A Methodology for Characterizing Reactive Coatings: Time–Temperature–Transformation (TTT) Analysis of the Competition between Cure, Evaporation, and Thermal Degradation for an Epoxy-Phenolic System

S. GAN and J. K. GILLHAM, *Polymer Materials Program,
Department of Chemical Engineering, Princeton University,
Princeton, New Jersey 08544* and R. B. PRIME, *IBM General
Products Division, 5600 Cottle Road, San Jose, California 95193*

Synopsis

A methodology, in terms of a macroscopic isothermal time–temperature–transformation (TTT) diagram, is presented for characterizing the changes that occur isothermally in a reactive thermosetting system in which evaporation, cure, and thermal degradation occur. Iso-weight loss contours show the progress of the loss of volatile material (mostly solvent). The gelation contour corresponds to the macroscopic viscosity rising to a definite level. The vitrification contour corresponds to the glass transition temperature (T_g) rising to the temperature of cure (T_{cure}). Iso-T_g contours show the progress of cure in terms of the easily measured T_g (rather than chemical conversion). The iso-T_g contours also show the influence of thermal degradation competing with cure. Degradation is responsible for difficulties in assigning the glass transition temperature of the fully cured material (i.e., $T_{g\infty}$).

INTRODUCTION

This report is concerned with a general macroscopic method for monitoring the progress of the change from the liquid state to the rubbery state and/or to the glassy state which occurs during the setting of reactive systems.[1] Cure can occur in conjunction with loss of material (solvent, some of the reactants, reaction and degradation byproducts), and thermal degradation. The glass transition temperature (T_g) is used as an index of the extent of setting which involves T_g rising as a consequence of evaporation and chemical cure reactions, and decreasing or increasing as a consequence of thermal degradation. Solidification (vitrification) occurs when T_g rises to the temperature of reaction (T_{cure}). Devitrification occurs when T_g decreases to T_{cure}. The glass transition temperature is a directly useful, sensitive, and unifying macroscopic parameter for monitoring changes in the setting of amorphous systems by being affected by diluent (e.g., solvent), extent of chemical conversion of the curing reactions, and by degradation. Unlike macroscopic viscosity, which is useful until gelation in crosslinking systems, the parameter T_g is applicable and easily measured throughout the process of setting. (However, in this report it is used as an index of change only after gelation and after loss of

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solvent.) The macroscopic parameter T_g can in principle be calculated from molecular parameters (e.g., from T_g versus composition).

In this work T_g is measured by the torsional braid analysis (TBA) technique[2] in which the specimen for a freely oscillating torsion pendulum experiment consists of an inert substrate coated with the reactive system. Thus a setting system can be monitored during the change from liquid to rubber to glass. In general T_g is measured in three types of experiment: (1) vitrification times are obtained when T_g rises to T_{cure}; (2) the progress of setting before vitrification at T_{cure} can be obtained from measurements of T_g obtained during intermittent cooling; (3) temperature scans, first to a temperature below and then to temperatures above T_{cure}, give T_g values which reflect the state of cure obtained at T_{cure}, and the stability of the material to temperatures higher than T_{cure}.

The results are summarized in an isothermal time–temperature–transformation (TTT) diagram in which the progress of setting is seen in terms of iso-T_g and related contours.[1,3,4] The related contours include iso-weight curves,[4] macroscopic gelation, vitrification (i.e., $T_g = T_{cure}$); and (not in this work, but in principle) isothermal devitrification due to degradation when again $T_g = T_{cure}$. [Gelation is defined at the macroscopic level to be the incipient attainment of an infinite viscosity, or as the incipient development of long-range elasticity, in the change from the liquid to the rubbery state: in practice the time to reach a finite viscosity or rubbery modulus is measured. At the molecular level gelation is defined[5] to be the incipient formation of molecules of infinite molecular weight which corresponds to a particular chemical conversion for each system (and for a simple system, a particular glass transition temperature, $_{gel}T_g$)]. The system investigated for this report is of interest in being reactive above its maximum glass transition temperature, $T_{g\infty}$. Therefore, vitrification is not easily encountered—it is predicted herein by direct extrapolation of T_g values from high temperatures to $T_g = T_{cure}$ at lower temperatures and from other analysis of time-temperature-T_g data. A preliminary report has been published.[6]

MATERIALS

The material used was a solution of a thermally crosslinkable mixture of a diglycidylether of bisphenol A resin with a phenolic resole resin.[7] The solvent content was about $57\frac{1}{2}$%; the boiling point of the least volatile solvent was about 215°C. Besides loss of solvent, an additional weight loss of 4–6% is expected from loss of condensation reaction byproducts and volatile components of the phenolic resin [unpublished results using the techniques of ref. 8].

