

Modification of a Two-Component System by Introducing an Epoxy-Reactive Diluent: Construction of a Time–Temperature–Transformation (TTT) Diagram

Lisardo Núñez, M. Villanueva, M. R. Núñez, B. Rial, L. Fraga

Research Group TERBIPROMAT, Departamento de Física Aplicada, Universidade de Santiago de Compostela, Campus Sur, 15782, Santiago, Spain

Received 25 January 2003; accepted 20 October 2003

ABSTRACT: Curing reactions of a three-component system consisting of an epoxy resin diglycidyl ether of bisphenol A (DGEBA $n = 0$), 1,2-diaminocyclohexane as curing agent, and vinylcyclohexene dioxide as a reactive diluent were studied to calculate a time–temperature–transformation isothermal cure diagram for this system. Differential scanning calorimetry (DSC) was used to calculate the vitrification times. 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. The activation energy for the polymerization overall reaction was calculated from the gel times obtained using the solubility test (58.5 ± 1.3 kJ/mol). This value was similar to the results obtained for other similar epoxy systems. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1190–1198, 2004

Key words: gelation; thermosets; time–temperature–transformation (TTT) diagram; differential scanning calorimetry (DSC); resins

INTRODUCTION

Curing reactions of thermoset materials generate a tridimensional network after chemical reaction of the epoxy resin and the appropriate hardener. During the cure process of a thermoset, the glass-transition temperature (T_g) of the material increases as a consequence of the increase in both the crosslinking density and the molecular weight.¹ Because of this, there is a decrease in the free volume of both epoxy groups and primary amine not reacted, attributed to the fact that some chains become hindered in an infinite molecular weight network. The transformation from a viscous liquid to an elastic gel is sudden and irreversible and marks the first appearance of the infinite network—called the gel point. Gelation is characteristic of thermosets, and it occurs at a well-defined and calculable stage in the course of the reaction, that is, at specific values of conversion and T_g . One other phenomenon that may occur at any stage during cure is vitrification. This transformation from a viscous liquid or elastic gel to a glass begins to occur as the glass-transition temperature of the system becomes coincidental with the cure temperature. The vitrification point marks a change in the reaction mechanism passing from chemically kinetically controlled to become diffusion controlled. Samples vitrified during an isothermal curing

[$T_g > T_c$ (crystallization temperature)] show an endothermic physical aging peak in the vicinity of T_g .²

Viscosity is a key factor in epoxy resin processing. Diluents are usually used to reduce viscosity to aid general processability. Epoxy-based reactive diluents can participate, together with a resin and a curing agent, in polymerization and crosslinking reactions, thus permitting the diluent to become chemically bound into the crosslinked network. In an attempt to preserve the physicomechanical properties at elevated temperatures, the use of a polyfunctional epoxy diluent has been considered.³

The use of this kind of additive can promote modifications in the properties of an epoxy system during a curing reaction. In the case of a multifunctional epoxy reactive diluent, the behavior of the diluent is considered to be similar to that of the basic component and the crosslink density seems not to be affected. The objective of this work was to construct the time–temperature–transformation (TTT) diagram for this three-component system.

The isothermal TTT cure diagram, which was developed to study epoxy systems, is a very useful tool for studying cure processes of epoxy systems.^{4,5} This diagram is calculated by 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. In this diagram other different con-

Correspondence to: L. Núñez (falisar1@usc.es).

tours can be included, 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.

EXPERIMENTAL

Materials

The epoxy resin was a commercial DGEBA ($n = 0$; Resin 332, Sigma Chemical Co., St. Louis, MO) and the epoxy reactive diluent was vinylcyclohexane dioxide (Fluka Chemie, Buchs, Switzerland), with equivalent molecular weights of 173.6 and 71.3 g/eq, respectively, as determined by wet analysis.^{6,7} The curing agent was 1,2-diaminocyclohexane (1,2-DCH; Fluka), with an amine hydrogen weight of 28.5.

Sample preparation

Epoxy resin and diluent were carefully and homogeneously mixed before the curing agent was added at a stoichiometric ratio with respect to the total epoxy weight (DGEBA + epoxy diluent). The order of mixing was to prevent the start of reaction before the addition of the three components. The amount of diluent was 15% of the total weight of mixture (DGEBA/curing agent/diluent).

Techniques

Experimental data reported in this work were obtained from DSC studies using a Perkin-Elmer DSC-7 unit (Perkin Elmer Cetus Instruments, Norwalk, CT) under a control of a 1020 system controller. The calorimeter was used to measure glass-transition temperatures and was operated in both dynamic and isothermal modes.

