Cure Kinetics, Glass Transition Temperature Development, and Dielectric Spectroscopy of a Low Temperature Cure Epoxy/Amine System

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ABSTRACT: This article reports a study of the chemical cure kinetics and the development of glass transition temperature of a low temperature (40°C) curing epoxy system (MY 750/HY 5922). Differential scanning calorimetry, temperature modulated differential scanning calorimetry, and dielectric spectroscopy were utilized to characterize the curing reaction and the development of the cross-linking network. A phenomenological model based on a double autocatalytic chemical kinetics expression was developed to simulate the cure kinetics behavior of the system, while the dependence of the glass transition temperature on the degree of cure was found to be described adequately by the Di Benedetto equation. The resulting cure kinetics showed good agreement with the experimental data under both dynamic and isothermal heating conditions with an average error in reaction rate of less than 2×10^{-3} min^{-1}. A comparison of the dielectric response of the resin with cure kinetics showed a close correspondence between the imaginary impedance maximum and the calorimetric progress of reaction. Thus, it is demonstrated that cure kinetics modeling and monitoring procedures developed for aerospace grade epoxies are fully applicable to the study of low temperature curing epoxy resins. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1899–1905, 2012

Key words: curing of polymers; kinetics; glass transition; differential scanning calorimetry; dielectric spectroscopy

INTRODUCTION

The manufacture of thermoset based composites involves the irreversible chemical process of cure during which a reactive resin system is transformed from liquid to solid via the formation of a three dimensional cross-linking network. Phenomena occurring during the cure, such as the development of residual stress and the corresponding microcracking, significantly influence the final properties of produced components, while the kinetics of cross-linking of the thermosetting polymer governs the design of the process. A cure kinetics model combined with knowledge of the dependence of the glass transition temperature on the degree of cure can be used to track the material state, given known temperature history. This combination of quantitative information is a central component of detailed process model for composites manufacturing.

Differential scanning calorimetry (DSC) is the most widely used method for the study of cure kinetics of thermosets.[1–3] In the context of DSC the heat of reaction, $\Delta H(t)$ is assumed to be proportional to the degree of cure, a, which is calculated as follows[4]:

$$a = \frac{\Delta H(t)}{\Delta H_T}, \tag{1}$$

where ΔH_T is the total heat of reaction measured in dynamic DSC tests. Consequently, the reaction rate, da/dt, is calculated from the heat flow released during the curing reaction and directly measured during a DSC experiment as follows:

$$\frac{da}{dt} = \frac{1}{\Delta H_T} \frac{dH(t)}{dt}, \tag{2}$$

Cure kinetics models fall into two main categories: (i) phenomenological models which are based on empirical expressions that resemble chemical kinetics equations; and (ii) mechanistic models which consider balances of chemical species and are based on information on the reaction path. Both types result in an expression that represents the reaction rate as a function of the degree of cure, a, and temperature, T. Phenomenological models

require a demanding parameter estimation step, which usually involves nonlinear fitting over a wide range of experimental conditions. In contrast, the chemical information implied in mechanistic models allows relatively easy estimation of model parameters. Mechanistic models are predictive in the sense that they can be valid outside the experimental window used for parameter estimation, whereas the range of validity of phenomenological models is strictly limited to the range of temperatures covered by experiments. Although mechanistic models appear to be advantageous, the complexity of the chemistry of industrial resin systems, as well as the sensitive nature of information related to their formulation, makes phenomenological modeling the preferred option.

The great majority of kinetics models for the curing of epoxies is based on the Kamal-Sourour model[2,5]:

$$\frac{da}{dt} = (k_1 + k_2 a^m)(1 - a)^n. \tag{3}$$

Here, m and n are reaction orders independent of temperature and k_1 and k_2 are rate constants following an Arrhenius dependence on temperature:

$$k_i = A_i e^{-E_i/RT}, \tag{4}$$

where A_i is the pre-exponential factor and E_i the activation energy of rate constant k_i and R is the universal gas constant. An extension of this model splits the nth order and autocatalytic terms as follows[6]:

$$\frac{da}{dt} = k_1 a^m (1 - a)^n + k_2 (1 - a)^k, \tag{5}$$

Other extensions of the Kamal-Sourour model include the combination of two autocatalytic terms[7] or of two autocatalytic and an nth order term.[8]

Incorporation of the influence of diffusion control in the latest stages of the curing reaction requires a modification of chemical cure kinetics models. This is usually performed by modifying the rate constant expression. A simple phenomenological approach based on the expression[9]:

$$k_i = \frac{k_{ci}}{1 + e^{C[a - a_c(T)]}}, \tag{6}$$

uses a scaling factor to reduce the rate constant as the degree of cure approaches a critical degree of cure, α_c, which depends on temperature. The coefficient C controls the breath of transition from chemical to diffusion control.