EXPERIMENTAL

Torsional Braid Analysis (TBA)

Macroscopic gelation times (t_{gel}) and glass transition measurements [T_g, and times to vitrification (t_{vit})], were made at about 1 Hz using the TBA technique.[2] Specimens were prepared using heat-cleaned glass braids impregnated with the resin solution ("as-received"). Specimens were heated isothermally at different temperatures for pre-established times. Representative
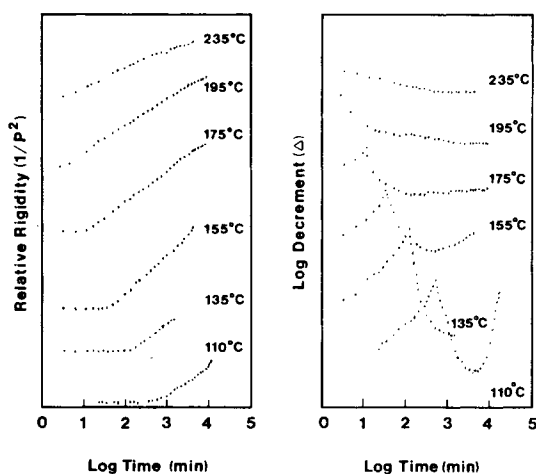
Fig. 1. Representative isothermal TBA spectra at different temperatures for different times. Relative rigidity (left) and logarithmic decrement (right) versus log time. Macroscopic gelation is identified by the peak in the logarithmic decrement (T_{cure} = 110, 135, 155, and 175°C). Vitrification is identifiable for T_{cure} = 110°C.

isothermal TBA spectra at different temperatures for different times are shown in Figure 1. The specimens were then taken through temperature scans from T_{cure} to -175 to 255 to -175 to 255 to 35°C at 2°C/min in a slowly flowing atmosphere of helium. Representative TBA spectra for temperature scans after isothermal heating for 10 h at different temperatures are shown in Figure 2. Each isothermal scan provides in principle the time to macroscopic gelation, and the time to vitrification (for $T_{cure} < T_{g\infty}$), whereas subsequent temperature scans provide the values of transition temperatures, T_g (maximum value about 140°C) and T_{sec} ($< T_g$, in the vicinity of -90°C). (Subscript 1 was used for transitions in the initial temperature scan, T_{cure} to -175 to
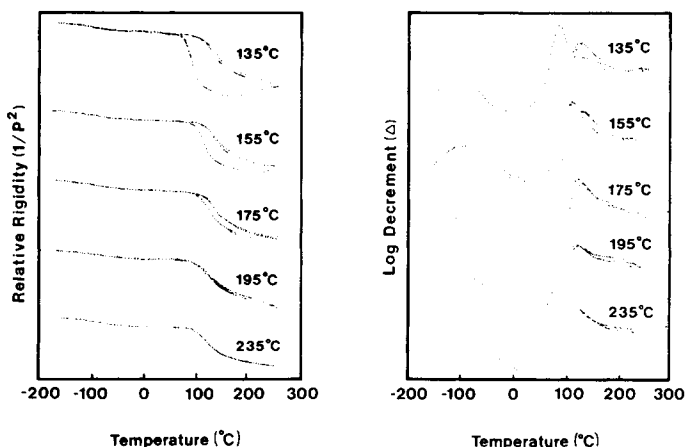

Fig. 2. Representative TBA spectra for temperature scans after isothermal heating for 10 h at different temperatures (as labelled). Relative rigidity (left) and logarithmic decrement (right) versus temperature.

225°C; subscript 2 was used for the scan 255 to −175 to 255°C; subscript 3 was used for the scan 255 to 35°C.

The automated TBA torsion pendulum is available from Plastics Analysis Instruments, Inc., P.O. Box 408, Princeton, NJ 08540.

Thermogravimetric Analysis (TGA)

Loss of weight during temperature scans (30–400°C) and isothermal heating (100–230°C) on the as-received resin solution was measured in flowing helium using a thermogravimetric analyzer programmed with a controller (Perkin Elmer TGS-2/System 4 microprocessor). The rate of change of temperature was 10°C/min.

