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Modelling and prediction of the diglycidyl ether bisphenol-A/2,2'-dimethyl-4,4'-methylenebis (cyclohexylamine) reaction

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Abstract: Differential scanning calorimetry is used for the analysis and quantitative evaluation of the reaction between diglycidyl ether bisphenol-A and 2,2'-dimethyl-4,4'-methylenebis (cyclohexylamine) according to changes in concentrations of reactants and products. First, this concerned determining the variation in enthalpy of reaction over time for different curing temperatures, plotting of glass transition temperatures versus time, calculation of a polynomial for glass transition temperature against fractional conversion, and the production of plots of fractional conversions versus time. Secondly, the fractional conversion data were used for the kinetic analysis. The line of best fit to these data points revealed an essentially logarithmic relationship that was used to evaluate the reaction rate, dx/dt corresponding to the conversion x , then plot the changes in concentrations (in moles) of all the reactants and products involved in the reaction versus time. This produced a quantitative prediction of the reaction over the curing period.

Keywords: epoxy resins, cure behaviour, processing composites, kinetics of cure

1 INTRODUCTION

Curing of thermosetting materials involves transformation of low-molecular-weight liquids into high-molecular-weight amorphous solids by means of chemical reactions. This transformation reaches an optimal value and then starts to degrade over time because of material ageing and external conditions (including exposure to light radiations, changes in temperature, vibrations, etc.). Therefore, if these materials are to be used in critical applications, one must be able to accurately predict these changes and subsequent performance over time. Differential scanning calorimetry (DSC) analysis is capable of monitoring such changes over time, but would be highly impractical as an *in situ* monitoring tool. The intention of this work was to

measure and plot the changes in the glass transition temperature and fractional conversion over time of an epoxy resin/amine reaction and then to obtain predictive curves of changes according to variations in the concentrations of reactants and products of the reaction.

Previous work [1] has utilized DSC together with Fourier Transform Infrared (FT-IR) to study the curing of epoxy resins. The plot of fractional conversion from an optical fibre sensor that used FT-IR spectroscopy was compared with that produced by DSC and the degree of correlation was found to be satisfactory up to 75 per cent of the chemical conversion. As a result, a sensor designed for embedding into a system curing at an elevated temperature was constructed and tested.

In this article, a plot for the variation of the glass transition temperature with cure time was performed and a relationship for the rate of reaction was defined. The activation energy of the reaction was calculated and a universal plot for fractional conversion against time at all temperatures was produced.

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Consequently, a model for the autocatalytic diglycidyl ether bisphenol-A (DGEBA)/2,2'-dimethyl-4,4'-methylenebis (cyclohexylamine) (DMMB-CHA) reaction was proposed. This model is used to calculate the variation of concentrations with time, and then the optimum rate constants were chosen to describe the curing process.

2 LITERATURE REVIEW

The matrix in many advanced composite materials is epoxy resin, which is responsible for the linkage between the reinforcing fibres that constitute the solid structure. In this article, an attempt to monitor the changes of the reactants and products of the reaction involved using DSC information is proposed. The thermal analysis provided the knowledge of the changes in the enthalpy of reaction and glass transition temperatures due to different curing schedules. Then, a prediction of the changes in the enthalpy of reaction and glass transition temperatures of curing epoxy resin is converted to changes in concentrations of reactants and products using a conversion curve produced from the experimental data.

Of the many research works that have been reported using DSC, some are reviewed. Némec *et al.* [2], used DSC for a study of low temperature phase transition. Calorimetric study by Chen and Fu [3] was undertaken to investigate whether preferential orientation of dipoles in the microwave field, as opposed to random orientation in the thermal field, altered the rates of individual reactions. These results clearly showed that both the degree of cure and the glass transition temperature increased with time and temperature and occurred faster in the thermal field than in the microwave field. Another apparent characteristic of the microwave cure was a two-step glass transition. Chemical conversion was estimated from the heat released up to a certain time during isothermal cure divided by the total heat of the reaction. Another DSC study by Mijovic and Wijaya [4] showed that the autocatalytic model was capable of predicting the kinetics of curing. In contrast, when the cure properties of epoxies with varying chain length were studied by Gonis and Simon [5] using DSC, the heat of polymerization was shown to be relatively independent of the monomer structure and chain length when determined by isothermal DSC. The overall mechanism of the epoxy reaction relies on the presence of free-proton donors and on the formation of stabilizer complex intermediates. During the early stage of polymerization, the viscosity of the system was relatively low and molecular motion was not restricted. As the reaction proceeded, highly branched macromolecules began

to form and there was a step increase in viscosity, which was indicative of the onset of gelation. The dynamic mode analysis of scanning exotherms obtained by varying the scan rate gave an average activation energy E_a . Unfortunately, this method could only analyse the overall process. For an isothermal measurement analysis, it is assumed that the total area under exothermic peak, ΔH_{total} , is equal to the overall heat of polymerization once the reaction is completed. The fractional conversion, α , was determined by dividing the heat evolved during isothermal cure up to a particular time, ΔH_t , by the total exothermal energy.

Many attempts to understand the curing process of the epoxy resins have been described in a number of articles. However, none has shown a methodology that extracts the data required by the end users in industrial applications. The reviewed studies do not present a method capable of defining the onset of the glass transition temperature T_g , a particularly critical value in this application. What definitely occurs at the T_g on a molecular level is not known and may be different for each polymer. T_g also depends on the time scale over which it is measured. All these lead to questions about approaches used in predicting T_g . There is also an absence of methods capable of translating the data produced by different analysis techniques into chemical conversions occurring in the reaction. Owing to the non-existence of a coherent method to investigate the progress of the chemical reactions in epoxy resins, a study was undertaken to provide a clear and practical method to evaluate the changes in concentrations of the reactants and products involved in most epoxy resin-based matrices.

