TTT Isothermal Cure Diagram of a Dyglicidyl Ether of Bisphenol A/1,3-Bisaminomethylcyclohexane (DGEBA/1,3-BAC) Epoxy Resin System

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SYNOPSIS

The isothermal cure of an epoxy-cycloaliphatic amine system has been studied following the evolution of both glass transition temperature and conversion. A functional relationship between T_g and conversion is established. The cure reaction is satisfactorily described by a phenomenological model with parameters determined from DSC experiments. By applying the kinetic model, gelation and vitrification curves are calculated and compared with experimental times to gelation and times to vitrification determined at temperatures between 50 and 100°C. The isothermal time–temperature–transformation (TTT) curing diagram including iso-T_g contours has been established. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The isothermal time–temperature–transformation (TTT) cure diagram introduced by Gillham[1,2] is a useful tool for analyzing and designing curing processes of thermosetting systems. TTT isothermal cure diagram is based on the phenomenological changes that take place during cure, such as vitrification and macroscopic gelation, as a consequence of chemical reactions that convert a fluid to a solid in the thermosetting process.[3,4]

On the molecular level, gelation corresponds to the incipient formation of branched molecules of very high molecular weight. In principle, molecular gelation occurs at a fixed chemical conversion that can be predicted from the functionality of the reactants.[5] Vitrification, which usually follows gelation, is the transformation from liquid or rubbery material to glassy material. At vitrification the material solidifies and the chemical reactions can be retarded (or quench).

The properties of the final material are intimately related to gelation and vitrification, so information about these two phenomena is required to characterize an epoxy resin system and to specify an effi-

cient cure program to ensure that the properties of the thermoset are optimized for a specific application.[6,7]

In a previous work[8] we have studied by DSC, using an isothermal approach, the cure reaction of stoichiometric diglycidyl ether of bisphenol A/1,3-bisaminomethylcyclohexane (DGEBA/1,3-BAC) epoxy system over the temperature range of 60–110°C. A semiempirical equation for autocatalytic systems containing two rate constants and two reaction orders provided a good phenomenological description of the cure kinetics up to the onset of vitrification. With the inclusion of a diffusion factor into this model, it was, however, possible to predict with precision the cure kinetics over the whole range of conversion, covering both pre and postvitrification stages and over the entire temperature range 60–110°C employed for isothermal curing.

In this article we are now concerned with the study of the conditions in temperature and curing time for gelation and vitrification to appear and the representation of such conditions in an isothermal TTT cure diagram. The diagram is expanded to include ideal molecular gelation, vitrification, and iso-conversion or iso-T_g curves, which can be calculated both in the kinetic and diffusion controlled regimes by using the kinetic model of the reaction.[9,10]
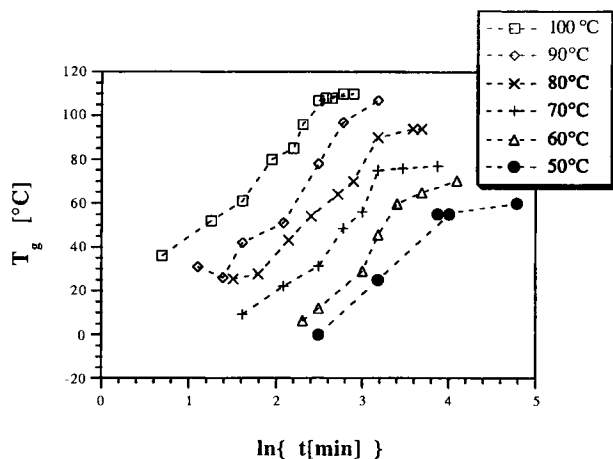

Figure 1 The increase of T_g with curing time at different temperatures, dashed lines are hand fitted.