A more general approach treats the overall reaction as the serial combination of chemical reaction and diffusion as follows[10]:

$$\frac{1}{k_i} = \frac{1}{k_{ci}} + \frac{1}{k_{di}}. \tag{7}$$

Here K_{ci} and K_{di} are the chemical and diffusion rate constants, respectively. The diffusion rate constant can be assumed to follow a modified WLF-type of behavior[11]:

$$k_{di} = k_{do} e^{[(C_1(T - T_g))/(C_2 + |T - T_g|)]} \tag{8}$$

where C_1 and C_2 are fitting parameters and k_{do} is an Arrhenius function of temperature.

To fulfil the condition that the reaction rate approaches zero as the material approaches vitrification, reaction rate expressions incorporating a maximum degree of cure (α_{max}) explicitly were introduced. Gonzalez-Romero and Casillas[12] utilized the following expression:

$$\frac{d\alpha}{dt} = A e^{-(E_a/RT)} (\alpha_{max} - \alpha)^n e^{m\alpha}, \tag{9}$$

Batch and Macosko[13] adopted the following expression for the dependence of maximum degree of cure on temperature:

$$\alpha_{max} = \frac{1}{d} \left(\frac{1}{T_o} - \frac{1}{T_{cure}} \right) \tag{10}$$

where d is a fitting parameter, T_{cure} is the cure temperature, and T_o is the theoretical temperature where no reactions could occur ($\alpha_{max} = 0$). At high cure temperatures the maximum degree of cure is unity.

This work investigates the cure kinetics and the glass transition temperature advancement of a diglycidyl ether of Bisphenol A based epoxy cured with a high molecular weight polyoxypropylene diamine hardener. DSC and temperature modulated DSC (TMDSC) are utilized to obtain experimental information from which appropriate models for both the cure kinetics and the development of the glass transition temperature during the cure. Dielectric Spectroscopy is utilized to monitor the cure reaction and to identify the correspondence between the calorimetric progress of reaction and dielectric metrics of the degree of cure. This approach has been used successfully in the characterization of high temperature curing aerospace grade epoxy systems[14] which are among the most widely studied of the epoxy systems. This article is concerned with the applicability of the same methodology to the characterization of a much less frequently studied type of epoxy, used in applications where cure temperature has to be kept low for the avoidance of exotherm, such as in situations when relatively large structures need to be potted in the resin. The particular resin studied here
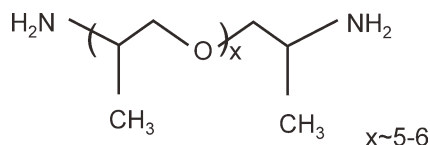
Figure 1 Chemical structure of Aradur HY 5922 curing agent.

would normally be cured at 40°C and achieve a maximum T_g of 45°C. For purposes of cure kinetics studies this cure temperature has to be exceeded, which is practical for the small sample sizes involved in the thermoanalytical measurements.

EXPERIMENTAL

Materials

The resin studied was a two-part epoxy/amine system based on a liquid diglycidyl ether of bisphenol A (Araldite MY 750, Vantico) with an epoxy equivalent mass of 192. The curing agent was an aliphatic polyetheramine, polyoxypropylene diamine, with a commercial name of Aradur HY 5922. It has repeating oxypropylene units in the backbone with average molecular weight of about 430 and amine equivalent mass of 115 (Fig. 1). This hardener is suitable for use in applications where cure temperature has to be kept low. The combination of the low cure temperature and the relatively flexible structure of the hardener means that the fully cured resin can only achieve a correspondingly low glass transition temperature. The hardener was used in the stoichiometric weight ratio of 55 parts per 100 parts of epoxy resin. The samples were produced by mixing these components at room temperature for 15 min and then subdividing the mixture into several containers subsequently stored at −18°C for further use.