RESULTS AND DISCUSSION

Weight Loss

Figure 3 shows weight (percent) versus temperature during a temperature scan from 30 to 400°C. A plateau level occurs between 250 to 330°C at about 37% residue weight. Figure 4 shows iso-weight loss curves (50–63%) and the macroscopic gelation curve in the format of a time-temperature-transformation (TTT) diagram. The iso-weight loss data of Figure 4 were obtained from isothermal gravimetric experiments (100–230°C).
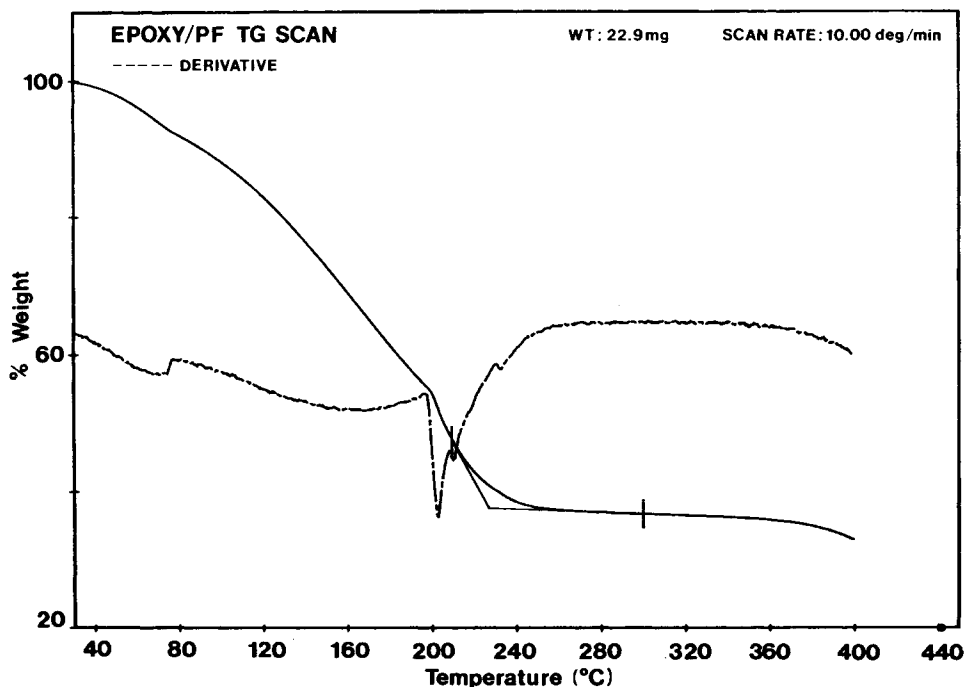

Fig. 3.   TGA: Weight percent (solid line) and derivative (dashed line) vs. temperature. (30 to 400°C, $\Delta T/\Delta t = 10°C/min$, helium atmosphere; initial weight = 22.9 mg).
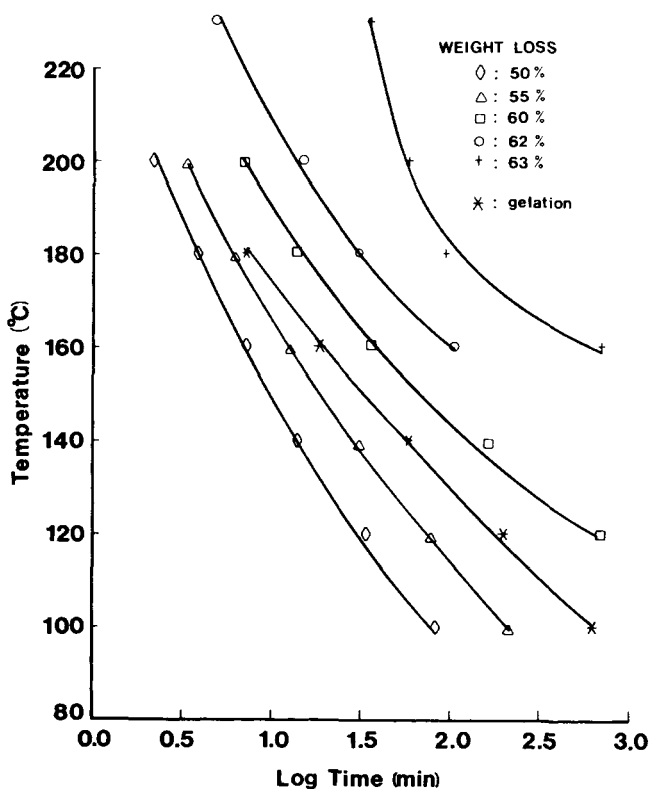
Fig. 4. Time-temperature-transformation (TTT) diagram: Iso-weight loss contours and gelation contour.

Macroscopic gelation occurs at approximately 56–57% weight loss. The spacing of the contours shows that the loss of residual volatiles (~ 5%) occurs slowly after gelation. Since vitrification occurs at prolonged times (see later), the material changes only from the liquid state to the rubbery state for the data of Figure 4. The volatiles will be composed of principally solvent, with small amounts of volatile reactants and reaction byproducts.

