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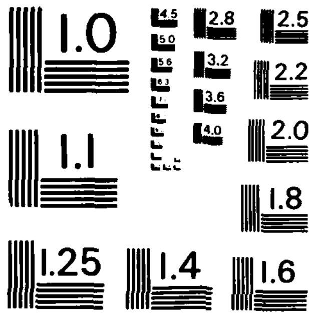
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TECHNICAL REPORT NO. 5

TIME-TEMPERATURE-TRANSFORMATION (TTT) CURE DIAGRAMS: RELATIONSHIP BETWEEN T_g AND THE TEMPERATURE AND TIME OF CURE FOR EPOXY SYSTEMS

by

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TIME-TEMPERATURE-TRANSFORMATION (TTT) CURE DIAGRAMS: RELATIONSHIP BETWEEN T_g AND THE TEMPERATURE AND TIME OF CURE FOR EPOXY SYSTEMS

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SYNOPSIS

A procedure is provided for estimating the time to full cure versus isothermal cure temperature for vitrified epoxy systems. An equation relating the glass transition temperature of vitrified epoxy systems to the time and temperature of cure is developed.

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INTRODUCTION

The glass transition temperature, T_g, of a thermosetting system is observed to be higher than the temperature of cure, T_{cure}, after prolonged isothermal cure below the system's maximum glass transition temperature, $T_{g\infty}$ (1-7). This implies that the cure reactions proceed after T_g has risen to T_{cure} (i.e., after vitrification). It is therefore important to investigate the cure behavior after vitrification. This communication is concerned with the relationship between T_g, T_{cure} and time of isothermal cure for two epoxy systems cured to beyond vitrification. The conclusions apply to both systems.

Linear T_g - T_{cure} relationships were obtained after cure at different temperatures for fixed times. The temperatures of cure for full cure to occur in the same fixed times could be obtained by extrapolation of the appropriate T_g - T_{cure} relationships to $T_{g\infty}$. The time to full cure versus T_{cure} is presented in a time-temperature-transformation (TTT) cure diagram together with the times to gelation and to vitrification (1-7). An empirical T_g - T_{cure} - time equation is also developed. The two epoxy systems investigated were a difunctional and a trifunctional epoxy resin each cured with the same tetrafunctional aromatic diamine.

EXPERIMENTAL

Materials

The difunctional epoxy was a diglycidyl ether of bisphenol A (DER 331, Dow Chemical Co.), the trifunctional epoxy was the triglycidyl ether of tris(hydroxy phenyl)methane (XD 7342.00, Dow Chemical Co.), and the curing agent was trimethylene glycol di-p-aminobenzoate ("TMAB", Polacure 740M, Polaroid Corp.). Stoichiometric formulations were prepared on the basis of one epoxy group per amine hydrogen.

Cure, T_g, and $T_{g\infty}$ Measurements

The epoxy resin systems were cured isothermally at different temperatures in a flowing atmosphere of dry helium in a torsional braid analysis (TBA) chamber (1). Each specimen was prepared using a multifilamented heated-cleaned glass braid impregnated with a solution of the reactants (1 g. solid/1 ml methyl-ethyl ketone). Changes due to cure were monitored as a function of time by measuring the frequency (~ 1 Hz) and decay of intermittently induced free oscillations; the times to gelation and to vitrification were located by maxima in the logarithmic decrement plots. Each specimen was cured for a preselected time, which was longer than the time to vitrification, at the temperature of cure, T_{cure}. After isothermal cure, dynamic mechanical spectra (~ 1 Hz) of the specimens were obtained on cooling from T_{cure} to -180°C and then on heating, to 240°C for the DER 331/TMAB system and to 280°C for the XD/TMAB system, at a rate of 1.5°C/min. Spectra were then obtained on subsequent cooling. The glass transition temperature, T_g, was identified by the temperature of the principal maximum in the logarithmic decrement plot during the heating scan. The maximum glass transition temperature, $T_{g\infty}$, was identified as the glass transition temperature during the subsequent cooling scan (from 240°C for DER 331/TMAB and from 280°C for XD/TMAB).