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (DGEBA), Shell Epikote 828, with weight per epoxy equivalent, WPE = 192.2 g/eq, as determined by hydrochlorination.[11] The curing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC from Mitsubishi Gas Chem. Co.) with molecular weight 142.18 and purity > 99% according to the supplier. Both components were used as received in stoichiometric amounts (mass ratio DGEBA/1,3-BAC = 100/18.5). Fresh samples were always prepared by mixing resin and hardener at room temperature (it took approximately 1 min).

EXPERIMENTAL

A differential scanning calorimeter, Perkin–Elmer DSC-7 was used in the determination of both T_g and conversion. The DSC was calibrated with high purity indium, and dry nitrogen was used as purge gas. Samples of about 5–10 mg were enclosed in aluminum DSC capsules and cured directly in the DSC.

Glass transition temperature of initial solution of monomers, $T_g = -37°C$, was determined in a dynamic scan at a heating rate of 10°C/min. This dynamically cured sample was quenched and rescanned at the same heating rate to give a glass transition temperature of $T_g = 131°C$.

Glass transition temperatures of partially cured samples were measured at six different isothermal temperatures (50, 60, 70, 80, 90, and 100°C). After various curing times, ranging from 1 to 150 min, all samples were quenched to $-10°C$ and then scanned at a heating rate of 10°C/min up to 200°C to determine their T_g.

For samples in an early stage of polymerization, T_g appears as an endothermic shift over a broad interval of temperature. In highly crosslinked samples, however, T_g reaches the temperature range where residual polymerization occurs and the superposition of both relaxation shift and exothermic reaction makes the determination of T_g more imprecise. In addition, samples that have vitrified could exhibit an endothermic peak in the glass transition region, just before the residual exotherm. In all cases, T_g has been taken as the temperature at which the derivative of the DSC curve reaches its maximum.

Gelation times were determined by curing samples in a thermostatic bath at five different temperatures: 60, 70, 80, 90, and 100°C and determining the solubility in tetrahydrofuran (THF). The gel times are the times for which one observes the appearance of insoluble particles.

Values of conversion for the temperatures analyzed were previously obtained[8,12] by curing samples isothermally in the DSC. The degree of conversion at a given time, is

$$\alpha = Q_t/Q_0 \tag{1}$$

where Q_t is the heat generated up to time t, and Q_0 is the total heat liberated when the uncured material is taken to complete cure. Q_0 was determined from scanning experiments at different heating rates as it is recommended by Prime.[13]

T_g vs. Curing Time. Vitrification

During cure to full conversion the glass transition temperature, T_g, increases from an initial value of T_{g0} up to $T_{g\infty}$, the glass transition temperature of the fully reacted material.

For cure temperatures well above T_g, the reaction rate between the epoxy and hardener reactive groups is controlled by chemical kinetics. When T_g ap-

Table I   Reaction Times Required for the System to Vitrify at Different Curing Temperatures