T_g, T_{cure}, and t_{cure} Relationships

T_g versus T_{cure}

Figure 5 shows T_g versus T_{cure} data for three cure times (t_{cure} = 10, 24 and 72 h). The maximum value of the glass transition temperature (i.e., $T_{g\infty}$) is about 147°C (see later). The system is not highly reactive since $T_g < T_{cure}$ for $T_{cure} < T_{g\infty}$, even for t_{cure} = 72 h. There is a maximum in each of the T_g versus T_{cure} plots. This is a result of competition between cure (which raises T_g) and thermal degradation (which decreases T_g). T_{g2} and T_{g3} were obtained from two consecutive temperature scans to 255°C after isothermal heating for 10 h.
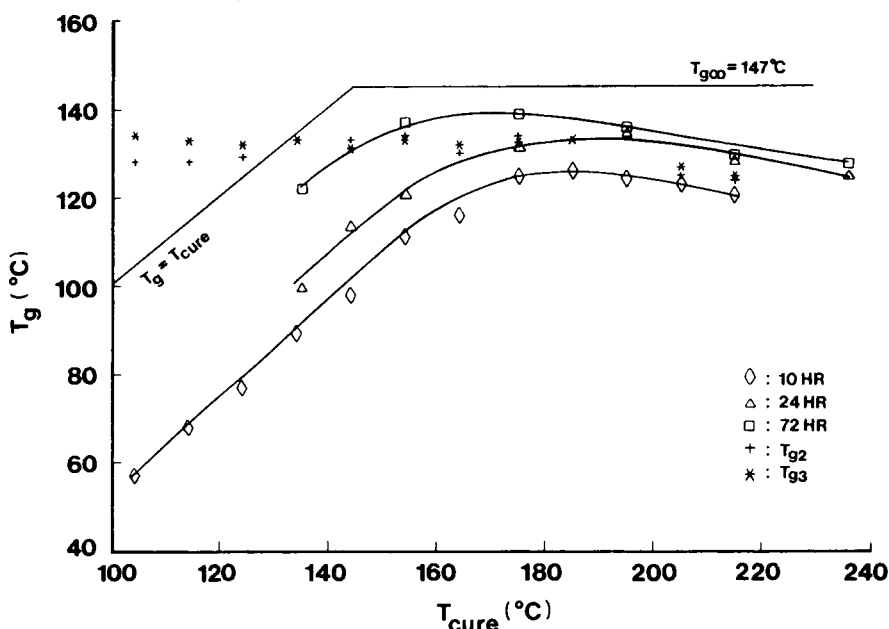
Fig. 5. T_g(°C) vs. T_{cure}(°C) for different isothermal heating times (10, 24 and 72 h). Note T_{g2} and T_{g3} were obtained from two consecutive scans to 255°C after 10 h isothermal heating. Also included for reference are the lines $T_g = T_{cure}$ and $T_{g\infty} = 147$°C.

For low values of T_{cure}, $T_{g3} > T_{g2}$ as a result of further cure. For high values of T_{cure}, T_{g3} and T_{g2} are approximately equal but with values decreasing with increasing T_{cure} due to thermal degradation.

T_g versus t_{cure}

Figure 6 shows the variation of T_g with log time at different isothermal temperatures. T_g increases with time of cure, t_{cure}, for all temperatures to a limiting value which depends on T_{cure}. The approximately parallel T_g versus log time relationships for temperatures of cure from 135 to 195°C for $T_g <$ 130°C suggests a single reaction process without degradation. At higher cure temperatures the progressively changing initial slope suggests a more complicated process for the increase of T_g with time from the start ($T_g > 100$°C).

Figure 7 shows the limiting value of T_g versus T_{cure}. Degradation is held responsible for the limiting value of T_g decreasing with increasing T_{cure} for $T_{cure} > 155$°C. The highest T_g value observed in this set of data is 147°C obtained at 155°C. Therefore 147°C is the operational value assigned to $T_{g\infty}$.

Iso-T_g Contours

Figure 8, which shows iso-T_g contours (solid lines) in the format of a time-temperature-transformation (TTT) diagram, was obtained from the data of Figure 6. At low conversions ($T_g \leq 115$°C), and for $T_{cure} \leq 175$°C, the
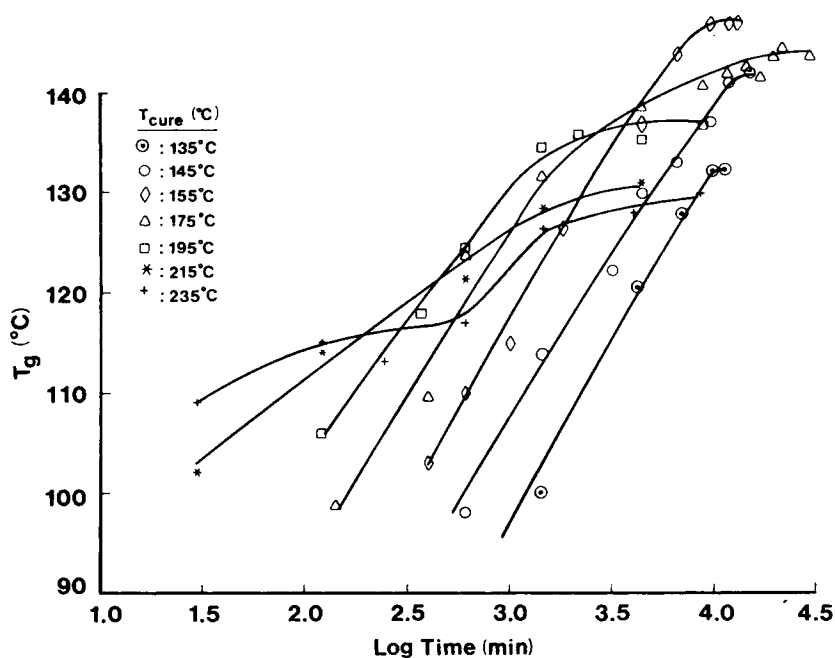
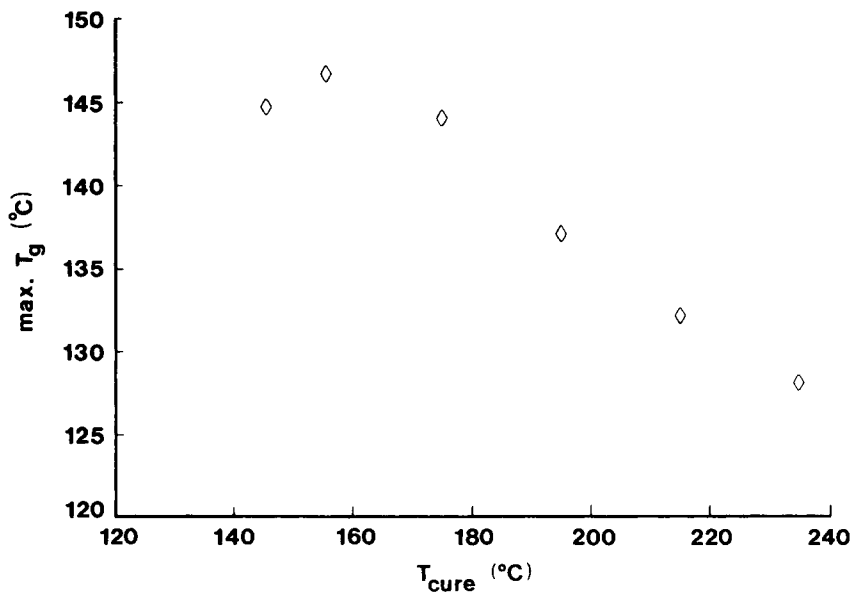Fig. 6. T_g(°C) vs. log time (min.) for different isothermal temperatures (T_{cure}).

