

Time-Temperature-Transformation (TTT) Cure Diagrams: Relationships Between T_g , Cure Temperature, and Time for DGEBA/DETA Systems

C. GUIBE and J. FRANCILLETTE*

DGA/CREA, Département Polymères et Composites, 16 bis, avenue Prieur de la Côte d'Or, 94114 Arcueil, France

SYNOPSIS

Isothermal curing of a bisphenol A diglycidyl ether-based epoxy-resin-based, using an aliphatic polyamine, has been performed at temperatures between 20 and 60°C. Samples were cured isothermally at various intervals of time, and analyzed by differential scanning calorimetry (DSC). The glass transition temperature (T_g) and the conversion ratio cure determined by residual enthalpy analysis is used as an isothermal cure-controlled reaction. A time-temperature-transformation (TTT) isothermal cure diagram was carried out to include the time to vitrification and iso- T_g curves. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The conversion of linear epoxy resins into three-dimensional cross-linked or thermosetting materials is performed by curing reaction. Curing kinetics of epoxy resins has been studied with different techniques. In the present work, isothermal cure was studied by differential scanning calorimetry (DSC).^{1,2}

The isothermal curing reaction of an epoxy resin is complicated as a consequence of the interaction between curing chemical kinetics and other physical processes, such as gelation and vitrification, which causes important changes in the reacting system macroscopic physical properties.^{1,3}

A convenient summary of the changes occurring during cure of a thermosetting system is the isothermal time-temperature-transformation (TTT) cure diagram described by Gillham et al.^{3,4} and schematically shown in Figure 1. It displays the changes of the material states and characterizes the changes in the material during isothermal cure as a function of time. Material states include liq-

uid, sol-glass, sol/gel-rubber, gel-rubber, sol/gel-glass, gel-glass, and char. The various changes occurring in the material during isothermal cure are characterized by contours of the time to reach the events.

This paper studies the temperature and time conditions of an epoxy resin isothermal cure. The glass transition temperature (T_g) is used as a parameter to monitor the curing reaction. T_g does not increase linearly with conversion. The unreacted material $T_g = T_{g_0}$ and the fully reacted material $T_g = T_{g_\infty}$. Vitrification occurs when the glass transition temperature T_g becomes equal to the curing temperature T_c .

The aim of this work is to study the feasibility of using T_g as a measure of the chemical conversion. The time-temperature superposition of T_g versus \ln time DSC data provides a kinetically controlled master curve, as well as the apparent activation energy of polymerization. The master curve and the reaction activation energy are used in the calculating iso- T_g contours prior to vitrification and also the vitrification contour. The basis of the approach is the fact that there is a one-to-one relationship between T_g and conversion which is independent of cure temperature, and the kinetically controlled reaction is over vitrification.

* To whom correspondence should be addressed.

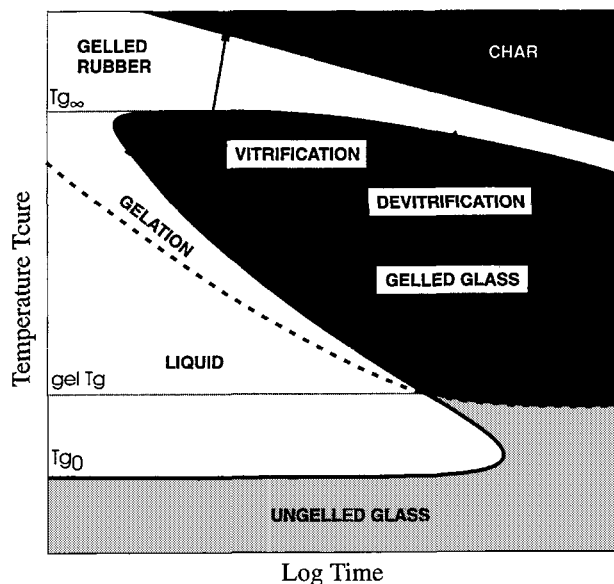


Figure 1 Time-temperature-transformation isothermal cure diagram for a thermosetting system. Source: Gillham.³

EXPERIMENTAL PART

Starting Materials Reactants

The difunctional epoxy monomer used for this work was a diglycidylether of BisphenolA (DGEBA) (DER 332, DOW Chemical Co.) cured with a pentafunctional aliphatic amine. The chemical structures of the reactants are shown in Figure 2. The reaction was stoichiometric, with one epoxy group reacting with one amine hydrogen according to their respective equivalent weights: DER 332 = 170 g/Eq; DETA = 20.63 g/Eq. The mixture was prepared at room temperature; immediately after mixing, the viscous liquid was weighted accurately in open aluminium pans and cured in the DSC oven. The reactive mixture was poured into numerous aluminium weighing pans and stored in the freezer part of a refrigerator (-15°C) for no more than 8 h. The glass transition temperature of the uncured mixture T_{g0} was -40°C .

DSC Measurements

A Perkin-Elmer instrument (DSC 7) was used to measure the T_g and the residual exotherm (ΔHr) of the reaction the material being firstly isothermally cured at prespecified times.

The samples were kept cold before the experiments. Handling was carried out at room tempera-

ture just before curing. The isothermal curing was performed at five different temperatures ($20, 30, 40, 50,$ and 60°C).

The instrument operated with a nitrogen flow rate of about $30 \text{ cm}^3 \text{ min}^{-1}$ through the cell. An empty pan was used as the reference material. For isothermal measurements, samples were inserted at -15°C , then heated at T_c with a programmed rate of $100^{\circ}\text{C min}^{-1}$.

