Kinetic Study and Time–Temperature–Transformation Cure Diagram for an Epoxy–Diamine System

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ABSTRACT: The different steps involved in the curing reaction of a purified ether of bisphenol A (BADGE $n = 0$) and 1,2-diamine cyclohexane (DCH) were studied with the objective to calculate a time–temperature–transformation (TTT) isothermal cure diagram for this system. A kinetic model proposed by Horie et al.[6] was used and compared to the experimental data. Gelation times and conversions were measured using two different methods: solubility test and dynamic mechanical analysis (DMA). Results obtained by both methods show a reasonable agreement.

Differential scanning calorimetry (DSC) data show a one-to-one relationship between T_g and fractional conversion, α, independent of cure temperature. As a consequence, T_g can be used as a measure of conversion.

Using the model parameters and the relationship between T_g and conversion, T_g versus ln time are calculated and found to agree with DSC experimental results for isothermal cure temperatures from 60 to 100°C.

A kinetically controlled master curve for isothermal cure is obtained by shifting T_g versus ln time data to a reference temperature, $T_r = 80$°C. The apparent activation energy was calculated from gel times measurements ($12.63 \text{ kcal mol}^{-1} = 52.88 \text{ kJ mol}^{-1}$ from solubility test and $12.28 \text{ kcal mol}^{-1} = 51.42 \text{ kJ mol}^{-1}$ from DMA measurements).

Isoconversion contours were calculated by numerical integration of the kinetic model. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1377–1388, 1997

INTRODUCTION

The curing of a thermoset and, particularly, the cure of epoxy resins, involves the formation of a rigid three-dimensional network by reaction with hardeners that have more than two reactive functional groups. The chemistry of cure begins by formation and linear growth of the chain that soon begins to branch and then to crosslink. As the cure proceeds, the molecular weight increases rapidly. The molecular size increases, and several chains become linked together into networks of infinite molecular weight. This transformation from a viscous liquid to an elastic gel is sudden and irreversible and marks the first appearance of the infinite network. It is called the gel point. Gelation is characteristic of thermosets.[1] Prior to gelation, the sample is soluble in appropriate solvents; but after the gel point, the network will not dissolve but swells as it imbibes solvent. At the gel point, small and branched molecules are present, which are soluble; hence, the curing sample contains sol as well as gel fraction.

One other phenomenon that can appear during a curing reaction is vitrification; that is, the transformation of a viscous liquid or elastic gel to a vitrous solid. The vitrification point marks a change in the reaction mechanism passing from chemically kinetically controlled to become diffusion-controlled. The reaction will eventually become very slow and finally stops.[2]

Once an epoxy resin has vitrified, chemical reactions continue to occur, but at a much slower rate, which further raises its density and some other physical properties.[1] Samples that have vitrified during isothermal cure ($T_g > T_c$) show an
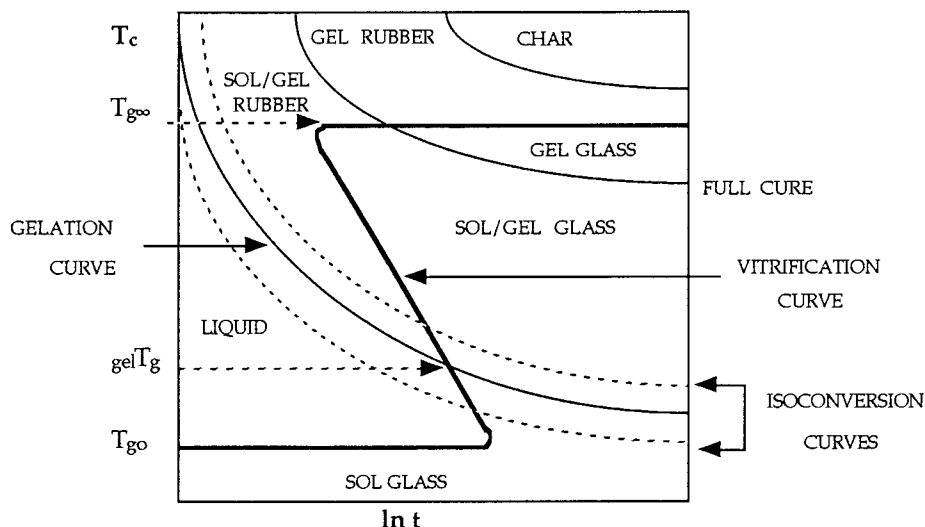
Figure 1 Generalized TTT isothermal cure diagram in which the time to reach various events during isothermal cure at different cure temperatures, T_c, is displayed.

endothermic physical aging peak in the vicinity of T_g.[3] This aging peak is in some ways a thermal degradation of material and should be avoided. Because of this, samples scanned at an appropriate heating rate to just beyond the physical aging peak are quenched to a low temperature ($-30°C$) and then rescanned to the final experimental temperature.

The isothermal time–temperature–transformation (TTT) cure diagram, which was developed to study epoxy systems, is a very useful tool for studying cure processes of epoxy systems.[4,5] Figure 1 shows a generalized TTT isothermal cure diagram. This diagram is calculated plotting the experimental times to reach various events during isothermal cure versus cure temperature.
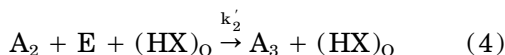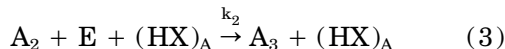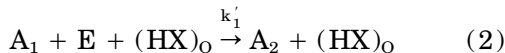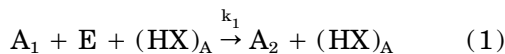
The TTT isothermal cure diagram records the phenomenological changes that occur during the cure reaction of the epoxy, such as vitrification and macroscopic gelation. As it can be seen in the figure, the diagram has been expanded to include other different contours, such as carbonization (char), or thermal degradation curve and isoconversion or iso-T_g curves, in which full cure or maximum experimental isoconversion is included.

