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Disciplines

Industrial Engineering | Manufacturing | Polymer and Organic Materials | Process Control and Systems | Systems Engineering

Cure kinetics characterization and monitoring of an epoxy resin using DSC, Raman spectroscopy, and DEA

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Abstract

The use of thick sections of fiber-reinforced polymers (FRPs) is increasing for numerous industrial applications such as wind turbine blades. In situ cure monitoring is very important to directly observe the cure process of FRPs during the manufacturing process. In this work, Raman spectroscopy and dielectric analysis (DEA) are investigated for in situ cure monitoring of an epoxy resin. The cure behavior is first characterized using differential scanning calorimetry (DSC) as a baseline comparison, and the best-fit phenomenological reaction model is 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 is also established. The degree of cure obtained from Raman spectroscopy and DEA under isothermal conditions is compared to that obtained from DSC. A good agreement is observed among the three methods, supporting the potential of these in situ cure monitoring methods during manufacturing. An implementation plan for in-plant monitoring is also discussed.

Keywords

- Thermosetting resin;
- Cure behavior;
- Thermal analysis;
- Process monitoring

1. Introduction

Large and complicated structures from fiber-reinforced polymers (FRPs) are used in numerous industrial applications, including the growing wind energy field, which has become one of the

dominant markets for composite materials. For structural and engineering applications, where both strength and elasticity are critical, FRPs are used due to their excellent physical and mechanical properties, especially their relatively high specific strength and stiffness (strength and stiffness divided by density) [1], [2], [3] and [4]. In the wind energy sector, FRPs are the materials of choice for manufacture of 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 premature vitrification and high temperatures at which undesirable side reactions or degradation may occur [5].

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) [3], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15] and [16]. 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 non-isothermal measurements of diglycidyl ether of bisphenol A (DGEBA) with m-phenylenediamine (m-PDA) using an advanced isoconversional method [17] and [18]. Flammersheim and Opfermann also examined the cure kinetics of isothermal and non-isothermal measurements of the same materials used by Sbirrazzuoli et al. and determined that phenomenological modeling would be a useful tool to

adequately describe the experimental cure kinetics data [19]. Kessler and White observed the cure kinetics of polydicyclopentadiene prepared by ring-opening metathesis polymerization using DSC by fitting different phenomenological kinetic models [12]. Sheng et al. studied the degree of cure vs. time of thermosetting bisphenol E cyanate ester by performing isothermal cure [13]. 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 [3].

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 [4], [7], [9], [20], [21], [22] and [23]. 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 [20]. The epoxide ring vibration was identified 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 [21]. 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 [7]. The degree of cure was compared to the one obtained 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 [9]. 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 [23]. Sernek and Kamke observed the dielectric analysis for continuous online monitoring of phenol formaldehyde adhesive cure in a hot press by putting sensors in between the two hot presses [22].

In order to observe the cure through the thickness of composite materials, sensors for the dielectric system must be implanted within the fabrics; however, this technique has been reported to adversely affect the mechanical performance of the parts [4] and [6]. 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 [4]. This method 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. Furthermore, the wind blade components are typically cured under near isothermal conditions, but there has been little study about determining the end of cure of an epoxy resin under isothermal conditions using Raman spectroscopy and DEA. By defining the end of cure, the cure cycle time can be estimated or even predicted in order to decrease the production cycle.

In this study, an epoxy system used for the manufacture of wind turbine blades is investigated; it is based on standard diglycidyl ether of bisphenol A (DGEBA) epoxy resin and a modified aliphatic amine as a curing agent. The cure kinetics of the epoxy system was characterized by differential scanning calorimetry (DSC) using both non-isothermal and isothermal methods. Several phenomenological reaction models were fitted with the non-isothermal 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 novel study interestingly compares the results of the degree of cure obtained from DSC, Raman spectroscopy, and DEA to investigate the possible use of these methods for in situ cure monitoring of thick section composites such as spar caps for wind turbine blades.

2. Experimental

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.

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 at room temperature for approximately 1 min to ensure a homogeneous mixture. The sample was then immediately flash frozen using liquid nitrogen to avoid premature curing reactions.