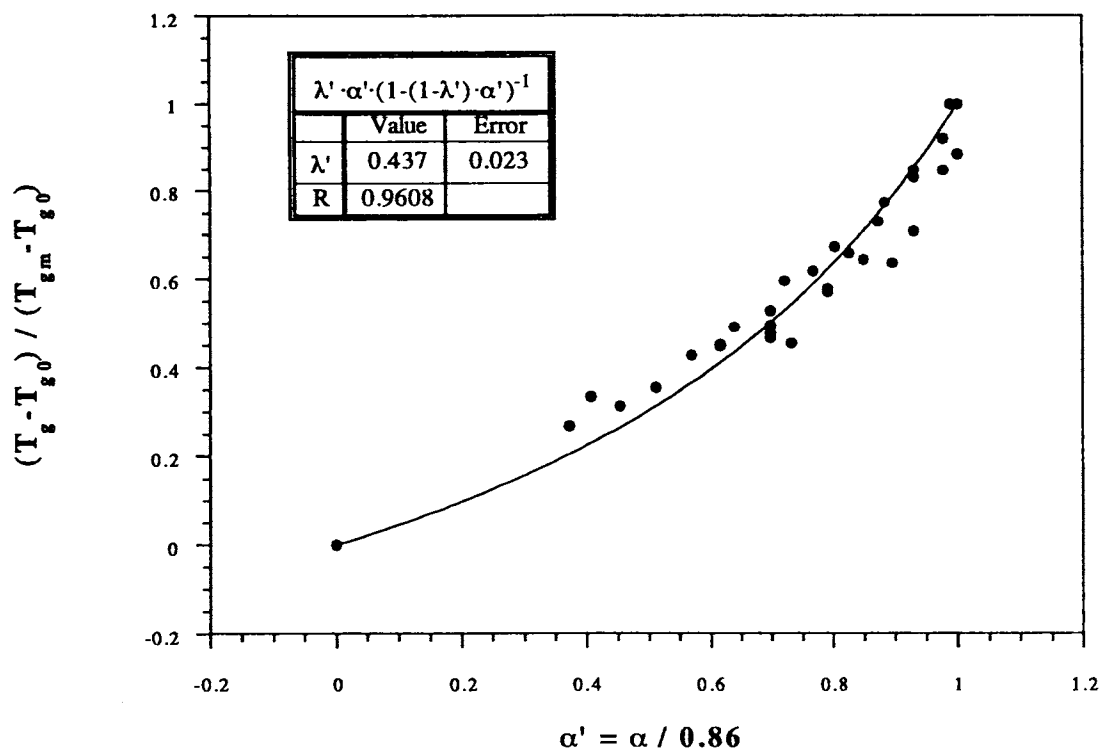| T_c [°C]	ln (t_v [min])
50	4.0
60	3.5
70	3.3
80	3.1
90	2.7
100	2.5

Figure 2   The fit of $(T_g - T_{g0})/(T_{gm} - T_{g0})$ vs. α' with $\alpha_m = 0.86$ and $T_{gm} = 101°C$.

proaches the cure temperature, curing reactions become diffusion controlled because molecular mobility is rapidly reduced. When T_g reaches T_c, the system is defined to vitrify and in the region where $T_g > T_c$, the glass transition temperature increases very slowly with time. The reaction rate in this regime is affected by both chemical and physical aging. If the cure temperature is above $T_{g\alpha}$, by definition the material cannot vitrify at T_c, and chemical kinetics governs the progress of reaction.[14]

In Figure 1 the increase in T_g with curing time is shown at different temperatures, T_c, below $T_{g\alpha}$. When T_g reaches T_c, the glass transition temperature shows a slow increase with time.

The reaction times required for the system to vitrify at different curing temperatures, t_v (i.e., times to $T_g = T_c$), are given in Table I.

Table II   Times to Gelation at Different Curing Temperatures and the Standard Deviation

T_c [°C]	t_{gel} [s]	$\sigma\ t_{gel}$ [s]
60	950.4	20.4
70	609.0	20.4
80	345.0	19.8
90	198.0	21.6
100	129.6	23.4

T_g vs. Conversion Relationship

Many authors have found a one-to-one relationship between glass transition temperature and conversion, and the empirical DiBenedetto equation as reported by Nielsen[15] has been widely used to fit the experimental T_g vs. α data. In this approach, the glass transition temperature of a partially cured thermoset up to an extent of reaction α is given by

$$\frac{T_g - T_{g0}}{T_{g\alpha} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \tag{2}$$

where λ, originally an adjustable parameter, is theoretically equated[16] to the ratio $\Delta C_{p\alpha}/\Delta C_{p0}$, where ΔC_{p0} and $\Delta C_{p\alpha}$ are the isobaric heat capacity changes in the glass transition region of the monomer and of the fully reacted network, respectively.