On the diagram, the times to gelation and the times to vitrification are plotted as a function of the isothermal temperature of curing. Three temperatures play an important role in this diagram. T_{go} is the temperature below which no significant reaction of the mixture epoxy–hardener occurs. It may be considered as the storage temperature for uncured resin mixture. (The reaction, if any, is so slow that may be considered negligible).

In an ideal system, gelation and vitrification can occur simultaneously. The temperature at which this phenomenon happens is $_{gel}T_g$. After vitrification, the reaction rate becomes to be controlled by diffusion of the reacting species. In this regime, the rate of reaction is affected by both chemical and physical aging. $T_{g\infty}$ is the cure temperature at which the degree of conversion reaches its maximum value (theoretically, $\alpha = 1$). From the experimental point of view, it is impossible to reach this α value. For this reason, a curve of maximum curing, corresponding to the maximum isoconversion curve, is included. Between T_{go} and $_{gel}T_g$, the liquid resin will react until its glass transition temperature becomes coincidental with the cure temperature, at which point vitrification will start. Between $_{gel}T_g$ and $T_{g\infty}$, gelation precedes vitrification. If the cure temperature is above the T_g of the fully cured material, $T_{g\infty}$, the material cannot vitrify at T_c.

Isoconversion (iso-T_g) curves included in the TTT diagram are calculated by numerical integration of the kinetic model proposed by Horie et al.[6] This model does not allow for diffusion phenomena. Because of that, theoretical and experimental results may deviate after vitrification. However, the agreement between experimental and theoretical values is better with increasing temperatures, and it is reasonably good when cure temperatures are close to $T_{g\infty}$.

The reactions considered in the kinetic model are the epoxy–amine reactions, catalyzed by the hydroxyl generated by the reaction $(HX)_A$ or by initial hydroxyl or impurities $(HX)_O$.

$$A_1 + E + (HX)_A \xrightarrow{k_1} A_2 + (HX)_A \quad (1)$$

$$A_1 + E + (HX)_O \xrightarrow{k_1'} A_2 + (HX)_O \quad (2)$$

$$A_2 + E + (HX)_A \xrightarrow{k_2} A_3 + (HX)_A \quad (3)$$

$$A_2 + E + (HX)_O \xrightarrow{k_2'} A_3 + (HX)_O \quad (4)$$

Where E, A_1, A_2, and A_3 designate epoxy, primary amine, secondary amine produced by addition of an epoxide, and tertiary amine as a final product, respectively.

Cole et al.[7] proposed the following etherification reaction:

$$mA_3 + E + n(OH) \xrightarrow{k_3} \text{ether} + mA_3 + n(OH) \quad (5)$$

In this last equation, an epoxide ring is transformed into an ether linkage, and there is no change in the number of hydroxyl groups (OH). Etherification refers to both the epoxide–hydroxyl reaction and the homopolymerization reaction. To cover the different possibilities, the equation contains a coefficient n, representing the number of hydroxyl groups involved (as either reactant or catalyst) and m, the number of tertiary amine groups (as catalyst). Both n and m could be zero. In our case, owing both to the nature of reactants and to the experimental conditions, the etherification reaction is neglected.

From eqs. (1) to (4), assuming equal reactivity for all the amine hydrogens, the reaction rate, in terms of basic concentrations, can be described by a semiempirical equation:

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha^m)(1 - \alpha)^a(B - \alpha)^b$$

where K_1' and K_1 are constants proportional to rate constants, and B is the initial ratio of diamine equivalents to epoxide equivalents (B equals 1.0 when stoichiometric quantities of the reactants are mixed).

In a previous article,[8] it was concluded that for the system studied here,

$$\frac{d\alpha}{dt} = (K_1\alpha + K_1')(1 - \alpha)^2$$

EXPERIMENTAL

Materials

The thermosetting system studied is a stoichiometric mixture of epoxy resin–diamine. The epoxy resin is a liquid diglycidyl ether of bisphenol A (BADGE $n = 0$) (Resin 332, Sigma Chemical Co) with an equivalent epoxy molecular weight, after purification, of 175.6 g eq, as determined by wet analysis.[9,10] The curing agent was 1,2-diaminecyclohexane (DCH) (Fluka), with an amine hydrogen equivalent weight of 28.5.[8] It was used as received.

Techniques

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to obtain all the experimental data reported in this work.

A Perkin-Elmer DSC-7 unit, under control of a 1020 system controller, was used for calorimetric measurements.

The experiments were carried out in a temperature range from −30 to 250°C. Owing to the low temperature necessary for the performance of measurements, a cooling device (Intercooler II supplied by Perkin-Elmer) was adapted to the DSC-7 equipment. The calorimeter was calibrated following the procedure given in the Perkin-Elmer DSC-7 Manual.[11] Two standards (indium and bidistilled water obtained by the Milipore method) were used.

The calorimeter was used to measure glass transition temperatures, and it was operated in both dynamic and isothermal modes.

Dynamic mechanical properties were measured using a Perkin-Elmer DMA-7 operated in the parallel plate measuring system. The DMA was calibrated using indium as a standard. Samples were under constant dynamic force of 60 mN.

RESULTS AND DISCUSSION

Gelation Study

Gelation is a phenomenon that takes place during thermosetting polymer cure reactions. It corresponds to the incipient formation of a network with an infinite weight-average molecular weight. Gelation occurs at a well-defined stage in the course of the cure reaction and is dependent on the stoichiometry, functionality, and reactivity of the reactants. This phenomenon typically occurs for conversions between 55 and 80% (conversion degree $\alpha = 0.55-0.80$).