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 pan. The sample pan was then put in the DSC cell which was pre-cooled to −50 °C. For the non-isothermal 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 purge gas at a rate of 25 mL/min. Three isothermal cure temperatures (T_c = 60, 80 and 100 °C) between the onset of the reaction and the peak heat flow from the non-isothermal 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 to the desired cure temperature and then isothermally held at that temperature for various times ranging from 2 min to 2 h. Following this scan, the DSC cell was immediately cooled 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 residual heat of reaction was determined by integrating over the exothermic peak with respect to time. 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.

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 used to induce the Raman scattering effect, measuring 200 mW at the sample. The exposure time for each spectrum was 5 s, and the acquisition interval was approximately 1 s. 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 a temperature-controlled sample holder and allowed to cure as the Raman spectra were collected.

2.5. DEA measurements

The dielectric analysis measurements were conducted using a broadband dielectric spectrometer from 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. Results and discussion

3.1. DSC cure characterization

3.1.1. Non-isothermal 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:

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

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

The non-isothermal 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 Fig. 1. 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 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.
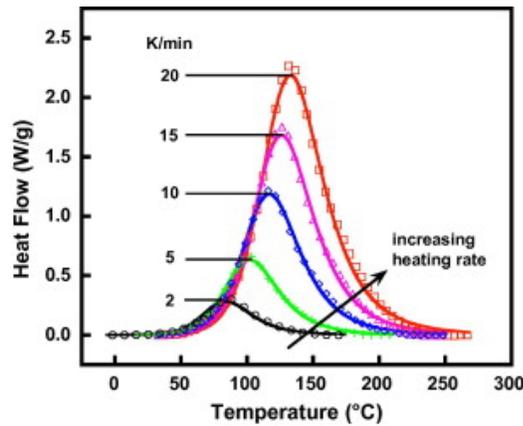

Fig. 1: Non-isothermal DSC cure behavior of the resin. The experimental data are shown as symbols, and the lines represent the best model fits.

The peak temperature, T_p, shifts to a higher temperature range with increasing heating rate, β. Hence, the Kissinger method can be used 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]:

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

where R is the universal gas constant. By plotting $\ln(\beta/T_p^2)$ vs. $1/T_p$, the values of activation energy, E_a, and pre-exponential factor, A, can be estimated by calculating the slope of the linear fit and the y-intercept, as shown in Fig. 2. It can be assumed that the maximum reaction rate, $d\alpha/dt$, occurs at the peak temperature, at which point $d^2\alpha/dt^2$ is equal to zero. The Kissinger method provides the value of activation energy as 52.37 kJ/mol and the value of log A as 15.22 s^{-1}.
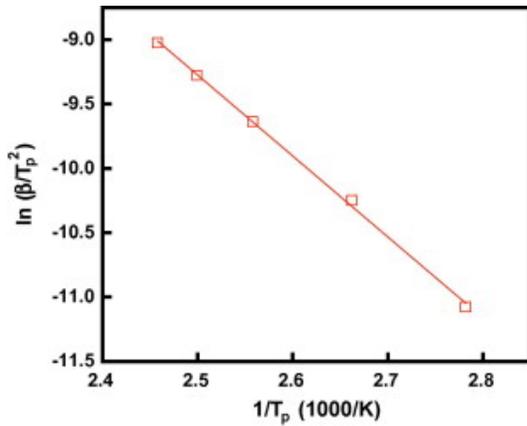
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Fig. 2: Kissinger's plot to determine activation energy (E_α). The slope of the linear fit represents E_α.

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 [3] and [8]. 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:

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

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

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

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:

$$K(T) = A \exp\left(\frac{-E_\alpha}{RT}\right)$$

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where E_α 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:

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

Therefore, if the reaction model that 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 nth order or autocatalytic models, which are shown in Table 1.

Table 1.
Phenomenological reaction models used in this study.

Model	Designation	$f(\alpha)$	Parameters
nth Order	Fn	$(1 - \alpha)^n$	A, E_α, n
nth Order autocatalytic	FnA	$(1 - \alpha)^n(1 + K_{cat}\alpha)$	A, E_α, n, K_{cat}
Prout–Tompkins autocatalytic	PT	$(1 - \alpha)^n\alpha^m$	A, E_α, n, m