Thermal analysis

A TA Instruments 2920 TMDSC equipped with an RCS cooling system under nitrogen flow was utilized for the cure characterization. Nitrogen was used as the purge gas at 30 mL/min. An amount of resin in the range of 8–10 mg was encapsulated in aluminum pans and placed in the instrument cell at ambient temperatures. Several dynamic runs were carried out at constant heating rates of 7.5, 5, 2.5, 1, and 0.5°C/min. The total heat of reaction and the evolution of the degree of cure with time were calculated using Bandara's method for the generation of an iterative sigmoidal baseline.[15] For isothermal cure experiments the sample was first heated up to the required temperature at a heating rate of 20°C/min and then left to cure until the reaction was complete. Isothermal cure experiments were carried out at 50, 60, 70, 80, and 90°C. A horizontal baseline was

used for the integration of isothermal heat flux signals.

TMDSC was used for the measurement of the glass transition temperature of uncured, partially cured and fully cured samples. Partially cured samples were produced under dynamic heating conditions at a rate of 1°C/min up to the predefined degree of cure, at which point the temperature scan was interrupted and the sample was rapidly cooled. An underlying heating rate of 1°C/min and a temperature modulation of 1°C with a period of 1 min were utilized in the TMDSC experiments. The glass transition temperature was identified as the inflection point of the specific heat capacity versus temperature curve (Fig. 2).

Dielectric measurements

Dielectric measurements under isothermal heating conditions at 80°C and 90°C were performed using a Solartron SI 1260 frequency analyzer. The dielectric sensors used (Weniger Scholz, Gmbh) comprise an assembly of interdigitated electrodes, printed on a thin polymeric film. The sensor was immersed in a glass tube containing the liquid resin which was then placed in a hollow copper cylinder, surrounded by heating elements controlled by a Eurotherm temperature controller. A control thermocouple was placed in an opening on the wall of the hollow cylinder. A second thermocouple was placed in the glass tube to record the actual thermal profile followed by the resin. The measurements were performed in the frequency range of 1 Hz to 1 MHz. Twenty five frequencies were swept on a logarithmic scale.

RESULTS AND DISCUSSION

Cure kinetics

The results of dynamic DSC tests at different heating rates for the cure of the MY 750/HY 5922 resin
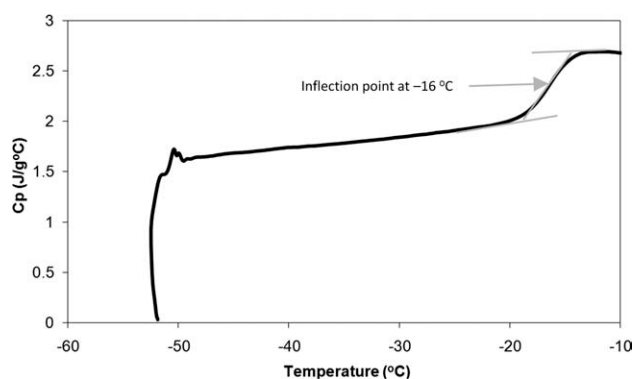

Figure 2 Determination of the glass transition temperature of partially cured resin using a dynamic heating rate of 1°C/min and a modulation of 1°C every 60 s. T_g is taken as the inflection point of the heat capacity signal, C_p, versus temperature.
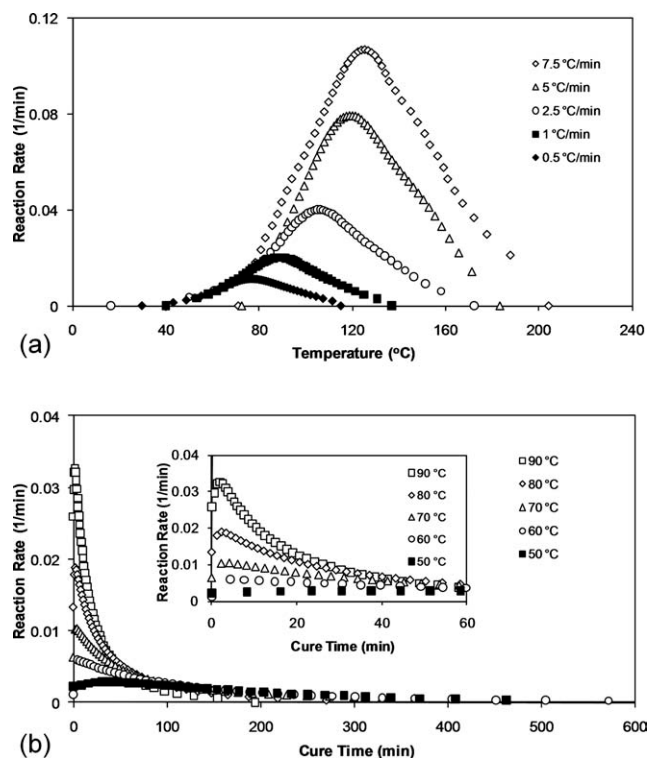
Figure 3 (a) Dynamic and (b) isothermal DSC tests.