3 METHODS

3.1 Sample preparation

The chemical system involved in this study was DGEBA cured with DMMB-CHA, as described by the diagram shown in Fig. 1. The epoxy monomer was a viscous liquid with an epoxide equivalent weight of 186.56 g, and the amine hardener was a liquid with an amine equivalent weight taken as 59.5 g. The amine was added to the resin and mixed manually (in stoichiometric ratio of 10 g of DGEBA with 3.2 g of amine). The mixing was repeated for each curing temperature for 3 min in a vacuum chamber, and the procedure was carried out in the same manner for every sample. For the kinetic study, the chemical conversion during mixing was neglected. A Perkin-Elmer (DSC-4) instrument was used to measure the glass transition temperature, T_g , and the residual exotherm, ΔH_r , of

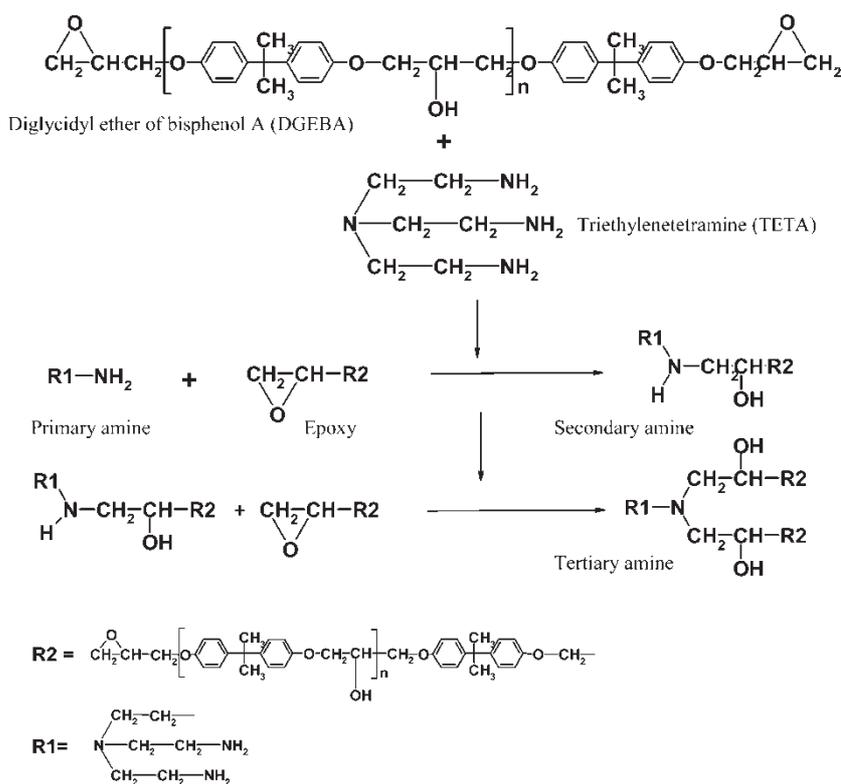


Fig. 1 Schematic diagram of the DGEBA and DMMB-CHA reaction

the epoxy resin samples cured for various time periods.

3.2 Method used in the prior work

The procedure used in the previous paper was to run DSC scans from -40 to 320 °C for samples cured at six different curing temperatures. The glass transition temperature and the residual enthalpy of reaction were measured from scans for samples cured for different lengths of time. The residual enthalpy changes against the glass transition temperature for different curing temperatures were plotted, and a polynomial to fit the plotted curve was obtained. The chemical conversions of samples cured at specific temperatures were examined. The results were correlated with the glass transition temperatures, and a plot of glass transition temperature against fractional conversion was prepared.

3.3 Method used in the current paper

In the present work, data from DSC scans from -40 to 320 °C for samples cured at six different curing temperatures produced in the previous work [1] were used to define the extent of the reaction. This is obtained from the fractional conversion versus time under specified conditions. These data were

also used to carry out a quantitative study of a chemical reaction by means of a mathematical model based on the kinetics of reaction. This provides relevant information about the detailed manner in which the chemical reaction takes place. It considers the experimental measurements and the empirical and theoretical approaches in the interpretation of these measurements. Finally, it shows the changes occurring to the concentrations of the reactants and products in DGEBA/DMMB-CHA reaction versus time.

4 RESULTS AND ANALYSIS

4.1 Introduction

From the DSC runs for samples cured at 80, 100, 120, 140, 150, and 160 °C performed for different lengths of time, graphs of enthalpy of reaction, ΔH_r , versus glass transition temperature, T_g , were produced. In the prior work [1], both glass transition temperature, T_g , and enthalpy of reaction, ΔH_r , changed with time: T_g increased while ΔH_r decreased until the reaction was completed. The residual exotherm was used to calculate the extent of reaction, according to equation [1]. The total enthalpy of reaction ($\Delta H_T = -102.6$ cal/g of epoxide) was determined in a similar way by scanning an initial (uncured) sample. The fractional

conversion x was quantitatively calculated [4] as

$$x = 1 - \frac{\Delta H_r}{\Delta H_T} \quad (1)$$

The kinetic rate of reaction changed with curing temperature and the collected data were used for the prediction of the chemical conversion achieved after any cure schedule. To plot the curve of the glass transition temperature against fractional conversion, same procedure used by Wang and Gillham [6] was adopted. A universal graph was also developed to enable fractional conversion to be obtained as a function of time and curing temperature.