The non-isothermal DSC measurements in this study were fitted with the reaction models displayed in Table 1 by using multivariate least squares regression. All the parameters, the F-values, and the least-squares correlation coefficients were calculated based on the respective reaction models and are shown in Table 2. The F-values were computed using a statistical F-test method, which determines the best model fit by comparing the individual models' variances against each other. The F-test method is employed to evaluate if there is a statistically significant difference between the models in regard to the fit quality to the experimental data. Based on the residual mean square (the lowest value), the Prout–Tompkins autocatalytic model provides the best description of the cure behavior of the epoxy resin studied in this work, and the F-test analysis confirms that the model is a statistically significant better fit for the data (assuming a 95% confidence interval), as shown in Fig. 1, where $\log A = 4.82$ s^{-1}, $E_\alpha = 50.58$ kJ/mol, $n = 1.89$ and $m = 0.39$. Some minor deviations are present between the experimental data and the model fit as the phenomenological models are unable to sufficiently describe the complicated cure behavior of epoxy resin in the non-isothermal DSC measurements. The difference could also be attributed to experimental uncertainties in the measured data.

Table 2.
Kinetic parameters determined by fitting non-isothermal DSC measurements with phenomenological reaction models.

Model	E_α (kJ/mol)	log A (s^{-1})	n	log K_{cat}	m	F-value [a]	Residual mean square
Fn	73.59 ± 1.417	7.70 ± 0.190	1.92 ± 0.020			5.34	0.04767
FnA	52.02 ± 0.500	4.39 ± 0.068	2.26 ± 0.026	0.81 ± 0.017		1.82	0.02627
PT	50.58 ± 0.423	4.82 ± 0.059	1.89 ± 0.016		0.39 ± 0.004	1.00	0.02117

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

When comparing the values of activation energy obtained from the Prout–Tompkins autocatalytic model and the Kissinger method, the numbers are similar (50.58 and 52.37 kJ/mol). Therefore, the two methods are a good approximation to determine the constant values of activation energy. However, a discrepancy on the pre-exponential factor was noted: 4.82 s^{-1} and 15.22 s^{-1} from the Prout–Tompkins autocatalytic model and the Kissinger method, respectively. This discrepancy could be due to the fact that the Kissinger method only uses the peak temperature for the analysis and does not account for the rest of the data in the DSC curves, whereas the Prout–Tompkins autocatalytic model is based on a fit of all of the data.

3.1.2. Model-free isoconversional method: Ozawa–Flynn–Wall analysis

If the activation energy is not assumed to be constant throughout the curing reaction, but rather allowed to vary with 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 [25], [26] and [27]:

$$\log \beta = -\frac{0.4567 E_\alpha}{R T_i} + A'$$

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

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

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 β vs. $1/T_i$ was drawn at each degree of cure, as shown in Fig. 3. The resulting slope is proportional to the activation energy, E_α, and the intercept is proportional to the pre-exponential factor, A'.
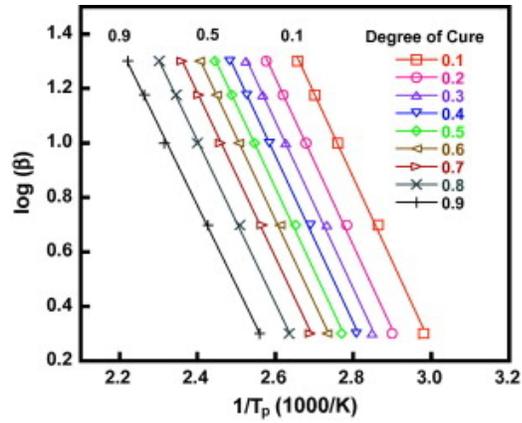
Fig. 3: Ozawa–Flynn–Wall analysis to determine E_α and A'.

When plotting the activation energy separately as a function of cure, the activation energy slowly decreases as the degree of cure increases, as shown in Fig. 4. 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.
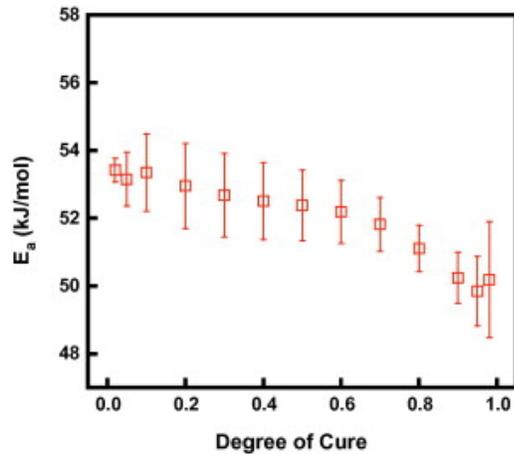

Fig. 4: Ozawa–Flynn–Wall's activation energy as a function of degree of cure.