After curing, each specimen was quenched from T_{cure} to -40 or -60°C at a programmed rate of $200^{\circ}\text{C min}^{-1}$ and then submitted to a temperature scan from -40 or -60°C to 250°C at $10^{\circ}\text{C min}^{-1}$ to determine the T_g of the material after cure and ΔHr of the remaining reaction.

The highest T_g value observed for extended cure times in this data set is 86°C , obtained at 60°C .

Loss of weight during temperature scans ($30\text{--}850^{\circ}\text{C}$) on the uncured resin-hardener mixture was measured in flowing nitrogen using a thermogravimetric analyzer equipped with a controller (Perkin-Elmer TGS2, system 4 microprocessor). The rate of temperature change was $10^{\circ}\text{C min}^{-1}$. Figure 3 shows that the onset temperature was located at 320°C . The material's relatively good temperature stability should not hide the fact that we worked with a low temperature system because of the presence of a very reactive aliphatic hardener. Furthermore, at 250°C , the loss of weight was approximately 4%, which might have a negative effect for high temperature composite applications.

RESULTS AND DISCUSSIONS

T_g was measured as the halfway point of ΔCp , when the polymer undergoes a transition from the

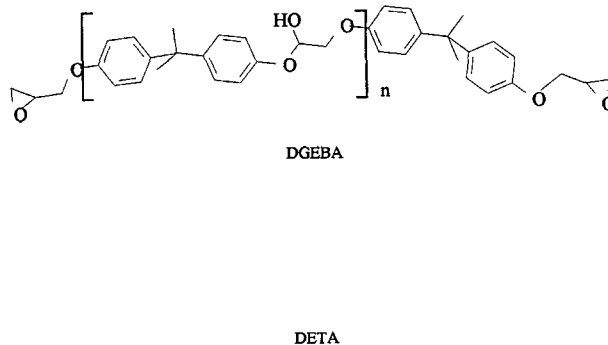


Figure 2 Chemical structures of the reactants.

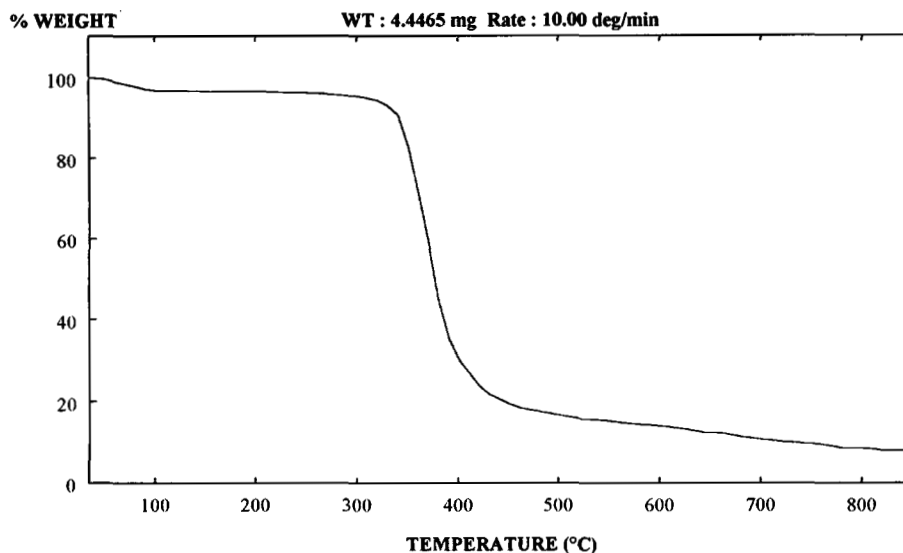


Figure 3 T_g temperature scan for uncured DER 332/DETA.

glassy state to the rubbery state. The apparent conversion ratio of the curing reaction is calculated from the residual enthalpy ΔH_r of the partially cured resin and from the total enthalpy of reaction ($\Delta H_T = -581.5 \text{ J g}^{-1}$) corresponding to one ideal unreacted mixed sample without curing treatment:

$$\alpha = [\Delta H_T - \Delta H_r] / \Delta H_T$$

Experimental T_g Versus Residual Heat of Reaction

T_g evolution and the corresponding residual heat of reaction ΔH_r of the material cured at 40°C for different times are shown in Figure 4. Both T_g and ΔH_r