Equation (2) is defined between $\alpha = 0$ and $\alpha = 1$; for instance, it is supposed that the epoxy/amine system reaches the 100% of conversion ($\alpha = 1$). Nevertheless, many authors consider the existence of topological limitations at the end of cure. Oleinik[17] showed that theoretically the maximum extent of reaction that can be expected in an epoxy/amine system is $\alpha = 0.95$–0.96%. Thus, the infinite properties of the network cannot be determined by the

Table III   Values of Parameters in Eq. 6 Obtained at Six Different Temperatures

T_c [°C]	k_1 [s^{-1}]	k_2 [s^{-1}]	m	n	$m + n$	C	α_c
60	0.00066	0.0021	0.98	2.1	3.1	21.16	0.660
70	0.0012	0.0021	0.72	2.0	2.7	14.78	0.680
80	0.0025	0.0034	0.52	2.1	2.6	18.10	0.709
90	0.0036	0.0072	0.57	2.1	2.7	25.33	0.790
100	0.0038	0.016	0.49	2.1	2.6	20.02	0.857
110	0.0054	0.024	0.59	2.3	2.9	43.24	0.850

experiment. To take this into account, Hale et al.[18] modified the DiBenedetto equation in the form

$$\frac{T_g - T_{g0}}{T_{gm} - T_{g0}} = \frac{\lambda' \alpha'}{1 - (1 - \lambda') \alpha'} \qquad (3)$$

with $\alpha' = \alpha / \alpha_m$ and $\lambda' = \Delta C_{pm} / \Delta C_{p0}$, α_m is the perfectly known extent of reaction of an almost fully cured network showing $T_g = T_{gm}$.

The fit of $(T_g - T_{g0})/(T_{gm} - T_g0)$ vs. α' with α_m = 0.86 and T_{gm} = 101°C is shown in Figure 2 and gives a value λ' = 0.437.

The one-to-one correspondence between T_g and conversion, independent of the cure temperature, allows one to convert α values into T_g values and inversely when it is necessary.

We can consider at this point the values of maximum T_g obtained by curing samples with different schedules. As we have indicated above, samples cured dynamically gave a glass transition temperature of 131°C, which, through eq. (3), corresponds to a conversion of α = 0.93. However, glass transition temperature of step-cured samples increased to 145–150°C when samples were postcured[19] at 154°C for periods of time up to 1500 h. These values of T_g correspond to 96–97% of conversion, which is in the topological limit proposed by Oleinik.[17] Taking these differences into account we have considered for the stoichiometric mixture of DGEBA/1,3-BAC, $T_{g\alpha}$ = 166°C (the value obtained by extrapolation of eq. (3) to α = 1).

Table IV   Dependence with Temperature Assumed for the Parameters in Kinetic Model Used to Obtain $a(t)$, through the Entire Range of Cure by Numerical Integration of Eq. 6

$k_1 = 5.943 \cdot 10^3 \exp(-5.2732 \cdot 10^3/T)$
$k_2 = 1.36 \cdot 10^6 \exp(-6.8805 \cdot 10^3/T)$
$\alpha_c = 0.46371 + 0.0033486 \cdot T$
$m = 0.5$
$n = 2$
$C = 20$

Gelation

Table II shows times to gelation, t_{gel}, determined as the average value of three measurements at each curing temperature. By combining the gel time measurements and DSC data of conversion vs. time, previously reported values for fractional conversion at gelation were obtained.[12] Conversion at gelation is almost constant, irrespective of the curing temperatures, within the measurement uncertainty. It ranges from 0.52 to 0.59.

Kinetic Model of the Curing Reaction

The semiempirical equation proposed by Kamal[20] with two rate constants k_1 and k_2 and two reaction orders, m, n, given by eq. (4), provided a good fit of the experimental data in isothermal cure of 1 : 1 DGEBA/1,3-BAC up to the onset of vitrification[8]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (4)$$

To consider diffusion control that becomes important near vitrification, for instance, typically when $(T_c - T_g) \approx \pm 20$ or 30°C, a diffusion factor, $F(\alpha)$, was introduced on the basis of a combination of two equations proposed by other workers.[21,22] $F(\alpha)$, given by eq. (5), was defined as the ratio k_e/k_c, k_e being the rate constant for chemical kinetics and k_c the overall effective rate constant that includes the effect of both chemical kinetics and diffusion.

$$F(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \qquad (5)$$

In eq. (5), C is a constant and α_c represents the critical value of conversion at which the effect of diffusion becomes important.