In the current work, variations of T_g versus time for six isothermal curing temperatures were plotted. On the basis of the fact that the reaction is kinetically controlled, the usual rate equation was used to calculate and plot T_g versus $\ln(\text{time})$. Rearrangement and manipulation of the rate equation led to the development of an equation for the shift factor. Consequently, shift factors in $\ln(\text{time})$ corresponding to five curing temperatures apart from 140 °C were calculated and plotted versus $1/T$, and graph showing the plot of glass transition temperature T_g versus $\ln(\text{time})$ for the sample cured at 140 °C was produced. By assuming equal reactivity of all the amino hydrogens, the reaction rate for an initial stoichiometric mixture of epoxy and amine was expressed on a fractional conversion basis (x). Fractional conversion of reactions cured at 80, 100, 120, 140, 150, and 160 °C was then plotted versus time. After rearrangement of the equation for fractional conversion combined with equation (1), a plot of glass transition temperatures versus fractional conversion, which is used as fitting polynomial for the reaction, was prepared. A graph of fractional conversion versus time, as converted from T_g versus $\ln(\text{time})$ via the produced fitting polynomial, was also plotted. Finally, a graph showing the changes in concentrations of the reactants and products in DGEBA/DMMB-CHA reaction against time was plotted.

4.2 Glass transition temperature versus time

The variations of T_g with cure time for the six isothermal cure temperatures are shown in Fig. 2. Isothermal vitrification points ($T_g = T_{\text{cure}}$) for cure temperatures below $T_{g\infty}$ are marked by arrows. It is found that these points are on average 90 per cent of the high limiting value of T_g . It is also where the reaction rate starts to decrease rapidly to zero because of diffusion control dominating the kinetics. The T_g values after vitrification increase slowly and level off at lower limiting values for lower cure temperatures and at higher limiting values for higher cure temperatures.

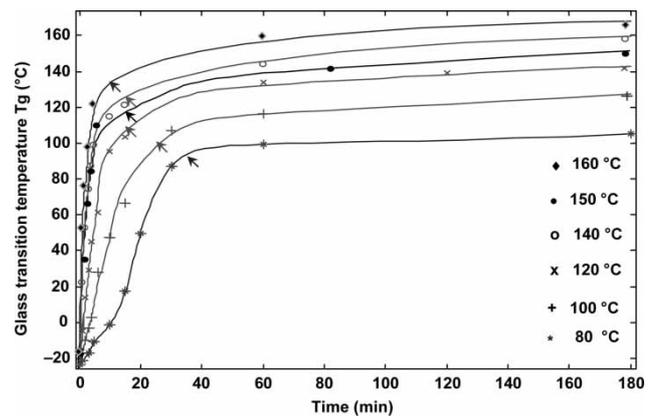


Fig. 2 Variation of T_g plotted versus time for six isothermal curing temperatures, and the isothermal vitrification points ($T_g = T_{\text{cure}}$) for cure temperatures below $T_{g\infty}$ are marked by arrows

For a reaction that is kinetically controlled, the usual rate equation is written as

$$\frac{dx}{dt} = k(T) \times f(x) \quad (2)$$

where $k(T)$ is the reaction rate constant, which is a function of temperature only, $f(x)$ a function of conversion, and t the cure time. The plot of T_g versus $\ln(t)$ for reactions occurring at the six curing temperatures is given in Fig. 3.

Rearranging equation (2), integrating at constant temperature, and taking the natural logarithm yield

$$\ln\left(\int_0^x \frac{dx}{f(x)}\right) = \ln k(T) + \ln(t) \quad (3)$$

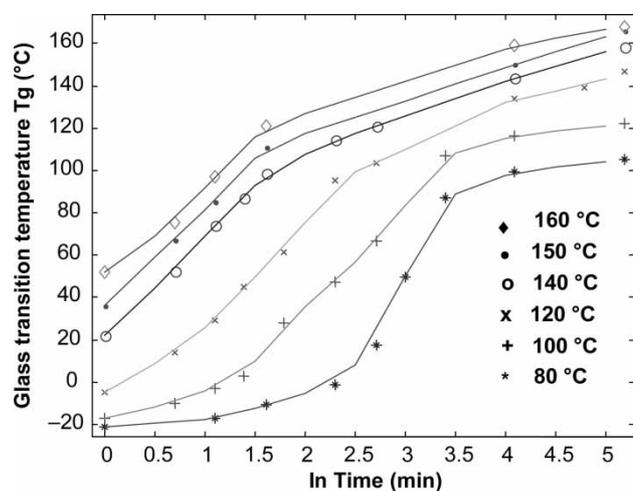


Fig. 3 Plot of T_g versus $\ln(\text{time})$ for reactions occurring at six curing temperatures

The left-hand side of this equation is a function of conversion and, therefore, may be expressed as a function of T_g only, as T_g was shown to be related to the fractional conversion. If $Y(T_g)$ is the left-hand side of equation (3), then

$$Y(T_g) = \ln k(T) + \ln(t) \quad (4)$$

Equation (4) describes the variation of the glass transition temperature with cure time and curing temperature. Therefore, for a particular value of $Y(T_g)$ that occurs at time t_1 when the cure temperature is T_1 , and also at time t_2 for cure temperature T_2 , then

$$Y(T_g) = \ln k(T_1) + \ln(t_1) = \ln k(T_2) + \ln(t_2) \quad (5)$$

Rearranging equation (5)

$$\ln(t_1) - \ln(t_2) = \ln k(T_2) - \ln k(T_1) \quad (6)$$

For any two reaction temperatures, $[\ln k(T_2) - \ln k(T_1)]$ is a constant. Therefore, for a kinetically controlled reaction, the variation of T_g with time at two different cure temperatures (T_1 and T_2) when plotted as a function of $\ln(\text{time})$ will have the same functional form except that the curve for the cure temperature T_2 will be displaced from that at temperature T_1 by a constant factor. By shifting each curve along the $\ln(\text{time})$ axis by a factor $A(T)$, the experimental results for each reaction temperature can be made to coincide with the results at a chosen reference temperature.