system are presented in Figure 3(a). The average total heat of the reaction and temperature maxima measured at six different heating rates, as reported in Table I, is 344 ± 16 J/g. The cure starts at approximately 40°C and becomes faster at around 90°C for the low heating rates used. The reaction rate versus time results for the isothermal cure of the system are presented in Figure 3(b). The reaction rate increases with time initially and then decreases after passing through a maximum [inset of Fig. 3(b)], suggesting that an autocatalytic reaction mechanism is followed.

The curing reaction was modeled using a phenomenological double autocatalytic model. For the diffusion limitations, the glass transition temperature advancement was incorporated into the cure kinetics model using an extension of the Karkanas[6] model. The proposed model utilized is expressed as follows:

$$\frac{da}{dt} = k_1 a^k (1-a)^l + k_2 a^m (1-a)^n, \qquad (11)$$

where $\quad k_1 = \frac{k_{r1} k_d}{k_{r1} + k_d}$, $\quad k_2 = \frac{k_{r2} k_d}{k_{r2} + k_d}$, $\quad k_{r1} = A_1 e^{-E_1/RT}$, $k_{r2} = A_2 e^{-E_2/RT}$, $k_d = A_d e^{-E_d/RT} e^{\frac{(FT-G)}{K(T-T_g)}+P}$, $T_g(a) = f(a)$. α is the degree of cure, T is the temperature in Kelvin, A is the pre-exponential factor (min^{-1}), E is the activation energy (J/mol), A_d is the diffusion controlled pre-exponential factor (min^{-1}), k_{r1}, k_{r2} are the chemical region reaction rates, k_d is the diffusion region reaction rate, k, l, m, and n are fitting exponents, F, G, K, P are fitting parameters and $T_g(a)$ is the glass transition temperature, which is expressed as a function of the degree of cure.

A model of the type used in eq. (11) expresses the reaction rate as a function of the degree of cure and temperature. This type of approach implies an assumption regarding the uniqueness of the mapping of reaction rate on the conversion-temperature space. The validity of this assumption can be tested using the superposition of isothermal and dynamic cure reaction rate data.[16] Figure 4 illustrates isothermal rate of reaction—degree of cure curves under isothermal conditions alongside the data corresponding to the same temperature levels as measured under dynamic conditions. It can be observed that superposition holds with a satisfactory accuracy at lower temperatures. For temperatures above 70°C the errors observed are relatively higher when the degree of cure exceeds 35%. This can be attributed to the fact that low rate dynamic data which yield results in the higher degree of cure part of the superposition plot shown in Figure 4 have a significant part of the reaction occurring at lower temperatures. As a consequence any differences in the curing reaction due to the different temperature range are maximized for this part of the degree of cure-temperature envelope. The average error due to lack of superposition calculated as the average absolute percentage difference between dynamic and isothermal data is approximately 15%. Consequently, conventional cure kinetics modeling based on the unique mapping of reaction rate in the degree of cure—temperature space can be considered valid for the resin system of this study.