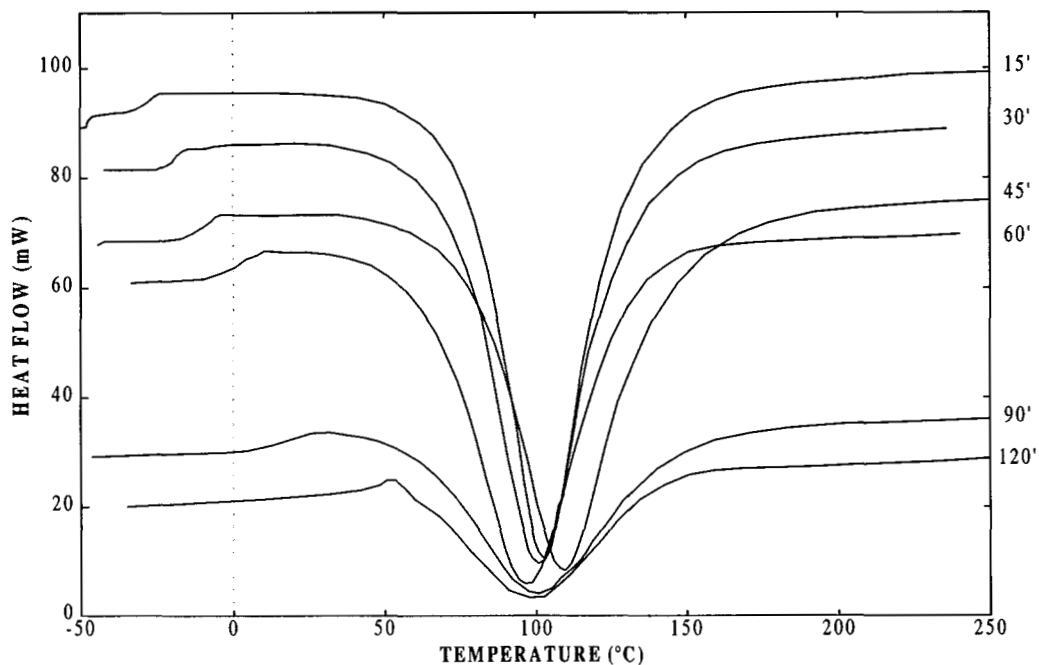


Figure 4 DSC temperature scans of samples isothermally cured at 40°C for different times.

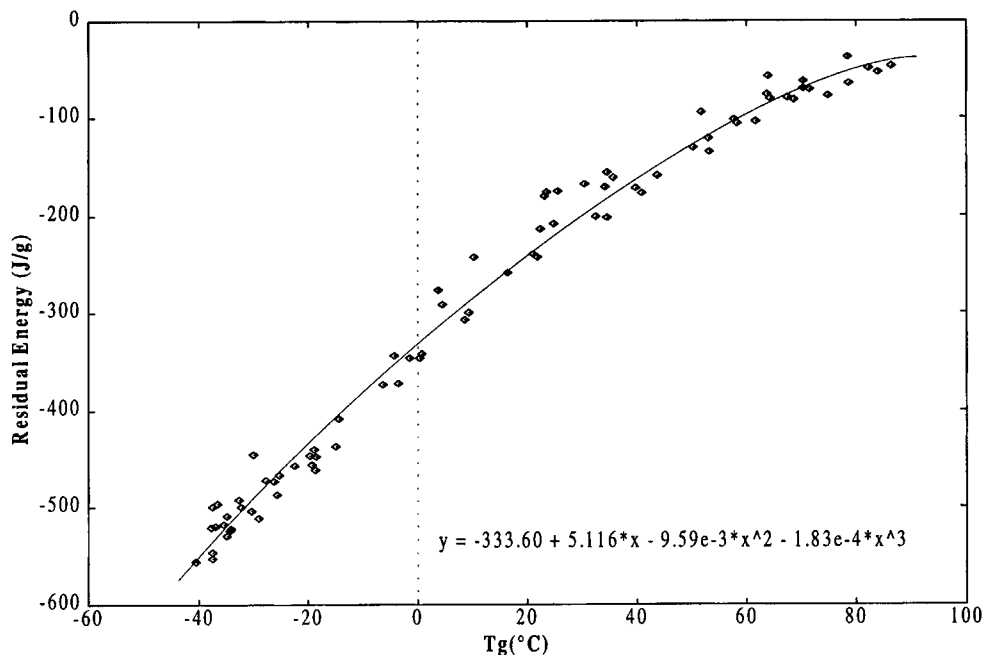


Figure 5 Residual exotherm versus T_g for DER 332/DETA (1 : 1).

change regularly with cure time; T_g increases while ΔH_r decreases until the reactants are fully consumed (because of the crosslinking increase density in the network).

Figure 5 shows the residual exotherm versus T_g plotted for different cure temperatures (20, 30, 40, 50, and 60°C). The data are fitted with a third-order polynomial shown by the solid line in this

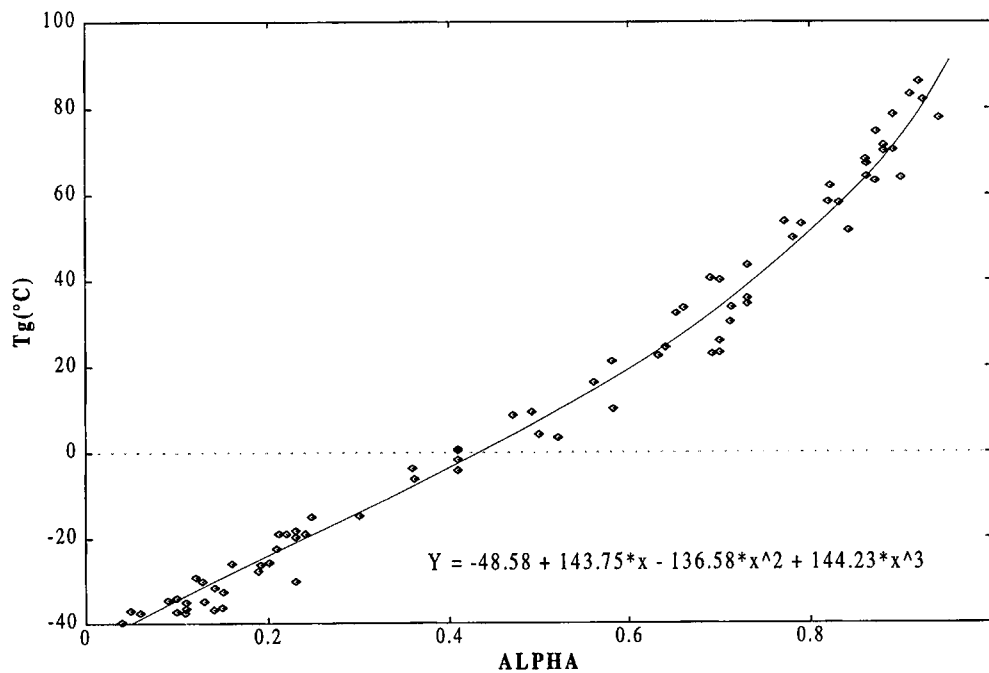


Figure 6 T_g versus fractional conversion (also illustrated is α_v , the conversion ratio at vitrification).