According to Flory,[12] for epoxy–diamine reactions, gelation occurs when conversion degree reaches the following value:

$$\alpha_g = \sqrt{\frac{B}{3}}$$

where B is the ratio of amine hydrogen equivalents to epoxide equivalents initially. In our case $B = 1$ as stoichiometric quantities are mixed. This leads to a value of $\alpha_g = 0.58$; that is, 58% of conversion.

Prior to gelation, the polymers remain soluble in suitable solvents; after gelation, samples show a rubber viscoelastic behavior and become insoluble.

As cure reaction proceeds, the molecular weight increases, and several chains link together into networks of infinite molecular weight. This sudden and irreversible transformation, from a viscous liquid to an elastic gel, is the gel point; and the time at which it occurs, at a given isothermal cure temperature, is the gel time. This gel time can be determined experimentally following different procedures. In the present study, we have followed two experimental methods: a solubility test and DMA.

Solubility Test

In this method, the time to reach a fibriform structure in tetrahydrofurane is measured.[13] The experimental procedure is as follows. An aluminium can containing the sample is introduced into a thermostatted bath filled with polyethylene glycol. The sample was continuously shaked; and at different times, a part of same was taken out from the container and poured into a beaker containing tetrahydrofuran trying to determine the time necessary for the sample to become insoluble at which a fibriform structure is visualized. Table I shows the gel formation (gel times) and the corresponding conversions at the different temperatures used in this study.

Dynamic Mechanical Analysis

DMA was used to measure dynamic mechanical properties of the epoxy. The equipment was operated in the parallel plate measuring system. Gel time was assigned as that corresponding to the maximum value of tan δ,[14] where δ is the phase angle between the imaginary part and the real part of the complex viscosity. Samples (10–20 mg) were placed into aluminium pans and covered with an aluminium disk, which was pressed by a parallel plates platform until the disk is totally submerged into the sample. This procedure assures a good contact between the platform and the sample, so improving the correctness of mea-

Table I   Times and Conversions at Gel Point from the Solubility Test

T (°C)	t_{gel} (min)	α
60	40.13	0.58
70	21.63	0.59
80	13.06	0.65
90	8.46	0.63
100	4.96	0.64

surements. A quasi-isothermal regime can be achieved by cooling the sample from the experimental chosen temperature to 5°C below it at a constant cooling rate of 0.1°C min. Once the sample is inside the DMA furnace, the parallel plates experiment is programmed by means of a rounded point probe. Figure 2 shows the gelation processes at the various temperatures used in this study. Gel times and the corresponding conversions data obtained by DMA are listed in Table II.

Tables I and II show a reasonable agreement between gel time values obtained by using both methods. In addition, the values measured for conversions at gel point are very closed to the value predicted by Flory (58%). For this reason, it can be reasonably assumed that for the system here studied, gelation corresponds to an isoconversion process, $\alpha_g = 0.58$.

An overall activation energy for polymerization can be obtained from gel times, assuming that cure reactions may be described by differential equations containing one unique apparent activation energy,[15,16] as follows:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT_c}\right) f(\alpha) \tag{6}$$

where A is a constant factor, E is the apparent activation energy for the overall reaction, T_c is the isothermal cure temperature, and $f(\alpha)$ is assumed to depend on α and to be independent of the cure temperature.

Integration of this equation from $\alpha = 0$ to $\alpha = \alpha_g$ and taking natural logarithms leads to

$$\ln \int_0^{\alpha_g} \frac{d\alpha}{f(\alpha)} = \ln A + \ln t_g - \left(\frac{E}{RT_c}\right) \tag{7}$$

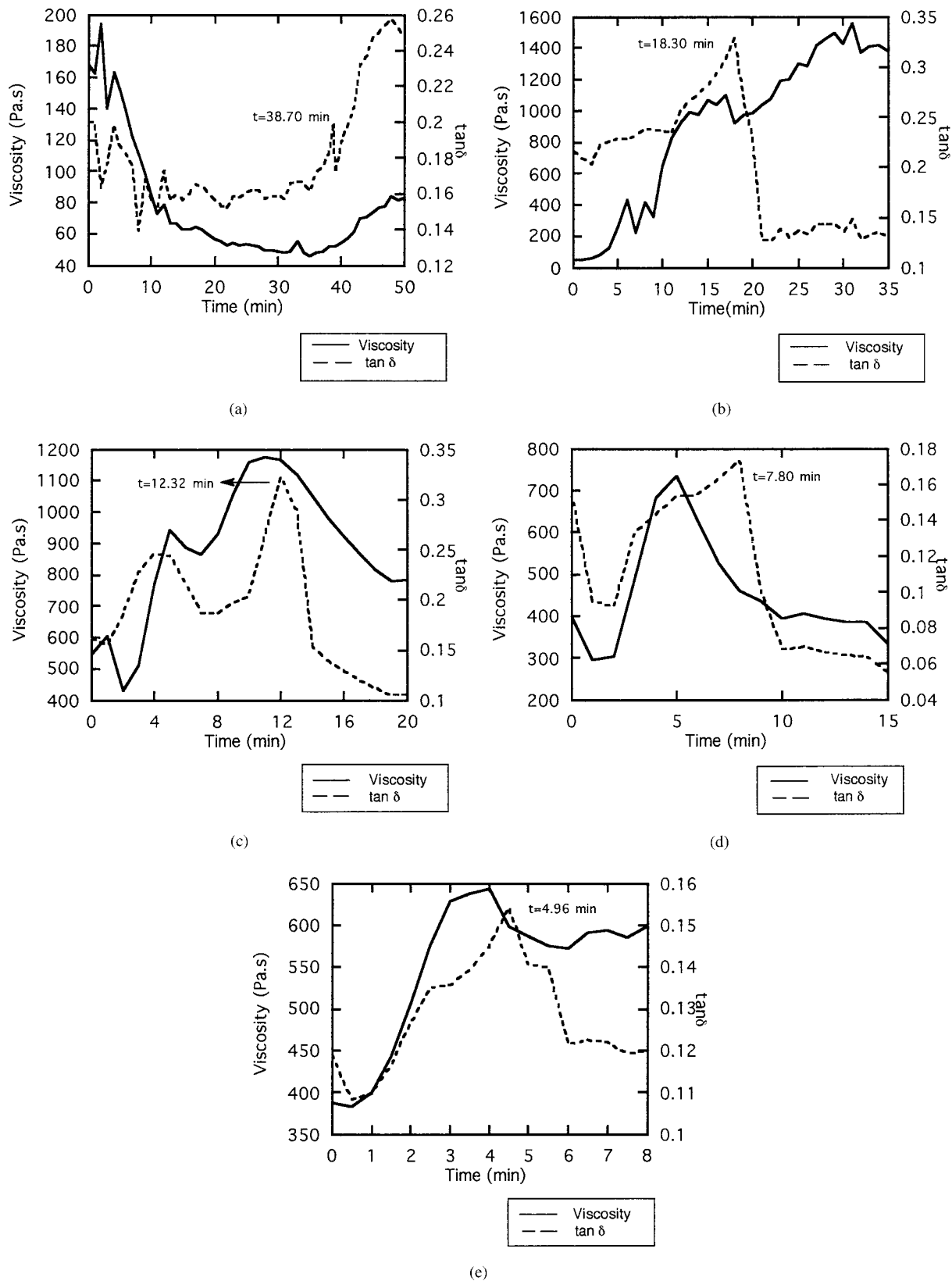The left-hand side of this equation is independent of T_c, so

