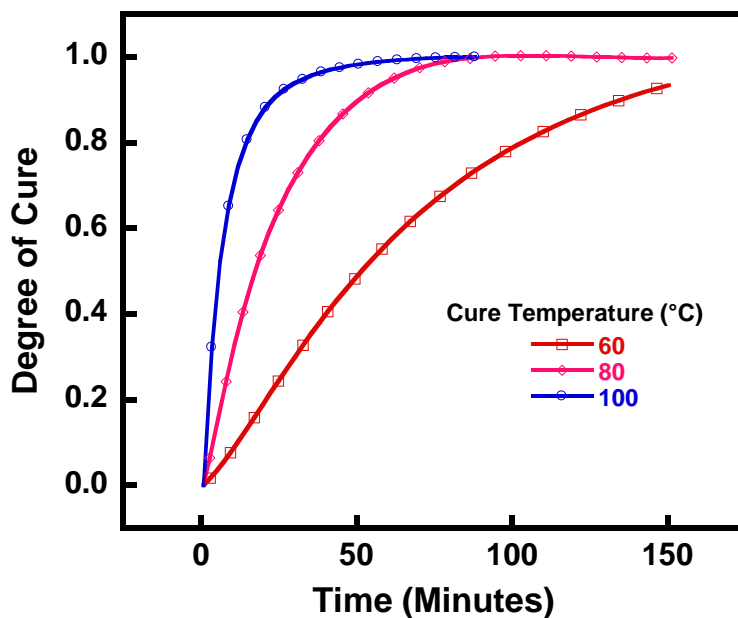


Figure 15: DEA degree of cure as a function of time at three isothermal cure temperatures

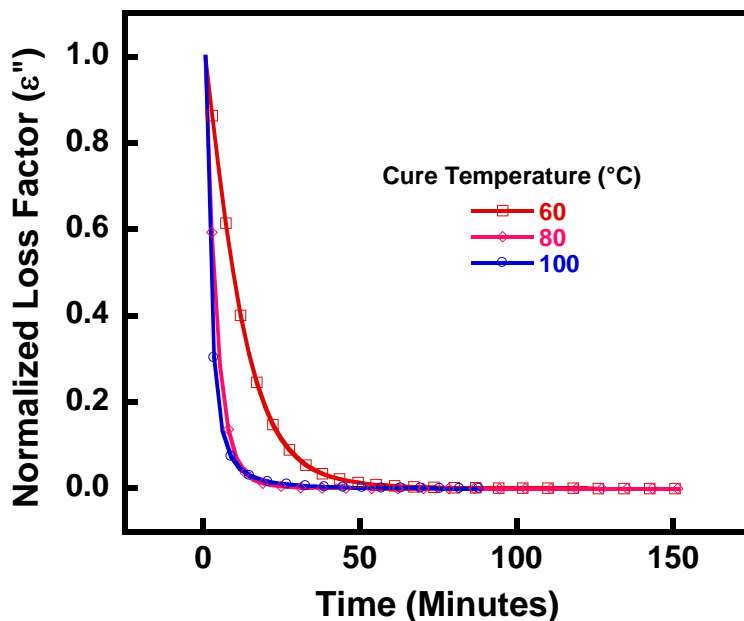


Figure 14: DEA loss factor as a function of time at three isothermal cure temperatures

where ε''_∞ is dielectric loss factor at infinity, ε''_t corresponds to dielectric loss factor at time t and ε''_0 is dielectric loss factor at the beginning. The degree of cure at three isothermal temperatures with increasing cure time is shown in Figure 15. As mentioned in the DSC analysis, the degree of cure increases with increasing cure temperature and cure

time. However, when the sample is about to reach full cure ($\alpha = 1$), the dielectric analysis is thought to be overestimating the degree of cure.