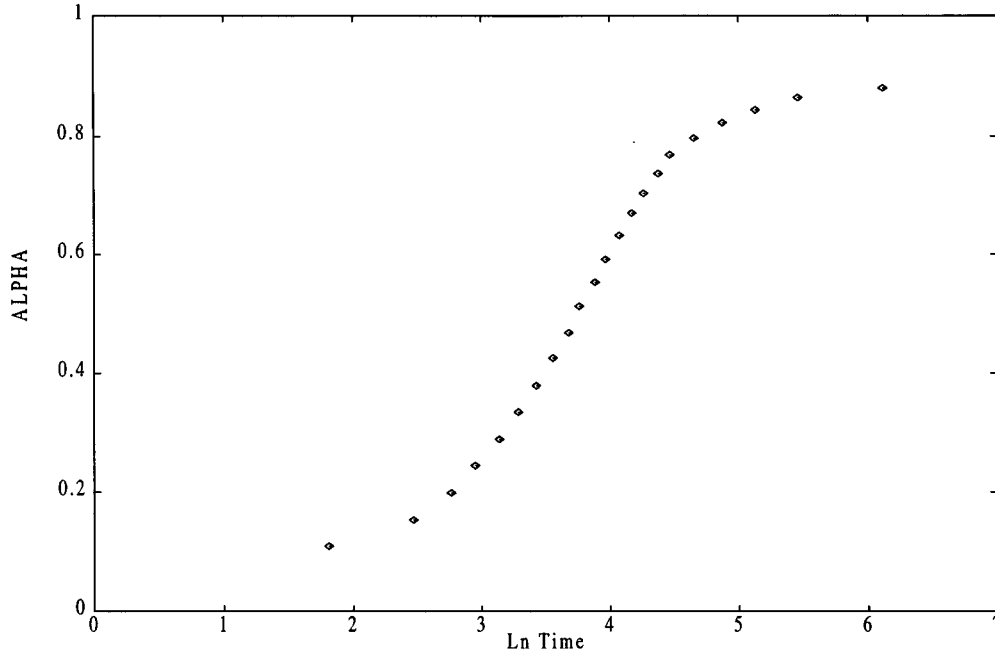


Figure 7 Conversion ratio versus time at $T_c = 50^\circ\text{C}$.

figure. For this epoxy-amine system, there is a unique one-to-one relationship, independent of cure temperature between either T_g and the residual exotherm or between T_g and conversion. The

same data are also plotted in Figure 6 as T_g versus fractional conversion. In the following analysis and discussions, T_g will be treated as a direct measure of the extent of reaction.

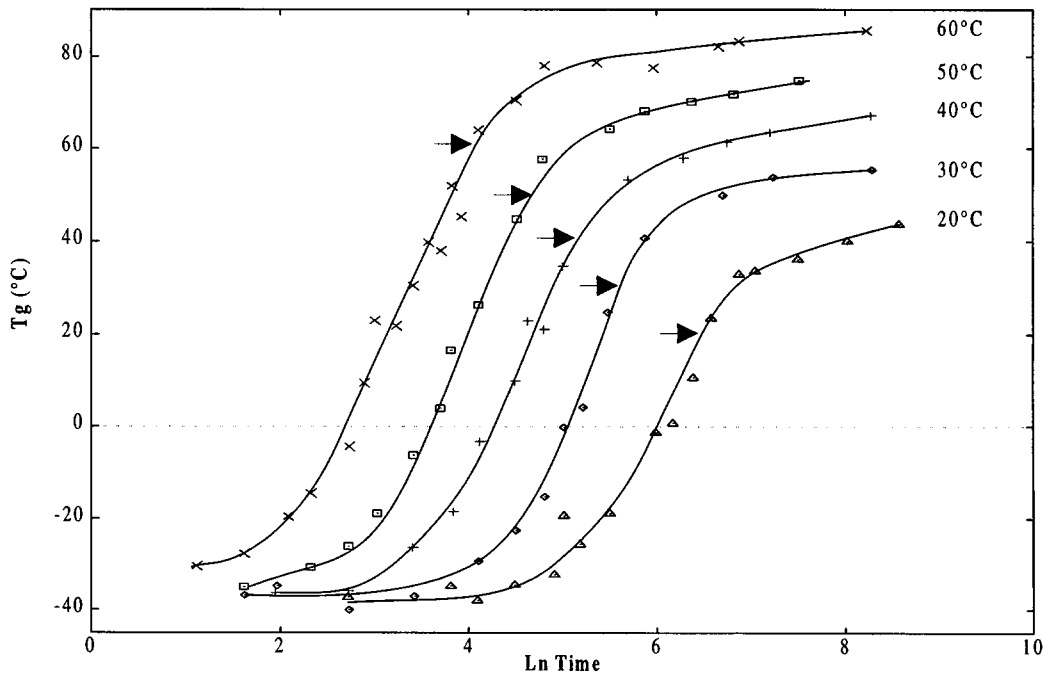


Figure 8 T_g versus ln (time) at different cure temperatures.