Dynamic experiments were carried out in a temperature range from -50 to 250°C . Because of 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.⁸ Two standards (indium and bidistilled water obtained by the Millipore method) were used.⁹⁻¹¹

Samples of uncured resin (5-7 mg) were sealed in aluminum pans and cured in the preheated DSC unit at isothermal cure temperatures from 80 to 130°C for various cure times.

These samples were then quenched to -50°C to keep them at their polymerization state.^{12,13} The samples were then scanned to 250°C at $5^\circ\text{C}/\text{min}$. This heating rate value was found to be the optimum so that further relaxation of the glass to its equilibrium

rate would not proceed during the heating period, and the T_g value would be independent of the heating rate.

It was mentioned that as a thermoset cures, its glass-transition temperature increases from a minimum, initial value (T_{g0}) 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 $T_{g0} = -46.8^\circ\text{C}$ and $T_{g\infty} = 163.7^\circ\text{C}$.

RESULTS AND DISCUSSION

Gelation study

Gelation is a phenomenon that occurs 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 cure reaction and is dependent on the stoichiometry, functionality, and reactivity of the reactants.

According to Flory,¹⁴ for epoxy-diamine reactions, gelation occurs when conversion degree reaches the value

$$\alpha_g = \frac{1}{\sqrt{(f_a - 1)(f_e - 1)}} \quad (1)$$

where f_a and f_e are the amine and epoxy functionalities, respectively. In our case $f_a = f_e = 4$. This leads to a value of $\alpha_g = 0.33$, that is, 33% of conversion.

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

As the 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 the solubility test.

Solubility test

In this method, the time to reach a fibriform structure in tetrahydrofuran is measured.¹⁵ The experimental method is as follows. An aluminum can containing the sample is introduced into a thermostatted bath filled with polyethylene glycol. The sample was continuously shaken; and at different times, a part of the sample was removed from the container and poured into a beaker containing tetrahydrofuran 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

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

T (°C)	t _{gel} (min)	α _{gel} (%)
60	38.6	22.5
70	21.0	22.3
80	10.5	24.5
90	6.4	27.0
100	4.0	27.2
110	2.7	34.5
120	1.4	31.0
130	1.5	43.1

corresponding conversions at the different temperatures used in this study. As may be observed, the gelation of this system does not correspond to an isoconversional event. This behavior is similar to that observed in other epoxy systems, as may be observed in Table 1 of Núñez et al.¹⁶

The overall activation energy for the cure reaction process can be obtained from gel time data, assuming that all reactions that occur during the curing process can be described through differential equations containing one unique apparent activation energy E_a, according to the following equation^{17,18}:

$$\frac{d\alpha}{dt} = Ae^{-(E_a/RT)}f(\alpha) \tag{2}$$

where A is a constant, E_a is the apparent activation energy for the overall curing reaction, T is the isothermal curing temperature, and f(α) is a temperature-independent function of conversion.

Integration of eq. (2) from α = 0 to α = α_g and taking natural logarithms, gives

$$\ln \int_0^{\alpha_g} \frac{d\alpha}{f(\alpha)} = \ln A + \ln t_g - \frac{E}{RT} \tag{3}$$

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

$$\ln t_g = \text{const} + \frac{E}{RT} \tag{4}$$

The activation energy can be calculated as the slope of a ln t_g versus 1/T plot, as shown in Figure 1. The cure reaction activation energy for the two-component system obtained using the gel times calculated through the solubility test method was 58.5 ± 1.3 kJ/mol. This value is similar to values obtained for other similar epoxy systems.¹⁹⁻²⁸

Vitrification study

DSC plots of dH/dT as a function of T show an endothermic step change in heat capacity at the glass transition. The glass-transition temperature T_g is taken as the midpoint of this transition.¹²

Figure 2 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_c¹⁹; then the increase in T_g becomes slower because of diffusion