The shift factor is then given by

$$A(T) = [\ln(t_{T_{\text{ref}}}) - \ln(t_T)] \quad (7)$$

4.3 Calculation of the activation energy and the shift factor

The temperature dependence of the rate constant is normally given by an Arrhenius relationship [7, 8]

$$k(T) = A_0 \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

All parameters have usual Arrhenius significance and T is in units of absolute Kelvin.

Equation (6) may be combined with equation (7) to obtain an expression for the Arrhenius activation energy, E_a

$$\begin{aligned} \ln(t_{\text{ref}}) - \ln(t_T) &= \ln k(T) - \ln k(T_{\text{ref}}) \\ &= -\frac{E_a}{RT} + \frac{E_a}{RT_{\text{ref}}} \end{aligned} \quad (9)$$

When T_{ref} of equation (9) is fixed and all other data are shifted relative to the reference temperature (e.g. in the present case, $T_{\text{ref}} = 140^\circ\text{C}$), plotting the shift factor $[\ln(t_{\text{ref}}) - \ln(t_T)]$ against $1/T$ should yield a straight line with gradient $-E_a/R$ and intercept equal to E_a/RT_{ref} . The shift factors in $\ln(\text{time})$ corresponding to five remaining curing temperatures are plotted versus $1/T$ in Fig. 4. The resulting plot is, in fact, a straight line of the form $w = -5386.2 v + 13$, which has a slope given by $-E_a/R$ and intercept equal to E_a/RT_{ref} . The activation energy for the reaction is found to be 43.81 kJ/mol; these results also suggest, for the present system, that there is only one overall reaction mechanism with a single overall apparent activation energy.

The relationship between the times to reach a fixed T_g at different cure temperatures for a kinetically controlled reaction is given by equation (9), which is rearranged as follows

$$-\frac{E_a}{RT_1} + \ln(t_{T_{g,1}}) = -\frac{E_a}{RT_2} + \ln(t_{T_{g,2}}) \quad (10)$$

where $t_{T_{g,1}}$ is the time needed to reach a given glass transition temperature T_g at cure temperature T_1 and $t_{T_{g,2}}$ is the time needed to reach the same T_g at cure temperature T_2 . Thus, if the time to reach a particular T_g at one cure temperature is known, then the time to reach the same T_g at different temperatures can be calculated from equation (9), provided that the activation energy of the reaction is available. The plot of T_g versus $\ln(t)$ for samples cured at 140°C taken from the graphs shown in Fig. 3 is given in Fig. 5; the best fitting curve is plotted to reveal a master curve for this reaction scheme among other curing temperatures. It is indicative of the general trend of T_g versus $\ln(t)$ at any curing temperature.

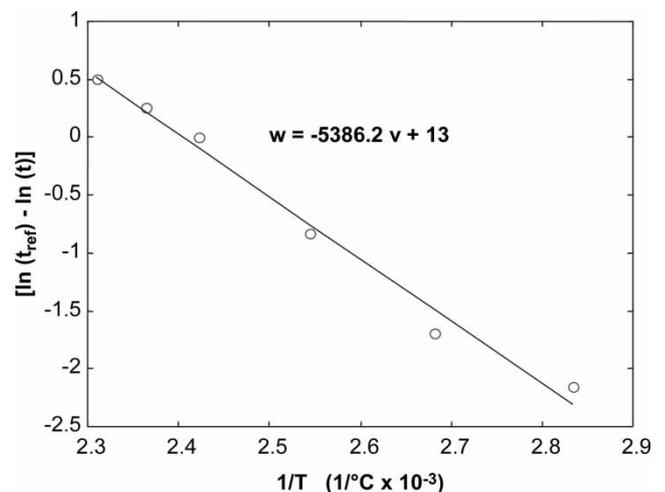


Fig. 4 Shift factor $\ln(\text{time})$ corresponding to five curing temperatures apart from 140°C plotted versus $1/T$

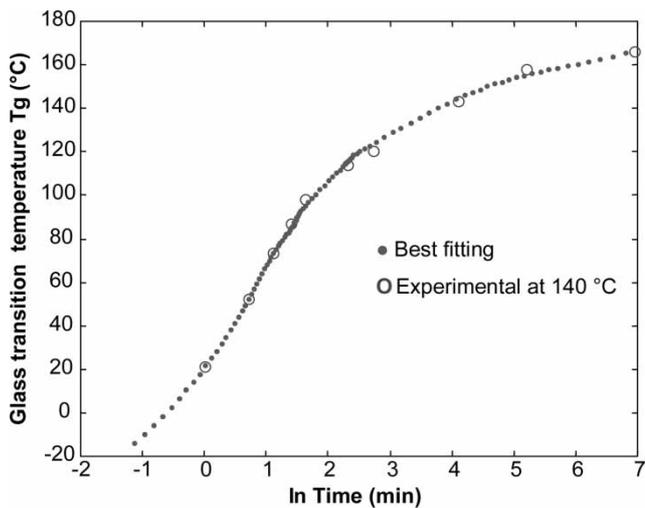


Fig. 5 Graph showing the plot of glass transition temperature T_g versus $\ln(\text{time})$ for the sample cured at 140°C

4.4 Fractional conversion versus time

Assuming equal reactivity of all amino hydrogens, the reaction rate for an initial stoichiometric mixture of epoxy and amine can be expressed on a fractional conversion basis (x) [9] as

$$\frac{dx}{dt} = \left(\frac{k_1 e_0^2}{2}\right)(1-x)^2 \left(\frac{x+k_2 n_0}{k_1 e_0}\right)$$

$$\frac{dx}{dt} = k(1-x)^2(x+B)$$
(11)

where $k = k_1 e_0^2/2$, $B = k_2 n_0/k_1 e_0$, and e_0 and n_0 are initial concentrations of the epoxide and amine groups, respectively, and k_1 and k_2 are the rate constants of the two reactions producing secondary and tertiary amines, respectively.