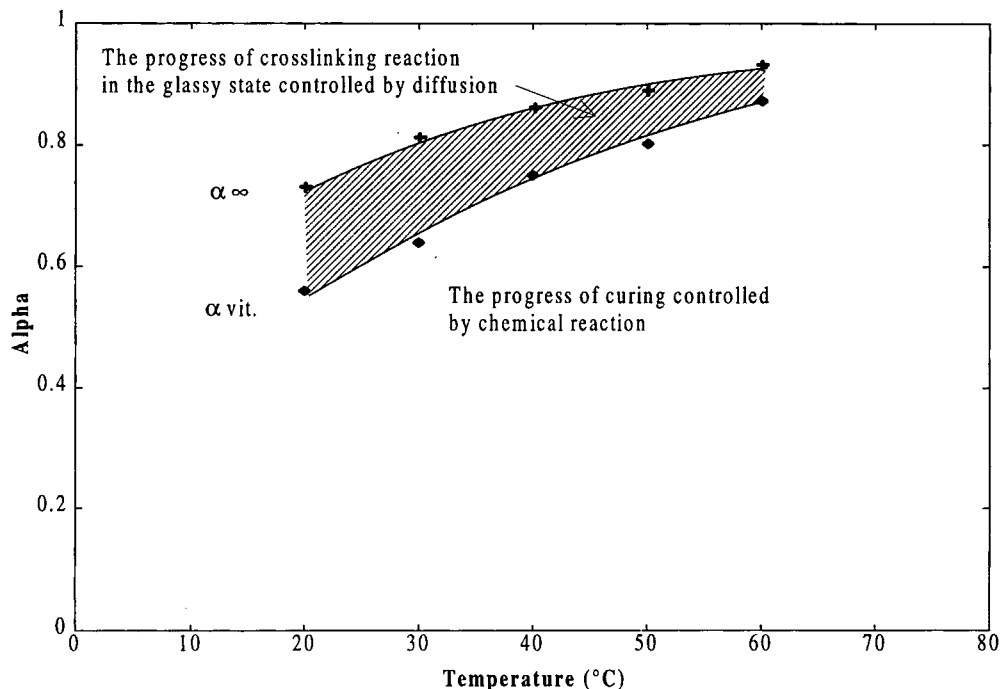


Figure 9 Dependence of limiting conversion ratio α_{∞} and conversion degree at vitrification α_v on the cure temperature.

Dependence of the Conversion Ratio with the Curing Conditions

For a given curing temperature, the conversion ratio increases with a sigmoidal shape and tends to have a limiting conversion ratio, which depends on this cure temperature (Fig. 7).

When $T_c < T_{g\infty}$, isothermal curing undergoes two different stages. The first one is controlled by the chemical reactivity of functional groups; the curing reaction takes place in the liquid state, and the T_g of the system is lower than the T_c . The reaction rate depends on T_c until $T_g = T_c$. At this point, the second stage of curing starts. The system vitrifies, and the reaction decreases considerably until the reaction becomes practically inhibited by a restricted reacting groups mobility, which prevents full conversion. The reaction time required for reaching $T_g = T_c$ is called vitrification time t_v . Its values at different T_c obtained from T_g data versus time are shown in Figure 8. Isothermal vitrification ($T_g = T_c$) at each cure temperature is designated by an arrow. When the system reaches the glassy state, the chemical reaction becomes controlled by diffusion,^{3,5} and the conversion ratio tends to a practically constant limiting value α_{∞} . Figure 9 shows the two stages in a diagram of conversion ratio versus curing temperature. The conversion at vitrification (when $T_g = T_c$) was

graphically obtained using the relationship between T_g and conversion. The conversion ratio at vitrification time α_v determines the progress of curing controlled by chemical processes. The difference between α_{∞} and α_v shows the progress of the cross-linking reaction in the glassy state controlled by diffusion.

The data for the extrapolated time to vitrification versus the temperature of isothermal cure were plotted using a Arrhenius law: logarithmic time versus $1/T$ (K). The activation energy of vitrification for isothermal transformation is ($\Delta E = 11.24$ kcal mol⁻¹).

Dependence of the Glass Transition Temperature on the Curing Conditions

During the isothermal curing at T_c , the T_g of the system increases with the curing time t_c due to the increase in the network crosslinking density. For samples cured at $T_c < T_{g\infty}$, deceleration has been noticed to occur near $T_g = T_c$ because of system vitrification. Beyond the vitrification time, T_g becomes higher than the curing temperature; as a result, the system is annealed at a lower temperature than T_g , thus, a structural relaxation process or physical aging in the amorphous phase. On the DSC scanning up from -40 or -60°C through T_g , these