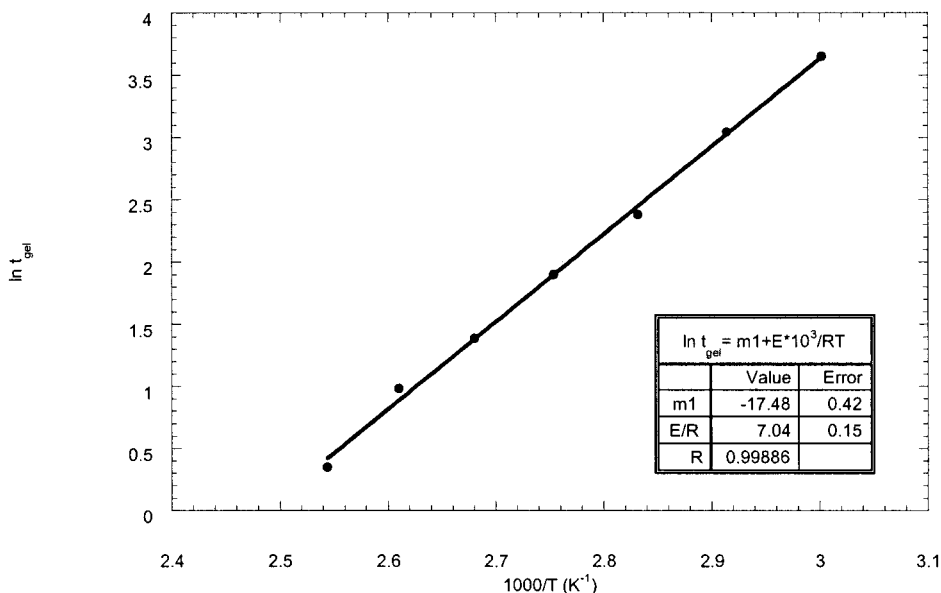


Figure 1 Plot of ln t_{gel} versus 1000/T.

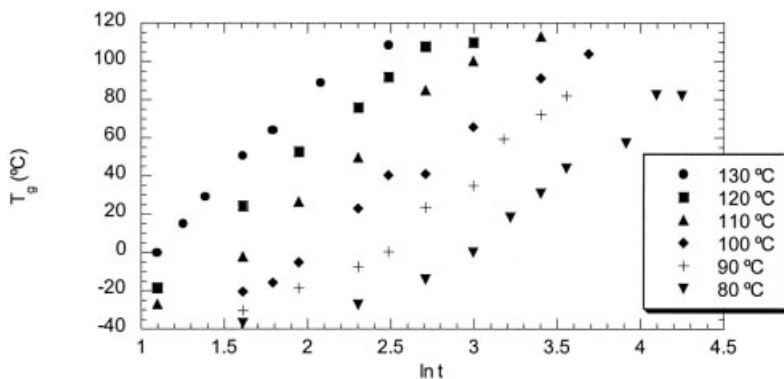


Figure 2 Plots of T_g versus $\ln t$ for various cure temperatures from DSC isothermal cure experiments.

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 ageing of the sample in the glassy state leads to an increase in T_g . To remove all traces of physical ageing, it is necessary to heat the samples, previously cooled, to a temperature just beyond the observed T_g , then to cool it rapidly, and finally to heat a second time to determine the correct T_g . This procedure can be used when the curing rate during the first heating may be neglected. To determine the T_g versus α relationship, it is recommended to use the T_g versus $\ln t$ plot only up to t_v .¹²

The experimental T_g versus α DSC data are shown in Figure 3. According to other similar studies reported in the literature,^{12,13} the relationship between T_g and conversion should be independent of the cure

temperature. In our system, even this independence is not clear (use of the DiBenedetto equation to calculate the vitrification times was assumed). The one-to-one relationship between T_g and conversion implies that either the molecular structure of the materials cured at different temperatures does not present significant changes or, if it does, these changes do 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).

A modified form of the empirical DiBenedetto equation was reported by Nielsen:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda)\alpha} \tag{5}$$

where T_{g0} is the T_g of the uncured monomer, $T_{g\infty}$ is the maximum glass-transition temperature obtained ex-