Figure 2 DMA gelation plots for the various isothermal cure temperatures: (a) T_c = 60, (b) 70, (c) 80, (d) 90, (e) 100°C.

Table II Times and Conversions at Gel Point from DMA Experiments

T (°C)	t_{gel} (min)	α
60	38.70	0.58
70	18.30	0.58
80	12.32	0.64
90	7.80	0.63
100	4.96	0.63

$$\ln t_g = C + \frac{E}{RT_c} \qquad (8)$$

The activation energy can be calculated from the slope of the straight line, which results when experimental values of ln t_g are plotted as a function of $(1/T_c)$. From experimental values given in Table I (solubility test), an activation energy E = 12.63 kcal mol^{-1} = 52.88 kJ mol^{-1} is found.

This same activation energy can be calculated from DMA data given in Table II and the results are that E = 12.28 kcal mol^{-1} = 51.42 kJ mol^{-1}.

As it can be seen, the results obtained using both methods show a reasonable agreement, which leads us to believe that both of them can be used to characterize gelation parameters.

Vitrification Study

DSC plots of dH/dT as a function of T show an endothermic step change in heat capacity at the glass transition. Glass transition temperature, T_g, is taken as the midpoint of this transition.[17]

It was mentioned that as a thermosetting cures, its glass transition temperature increases from a minimum, initial value, T_{go}, to a maximum value, $T_{g\infty}$, which corresponds to the fully cured material.

For the epoxy system reported in this article, both values were measured in our laboratory, resulting in T_{go} = −30.1°C and $T_{g\infty}$ = 146.3°C.

Experimental data reported in this work were obtained from DSC studies using a Perkin-Elmer DSC-7 unit. Five to seven milligram samples of uncured resin were sealed in aluminium pans and cured in the preheated DSC unit at isothermal cure temperatures from 60 to 100°C for various cure times in the range from 1 to 50 minutes.
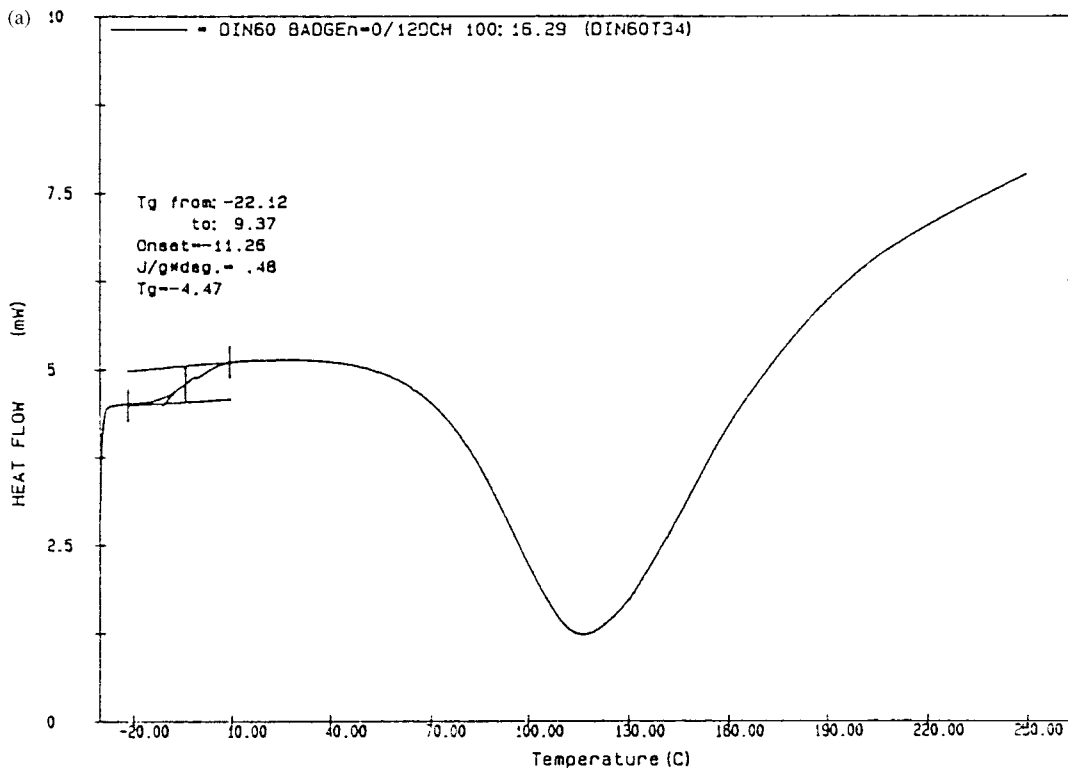
These samples were then quenched to −30°C in order to keep them at their polymerization state.[17,18] The samples are then scanned to 250°C at 10°C min. This heating rate value was found to be the optimum in order that further relaxation of the glass to its equilibrium rate does not proceed during the heating period, and T_g is independent of the heating rate.