Estimation of the parameters of the cure kinetics model expressed by eq. (11) was carried using a binary genetic algorithm (GA). Details of the implementation which involved roulette wheel selection and strong elitism are given in reference.[17] The GA

TABLE I
Total Heats of Reaction and Peak Temperature Under Dynamic Curing Conditions

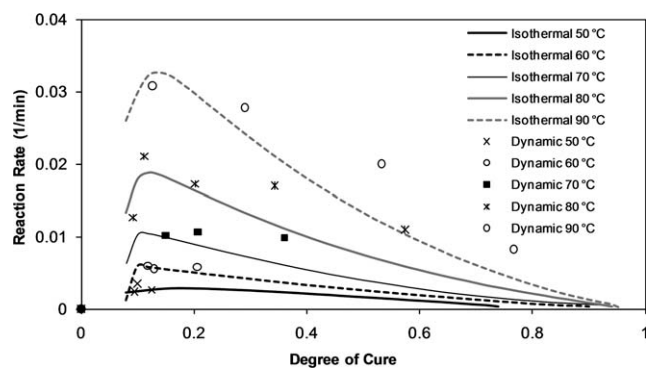| Heating rates (°C/min)		10.0	7.5	5.0	2.5	1.0	0.5	μ^{a}	σ^{b}
MY 750/HY 5922	ΔH (J/g)	333	334	348	340	335	353	344	16
	$T_{\max}$ (°C)	135	126	120	106	89	78	–	–

[a] Average.
[b] Standard deviation.

Figure 4 Superposition of dynamic and isothermal DSC data.

operates with successive generations of solution vectors that are encoded in binary strings which are called individuals. The algorithm starts with the production of the first generation of individuals using random values for the model parameters in the search space. The performance of each individual (fitness) is evaluated as the inverse average error of the model. Subsequently, pairs of individuals are selected for reproduction with the selection probability of an individual being proportional to its fitness. The reproduction involves a cross-over operation, in which parts of the binary string of each of the parents are copied in the string of the new individual, and a mutation operation, in which bits of the new individual are flipped with a very low probability. This procedure is repeated until a new generation is produced. Subsequently, the operations of fitness computation, selection and reproduction are repeated to produce new generations, while the best individuals in each generation of the algorithm are directly passed to the next generation (elitism). The algorithm terminates when a preset number of generation has been produced. Fourteen parameters are involved in the estimation. A population of 51 individuals was used in the GA while the algorithm was executed for 200 generations and the length of the binary string was 31 digits. The search space of the parameter estimation problem addressed in this study is detailed in Table II.

The results of fitting are summarized in Table III and illustrated in Figures 5 and 6 for the dynamic and isothermal cure of the resin system, respectively. The average absolute error over the whole experimental range comprising both isothermal and dynamic experiments is 1.97×10^{-3} 1/min. Table III also reports the sensitivity of the quality of the fit to the values of the fitting parameters. This is computed by applying a 5% shift to one of the parameters while keeping the rest of them constant and calculating the average absolute error corresponding to the new value. The ratio of percentage change of average absolute error and of the parameter yields the

TABLE II
Search Space for the Parameters of the Cure Kinetics Model Used in the Genetic Algorithm Fitting

Parameters	Minimum	Maximum
A_1 (min^{-1})	10^4	2×10^7
E_1 (kJ/mol)	10^2	2×10^5
A_2 (min^{-1})	10^4	2×10^7
E_2 (kJ/mol)	10^2	2×10^5
k	0.01	1
l	0.01	4
m	0.01	1
n	0.01	4
A_d (min^{-1})	10^4	2×10^{20}
E_d (kJ/mol)	10^2	2×10^5
F	10^{-4}	1
G	10^{-4}	1
K	10^{-4}	1
P	10^{-4}	1

sensitivity coefficient. It can be observed that the model error is most sensitive to the activation energies, while the diffusion limitations related terms have a relatively small influence.

The model follows the isothermal experimental cure kinetics results closely. This is evidenced by the high accuracy of the fitting in the early stages of the curing reaction and the successful simulation of the behavior at the latest part of the reaction (Fig. 6). Relatively higher discrepancy is observed in dynamic experiments at low heating rates for the epoxy resin, i.e., 0.5 and 1°C/min. This can be explained by the fact that large part of the cure in the low heating experiments occurs in a temperature-degree of cure region where the superposition between dynamic and isothermal data yields significant errors. As a consequence, the fitting which is influenced significantly by the isothermal data in this region does not reproduce very accurately the results of dynamic experiments. The validity of the

TABLE III
Estimated Cure Kinetics Parameters Obtained From the Fitting of Isothermal and Dynamic DSC Data and the Corresponding Sensitivities