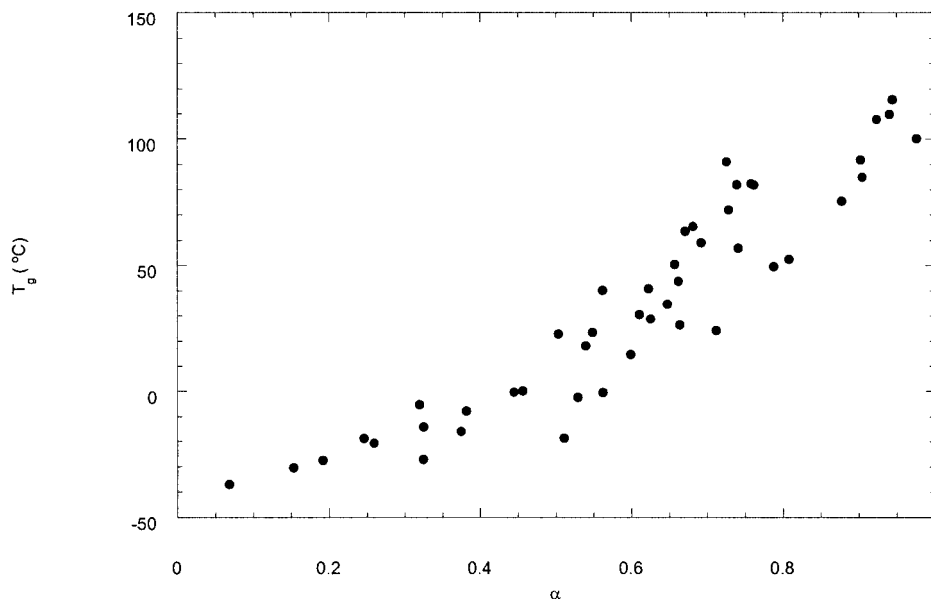


Figure 3 Plots of one-to-one relationship between transition temperature (T_g) and conversion (α).

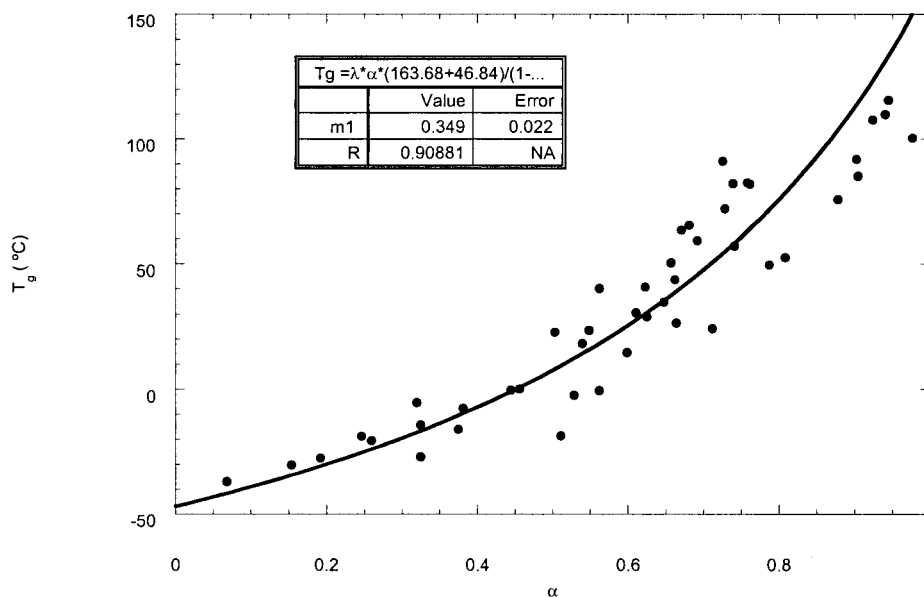


Figure 4 Plots of one-to-one relationship between T_g and α using the DiBenedetto equation.

perimentally for the fully cured material, and λ represents an adjustable structure-dependent parameter between 0 and 1. Pascault and Williams²⁹ showed that λ is theoretically equated to $\Delta C_{p\infty} / \Delta C_{p0}$, where $\Delta C_{p\infty}$ and ΔC_{p0} are the differences in heat capacity between the glassy and rubbery (or liquid, before gelation) states at T_g for the fully cured network and monomer, respectively.

The DiBenedetto equation will be used when it is necessary to convert T_g to conversion and vice versa. To calculate vitrification times, DSC data of experimental T_g versus α were fitted to the DiBenedetto equation, as shown in Figure 4. In this equation, λ was treated as an adjustable parameter resulting in 0.349 ± 0.022 . This value is in good agreement with values obtained for other similar systems.^{29,30}

Vitrification times corresponding to the different isothermal cure temperatures are shown in Table II. Compared to the vitrification values obtained by thermomechanical DSC (TMDSC) for the same three-component epoxy system,³¹ the values calculated through the DiBenedetto equation are practically within the

limited range of vitrification determined from the c_p curves registered in the TMDSC isothermal experiments, as seen in Figure 5. Differences between the DSC and TMDSC data have been attributed to the frequency dependency of the vitrification time.^{32,33}