The data for $T_{g\infty}$ versus T_{cure} for different cure times were compared (not shown). A small increase in $T_{g\infty}$ with increasing temperature of isothermal cure for DER 331/TMAB was observed. This behavior is attributed to the cure not being completed by heating to and cooling from 240°C after the isothermal cures. The $T_{g\infty}$ data for the XD/TMAB system followed a trend in which the higher values of $T_{g\infty}$ were obtained with high cure temperatures for short cure times, low cure temperatures for long cure times, and intermediate cure temperatures for intermediate cure times. This behavior could be attributed to the competition between cure (which increases T_g) and thermal degradation (which decreases T_g) at the high temperatures which are necessary for curing this high $T_{g\infty}$ system. Average values of $T_{g\infty}$ were used for the calculations in this paper: 168°C for the DER 331/TMAB system (range 166 to 170°C), and 268°C for the XD/TMAB system (range 261 to 278°C).

RESULTS AND DISCUSSION

T_g vs. T_{cure}

The data for T_g vs. T_{cure} for the DER 331/TMAB and XD/TMAB systems for different times of isothermal cure are given in Tables 1 and 2, and are plotted as T_g vs. T_{cure} in Figures 1 and 2. A set of approximately parallel lines was obtained for each system. Each line represents a linear relationship between T_g and T_{cure} for the same cure time (which was longer than the time to vitrification). Therefore

$$T_g = A + B\ T_{cure} \qquad (1)$$

where A depends on, and B is independent of, the cure time. The values of A and B for different cure times for the DER 331/TMAB and XD/TMAB systems are presented in Tables III and IV. The average values of B are 0.98 and 1.24 for the DER 331/TMAB system and the XD/TMAB system, respectively (ratio = 0.79). Also, the apparent activation energies, ΔE, for full cure are 71.6 and 92.7 kcal/mol for the DER 331/TMAB and the XD/TMAB systems, respectively (ratio = 0.78) (see later, Table 7). It is possible therefore that the slope, B, is related to the activation energy and hence to the reaction mechanism. Since the cure reaction for the XD/TMAB system has the higher activation energy after vitrification, the effect of increasing T_{cure} on T_g (which increases with the extent of cure) is greater for the XD/TMAB system than for the DER 331/TMAB system.

T_{cure} vs. Time to Full Cure

Assuming that the materials are fully cured when T_g reaches $T_{g\infty}$, the temperature for full cure to occur in a specified time, $T_{\infty(t)}$, was determined by extrapolation of the T_g - T_{cure} relationship line for the same cure time to $T_{g\infty}$ using equation 1. For example, since for the XD/TMAB system T_g = -2.67 + 1.20 T_{cure} for the sixty minute cure time, then when $T_g = T_{g\infty}$ = 268°C, T_{cure} =

$T_{x(60)}$ = 226°C. In other words, the time to full cure at the cure temperature of 226°C, $t_{x(226)}$, should be 60 minutes. Times to full cure, t_x, at different cure temperatures were calculated in this manner. They are presented in Table 5.

For testing the extrapolated conditions for obtaining full cure shown in Table 5, the DER 331/TMAB system was cured at 148°C/1440 min, 146°C/2880 min, and 141°C/8640 min, and the XD/TMAB system was cured at 211°C/1440 min, and 207°C/2880 min. The corresponding values of T_g obtained from these cure conditions for the DER 331/TMAB system were 165°C, 166°C, and 166°C, and for the XD/TMAB system were 268°C and 265°C (Figures 1 and 2). They are close to, but in general below, the average values of T_{gx} for the DER 331/TMAB system (168°C) and for the XD/TMAB system (268°C).