This equation corresponds to equation (2) $dx/dt = k(T) \times f(x)$, in which $f(x) = (x+B)(1-x)^2$. Constant B in $f(x)$ is only a weak function of temperature. Rate constants k_1 and k_2 are expected to have similar temperature dependence and thus the ratio will be approximately constant for all temperatures. Equation (11) is used to analyse the reaction kinetics of the present system by rearranging in the following form

$$\frac{dx/dt}{(1-x)^2} = kx + kB$$
(12)

Fractional conversions, x , of resin cured for specified times and temperatures are plotted versus time, as shown in Fig. 6. The kinetic rate of reaction changed with curing temperature. These data are used for the prediction of the chemical conversion achieved after any cure schedule.

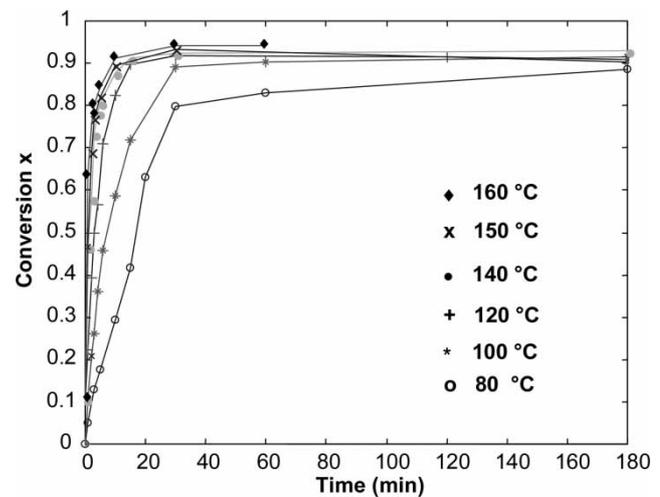


Fig. 6 Plot of fractional conversion of reactions cured at 80, 100, 120, 140, 150, and 160°C specified temperatures versus time

The chemical conversion during cure of a thermosetting resin can be correlated with an increase in the glass transition temperature T_g . The fact that T_g increases non-linearly with conversion, in cross-linking systems, makes it more sensitive in the later stages of cure where the chemical kinetics is complicated. Therefore, T_g , determined by DSC, may be used to measure the fractional chemical conversion for an amine-cured epoxy system.

The glass transition temperature, T_g , was therefore plotted against fractional conversion x according to equation (1) and the results are shown in Fig. 7. As can be seen, a single curve fits the different plots corresponding to samples cured at different temperatures, and consequently, a fitting polynomial is produced.

The master curve shown in Fig. 5 is converted into a fractional conversion basis through the use of the

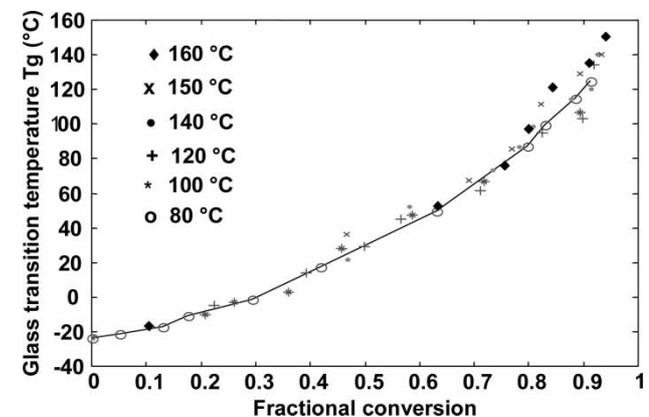


Fig. 7 Plotting of glass transition temperatures versus fractional conversion, which is used as fitting polynomial for the reaction

fitting polynomial shown in Fig. 7. The results are shown as data points on a plot of conversion, x , against time in Fig. 8. These data are used for the kinetic analysis according to equation (11). The line of best fit to these data points reveals an essential logarithmic relationship of the form $g = 0.1292 \ln(u) + 0.0062$, showing that the reaction is fast at the beginning and quickly slows down to level up at ~ 90 per cent of conversion. These data are used to evaluate the reaction rate dx/dt corresponding to the conversion x .

It might be inferred from the unique one-to-one relationship between T_g and conversion, which is independent of the cure temperature, that the ratio of the rate constant for the reaction between the primary amine group and epoxy to that between the secondary amine group and epoxy is unity. The relationship could also imply that the activation energies for both reactions are the same. Furthermore, the agreement between the experimental data and the results of calculations from the assumed kinetics suggests that all amino hydrogens show equal reactivity ($k_2/k_1 = 0.5$) or only with a weak negative substitution effect [10]. The analysis shows that the value of the ratio, k_2/k_1 , is between 0.4 and 0.5.

The autocatalytic reaction model has been used by other investigators to describe the chemical kinetics of a variety of aromatic amine-cured epoxy systems [11–13]. It has been found to be applicable over a wide conversion range before vitrification. In many investigations, the results for low-temperature curing deviated from the kinetic model predictions after vitrification. These deviations are expected, as the reactions become diffusion-limited after the material vitrifies. Few studies have attempted to incorporate the effects of diffusion control on the reaction kinetic model.