Time-temperature superposition of DSC data

A relationship between time and temperature can be established such that the behavior of the material for given time-temperature conditions is identical to the behavior that could be achieved by different appropriate combinations of values of the same variables. The theoretical basis for the superposition is the two-fold assumption that the polymerization is kinetically controlled with a single apparent activation energy and that there is a one-to-one relationship between T_g and α .^{12,13} This relationship allows the calculation of master curves at arbitrary reference temperatures. For this calculation, the knowledge of a relationship between reaction rate and conversion is necessary. The left-hand side in eq. (3) depends only on conversion, and because there is a one-to-one relationship between T_g and conversion, some function of T_g , $F(T_g)$, can be substituted for the left-hand side of the equation, as follows:

$$F(T_g) = \ln A + \ln t_c - \frac{E}{RT_c} \quad (6)$$

By substituting T_c with any arbitrary reference temperature (T_r), one obtains

$$F(T_g) = \ln A + \ln t_r - \frac{E}{RT_r} \quad (7)$$

TABLE II
Vitrification Time at Various Isothermal
Cure Temperatures

T_c (°C)	t_v (min)	α_v (%)
80	66	81.3
90	32	84.2
100	24	86.9
110	20	89.3
120	25	91.6
130	50.5	93.8

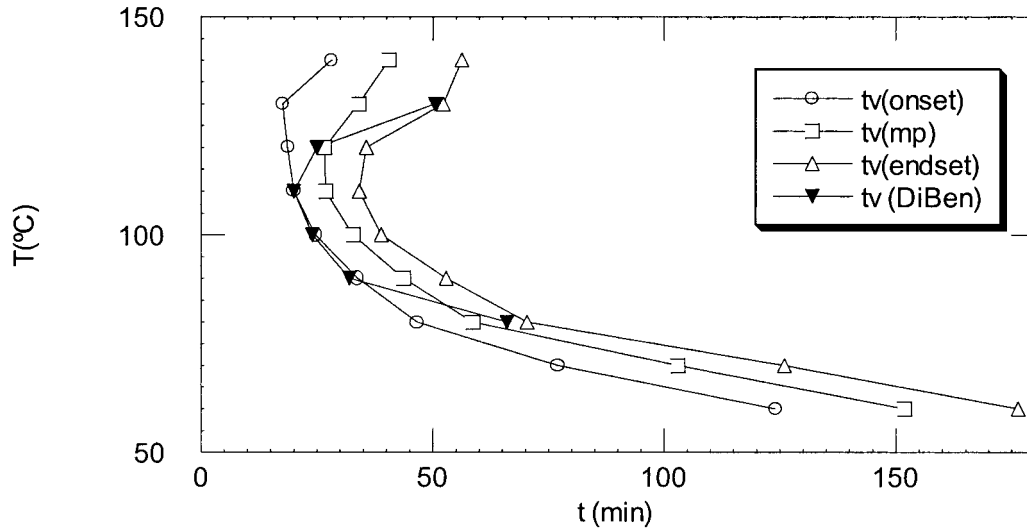


Figure 5 Experimental vitrification curves obtained by DSC and TMDSC techniques.

The shift factor a_T is the difference in $\ln t$ between two curves shifted at constant T_g (i.e., the same conversion):

$$a_T = \ln t_r - \ln t_c = \left(-\frac{E}{R} \right) \left(\frac{1}{T_c} - \frac{1}{T_r} \right) \quad (8)$$

Figure 6 shows T_g versus $\ln t$ master curve at $T_r = 100^\circ\text{C}$. From the master curve, values of T_g may be obtained at any T , provided that the T_g values corresponding to the cure reaction at a given reference temperature T_r are known. In this plot, a deviation at high conversions can be observed. This deviation, usually caused by vitrification, which marks the onset of diffusion, was reported by other investigators.^{12,34–37} For this reason, the diagram cannot be extended into the diffusion-controlled regime because the master curve is valid only for the kinetically controlled regime.

Table III shows values of shift factor a_T , at various isothermal temperatures for $T_r = 100^\circ\text{C}$. Because a_T depends Arrhenius-like on temperature, the activation energy for the polymerization reaction can be obtained as the slope of the a_T versus $1/T$ plot (Fig. 7). A value of 64.2 ± 4.2 kJ/mol for the activation energy was found in good agreement with the value obtained from gel time measurements.

TTT diagram

The TTT isothermal cure diagram was calculated from the contours of the time to gel and to vitrify as a function of the reaction temperature (Fig. 8). Data were fitted to the exponential best-fitting curves.

The vitrification curve was obtained by the fitting of the experimental data obtained by TMDSC to an exponential curve. Data clearly deviating from the curve were not taken into account for fitting.