With the inclusion of this diffusion factor the effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $F(\alpha)$
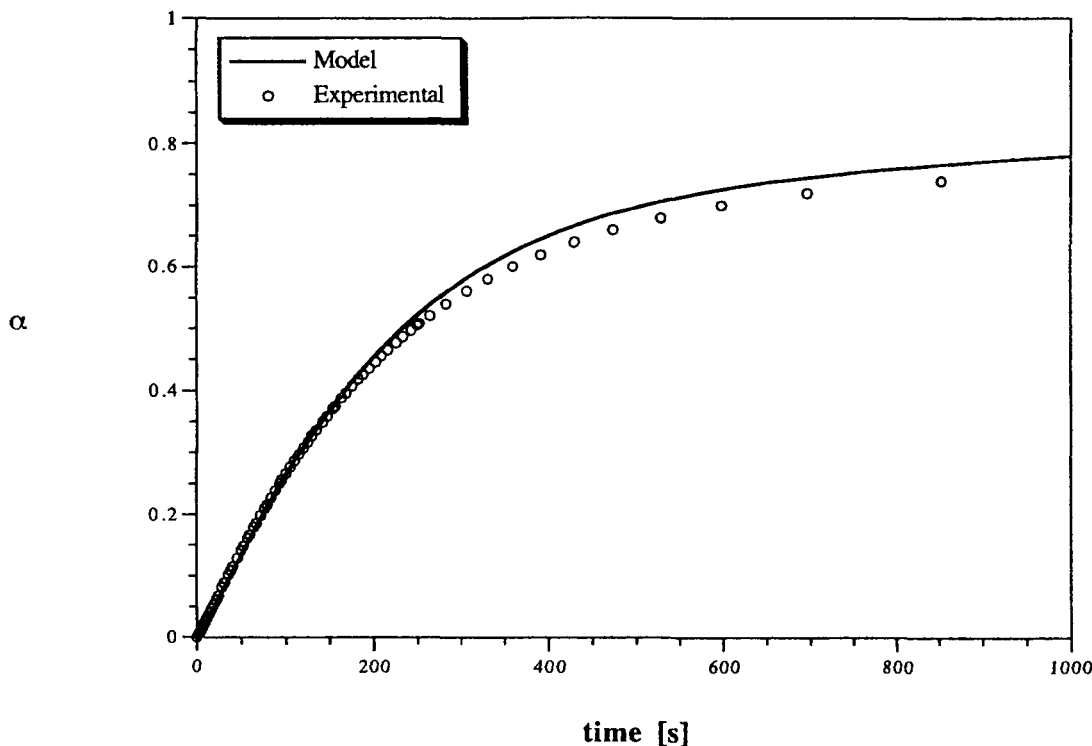
Figure 3   Values of conversion at the temperature of 80°C.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)$$

$$\times (1 - \alpha)^n \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (6)$$

When $\alpha \ll \alpha_c$, $F(\alpha)$ approximates unity, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches α_c, $F(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$,
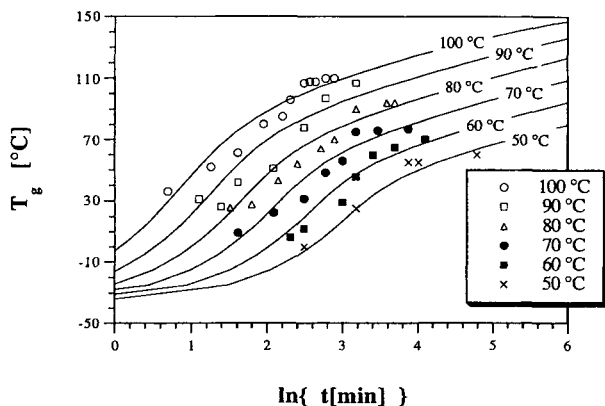

Figure 4 T_g vs. ln time data: (solid line) calculation using the model; (symbols) experimental data.

and beyond this point approaches zero as the reaction effectively stops.