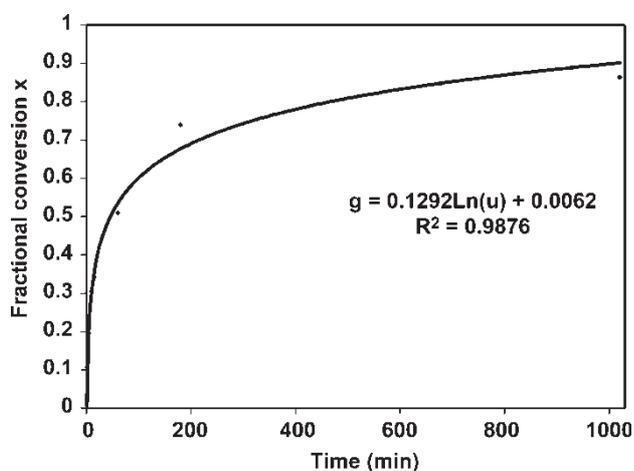


Fig. 8 Fractional conversion versus time as converted from T_g versus $\ln(\text{time})$ via the fitting polynomial of Fig. 7

4.5 Autocatalytic reaction model of the DGEBA/DMMB-CHA system for a quantitative study of the reaction

When alicyclic diamines are used to cure epoxy resins at temperature >100 °C, they give excellent heat resistance and high mechanical strengths. The low reactivity of the alicyclic primary amine is caused, in part, by steric hindrance caused by the cyclohexyl ring. This conveys an undoubted advantage for heat-cure application.

The work reported in the following section is about the quantitative study of a chemical reaction described from the knowledge of the extent of the reaction (obtained from the fractional conversion versus time graph shown in Fig. 8) expected under specified conditions. This study relates to the speed at which the chemical reaction occurs and involves a concept called the reaction rate. It provides relevant information about the detailed manner in which the chemical reaction takes place. It is sufficient to show that the total reaction process represented in the stoichiometric equation goes through a particular succession of events and it considers the experimental measurements and the empirical and theoretical approaches in the interpretation of these measurements.

To express the rate of reaction, which is the speed of the reaction in a quantitative manner, a definition of the reaction rate is required to denote the rate of change of concentration over the progress in the reaction. Consider the hypothetical reaction in which primary amine P is added to epoxy E to give tertiary amine T . Other workers [12, 13] have established that these reactions are catalysed by the hydroxyl ions. The following model can be used to describe the reaction mechanism for the DGEBA/DMMB-CHA system



E , P , S , and T represent the epoxy, primary, secondary, and tertiary amines, respectively. The rate equations for the two reactions are given by

$$\begin{aligned} r_1 &= k_1[E] \cdot [P] \cdot \left[\frac{n}{2}[E]_0 + [S] + 2[T] \right] \\ r_2 &= k_2[E] \cdot [S] \cdot \left[\frac{n}{2}[E]_0 + [S] + 2[T] \right] \end{aligned} \quad (15)$$

where n refers to the structure as shown in the schematic diagram of the reaction in the previous article [1]. Table 1 summarizes the parameters involved in this reacting system.

Table 1 Summary of the chemical activities in the DGEBA/DMMB-CHA reaction

Substances	$R_{1,i}$	$R_{2,i}$	Amount (mol) $t = 0$	Amount (mol) $t = t$	Concentrations
Epoxy	-1	-1	$2n_0$	$2n_0 - n_s - n_t$	$(2n_0 - n_s - n_t)/V$
Primary amine	-1	0	n_0	$n_0 - n_s$	$(n_0 - n_s)/V$
Secondary amine	+1	-1	0	$n_s - n_t$	$(n_s - n_t)/V$
Tertiary amine	0	+1	0	n_t	n_t/V

n_s and n_t are the extents of the two reactions (given in number of moles measured at different stages of the cure) and V is the volume of the material used in this reaction. The rate equations for the reactants and the products involved in this reaction are given by the following equations.

For the primary amine, it is

$$\frac{d}{dt}[P] = -\frac{1}{V} \frac{dn_s}{dt} = (-1)k_1 \frac{(2n_0 - n_s - n_t)}{V} \cdot \frac{(n_0 - n_s)}{V} \cdot \frac{(nn_0 + n_s - n_t + 2n_t)}{V} \quad (16)$$

This differential equation can be manipulated to produce the following equation, which may be written for both cases, $k_1 \neq k_2$ or $k_1 = k_2$ as

$$\frac{dn_s}{dt} = \frac{k_1}{V^2} (2n_0 - n_s - n_t)(n_0 - n_s)(nn_0 + n_s + n_t)$$

Passage from equations (16) to (37) is given in Appendix 2, the produced equation may be solved numerically to obtain n_s as a function of time.

The differential equation (37) was solved using the Runge-Kutta method; values of n_s were used to calculate n_t and the concentrations of the secondary amine and tertiary amine and residual concentrations of epoxy and primary amine were determined over the curing period, as can be seen from the graphs plotted in Fig. 9.

These curves reveal that the epoxy and primary amine concentrations decrease progressively over time. The secondary amine concentration shows an increase in the early stage followed by a decrease as the transformation to tertiary amine ultimately dominates the reaction.