3.3.4 Comparison between DSC, Raman Spectroscopy and DEA

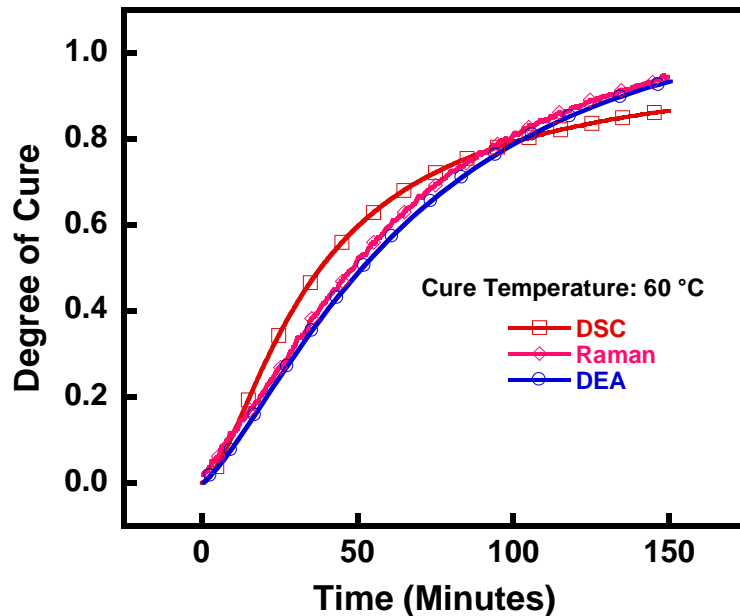


Figure 16: Degree of cure comparison between DSC, Raman and DEA isothermally at 60 °C

For the in-situ cure monitoring to be valid, the results from the Raman spectroscopy and DEA should provide the same, if not, comparable observations as given by the DSC. As shown in Figure 16, 17 and 18, a respectable agreement is obtained from the degree of cure comparison among the three methods. As each

It is important that information obtained from each cure method should lead to the same or similar results in order to investigate the possibility of in-situ cure monitoring. Hence, the degree of cure from the DSC, Raman spectroscopy and DEA was compared at three isothermal cure temperatures: 60, 80 and 100 °C, as shown in Figure 16, 17 and 18, respectively.

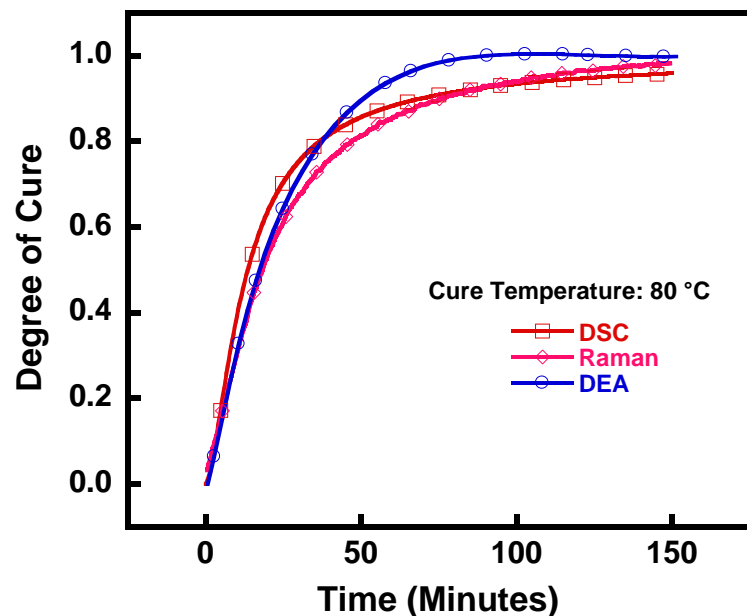


Figure 17: Degree of cure comparison between DSC, Raman and DEA isothermally at 80 °C

technique observes and measures a different phenomenon, the results were not expected to be identical. DSC measures the heat of reaction generated in a sample, Raman spectroscopy observes the rotational and vibrational transitions in molecules and detects chemical bonds and their changes during reaction, while DEA detects the changes in dielectric properties of the sample which are highly influenced by the mobility of ions and dipoles. As illustrated in the figures, the three methods deliver a good agreement in the degree of cure, and thus confirming the possible use for in-situ cure monitoring.