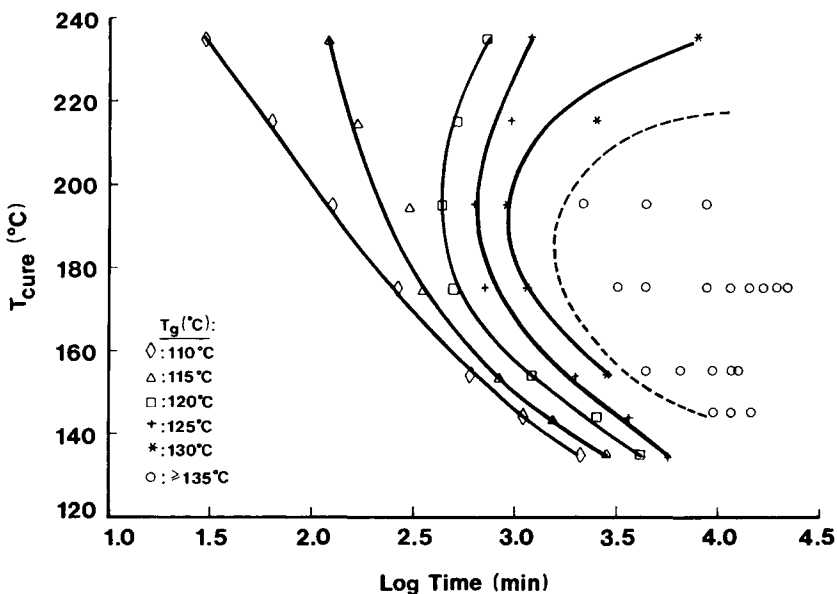Fig. 7. Limiting T_g (°C) [from Fig. 6] vs. T_{cure} (°C).

Fig. 8. Time-temperature-transformation (TTT) diagram: Iso-T_g contours. (Glass transition temperatures $\geq$ 135°C are bounded by the dashed contour.)

contours reflect mainly cure. For higher values of T_{cure} at higher conversions ($T_g \geq 120°C$), thermal degradation is revealed by the increasing t_{cure} to attain a given T_g. Glass transition temperatures $\geq 135°C$ are bounded by the dashed contour; therefore, for example, $T_g \leq 135°C$ for $T_{cure} \geq 215°C$.

It is noted that iso-T_g contours (e.g., $T_g = 98°C$ in Fig. 11) can be calculated from experimental T_{cure}, t_{cure}, and T_g data using Eq. (1) (see below).

Prediction of t_{vit}

Figure 9, which shows ln time to a fixed value of T_g versus reciprocal temperature (1/K), was obtained from the data of Figure 8. The relationship is linear for $T_{cure} \leq 175°C$ which corresponds to the dominance of cure. For higher values of T_{cure}, degradation competes overtly with cure.

Apparent activation energies, ΔE_a, can be obtained from the slope of the linear relationships (i.e., $T_{cure} \leq 175°C$ in Figure 9): ΔE_a values are 20.2, 19.0, 18.7, and 18.3 kcal/mol, for the iso-T_g values 110, 115, 120, and 125°C, respectively.