5 CONCLUSIONS

The DSC technique provided very consistent values of the energy involved in a reaction. The experimental work was a study of the DGEBA epoxy resin mixed with a DMMB-CHA hardener. The procedure ran

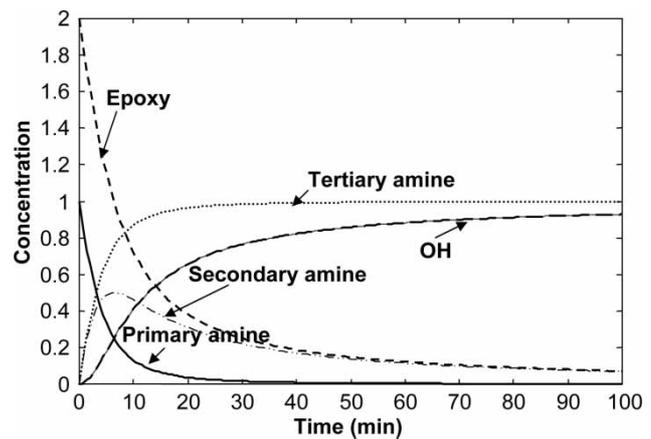


Fig. 9 Plotting of the concentrations of the reactants and products in the DGEBA/DMMB-CHA reaction

DSC scans for samples cured at six different curing temperatures. The glass transition temperature and the residual enthalpy of reaction were measured from the scans for samples cured for different lengths of time. For a sample, which was left out at room temperature, there was virtually no cure for a period of 1 h.

From the measured residual exotherm and the total enthalpy of reaction (102.6 cal/g), the extent of reaction was calculated and plotted. At late stages of cure, it was found that the glass transition temperature continued to increase, whereas the residual exotherm was not measurable any more.

For this kinetically controlled reaction, the variations of T_g with cure time for the six isothermal cure temperatures were plotted and the corresponding rate equation was written. Plots of T_g versus $\ln(t)$ were made and the temperature dependence of the rate constant was used to produce shift factors in $\ln(\text{time})$ corresponding to five curing temperatures, which were also plotted versus $1/T$. The resulting plot was a straight line with a slope given by $-E_a/R$ and intercept equal to E_a/RT_{ref} . The activation energy for this reaction was found to be 43.81 kJ/mol; it has also been shown that there is only one overall reaction mechanism with a single overall apparent activation energy. In addition, a curve fitting of T_g versus $\ln(t)$ at the curing temperature of 140 °C was produced.

Furthermore, by assuming equal reactivity of all amino hydrogens, the reaction rate for an initial stoichiometric mixture was expressed on a fractional conversion basis x for specified times and temperatures. The kinetic rate of reaction changed with curing temperature and was used for the prediction of the chemical conversion achieved after any cure schedule. The chemical conversion was correlated with an increase in the glass transition temperature T_g . The fact that T_g increases non-linearly with

conversion, in cross-linking systems, makes it more sensitive in the later stages of cure where the chemical kinetics is complicated. Therefore, T_g , determined by DSC is used to measure the fractional chemical conversion for an amine-cured epoxy system. From the curves of T_g plotted against fractional conversion x , a single curve fits the different plots corresponding to samples cured at different temperatures. Consequently, a fitting polynomial was produced. In addition the best fitting curve was plotted from T_g versus $\ln(t)$ for the samples cured at 140 °C, which was then used to reveal a master curve for this reaction scheme among other curing temperatures. This was indicative of the general trend of T_g versus $\ln(t)$ at any curing temperature. The master curve was converted into a fractional conversion basis through the use of the fitting polynomial already produced. The results were shown as data points on a plot of conversion, x , against time and were used for kinetic analysis. The line of best fit to these data points revealed an essential logarithmic relationship. The produced graph was used to evaluate the reaction rate dx/dt corresponding to the conversion x .

Then a quantitative study of a chemical reaction was started from the knowledge of the extent of the reaction obtained from the fractional conversion versus time. From a hypothetical reaction, in which primary amine P is added to epoxy E to become tertiary amine T, differential equation as a function of n_s and n_t , which are the extents of the two reactions given in number of moles measured at different stages of the cure, was written. This rate equation for the reactants and the products involved in the reaction was solved using the Runge–Kutta method. As a result, values of n_s were used to calculate n_t and the concentrations of the secondary amine and tertiary amine and residual concentrations of epoxy and primary amine were determined over the curing period. Plots of these concentrations revealed that the epoxy and primary amine decreased progressively over time. The secondary amine concentration showed an increase in the early stages followed by a decrease as the transformation to tertiary amine ultimately dominates the reaction.

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APPENDIX 1

NOTATION

$A(t)$	shift factor
B	constant in $f(x)$ as a weak function of temperature
C	is a constant
e_0	initial concentrations of epoxide groups
E_a	activation energy
$f(x)$	function of conversion
$k(T)$	reaction rate constant as a function of temperature
k_1	rate constant of the reaction producing secondary amine
k_2	rate constant of producing tertiary amine

n	structure of diglycidyl ether bisphenol-A
n_0	initial concentrations of amine
n_s, n_t	extents of the two reactions
R	constant
$R_{1,i}, R_{i,2}$	directions of reaction
t	is the cure time
T_{cure}	isothermal vitrification points
T_g	glass transition temperature
T_{ref}	reference temperature
V	the volume of the material used in this reaction
w, v, g, u	used in equations describing the curves of best fit
x	fractional conversion
$Y(T_g)$	function of glass transition temperature
ΔH_r	enthalpy of reaction
ΔH_{total}	the overall heat of polymerization once the reaction is completed
ΔH_T	total enthalpy of reaction of epoxide

APPENDIX 2

The manipulation of the differential equation (17) to produce an equation that might be solved numerically to obtain n_s as a function of time is given in this appendix

$$\frac{dn_s}{dt} = \frac{k_1}{V^2} (2n_0 - n_s - n_t)(n_0 - n_s)(nn_0 + n_s + n_t) \quad (17)$$