Figure 3 shows some of the dynamic experiments carried out in order to measure T_g. It can be seen that T_g increases as cure time increases [Fig. 3(a)–(d)]. The step change smooths in the vicinity of the exotherm of the residual reaction, making it difficult to determine T_g. Samples that have vitrified during the isothermal cure ($T_g > T_c$) show an endothermic physical aging peak in the vicinity of T_g [Fig. 3(e)]. To eliminate the physical aging peak and, therefore, the effects of physical aging on T_g, these samples are quenched to −30°C at 300°C min and then rescanned to 250°C at 10°C min [Fig. 3(f)]. This procedure allows the determination of T_g.
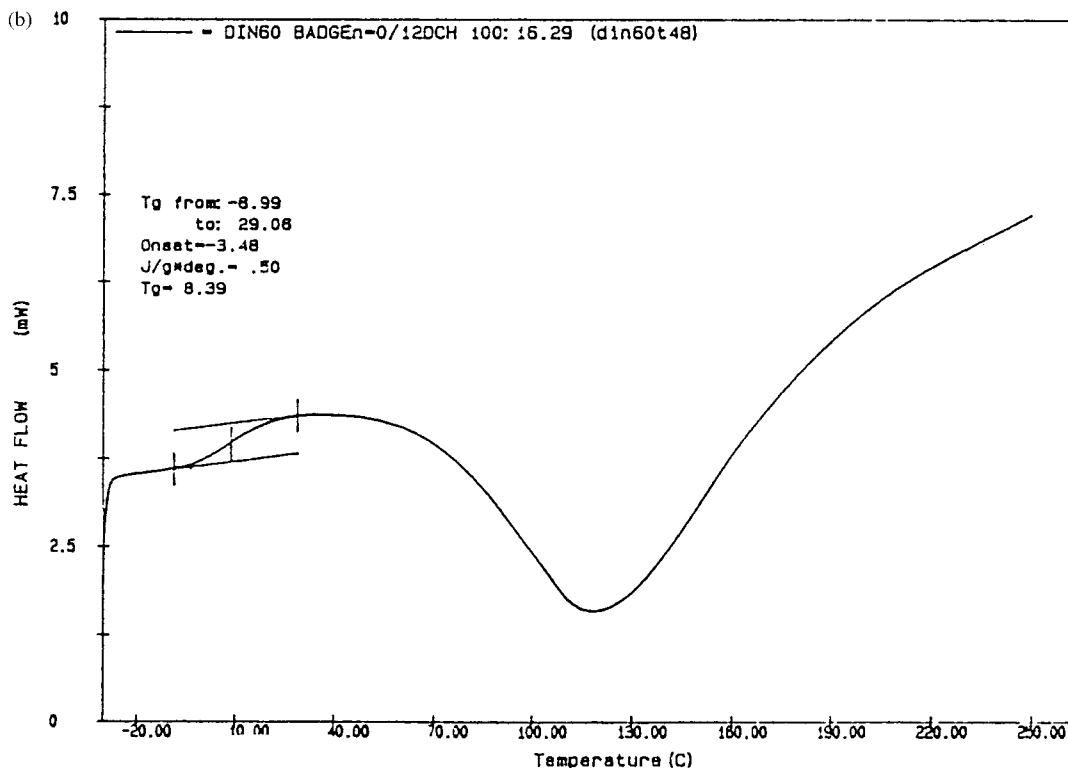
Figure 4 shows T_g values as a function of the cure time, t_c, for the different isothermal cure temperatures. As can be seen, T_g rapidly increases with cure time up to vitrification time, at which $T_g = T_c$[19]; then the increase in T_g becomes slower, owing to diffusion effects. In this sense, t_v denotes the time at which incipient vitrification takes place. For $t > t_v$, two different effects are associated with the further increase of T_g: on the one hand, conversion continues to increase, although at a greatly diminished rate; on the other hand, physical aging of the sample in the glassy state leads to an increase in T_g. To remove all traces of physical aging, it is necessary to heat the sample, previously cooled, to a temperature just beyond the observed T_g to cool it rapidly and heat a second time to determine the correct T_g. This procedure can be employed when the curing rate during the first heating may be neglected. In order to get the T_g versus α relationship, it is recommended to use the T_g versus ln t plot only up to t_v.[17] In order to calculate vitrification times, curves shown in Figure 4 were fitted to power functions of the nth degree, taking into account that vitrification takes place at $T_g = T_c$.