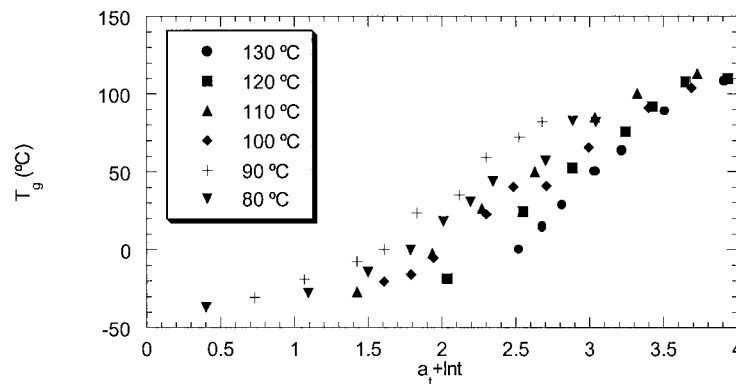


Figure 6 Plots of T_g versus $\ln t$ master curve ($a_t + \ln t$) at the reference temperature $T_r = 100^\circ\text{C}$.

TABLE III
Shift Factor Values at Various Isothermal Cure
Temperatures, for $T_r = 100^\circ\text{C}$

T_c ($^\circ\text{C}$)	$a_T [= \ln t_r - \ln t]$
80	-1.207
90	-0.878
100	0
110	0.327
120	0.939
130	1.428

As previously mentioned, gelation times do not correspond to an isoconversional event, so therefore gelation does not follow an isoconversion curve, as may be seen in Figure 8. Isoconversion curves corresponding to $\alpha = 0.10, 0.20, 0.30, 0.34, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90,$ and 0.94 are plotted. These curves were calculated taking into account the results obtained from the isothermal calorimetric experiments.^{21,26}

The isoconversion curve $\alpha = 0.94$ corresponds to the maximum achievable experimental extent of conversion.

To plot a TTT diagram, it is necessary to know three principal temperatures: T_{g0} , the initial T_g of the system; ${}_{\text{gel}}T_g$, 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 $T_{g\infty}$ (also indicated as $T_{g\text{max}}$), the maximum glass-transition temperature of the fully cured system.

For the system studied here (DGEBA/DCH/15%VCHD), T_{g0} and $T_{g\infty}$ were experimentally determined; and ${}_{\text{gel}}T_g$ was calculated as the temperature

corresponding to the intercept of the gelation and vitrification curves in a T_c versus $\ln t$ plot. Values of T_{g0} and $T_{g\infty}$ were measured by DSC. The values of the three characteristic temperatures were found to be $T_{g0} = -46.8^\circ\text{C}$; ${}_{\text{gel}}T_g = 45.7^\circ\text{C}$; and $T_{g\infty} = 163.7^\circ\text{C}$.

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_{g0} (-46.8°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_{g0} .

${}_{\text{gel}}T_g$ (45.7°C) is the temperature at which the system gels and vitrifies simultaneously.

Between T_{g0} and ${}_{\text{gel}}T_g$ ($-46.8^\circ\text{C} < T_c < 45.7^\circ\text{C}$), the system will react until its continuously increasing glass-transition temperature becomes coincidental with the cure temperature; at this stage vitrification will begin and the reaction becomes diffusion controlled, so gelation may not be achieved. For vitrification below ${}_{\text{gel}}T_g$, the resulting material will have a low molecular weight and it will flow on heating. $T_{g\infty}$ (163.7°C) is the maximum temperature at which glass transition can be achieved. Between ${}_{\text{gel}}T_g$ and $T_{g\infty}$ ($45.7^\circ\text{C} < T_c < 163.7^\circ\text{C}$), gelation precedes vitrification.

After gelation, the curing sample contains both sol and gel fractions. The gel initially formed is weak and