We have considered k_1, k_2, m, n, C, and α_c, in eq. (6) as adjustable parameters and have been determined at six different temperatures.[8] Results are sumarized in Table III.

Because a more general model is necessary to predict the advance of cure at different temperatures from that shown in Table III, several assumptions have been made: the Arrhenius dependence of the rate constants, k_1 and k_2 has been taken into account in addition to a linear dependence of α_c with temperature. The other parameters, m, n, and C, have been taken as constants, independent of curing temperatures. These assumptions are summarized in Table IV and allow us to solve numerically eq. (6) using the Runge–Kutta technique[23] to yield conversion as a function of time, $\alpha(t)$ through the entire range of cure.

In Figure 3, the experimental values of conversion and values obtained from the integration of the kinetic model are shown at the isothermal cure temperature of 80°C. Similar curves were obtained at the other temperatures studied. As the curing time increases, model calculations give higher values of conversion than the experimental ones. This
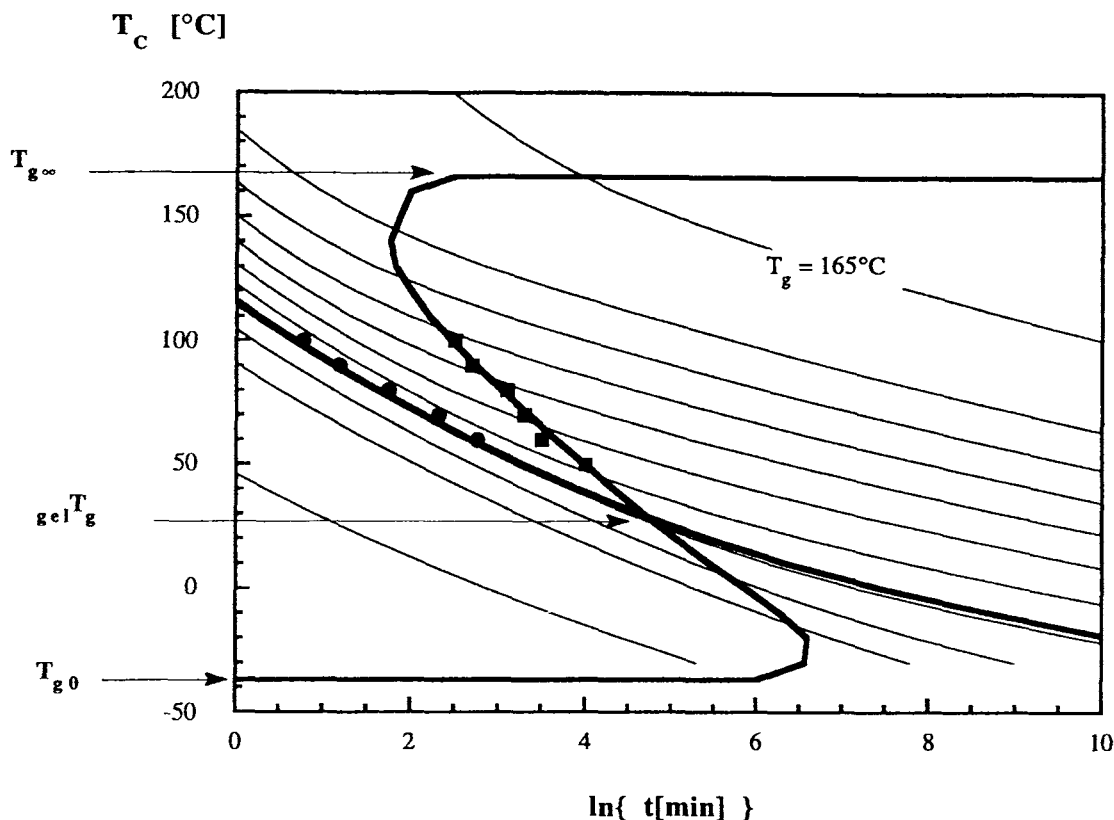
Figure 5 TTT isothermal cure diagram for DGEBA/1,3-BAC. ● and ■ correspond, respectively, to experimental gelation and vitrification times. Vitrification, gelation, and iso-T_g contours (T_g = −35 to 165, every 20°C) were obtained from the kinetic model.