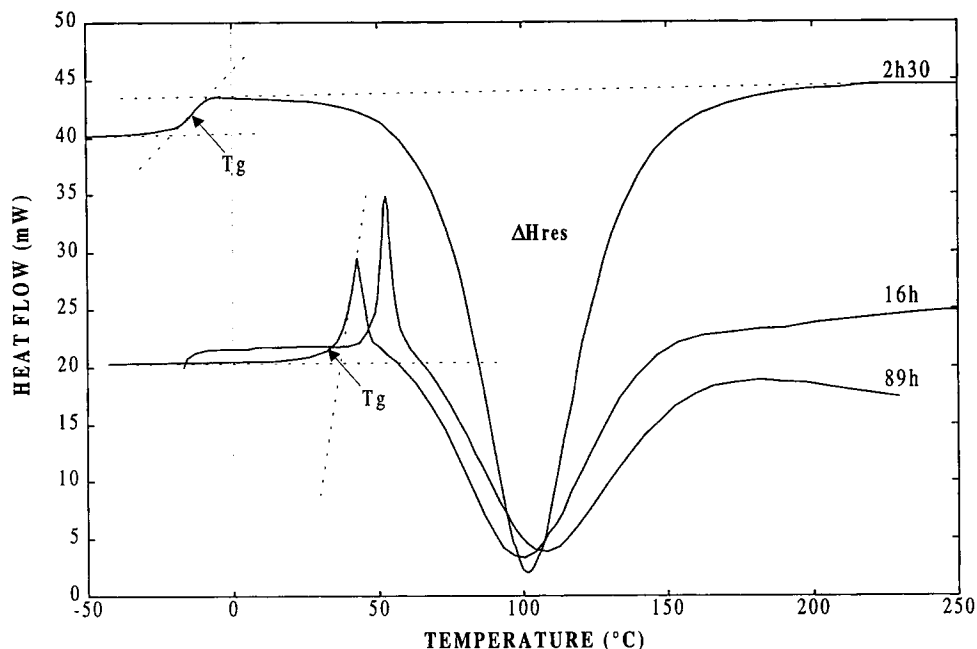


Figure 10 A typical DSC scan of samples isothermally cured at 20°C for different times, showing T_g and the endothermic annealing peak.

samples showed an endothermic peak superposed to T_g . Figure 10 illustrates the operational definition of T_g . Then T_g increases slowly with the annealing time at a temperature $T_c < T_g$ and approaches asymptotically to a limiting value depending on T_c .

Therefore, to be able to obtain curing in the glassy state, values of T_g cure must be greater than $T_c + 26^\circ\text{C}$ (Fig. 11).

Time-Temperature Superposition of DSC Data

Time-temperature shifts of T_g versus log time at different cure temperatures yields to a master curve for the reaction at an arbitrary reference temperature.⁵

For the time-temperature superposition, the rate expression of epoxide conversion is not needed.^{5,6} In a first approach, the data can be treated as if the reaction was only kinetically controlled, neglecting the diffusion contribution. Therefore, the reaction rate can be described mechanistically by the usual kinetic rate equation:

$$d\alpha/dt = k_{(T)} \times f(\alpha) \quad (1)$$

where $k_{(T)}$ is the reaction rate constant which depends on temperature only. $k = A \exp(-Ea/RT)$, with A , Ea , and R having their usual definition, and T is expressed in K . $f(\alpha)$ is assumed to be a function

of conversion independent of temperature. Rearranging eq. (1), integrating at constant temperature, and taking the natural logarithm, we obtain

$$\ln \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \ln k_{(T)} + \ln t \quad (2)$$

The left-hand side of the equation is only a function of conversion (α) and, thus, also a function of T_g only

$$F(T_g) = \ln k_{(T)} + \ln t \quad (3)$$

This equation describes the variation of T_g with cure time and temperature. This equation is valid for all cure temperature as long as the reaction mechanism remains kinetically controlled. Equation (2) suggests that for a kinetically controlled reaction, all isothermal T_g versus log (time) curves at different cure temperatures should be superimposed by simply shifting all curves horizontally (relative to a curve at a fixed reference temperature). A common master curve can be obtained. The resulting curve with $T_{\text{ref}} = 50^\circ\text{C}$ is shown in Figure 11. Note that vitrification points at all cure temperatures on the master curve are marked by arrows.

A satisfactory superposition is obtained. The deviations from the master curve occur near the system vitrification and obviously at $T_g > T_c$, which cor-

responds to diffusion control due to low segmental mobility.

The shift factors $A_{(T)}$ listed in Table I are defined as the \ln time difference at constant T_g (i.e., constant conversion) between the T_g versus \ln time curve for temperature T_c and the curve for an arbitrary reference temperature T_{ref}

$$A_{(T)} = \ln t_{(\text{ref})} - \ln t(T_c) \\ = (-Ea/R)(1/T_c - 1/T_{\text{ref}}) \quad (4)$$

Activation Energy

The apparent activation energy of the reactions is determined from eq. (4). Plotting the master curve shift factor against reciprocal cure temperature ($1/K$) gives a straight line with a slope $-E/R$, as shown in Figure 12. The apparent activation energy thus obtained is $16.05 \text{ kcal mol}^{-1}$ ($67.08 \text{ kJ mol}^{-1}$).

Construction of Iso- T_g Contours and Vitrification Curve in the Isothermal TTT Diagram

Iso- T_g Contours

The reaction activation energy determined in the previous section can be used for constructing an iso-

Table I Shift Factor Relative to 50°C for Different Cure Temperatures

Cure Temperatures (°C)	Shift Factors [$A(T)$] = [$\ln(t_{50}) - \ln(t_T)$]
20	-2.554
30	-1.481
40	-0.644
50	0
60	0.840

T_g contour if, in addition, a data point of the contour is known.

The relationship between times to reach a fixed T_g at different cure temperature for a kinetically controlled reaction is given by eq. (4), rearranged as follows:

$$-Ea/RT_1 + \ln(tT_{g_1}) \\ = -Ea/RT_2 + \ln(tT_{g_2}) \quad (5)$$

where $t(T_{g_1})$ is the time needed to reach a given T_g at cure temperature T_1 , and tT_{g_2} is the time needed to reach the same T_g at cure temperature T_2 . Thus, if a time to reach a particular T_g at one cure temperature (i.e., tT_{g_1} at T_1) is known, then the time to