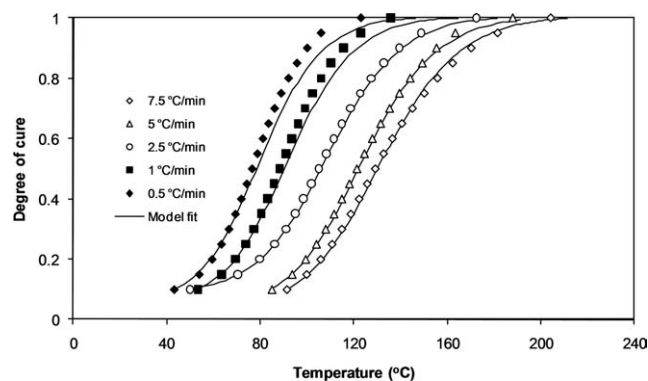| Parameters	Value	Sensitivity
A_1 (min^{-1})	7.79×10^6	7.67×10^{-1}
E_1 (kJ/mol)	55.95	8.26×10^1
A_2 (min^{-1})	5.97×10^6	1.46×10^{-1}
E_2 (kJ/mol)	62.03	1.02×10^1
K	0.295	6.06×10^{-1}
L	1.966	3.59
M	0.494	1.05×10^{-1}
N	1.032	4.11×10^{-1}
A_d (min^{-1})	8.17×10^8	2.16×10^{-2}
E_d (kJ/mol)	55.87	9.96×10^{-1}
F	0.023	1.43×10^{-1}
G	0.019	2.02×10^{-5}
K	0.139	9.15×10^{-3}
P	0.060	2.40×10^{-5}

Figure 5 Comparison between experimental and simulated values of degree of cure versus temperature for dynamic experiments.

model over the wide temperature-degree of cure addressed in this study demonstrates the feasibility of using phenomenological cure kinetics to fit both isothermal and dynamic data simultaneously. This is conditional on satisfactory superposition between isothermal and dynamic data such as the one illustrated in Figure 4, with inconsistencies in superposition propagating to the fitting error. Furthermore, the complexity of the fitting problem necessitates the use of an advanced model fitting procedure that can address multimodal error minimization problems and tackle parameter identification over a wide search space.

The model uses an expression for the dependence of glass transition temperature on the degree of cure based on the Di Benedetto equation. The fitting of this equation to the corresponding experimental data is described in the next section.

Glass transition temperature advancement

Figure 7 shows T_g as a function of the degree of cure obtained from different partially cured specimens along with the curve fit. The T_g of the uncured
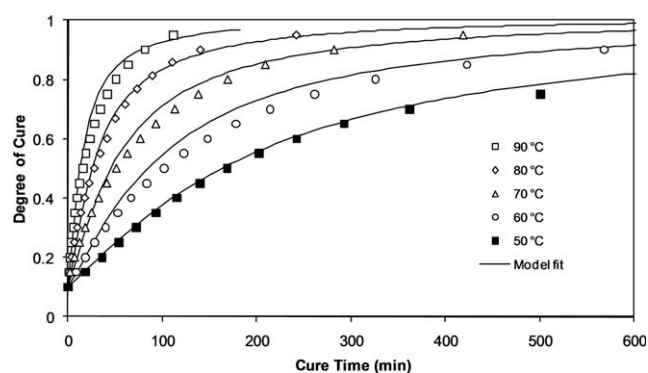

Figure 6 Comparison between experimental and simulated values of degree of cure versus time for isothermal experiments.
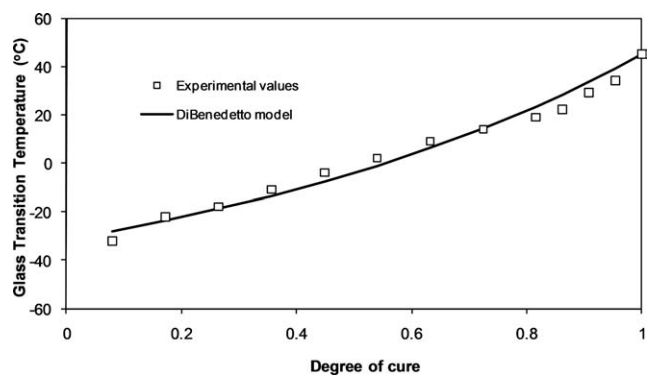
Figure 7 Experimental values and model fit of glass transition temperature as a function of degree of cure.

material is $-32°C$ and that of the fully cured resin is $45°C$.