Repeating the same procedure for the tertiary amine

$$\frac{d}{dt}[T] = \frac{1}{V} \frac{dn_t}{dt} = (+1)k_2 \frac{(2n_0 - n_s - n_t)}{V} \cdot \frac{(n_0 - n_t)}{V} \cdot \frac{(nn_0 + n_s + n_t)}{V} \quad (18)$$

$$\frac{dn_t}{dt} = \frac{k_2}{V^2} (2n_0 - n_s - n_t)(n_0 - n_t)(nn_0 + n_s + n_t) \quad (19)$$

$$\frac{dn_t}{dn_s} = \frac{k_2}{k_1} \cdot \frac{n_s - n_t}{n_0 - n_s} = \frac{k_2}{k_1} \cdot \frac{n_s}{n_0 - n_s} - \frac{k_2}{k_1} \cdot \frac{n_t}{n_0 - n_s} \quad (20)$$

The manipulation of the above equations results in a differential equation

$$\frac{dn_t}{dn_s} + \frac{k_2}{k_1} \cdot \frac{1}{n_0 - n_s} \cdot n_t = \frac{k_2}{k_1} \cdot \frac{n_s}{n_0 - n_s} \quad (21)$$

An integrating factor for this differential equation is

$$\begin{aligned} \exp\left(\int \frac{k_2}{k_1} \frac{dn_s}{(n_0 - n_s)}\right) &= \exp\left(-\frac{k_2}{k_1} \ln(n_0 - n_s)\right) \\ &= \exp(\ln(n_0 - n_s)^{-k_2/k_1}) \\ &= (n_0 - n_s)^{-k_2/k_1} \end{aligned} \quad (22)$$

Multiplying both sides by this integrating factor gives

$$\begin{aligned} (n_0 - n_s)^{-k_2/k_1} \frac{dn_t}{dn_s} + \frac{k_2}{k_1} \cdot (n_0 - n_s)^{-(k_2/k_1)-1} \cdot n_t \\ = \frac{k_2}{k_1} \cdot n_s \cdot (n_0 - n_s)^{-(k_2/k_1)-1} \end{aligned} \quad (23)$$

The left-hand side of equation (23) is a complete derivative and so

$$\frac{d}{dn_s} (n_t \cdot (n_0 - n_s)^{-k_2/k_1})_t = \frac{k_2}{k_1} \cdot n_s \cdot (n_0 - n_s)^{-(k_2/k_1)-1} \quad (24)$$

Integrating equation (24) above leads to

$$n_t \cdot (n_0 - n_s)^{-k_2/k_1} = \frac{k_2}{k_1} \int n_s \cdot (n_0 - n_s)^{-(k_2/k_1)-1} dn_s \quad (25)$$

which may be developed using integration by parts as

$$\begin{aligned} n_t \cdot (n_0 - n_s)^{-k_2/k_1} \\ = \frac{k_2}{k_1} \left(\frac{-n_s \cdot (n_0 - n_s)^{-k_2/k_1}}{-(k_2/k_1)} \right. \\ \left. - \int 1 \cdot \frac{k_1}{k_2} (n_0 - n_s)^{-k_2/k_1} dn_s \right) \\ = n_s (n_0 - n_s)^{-k_2/k_1} - \int (n_0 - n_s)^{-k_2/k_1} dn_s \end{aligned} \quad (26)$$

First, consider the case when $k_2 \neq k_1$, then direct integration will give

$$\begin{aligned} n_t (n_0 - n_s)^{-k_2/k_1} &= n_s (n_0 - n_s)^{-k_2/k_1} \\ &+ \frac{(n_0 - n_s)^{-k_2/k_1+1}}{(1 - (k_2/k_1))} + C \end{aligned} \quad (27)$$

where C is a constant, as $n_t = 0$ when $n_s = 0$

$$0 = 0 + \frac{n_0^{1-(k_2/k_1)}}{1 - (k_2/k_1)} + C \quad (28)$$

$$C = -\frac{k_1}{k_1 - k_2} n_0^{1-(k_2/k_1)} \quad (29)$$

Replacing C in equation (27) gives

$$n_t = n_s + \frac{k_1}{k_1 - k_2} (n_0 - n_s) - \frac{k_1}{k_1 - k_2} n_0^{1-k_2/k_1} \times (n_0 - n_s)^{k_2/k_1} \quad (30)$$

$$n_t = n_s + \frac{k_1(n_0 - n_s)}{k_1 - k_2} \left(1 - \frac{(n_0 - n_s)^{(k_2/k_1)-1}}{n_0^{(k_2/k_1)-1}} \right) \quad (31)$$

$$n_t = n_s + \frac{k_1(n_0 - n_s)}{k_1 - k_2} \left(1 - \left(\frac{n_0 - n_s}{n_0} \right)^{(k_2-k_1)/k_1} \right) \quad (32)$$

The alternative that needs to be considered is when $k_1 = k_2$, then

$$\begin{aligned} n_t(n_0 - n_s)^{-1} &= n_s(n_0 - n_s)^{-1} - \int (n_0 - n_s)^{-1} dn_s \\ &= n_s(n_0 - n_s)^{-1} + \ln(n_0 - n_s) + C' \end{aligned} \quad (33)$$

Again $n_t = 0$, when $n_s = 0$

$$C' = -\ln(n_0) \quad (34)$$

and so

$$n_t = n_s + (n_0 - n_s) \ln\left(\frac{n_0 - n_s}{n_0}\right) \quad (35)$$

In either case, $k_1 \neq k_2$ or $k_1 = k_2$, the relationship between n_s and n_t may be used to obtain a single differential equation of the form

$$\frac{dn_s}{dt} = f(n_s) \quad (36)$$

For both cases described earlier

$$\frac{dn_s}{dt} = \frac{k_1}{V^2} (2n_0 - n_s - n_t)(n_0 - n_s)(nn_0 + n_s + n_t) \quad (37)$$