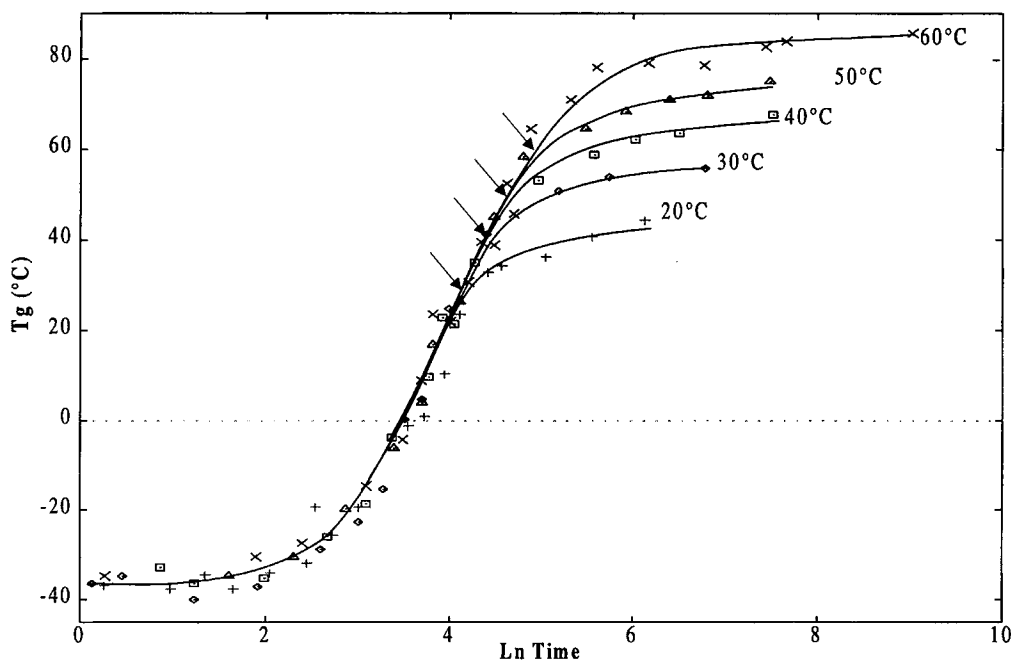


Figure 11 Time-temperature superposition: T_g versus \ln (shifted) time different cure temperatures for a reference temperature at $T = 50^\circ\text{C}$.

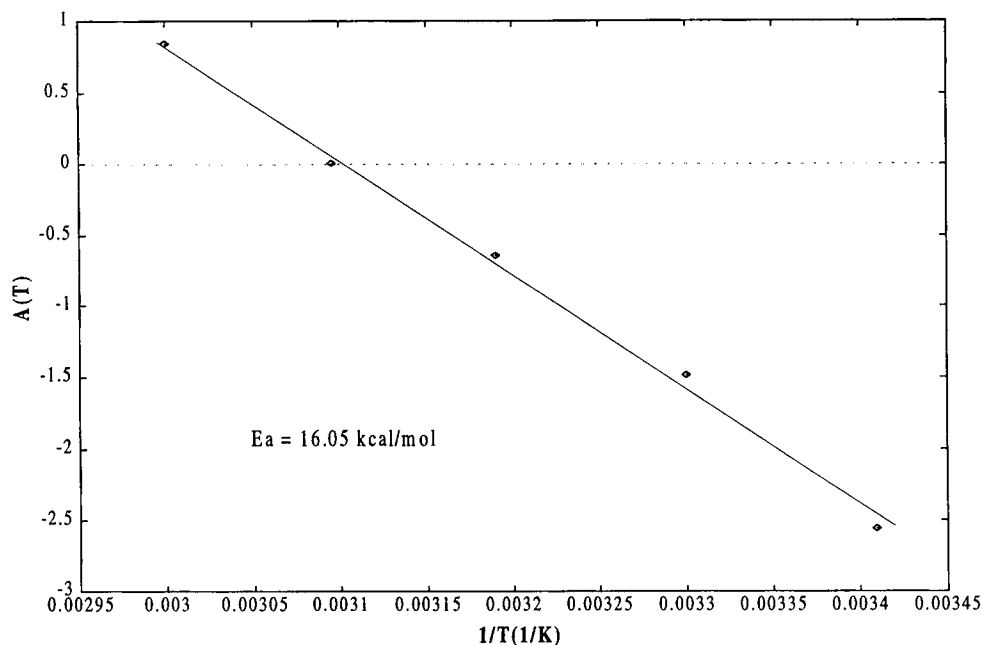


Figure 12 Arrhenius plot shift factor $A(T)$ versus reciprocal cure temperature ($1/K$).

reach the same T_g at different temperature (i.e., tT_{g2} at T_2) can be calculated from eq. (5).

Each point on the master curve provides a necessary data point (i.e., a time tT_{g1}) to reach a particular T_g^* at $T_1 = 50^\circ\text{C}$, which can be used in eq. (5), together with the activation energy for the reaction determined in the previous section, for the calculation of an iso- $T_g = T_g^*$.

The calculated results are incorporated into the TTT diagram in the form of a series of iso- T_g contours by plotting the cure temperature T_c against the logarithm of the times to reach a particular T_g^* . Figure 13 shows the calculated iso- T_g (for $T_g = -35$ to $+75^\circ\text{C}$).

Vitrification Curve

Vitrification reaction occurs when the glass transition increases up to the temperature of cure and indicates the transition from a rubber to a gelled glass (if gelation has occurred) or from a liquid to an ungelled glass (if gelation has not occurred).

Since the master curve covers the entire range of T_g , the vitrification curve can be calculated. The iso- T_g relation [eq. (5)] is valid until the material vitrifies and can be used to estimate the isothermal times of vitrification. Each point on the master curve (Fig. 11) provides a necessary data point [i.e., a time (tT_{g1}) to reach a particular T_g at $T_c = 50^\circ\text{C}$], which can be used for calculation, and t_{vit} is given by:

$$\ln t_{vit} = -Ea/R[1/T_{cure} - 1/T_g] + \ln t_{cure}.$$

Figure 13 shows the vitrification curve and different iso- T_g contours (for $T_g = -35 + 75^\circ\text{C}$) in the form of an isothermal TTT diagram. The vitrification curve is S-shaped.