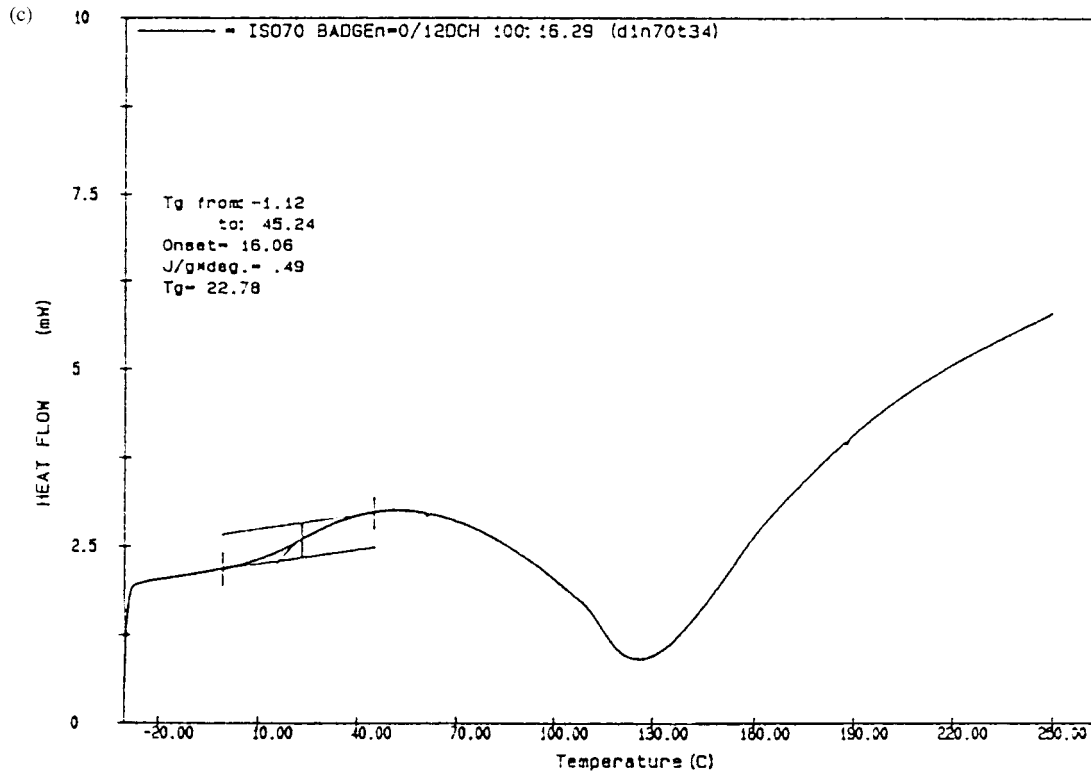Vitrification times corresponding to the differ-

Figure 3 DSC dynamic plots used for determination of T_g in partially reacted samples at different isothermal cure temperatures: (a) T_c = 60°C, t_c = 34 min; (b) T_c = 60°C, t_c = 48 min; (c) T_c = 70°C, t_c = 34 min; (d) T_c = 90°C, t_c = 12 min; (e) T_c = 80°C, t_c = 83 min (first scan); (f) T_c = 80°C, t_c = 83 min (second scan).

(a)

■ DIN60 BADGEn-0/12DCH 100: 16.29 (DIN60T34)

Tg from: -22.12
to: 9.37
Onset:-11.26
J/g×deg.- .48
Tg=-4.47

HEAT FLOW (mW)

Temperature (C)

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(b)

■ DIN60 BADGEn-0/12DCH 100: 16.29 (din60t48)

Tg from: -8.99
to: 29.08
Onset:-3.48
J/g×deg.- .50
Tg= 8.39

HEAT FLOW (mW)

Temperature (C)

TERBIPROMAT

(c)

Tg from -1.12
    to: 45.24
Onset= 16.06
J/g×deg.= .49
Tg= 22.78

- ISO70 BADGEn=0/12DCH 100: 16.29 (din70t34)

HEAT FLOW (mW)

Temperature (C)

TERBIPROMAT

(d)

Tg from 1.50
    to: 63.62
Onset= 16.98
J/g×deg.= .33
Tg= 41.29

- DIN90 BADGEn=0/12DCH 100: 16.29 (DIN90T12)

HEAT FLOW (mW)

Temperature (C)

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Figure 3 (*Continued from the previous page*)
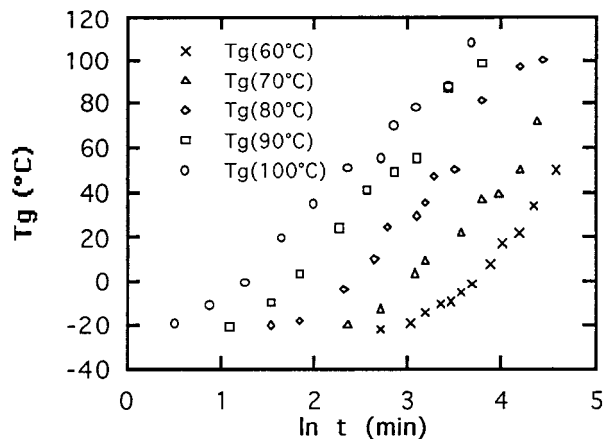
Figure 4 T_g versus ln time for various cure temperatures from DSC isothermal cure temperatures.

Figure 5 One-to-one relationship between glass transition temperature (T_g) and conversión (α).

ent isothermal cure temperatures are shown in Table III.

The experimental T_g versus α DSC data are shown in Figure 5. It can be noted that the relationship between T_g and conversion is independent of cure temperature. This fact agrees with studies reported in the literature.[17,18] The one-to-one relationship between T_g and conversion implies that either the molecular structure of the materials cured at different temperatures is the same or that the difference in molecular structure for materials cured at different temperatures does not have a significant effect on the glass transition temperature (i.e., the differences in structure occur on a size scale smaller than that measured by T_g).

Nielsen reported a modified form of the empirical DiBenedetto equation,[19]

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

where T_{go} is the T_g of uncured monomer, $T_{g\infty}$ is the maximum glass transition temperature obtained experimentally for the fully cured material, and λ is taken as an adjustable structure-dependent

Table III Vitrification Time at Various Isothermal Cure Temperatures

T (°C)	t_v (min)
60	109.61
70	80.28
80	48.87
90	36.03
100	35.51

parameter between 0 and 1. Pascault and Williams[19] show that λ is theoretically equated to $\Delta C_{p\infty}/\Delta C_{po}$, where $\Delta C_{p\infty}$ and ΔC_{po} are the differences in heat capacity between the glassy and rubbery (or liquid, prior to gelation) states at T_g for the fully cured network and monomer, respectively.