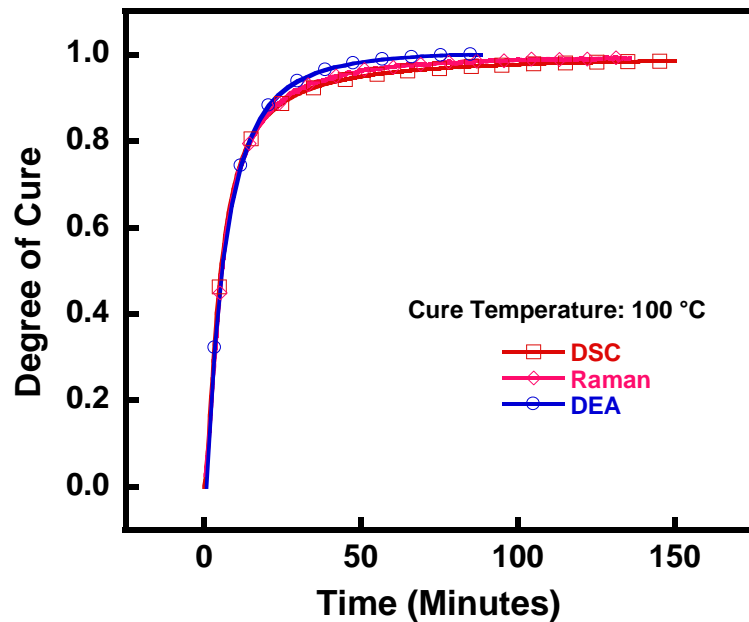


Figure 18: Degree of cure comparison between DSC, Raman and DEA isothermally at 100 °C

3.4 Conclusion and Implementation Plan

In this research, the possibility of in-situ cure monitoring of an epoxy resin was investigated by means of Raman spectroscopy and dielectric analysis (DEA). The cure behavior was first characterized using differential scanning calorimetry (DSC) as a baseline comparison. Several kinetic models were fitted with the dynamic DSC data, and it was found that the Prout-Tompkins autocatalytic model was able to best describe the cure behavior of the epoxy resin. The kinetic parameters were determined from the fitted model, and the activation energies obtained from the autocatalytic model, the Kissinger method and the Ozawa-Flynn-Wall analysis showed a reasonable agreement. The model can also be used to predict the degree of cure under isothermal conditions, which was found to be consistent with experimental results. The degree of cure was strongly affected by the cure temperature; a higher cure temperature accelerated the

cure process in general. The relationship between T_g and degree of cure was established and fitted with the DiBenedetto equation.

The degree of cure from Raman spectroscopy was determined quantitatively using a peak at 1255 cm^{-1} and a constant reference peak at 1609 cm^{-1} . The peak at 1255 cm^{-1} was observed to be decreasing due to the opening of the epoxide group during cure, and therefore was used to calculate the degree of cure. The DEA provided the dielectric loss factor data, which is mainly contributed by the ion conductivity at low frequencies. The loss factor data indicated that the ion mobility to migrate from one electrode to the other became more restricted as the sample turned into solids. Therefore, the dielectric loss factor data were used to calculate the degree of cure, and a new model was proposed for the calculation.

The degree of cure comparison obtained from the DSC, Raman spectroscopy and DEA under isothermal conditions was presented in this research, and a good correlation was established among the three methods. This correlation supports in-situ cure monitoring during the manufacturing process using Raman spectroscopy and DEA. Raman spectroscopy is an efficient and excellent technique for the analysis of epoxy resins cure because direct information on chemical bonds and their changes during reaction can be obtained. While DEA measures a different phenomenon, it is shown that DEA also has the capability of monitoring the cure reaction, and therefore can be incorporated in the manufacturing process for cure monitoring.

Now that the potential use for in-situ cure monitoring has been confirmed, an implementation plan for in-plant monitoring can be developed. The goal is to develop a method for utilizing Raman spectroscopy or DEA that can be implemented in the wind blade manufacturing industry to monitor the cure reaction in real time. With DEA, the use of parallel plate electrodes becomes impractical for complex-shaped and/or thick parts as well as when producing parts with an open mold. In manufacturing wind blades, particularly, the use of interdigitated sensors is significant, as shown in Figure 3. It has been reported that implanting sensors within the fabrics adversely affects the mechanical performance of the parts. Hence, future study should look into the possibility of placing the sensors on or near the surface of the mold before laying down

the fiberglass without interrupting the process being monitored. Although the DEA performed in this study used parallel plate electrodes, the trend in the degree of cure obtained by the sensors should offer similar results. After the sensors are placed on the surface of the mold, the dielectric properties can be recorded as a function of time to observe the cure.

With Raman spectroscopy, it is important for future study to investigate the possibility of developing a fixture to observe the cure reaction using a Raman spectrometer by projecting the laser light to a specific part location. As previously mentioned, since different areas of the part exhibit different reaction rates, projecting several laser lights is necessary to observe the cure cycle at different locations. The data generated from the DEA and Raman spectroscopy could also be used as input into computer simulation models such as finite element analysis to optimize the process parameters during cure.

Chapter 4: Conclusion and Future Work

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