Di Benedetto's equation was utilized for the simulation of the glass transition temperature advancement. The analytical form of this model is:

$$T_g(a) = T_{go} + \frac{\lambda a(T_{g\infty} - T_{go})}{1 - (1 - \lambda)a}. \tag{12}$$

Here T_{go} is the glass transition temperature of the uncured sample, $T_{g\infty}$ is the glass transition temperature of the fully cured sample and λ a fitting parameter. Nonlinear fitting of eq. (12) to the experimental data yields a value for λ of 0.527. The fitting achieved using this model is very good as evidenced in Figure 7.
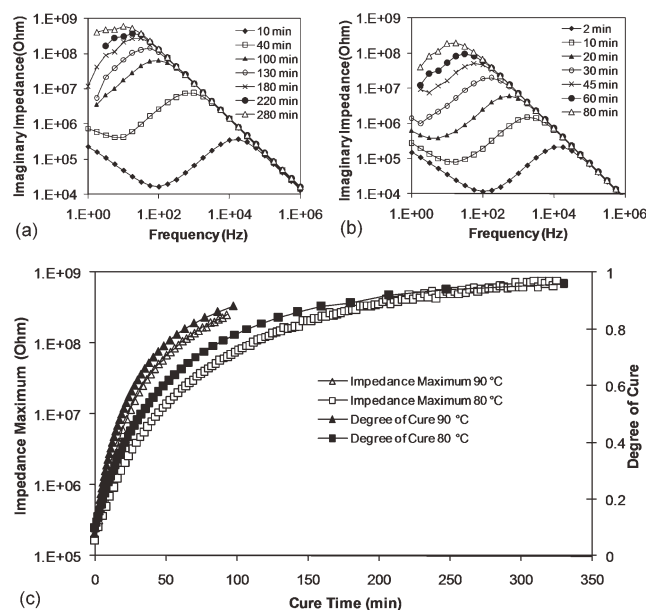

Figure 8 Dielectric response of the resin during isothermal cure (a) evolution of imaginary impedance spectra at $80°C$, (b) evolution of imaginary impedance spectra at $90°C$, and (c) correlation between the imaginary impedance maximum and degree of cure determined by DSC experiments.

Dielectric cure monitoring

The dielectric response of the epoxy resin system follows the typical behavior observed during the cure of thermosets. Figure 8(a) illustrates the evolution of the imaginary impedance spectrum with progressing cure. The spectrum comprises a minimum and a maximum separated by a linear region on the logarithmic scale. At very low frequencies the imaginary impedance decreases with increasing frequency, reaches a minimum value and then increases up to its maximum. A further increase in the frequency leads to a linear decrease of the imaginary impedance. This behavior is representative of the cases where the spectrum is dominated by the occurrence of charge migration.[18]

During the cure, as entities involved in the dielectric response of the material become less mobile and time constants of all processes increase, the imaginary impedance spectrum moves to higher impedance and lower frequencies. Figure 8(b) shows the evolution of the imaginary impedance maximum during the isothermal cure of the epoxy system at 80°C and 90°C alongside the results of calorimetric cure kinetics experiments. It can be observed that the evolution of the impedance maximum correlates very well with the evolution of the degree of cure determined by DSC experiments. This correlation which has also been observed in a wide range of other epoxy systems[14,18] can serve as the basis of online cure monitoring using dielectrics.

CONCLUSIONS

This study extends the use of cure analysis methodologies developed for "high temperature" aerospace epoxies to "low temperature" encapsulating resin systems. The kinetics of cure of the particular epoxy system under investigation follows a double autocatalytic phenomenological model which is valid under both dynamic and isothermal heating conditions. This model incorporates a diffusion term to describe adequately the later stages of the curing reaction. This is achieved in combination with a model of the development of glass transition temperature during the cure based on Di Benedetto's equation. A sensitivity study demonstrates that fitting can lead to robust estimation of the fourteen parameters involved in the cure kinetics model. The fitting is carried out using a GA which allows exploration of a wider parameter search space and elimination of the dependence on a guess solution vector. The capability to model the cure of the resin system of this study is combined with the means to monitor the process *in situ* using impedance spectroscopy. Dielectric experiments of the curing reaction showed that the evolution of the maximum of the imaginary impedance follows the progress of reaction closely.

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