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, Eq. (1) can be modified as:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T}$$

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) because T_g provides a more sensitive measure for monitoring the cure process, especially at high levels of conversion.

Fig. 5 displays the non-isothermal 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 (noted by the arrows), 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 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.
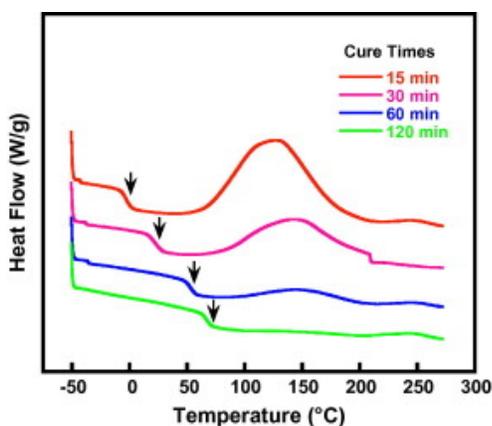

Fig. 5: A series of DSC curves for partially cured samples at 80 °C for various times.

The total heat of reaction, ΔH_T, was measured to be 425.3 J/g by performing a non-isothermal DSC scan of an uncured sample at 10 °C/min. The degree of cure obtained at three different isothermal temperatures for several time periods are shown in Fig. 6. 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 non-isothermal DSC scans can be used to predict the cure behavior under isothermal conditions. 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 predictions, which are represented by the lines, fit the experimental data quite well, which indicates that the Prout–Tompkins autocatalytic model is a good model fit for the epoxy system studied in this work.
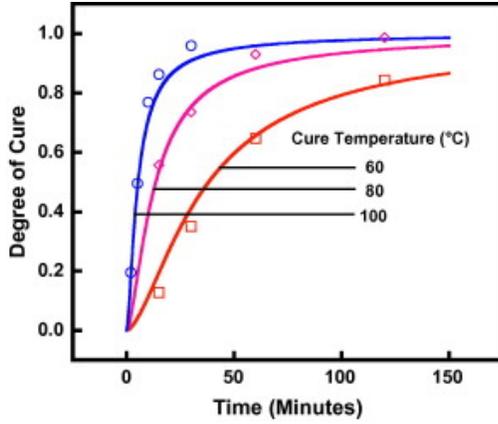
Fig. 6: DSC degree of cure as a function of time at three isothermal cure temperatures. The symbols represent the experimental data, and the lines correspond to the model prediction.

The glass transition temperature can 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 relationship between T_g and α can be mathematically developed using the empirical DiBenedetto equation, which is defined as [28]:

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

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 Fig. 7 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, respectively.
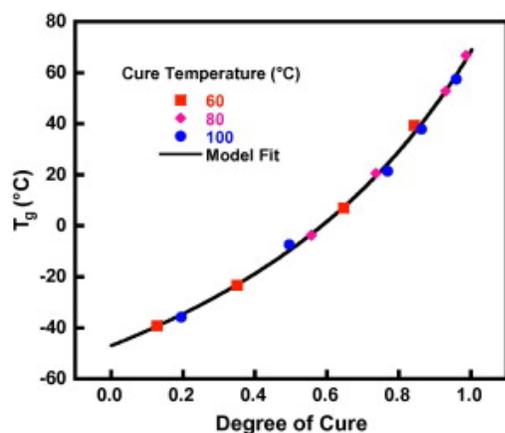
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Fig. 7: T_g vs. degree of cure plot with a model fit provided by the DiBenedetto equation.