is because $\alpha(t)$, obtained by numerical integration of eq. (6), increases continuously with time up to $\alpha = 1$ (which occurs at $t = \infty$) in contrast to the experimental $\alpha(t)$ data curve that tends asymptotically to certain limiting value lower than 1 that depends on T_c.

Values of calculated conversion can be transformed into T_g values by applying the functional relationship between glass transition temperature and conversion [eq. (3)]. Figure 4 shows the plot of experimental T_g and the curves calculated with the procedure described above vs. the logarithm of curing time for six isothermal curing temperatures. We must remember that the possible causes of imprecision in calculated values are the election of the parameters in the rate equation [eq. (6)] and the DiBenedetto's modified equation used to convert α into T_g. Nevertheless, the agreement between experiments and model calculations is satisfactory for each cure temperature.

TTT Isothermal Cure Diagram

The Time–Temperature–Transformation isothermal cure diagram for the DGEBA/1,3-BAC epoxy system is given in Figure 5. The diagram displays the experimental gelation points, for which the extent of reaction was found to be nearly constant, independent of temperature and experimental vitrification onsets, for instance, the times at which T_g reaches the different cure temperatures.

Vitrification and gelation curves calculated from the model are also plotted. The vitrification curve, the locus of cure times at which $T_g = T_c$, was calculated by transforming conversion values into T_g values through eq. (3). Ideal molecular gelation should theoretically[5] occur at a conversion of 58%. Thus, the ideal molecular gelation contour is an iso-T_g for $\alpha = 0.58$. The experimental and calculated gelation and vitrification values are in good agreement.

Three critical temperatures $T_{g0} = -37°C$, $_{gel}T_g = 28°C$, [temperature at which vitrification and

gelation occur simultaneously; calculated with α = 0.58 in eq. (3)] and T_g = 166°C, are indicated in Figure 5.

Iso-T_g contours are included in TTT diagram. They were calculated from the kinetic model as isoconversion curves and then transformed into T_g. The curve T_g = 165°C, which corresponds to a conversion value α = 0.998, is taken as the full cured line because, as we have explained above, with this kinetic model full conversion, for instance, α = 1 is not reachable in a finite time.

CONCLUSIONS

In summary, the cure of stoichiometric DGEBA/ 1,3-BAC epoxy system has been studied by means of glass transition temperature and conversion. The one-to-one correspondence between T_g and conversion, independent of the cure temperature, is correctly described by a DiBenedetto's approach in the form used by Hale et al.[18]

A general kinetic model with parameters determined in a previous work from isothermal DSC experiments in the range of 60–100°C, taking into account diffusion in the last stages of cure (near vitrification) was extended to describe the cure reaction in the complete range of conversion and over a wider range of temperature.

Using this model, ideal molecular gelation (α = 0.58) and vitrification curves ($T_c = T_g$) have been calculated and provide excellent fitting with experimental data.

A TTT isothermal cure diagram has been constructed in which Iso-T_g (isoconversion) contours, calculated from the kinetic model have been included.

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