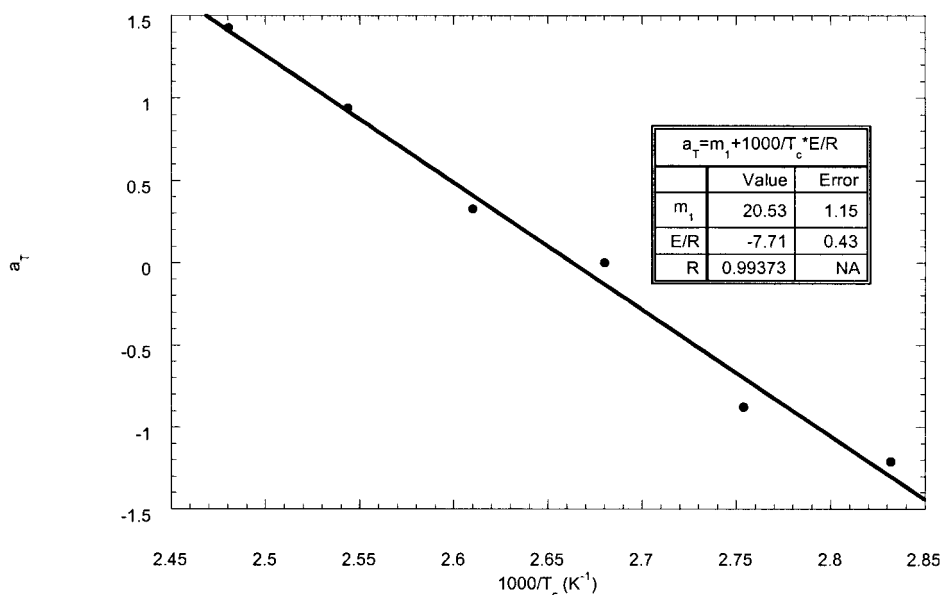


Figure 7 Plot of shift factor a_T versus $1000/T_c$.

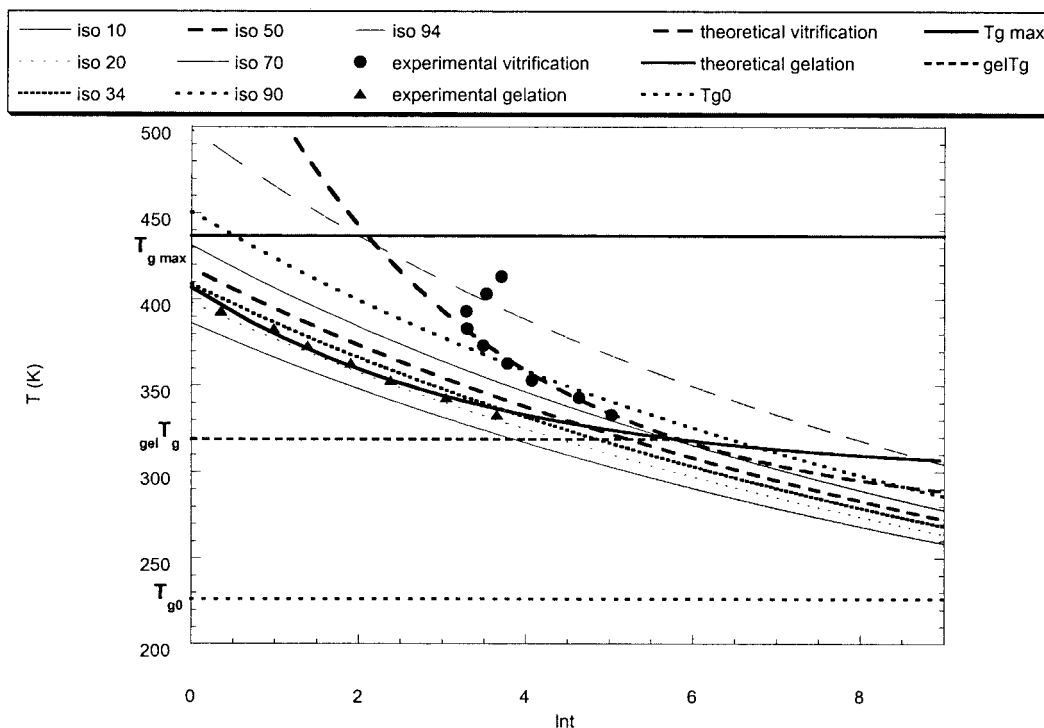


Figure 8 Calculated TTT isothermal cure diagram for the DGEBA ($n = 0$)/1,2-DCH/15% RD system.

can be easily disrupted. To produce a structural material, cure has to continue until most of the sample is interconnected within 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 $T_{g\infty}$ (163.7°C), no vitrification occurs; the reaction is kinetically controlled and total conversion may be theoretically achieved. However, as the time increases, a great amount of material is thermodegraded such that its useful properties are lost.

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

CONCLUSIONS

A TTT diagram for the three-component epoxy system DGEBA ($n = 0$)/1,2-DCH/15% VCHD was calculated. Its main recorded features indicate that a cure at 120°C for 35 min will give optimum results with a final conversion coincidental with the extent of conversion at $\alpha = 0.93$. The reliability of these values had to be corroborated through a dynamomechanical study of the system as well as the thermodegradation process and the lifetime of the system cured according to the conditions indicated.