3.2. Raman spectroscopy cure characterization

Raman spectroscopy measures rotational and vibrational transitions in molecules and can be used to detect chemical bonds and their changes during reaction [29]. 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. Fig. 8 shows the Raman spectra obtained at 80 °C at various cure times with the last four curves being shifted vertically for better illustration of the reaction progress. The peak at 1255 cm^{-1} corresponds to the epoxide group, and the intensity is observed to decrease 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 [20], [21] and [30]. 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 peak attributed to the epoxide group.
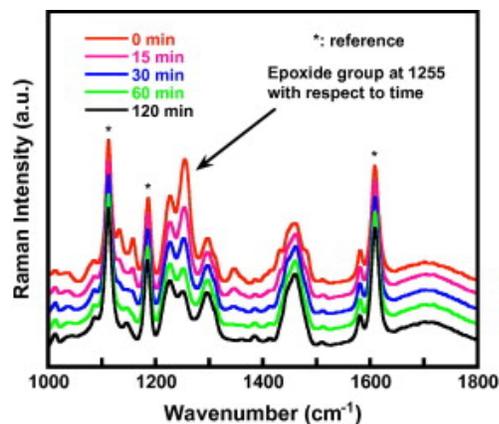
Fig. 8: Real-time Raman spectra featuring the reactive and reference peaks during cure at 80 °C. To calculate the degree of cure, it is important to normalize the peak intensity at 1255 cm^{-1} by dividing it by that of one of the reference peaks. Dividing by the reference peak cancels out background and instrument noise, including shifts in the spectral baseline over time. The degree of cure can be calculated using the equation below:

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

where $I(t)$ and $I(0)$ correspond to the intensity at time t and the beginning (time 0), respectively. Time 0 is the point when the Raman data collection starts as soon as the materials have been prepared. The subscripts 1255 and ref represent the values at 1255 cm^{-1} and at 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. Fig. 9 shows the degree of cure obtained by Raman spectroscopy at 60, 80 and 100 °C. Similar to the DSC results (see Fig. 7), the degree of cure increases with increasing cure temperature and cure time.
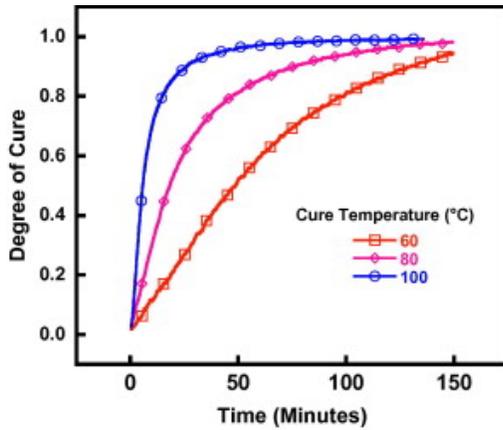

Fig. 9: Raman spectroscopy degree of cure as a function of time at three isothermal cure temperatures.

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 [31]:

14

$$\varepsilon * = \varepsilon' - i\varepsilon''$$

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 [9].

The loss factor decreases with cure time (see Fig. 10), with the decrease being more rapid at higher cure temperatures, which is consistent with DSC results (see Fig. 6). 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.
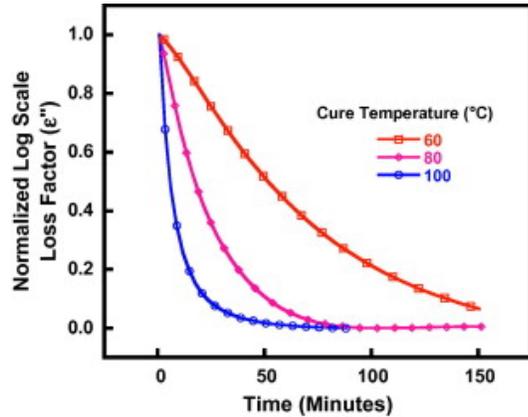

Fig. 10: DEA loss factor as a function of time at three isothermal cure temperatures.

The measurement of loss factor as a function of cure temperature and time allows for the calculation of degree of cure. The following formula is proposed for the degree of cure calculation:

$$\alpha(t) = \frac{\log(\varepsilon_0'') - \log(\varepsilon_t'')}{\log(\varepsilon_0'') - \log(\varepsilon_\infty'')}$$

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 Fig. 11. As mentioned in the DSC and Raman analysis, the degree of cure increases with increasing cure temperature and cure time.
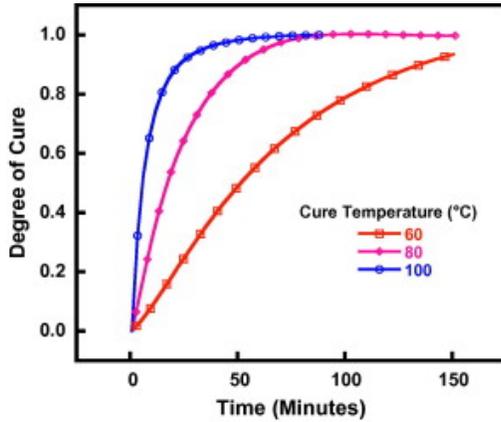

Fig. 11: DEA degree of cure as a function of time at three isothermal cure temperatures.