The linear equations for times to the above iso-T_g values ($T_{cure} \leq 175°C$) are:

$$\ln t = 10170/T - 17.2 \quad (r = 0.995) \quad \text{for iso-}T_g = 110°C,$$

$$\ln t = 9560/T - 15.5 \quad (r = 0.998) \quad \text{for iso-}T_g = 115°C,$$

$$\ln t = 9390/T - 14.8 \quad (r = 0.999) \quad \text{for iso-}T_g = 120°C, \text{ and}$$

$$\ln t = 9190/T - 13.9 \quad (r = 0.999) \quad \text{for iso-}T_g = 125°C.$$
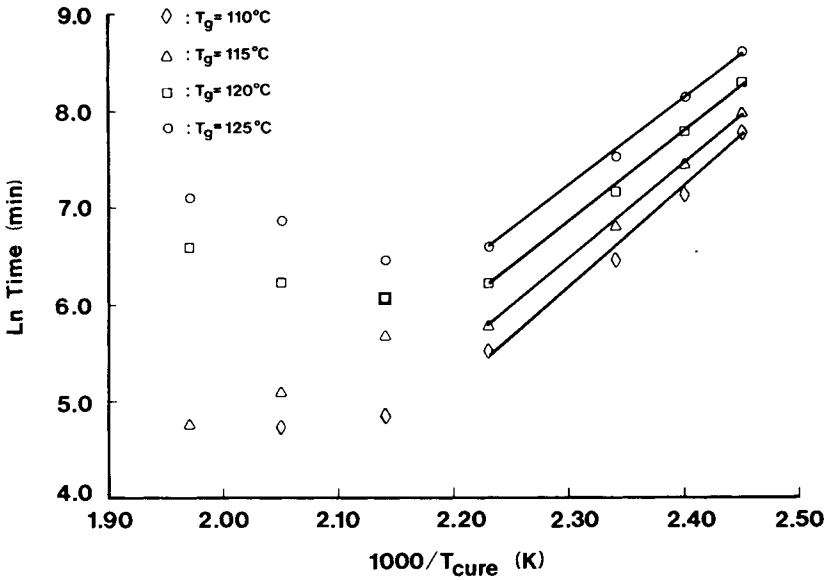
Fig. 9. Ln time (min) to fixed T_g values [from Fig. 8] vs. $1/T_{cure}$ (K).

The times to vitrification can be calculated by setting $T_g = T_{cure}$ in the iso-T_g equations (since vitrification is defined to occur when $T_g = T_{cure}$). For T_{cure} = 110, 115, 120, and 125°C, the logarithm$_{10}$ of the times to vitrify are 4.06, 3.97, 3.95, and 3.99 minutes, respectively (see dashed vitrification curve of Figure 11). Calculated values are required for constructing the isothermal TTT cure diagram, because of the long experimental times to vitrification at isothermal temperatures below $T_{g\infty}$.

The times to vitrification were measured experimentally for T_{cure} = 110 and 115°C (see open circles near the vitrification curve of Figure 11). These are longer than the extrapolated ones. The influence of diffusion control cannot be ignored for low values of T_{cure} and near vitrification.

The time to vitrify can be calculated more completely from experimental time-temperature-T_g data than from simple extrapolation of iso-T_g data. In the assumed absence of diffusion control, solvent evaporation, and thermal degradation, the simplest equation which describes the relationship between the rate of reaction ($-dx/dt$), concentration of reactant (x), activation energy (E), temperature (T, K), and time (t) is the Arrhenius:

$$-dx/dt = A * \exp(-E/RT) * f(x)$$

or integrating

$$F(x) = A * \exp(-E/RT) * t$$

where undesignated symbols $[R, f(x), F(x), A]$ have their usual significance. The vitrification curve in the isothermal TTT diagram (see Figure 11) corresponds to reaction at temperature T_g for time t_{vit} to conversion defined by T_g.

Therefore, the iso-T_g contour for any corresponding pair of values of T_g and t_{vit} is given by

$$\exp\left(-E/RT_{cure}\right) * t_{cure} = \exp\left(-E/RT_g\right) * t_{vit}$$

or $\qquad \ln t_{vit} = -\left(E/R\right)\left[1/T_{cure} - 1/T_g\right] + \ln t_{cure} \qquad (1)$

Using (a) Eq. (1), and (b) for example data for $t_{cure} = 10$ h of Figure 5, together with (c) $E/R = 10170$, obtained (above) from the time-temperature behavior to conversions corresponding to $T_g = 110°C$ (which is assumed to be constant for lower conversions), it follows that since cure at 125°C (398 K) for 10 h gives $T_g = 76°C$ then log $t_{vit} = 4.34$ for $T_{cure} = 76°C$. Similarly, since cure at 135°C (408 K) for 10 h gives $T_g = 89°C$ then log $t_{vit} = 4.15$ for $T_{cure} = 89°C$, and since cure at 145°C (418 K) for 10 h gives $T_g = 98°C$ then log $t_{vit} = 4.12$ for $T_{cure} = 98°C$, and since cure at 155°C (423 K) for 10 h gives $T_g = 110°C$ then log $t_{vit} = 3.99$ for $T_{cure} = 110°C$. The calculated values for (three of the four) corresponding temperatures and times to vitrify are included in the Summary TTT cure diagram of Figure 11 (see large solid circle symbols on vitrification contour above 50°C).