References

1. Prime, R. B. Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic Press: San Diego, CA, 1981.
2. Wisanrakkit, G.; Gillham, J. K. *J Appl Polym Sci* 1990, 41, 2885.
3. Ellis, B. *Chemistry and Technology of Epoxy Resins*, 1st ed.; Blackie Academic and Professional: Glasgow/London, 1993.
4. Gillham, J. K. *Polym Eng Sci* 1986, 26, 1429.
5. Enns, J. B.; Gillham, J. K. *J Appl Polym Sci* 1983, 28, 2567.
6. Lee, H.; Neville, K. *Handbook of Epoxy Resin*; McGraw-Hill: New York, 1967.
7. May, C. A. *Epoxy Resins: Chemistry and Technology*; Marcel Dekker: New York, 1988.
8. Perkin-Elmer Corp. Users Manual 1020 Series DSC-7 Thermal Analysis System, Norwalk, CT, 1991.
9. Höne, G. W. H. *J Therm Anal Calorim* 1991, 37, 1987.
10. Brown, M. E., Ed. *Handbook of Thermal Analysis and Calorimetry*; Elsevier: Amsterdam/New York, 1998.
11. Price, D. M. *J Therm Anal* 1995, 45, 1285.
12. Simon, S. L.; Gillham, J. K. *J Appl Polym Sci* 1992, 46, 1245.
13. Simon, S. L.; Gillham, J. K. *J Appl Polym Sci* 1993, 47, 461.
14. Flory, P. J. *Chem Rev* 1946, 39, 137.
15. Hagnaver, G. L. *Chemorheology of Thermosetting Polymers*; ACS Symposium Series 227; American Chemical Society: Washington, DC, 1983.
16. Núñez, L.; Fraga, L.; Núñez, M. R.; Villanueva, M.; Rial, B. *J Therm Anal Calorim* 2002, 70, 45.
17. Barton, J. M.; Greenfield, D. C. L.; Hodd, K. A. *Polymer* 1992, 33, 1977.
18. Oyanguren, P. A.; Williams, R. J. J. *J Appl Polym Sci* 1993, 47, 1361.
19. Núñez, L.; Taboada, J.; Fraga, F.; Núñez, M. R. *J Appl Polym Sci* 1997, 66, 1377.
20. Barton, J. M. *Adv Polym Eng Sci* 1985, 72, 111.
21. Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. *J Polym Sci Part A: Polym Chem* 1970, 8, 1357.
22. Abuín, S. P.; Pellín, M. P.; Núñez, L. *J Appl Polym Sci* 1993, 48, 905.

23. Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. J. *J Appl Polym Sci* 1984, 29, 2481.
24. Han, J. L.; Hsieh, K. H.; Chiu, W. Y. *J Appl Polym Sci* 1993, 50, 1099.
25. Abuín, S. P.; Pellín, M. P.; Núñez, L. *J Appl Polym Sci* 1990, 41, 2155.
26. Kamal, M. R. *Polym Eng Sci* 1974, 14, 23.
27. Riccardi, C. C.; Williams, R. J. J. *J Appl Polym Sci* 1986, 32, 3445.
28. Grillet, A. C.; Galy, J.; Pascault, J. P.; Bardin, I. *Polymer* 1996, 30, 2094.
29. Pascault, J. P.; Williams, R. J. J. *J Polym Sci Part B: Polym Phys* 1990, 28, 85.
30. Jordan, C.; Galy, J.; Pascault, P. *J Appl Polym Sci* 1992, 46, 859.
31. Villanueva, M.; Núñez, L.; Núñez, M. R.; Rial, B.; Fraga, L.; Montserrat, S. *J Therm Anal Calorim* 2002, 70, 45.
32. Van Asche, G.; Van Mele, B.; Saruyama, Y. *Thermochim Acta* 2001, 377, 121.
33. Scherrenberg, R.; Mathot, V.; Steeman, P. *J Therm Anal Calorim* 1998, 54, 447.
34. Dusek, K. *Advances in Polymer Science*; Springer-Verlag: Berlin/New York, 1986; p 78.
35. Montserrat, S. *J Polym Sci Part B: Polym Phys* 1994, 32, 509.
36. Montserrat, S. *J Appl Polym Sci* 1992, 44, 545.
37. Montserrat, S. *J Therm Anal* 1993, 40, 553.