Figure 6 shows a fit of T_g versus α using the DiBenedetto equation. In this equation, λ is treated as an adjustable parameter and is determined to be 0.165. The DiBenedetto equation will be used when it is necessary to convert T_g to conversion and vice versa. Application of this equation, using the value of $\alpha = 0.58$ given by the Flory theory, led to the calculation of $_{gel}T_g = 7.2$°C.

Time–Temperature Superposition of DSC Data

Time–temperature shifts of T_g versus log time data at different cure temperatures yield a master curve for the reaction at an arbitrary reference temperature.[17,18] The theoretical basis for the superposition is the one-to-one relationship between conversion and T_g and the assumption that the polymerization is kinetically controlled with a single apparent activation energy.

The rate of reaction is given by the Ahrrenius rate equation (6), from which equation (7) is derived. Since the left-hand side of this equation is only a function of conversion, and because there is a one-to-one relationship between conversion and T_g, some function of T_g, $F(T_g)$, can be substituted for the left-hand side of the equation, as follows:

$$F(T_g) = \ln A + \ln t_c - \left(\frac{E}{RT_c}\right) \qquad (9)$$

The shift factor, a_{T_c}, is the difference in ln time between two curves shifted at constant T_g (i.e., the same conversion).

$$a_{T_c} = \ln t_r - \ln t_c = \left(-\frac{E}{R}\right)\left(\frac{1}{T_c} - \frac{1}{T_r}\right) \quad (10)$$

where the subscript r corresponds to an arbitrary reference temperature.

Figure 7 shows T_g versus ln time master curve at 80°C. From the master curve, values of T_g (or α) may be obtained at any T_c, providing the knowledge of T_g values corresponding to the cure reaction at a given reference temperature, T_r.

Isoconversion curves have been determined by numerical integration of the kinetic model.[6] Only values prior to vitrification have been taken into account. Our diagram cannot be extended into the diffusion-controlled regime since the master curve used is only valid for the kinetically controlled regime.

TTT Diagram

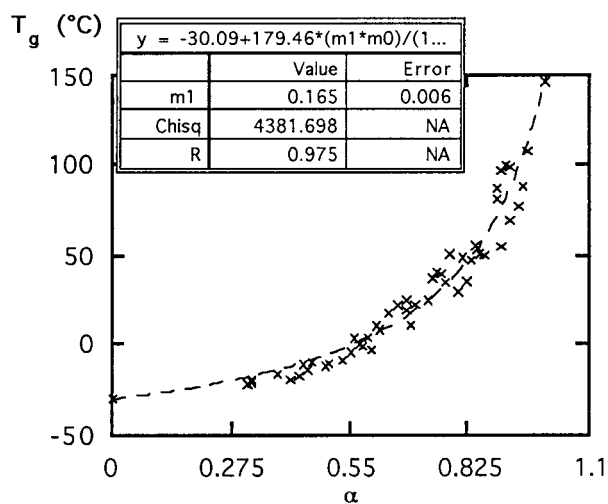The TTT isothermal cure diagram was calculated from the contours of the time to gel and to vitrify

Figure 6 One-to-one relationship between T_g and conversion using the DiBenedetto equation.
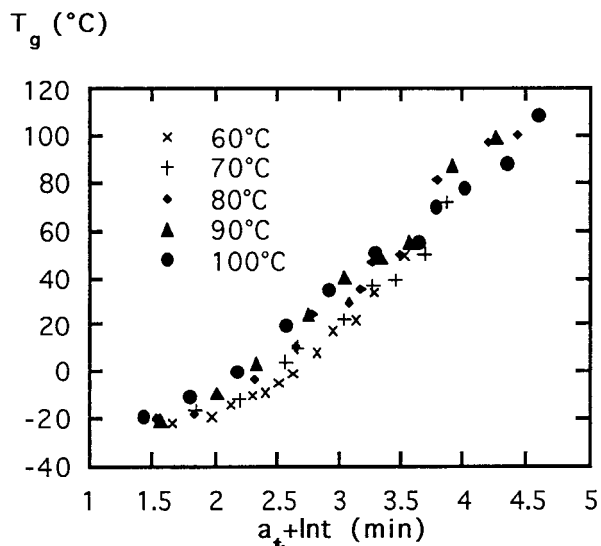
Figure 7 T_g versus ln time master curve for the system BADGE $n = 0/1,2$-DCH at a reference temperature, T_r, of 80°C.

as a function of the reaction temperature (Fig. 8). Data were fitted to curves, taking into account that the gelation curve and vitrification curve intersect at the curing time, corresponding to $_{gel}T_g$ calculated using the DiBenedetto equation and the value $\alpha = 0.58$ (theoretical gelation). Isoconversion curves corresponding to $\alpha = 0.32$, 0.45, 0.75, 0.80, and 0.96 are plotted.

The isoconversion curve $\alpha = 0.96$ corresponds to the maximum achievable experimental extent of conversion.

To plot a TTT diagram, it is necessary to know three principal temperatures: T_{go}, the initial T_g of the system; $_{gel}T_g$, the temperature at which vitrification and gelation occur simultaneously (i.e., the temperature at which the conversions for vitrification and gelation are the same); and $T_{g\infty}$, the maximum glass transition temperature of the fully cured system.