The times to vitrification undergoes a minimum at a cure temperature just below $T_{g\infty}$ because of the competing effects of both the reaction rate constant and the extent of conversion at vitrification increasing with temperature.

The data for an isothermal TTT diagram can be represented in a line versus $1/T$ (K) plot, from which the apparent activation energy for the transformation can be determined. The line time versus $1/T$ (K) plot is presented in Figure 14. The apparent energy for vitrification is given by the slope. The value of the vitrification energy is $12.34 \text{ kcal mol}^{-1}$.

CONCLUSION

The analysis of the relations between the cure time and temperature has led to the following conclusions.

- 1) T_g is an appropriate parameter for monitoring the cure process. The results show that

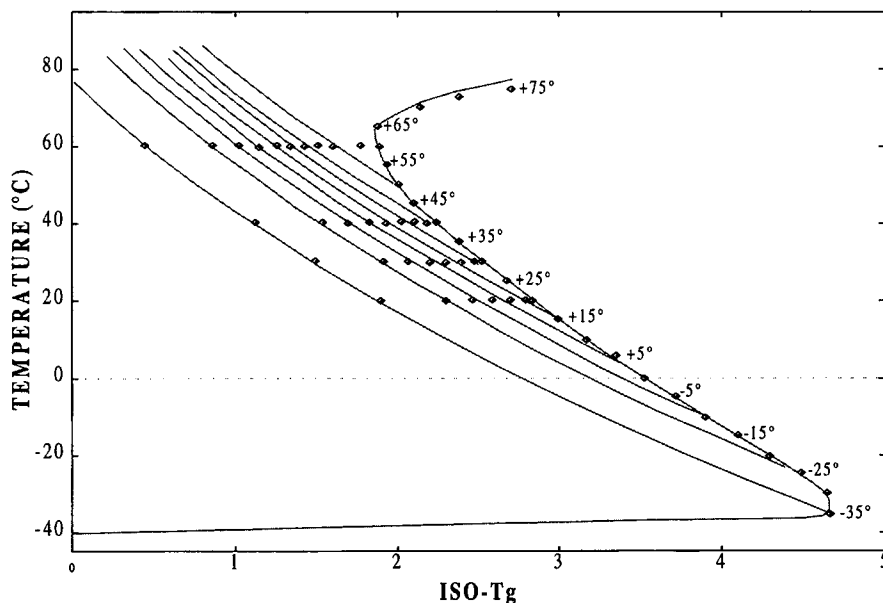


Figure 13 Calculated isothermal TTT diagram showing iso- T_g contours and vitrification curve.

T_g for an epoxy-aliphatic amine system is a function of conversion independent of the cure temperature. A one-to-one relationship between T_g and conversion is found for the DGEBA/DETA system.

2) By plotting time-temperature shifts of the

T_g versus $\ln(t)$ at different cure temperatures, we obtain a master curve at a reference cure temperature (50°C), according to the assumption that the reaction is purely kinetically controlled. From this curve, we found an activation energy is closed to 16.05

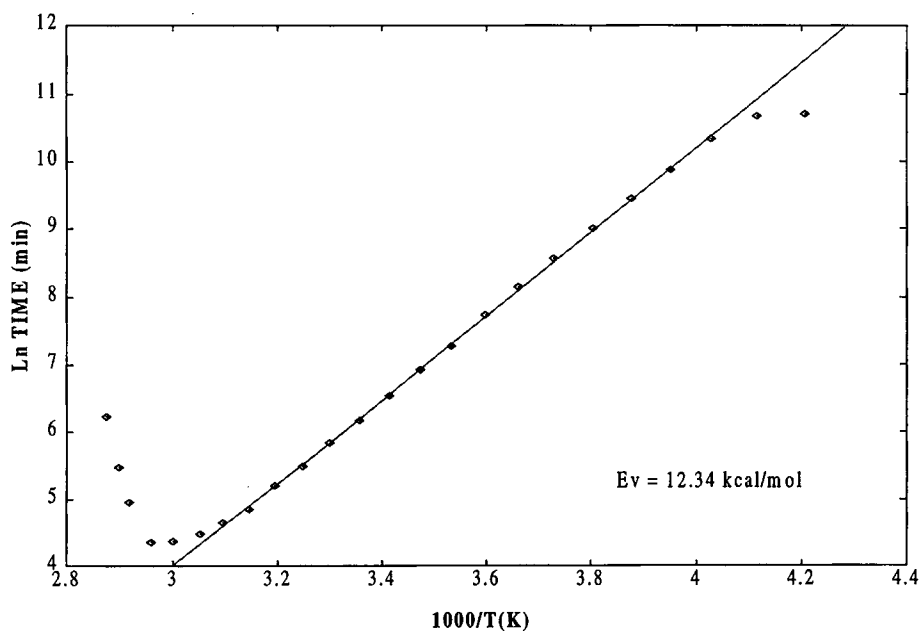


Figure 14 Ln time versus $1000/T$ (K) and apparent activation energy for vitrification.

kcal mol⁻¹. The isothermal vitrification points at all cure temperatures lie on the master curve, which indicates that the reaction before vitrification is only kinetically controlled. Perturbations of the data from the master curve occur after vitrification, revealing the onset of diffusion control.

- 3) In the TTT cure diagram, the master curve, together with the calculated activation energy, are used as a basis for a simple calculation of vitrification curves, and iso- T_g contours are presented.
- 4) The reaction vitrification energy determined from isothermal TTT diagram is calculated ($E_v = 12.34$ kcal mol⁻¹).

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