Equation (1) together with $T_g = 98°C$ and log $t_{vit} = 4.12$ was used to calculate the iso-T_g contour corresponding to $T_g = 98°C$ in Figure 11. It appears that this contour resides in the region between solvent loss and thermal degradation where chemical kinetics (cure) dominate. Iso-T_g contours can be converted into iso-conversion contours if the relationship between conversion and T_g is known.

Figure 10 shows the $\ln t$ to gelation versus reciprocal temperature (K) relationship

$$\ln t = 9860/T_{cure} - 19.8 \qquad (2)$$

for which the apparent activation energy is 19.8 kcal/mol (correlation coefficient, r, = 0.997). T_g at gelation was also measured at different temperatures by TBA (after quenching the specimen at the time it gelled). The T_g at gelation is expected to vary with T_{cure} since the measurement of gelation in this report is by a macroscopic technique in which gelation is assigned as the attainment of a specific viscosity ($\sim$ 140,000 cps, see ref. 2). The values of T_g at macroscopic gelation ranged from 50 to 60°C for corresponding values of T_{cure} from 75 to 155°C.

The isothermal temperature at which the time to vitrification equals the time to the extrapolated value of macroscopic gelation is indicated as $_{gel}T_g'$ in Figure 11. This can be calculated using (a) Eq. (1), where now t_{vit} corresponds to reaction at temperature $_{gel}T_g'$, together with (b) Eq. (2) and (c)

$$T_{cure} = 0.9 \, T_g + 84 \, \left(T_g < 110°C\right) \qquad (3)$$

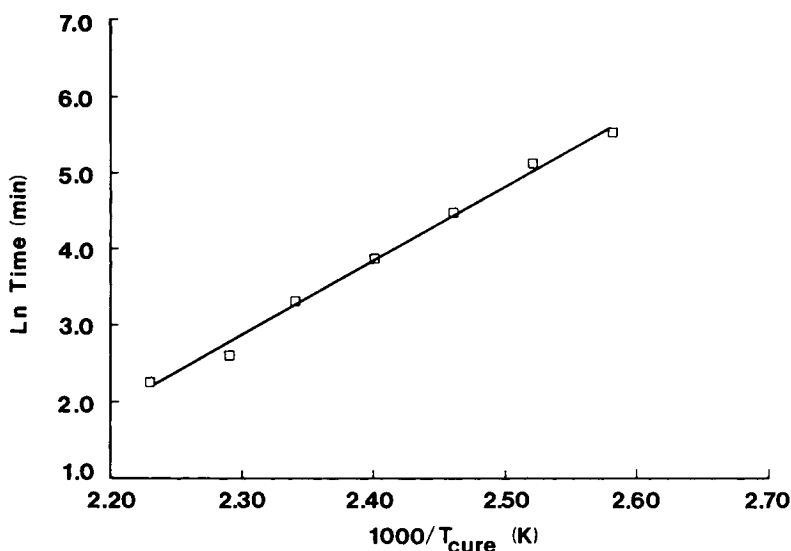which summarizes isochronal T_g versus T_{cure} data ($T_g < 110°C$) for $t_{cure} = 10$ h

Fig. 10. Ln time (min) to macroscopic gelation vs. $1/T_{cure}$ (K).

of Figure 5. The relevant expression becomes:

$$\frac{9860}{_{gel}T_g'} - 19.8 = 10170 \left[\frac{1}{_{gel}T_g'} - \frac{1}{0.9_{gel}T_g' + 84} \right] + 6.4$$

Solving, $_{gel}T_g' = 50°C$. Also $\log t_{vit} = 4.66$ for $T_{cure} = 50°C$ [from Eq. (2)] [see Fig. 11].

If molecular gelation is defined or measured as an isoconversion state then the glass transition temperature of the material at the conversion corresponding to molecular gelation, that is, $_{gel}T_g$, is independent of T_{cure} in simple chemical systems. Whereas the molecular gelation contour must intersect the vitrification curve at a unique temperature ($_{gel}T_g$) between temperatures T_{g0} and $T_{g\infty}$, an isoviscosity contour corresponding to a finite rather than an infinite viscosity will not intersect the vitrification contour: it will approximately parallel the vitrification contour at temperatures below $_{gel}T_g$.[9] Temperature $_{gel}T_g'$ is only an approximate estimate of the basic material parameter $_{gel}T_g$.

CONCLUSIONS

Time-Temperature-Transformation (TTT) Isothermal Diagram

Most of the results of this work can be summarized in the form of a time-temperature-transformation (TTT) isothermal diagram, as in Figure 11.