3.4. Comparison between DSC, Raman spectroscopy and DEA

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 Fig. 12, Fig. 13 and Fig. 14, respectively.
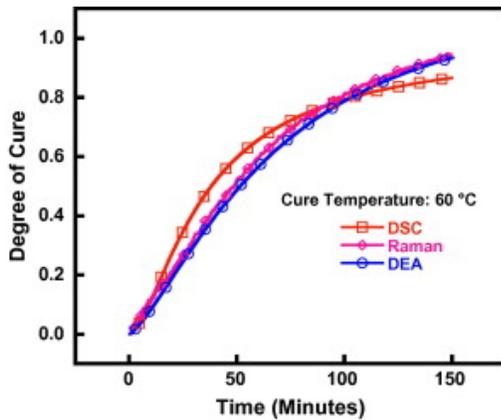

Fig. 12: Degree of cure comparison between DSC, Raman and DEA isothermally at 60 °C.
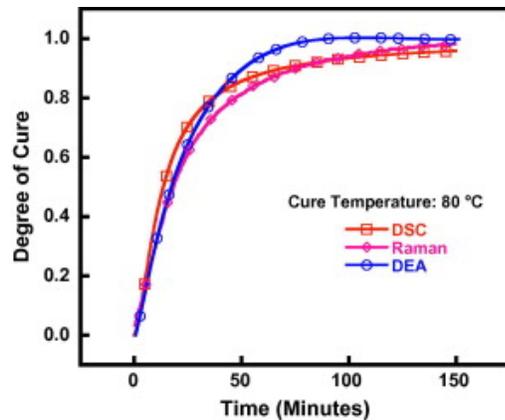
Fig. 13: Degree of cure comparison between DSC, Raman and DEA isothermally at 80 °C.
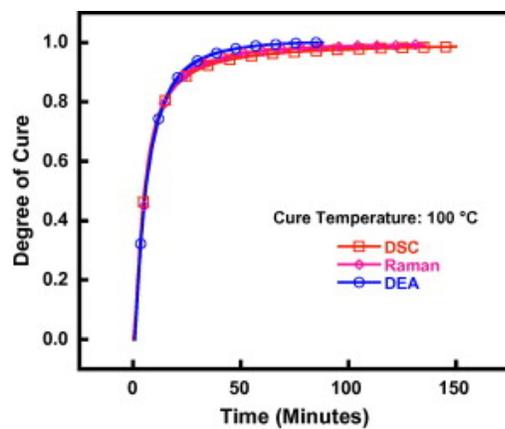

Fig. 14: Degree of cure comparison between DSC, Raman and DEA isothermally at 100 °C.

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 Fig. 12, Fig. 13 and Fig. 14, a respectable agreement is obtained from the degree of cure comparison among the three methods. It is shown that at higher temperatures (80 and 100 °C), DEA generally presents a higher degree of cure at given cure times. The degree of cure calculation proposed for DEA uses loss factor as the variable, which is highly influenced by the ion conductivity. 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. Hence, the viscosity of the materials is the key factor here in DEA, which makes it more sensitive in terms of detecting the cure.

As each technique observes and measures a different phenomenon, the results were not expected to be identical. DSC, which is not an in situ technique, measures the heat of reaction generated in a sample, and its results are dependent on the heat generated during the reaction, which may not be resolvable from other heat-related events. Raman spectroscopy observes the rotational and

vibrational transitions in molecules and detects chemical bonds and their changes during reaction, has an excellent time resolution, requires no special sample preparation, and can be used for remote analysis using optical fibers. However, it is a more expensive technique and may have a limited penetration depth depending on the refractive index and colour and fluorescence characteristics of the materials. On the other hand, DEA detects the changes in dielectric properties of the sample which are highly influenced by the mobility of ions and dipoles, possesses a wide frequency range in the measurement, and is very sensitive to small changes in material properties. However, in practice, more preliminary experiments need to be performed when it comes to using parallel-plate electrodes or interdigitated sensors to ensure correct measurements. Nevertheless, 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.

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 non-isothermal 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 during 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. Moreover, methods and calculation to determine the end of cure using Raman spectroscopy and DEA were fully demonstrated.

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. 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, because 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.

Acknowledgements

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