For the system studied here (BADGE–DCH), T_{go} and $T_{g\infty}$ were experimentally determined; and $_{gel}T_g$ was calculated using the DiBenedetto equation and the value $\alpha = 0.58$, which corresponds, according to Flory, to the theoretical gelation. Values of T_{go} and $T_{g\infty}$ were measured by DSC. $_{gel}T_g$ was determined as the temperature corresponding to the intercept of gelation and vitrification curves in a T_c(°C) versus ln t plot. The values of the three characteristic temperatures are found to be $T_{go} = -30.1$°C; $_{gel}T_g = 7.2$°C; and $T_{g\infty} = 146.3$°C.

The vitrification curves are, as usual, S-shaped. The times to vitrification pass through a maximum at a cure temperature just above T_{go} because

of the competing effects of increasing reactivity and decreasing viscosity with increasing temperature. In contrast, the times of vitrification pass through a minimum at a temperature of cure just below $T_{g\infty}$ because of the competing effects of the increasing reaction rate constant and the increasing extent of conversion at vitrification with increasing temperature.[20]

Figure 8 shows that iso-T_g contours are almost parallel to the gelation curve, which suggest that, in this case, this curve can be also considered as an isoconversion one. Extent of conversion slows after vitrification, but it does not cease.

According to the TTT cure diagram, as a thermosetting material cures, its glass transition temperature increases with the extent of conversion. When the T_g reaches the value of the isothermal cure temperature, T_c, the material vitrifies. In the vicinity of vitrification, the segmental mobility decreases, and the overall rate of the reaction may become controlled by the limiting diffusion of reacting species.

T_{go} ($-30.1°C$) corresponds to the glass transition temperature of the material with the degree of conversion $\alpha = 0$. Below this temperature, the thermoset is a glassy solid soluble in suitable solvents. The system does not react below T_{go}.
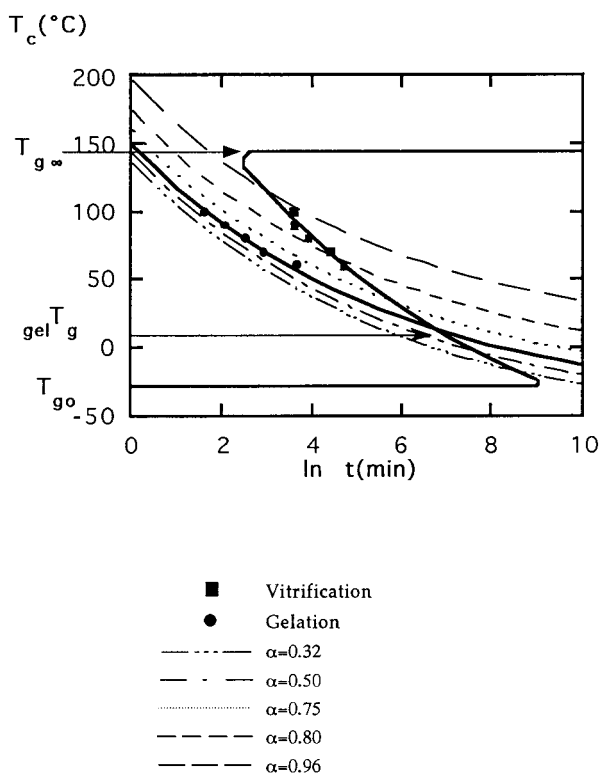
$_{gel}T_g$ ($7.2°C$) is the temperature at which the system gels and vitrifies simultaneously.

Between T_{go} and $_{gel}T_g$ ($-30.1°C < T_c < 7.2°C$), the system will react until its continuously rising glass transition temperature becomes coincidental with the cure temperature; at which stage vitrification will begin and the reaction becomes diffusion-controlled, so gelation may not be achieved. For vitrification below $_{gel}T_g$, the resulting material will have a low molecular weight and it will flow on heating. $T_{g\infty}$ ($146.3°C$) is the maximum temperature at which glass transition can be achieved. Between $_{gel}T_g$ and $T_{g\infty}$ ($7.2°C < T_c < 146.3°C$), gelation precedes vitrification. For our system, gelation occurs at an extent of conversion of $\alpha = 0.58$ (gel point).

After gelation, the curing sample contains sol as well as gel fractions. The gel initially formed is weak and can be easily disrupted. To produce a structural material, cure has to continue until most of the sample is connected into the three-dimensional network, in which case, the sol fraction becomes small; and for many cured materials, it has to be essentially zero. If the material achieves the maximum extent of conversion, no soluble fraction is present.

If the cure reaction is above $T_{g\infty}$ ($146.3°C$), no vitrification occurs; and the reaction is kinetically controlled, and total conversion may be theoretically achieved. However, as the time increases, a great amount of material is thermodegraded so that its useful properties are lost.

From the TTT isothermal cure diagram, the cure conditions for the cure reaction of an epoxy system studied may be determined.

From the observation of the TTT diagram for the system diglycidyl ether of bisphenol A−1,2-Diaminecyclohexane, it can be deducted that a cure at 23°C for 24 h and then 16 h at 70°C will allow an optimum result with a final conversion coincidental with the maximum achievable extent of conversion at $\alpha = 0.96$.

This same cure conditions are in complete agreement with those proposed by Dupont for the same epoxy system using commercial products.

Figure 8 Calculated TTT isothermal cure diagram for the system BADGE $n = 0/1,2$-DCH.

CONCLUSIONS

Phenomenom of gelation for the system BADGE $n = O$/DCH has been studied using two different experimental techniques: solubility test and DMA. The values of gel times and apparent activation energies obtained using both methods are in rea-

sonable agreement, which shows that these methods may be used for these kind of measurements.

DSC shows itself to be a suitable technique with which to determine experimental glass transition temperatures, and so with which to characterize the vitrification phenomenom.

A TTT isothermal cure diagram for the system BADGE n = O/DCH was calculated from the kinetic model and compared to experimental data. This diagram may be used as a basis for understanding the cure and properties of the system.

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