The progress of the transformation of liquid to glass or to rubber is shown by the macroscopic gelation, vitrification, iso-weight loss, and iso-T_g contours.
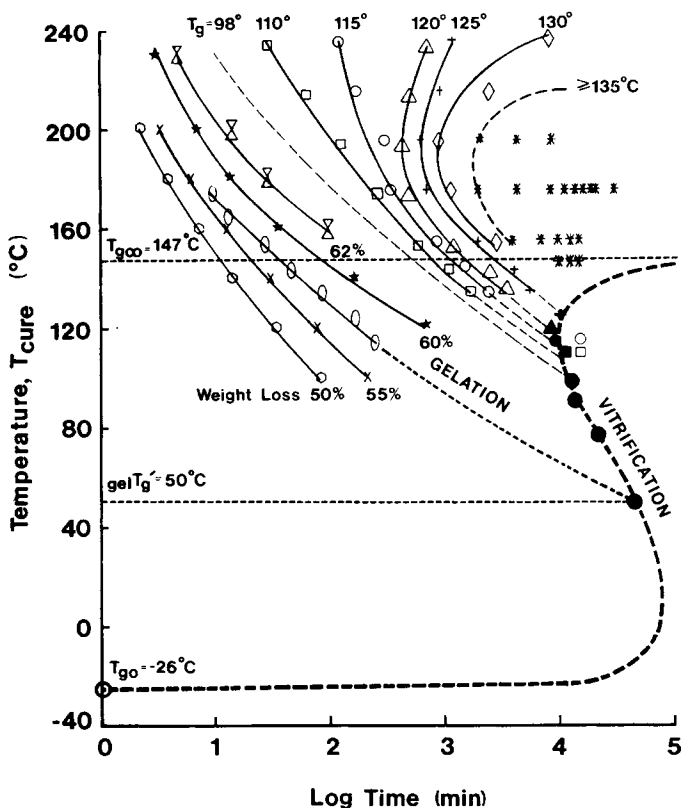
Fig. 11. Summary time-temperature-transformation (TTT) diagram. (Glass transition temperatures $\geq 135°C$ are bounded by the contour marked $\geq 135°C$.)

(Iso-T_g contours could have been obtained for the complete process of setting; however, for this report they were obtained after gelation and after loss of solvent.) Characteristic temperatures are T_{g0} ($-26°C$, obtained by cooling a TBA specimen of the solution of reactants), $T_{g\infty}$ (about 147°C) and $_{gel}T_g'$ (which is the extrapolated temperature at which the macroscopic isoviscosity contour on cooling intersects the vitrification contour).

Cure for this system is only rapid above $T_{g\infty}$ under which conditions the material does not vitrify. Cure reactions are therefore conducted in the fluid and rubbery states.

Cure above $T_{g\infty}$ can lead to thermal degradation which results in lowering of the glass transition temperature. For example, $T_g \leq 135°C$ for $T_{cure} \geq 215°C$. A value for the completely reacted system (i.e., $T_{g\infty}$) is difficult to obtain above $T_{g\infty}$ because of degradation, and also below $T_{g\infty}$ because of the slow kinetics to vitrification and the still slower kinetics beyond vitrification due to diffusion control of the reactions.

The vitrification curve is S-shaped.[1] The vitrification curve in Figure 11 (dashed line) was constructed from an estimated value for $T_{g\infty}$, analysis of

$t_{\text{cure}} - T_{\text{cure}} - T_g$ data, experimental vitrification times, analysis of $_{\text{gel}}T_g'$, and an experimental value for T_{g0}.

It follows from this report that for any reactive system with only a single mechanism for the curing reaction, and in the absence of competitive processes, that iso-T_g contours can be calculated throughout the kinetically controlled region of its TTT cure diagram from very limited amounts of experimental $T_g - T_{\text{cure}} - t_{\text{cure}}$ data. The corresponding vitrification contour of the TTT cure diagram for the same system can then be calculated from the relationship $T_g = T_{\text{cure}}$ and experimental data for T_{g0} and $T_{g\infty}$.

APPENDIX: NOMENCLATURE

A	Arrhenius pre-exponential factor
$F(x), f(x)$	Functions of x
T_{cure}	The temperature of isothermal cure
T_g	Glass transition temperature
T_{g1}	Glass transition temperature measured during first scan from T_{cure} to -175 to $255°C$ (two values)
T_{g2}	Glass transition temperature measured during second scan from 255 to -175 to $255°C$ (two values)
T_{g3}	Glass transition temperature measured during third scan from 255 to $35°C$ (one value)
T_{sec}	Glassy-state transition temperature
t	Time
t_{cure}	Time of isothermal heating
t_{gel}	Time to gelation
t_{vit}	Time to vitrification
ΔE_a	Apparent activation energy
R	Gas constant
r	Correlation coefficient
T	Temperature (K in kinetic expressions; otherwise °C)
$_{\max}T_g$	Limiting value of T_g attained on isothermal heating
iso-T_g	T_g contours for particular values of T_g attained by different combinations of time and temperature
$T_{g\infty}$	Maximum value of T_g (representing full cure)
$_{\text{gel}}T_g$	Glass transition temperature of the material at the molecular gel point
$_{\text{gel}}T_g'$	An estimate of $_{\text{gel}}T_g$ made by extrapolation of iso-viscosity data to the temperature at which the times to attain the iso-viscosity level and vitrification are equal
x	Concentration of reactant

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