If the extrapolated data for T_{cure} versus time to full cure (Table 5) are plotted as T_{cure} vs. log time of cure, a new line results which is designated the full cure line on a Time-Temperature-Transformation (TTT) cure diagram (Figure 3). The gelled glass region in the TTT diagram is divided into two parts by the full cure line. In the absence of degradation (Figure 3, devitrification and char formation), the top and lower parts could be designated fully cured gelled glass (gel glass) and undercured gelled glass (sol/gel glass) regions, respectively. The TTT diagrams with the full cure lines for the DER 331/TMAB system and for the XD/TMAB system are shown in Figures 4 and 5, respectively. These lines appear to be linear, which can therefore be expressed by

$$T_x = a + b \log t_x \qquad (2)$$

where T_x and t_x are the temperature and time to full cure, respectively. The intercepts (a) and slopes (b) for the two systems are provided in Table 6. The full cure line should be useful for designing cure processes which lead to full cure. Selection of the temperature or time of cure gives the time or temperature, respectively, to full cure.

The data for the extrapolated time to full cure versus temperature of isothermal cure for the two systems are plotted in an Arrhenius manner as the logarithmic time versus 1/T(K) in Figure 6, which also includes corresponding data for gelation and vitrification. The activation energies for full cure (after vitrification), gelation, and vitrification for the DER 331/TMAB and the XD/TMAB systems are presented in Table 7. That the activation energy for full cure is much higher than that for gelation is a result of the cure reactions being controlled by physical relaxations in the glassy state (which themselves have similarly high activation energies).

T_g - T_{cure} - Time Equation

An equation relating T_g, T_{cure} and time of cure can be derived from equations 1 and 2. From equation 1, with $T_g = T_{gx}$ and $T_{cure} = T_x$,

$$T_{gx} = A + B\,T_x \qquad (3)$$

For cure in the same time period, subtracting equation 1 from equation 3 results in

$$T_{gx} - T_g = B(T_x - T_{cure}) \quad (4)$$

Substituting for T_x in equation 4 in terms of time using equation 2 gives

$$T_{gx} - T_g = B(a + b \log t_x - T_{cure}) \quad (5)$$

where t_x could be any time, t.

Therefore equation 5 can be rewritten as

$$T_g = T_{gx} - B(a + b \log t - T_{cure}) \quad (6)$$

The T_g of the material cured at temperature T_{cure} for time t can be calculated using this T_g - T_{cure} - time equation.

The particular equations for the DER 331/TMAB and the XD/TMAB systems were formulated by substituting values for T_{gx}, B, a, and b in equation 6 with the data in Tables 3-6. For the DER 331/TMAB system,

$$T_g = 10.18 \log t + 0.98\, T_{cure} - 10 \quad (7)$$

and for the XD/TMAB system,

$$T_g = 14.48 \log t + 1.24\, T_{cure} - 38 \quad (8)$$

where t is in minutes, and T_{cure} and T_g are in degrees centigrade.

For both systems, the T_g calculated (T_g cal) by equations 7 and 8 are included in Tables 1 and 2 together with the corresponding experimental values for T_g. The agreement is good.

For an approximate calculation of T_g from T_{cure} and cure time for the epoxy systems, only two T_g vs. T_{cure} lines for two specified cure times are needed if $T_{g\infty}$ is known. The parameters B, a and b in equation 6 can be derived from these two lines. This procedure is a simple one for obtaining the relationship between T_g, T_{cure} and time of cure.

Correction of Cure Time

The relationship between T_g and T_{cure} for the same isothermal cure time observed in this work is for cure behavior after vitrification since the cure behavior after vitrification, where the cure reaction proceeds in the glassy state, should be different from that before vitrification where the cure reaction occurs in the liquid and rubbery states. This suggests that the time of cure should be measured from the vitrification time and that the time of cure in this work should be corrected by subtracting the vitrification time. For example, when the DER 331/TMAB system was cured at lower temperatures, the data points deviated from the straight line (Figure 1); presumably for shorter times the data would also deviate from linearity. They would be expected to be closer to the straight line if the times of cure were corrected. For the XD/TMAB system, the errors were less because the time to vitrification for the XD/TMAB system was shorter than for the DER 331/TMAB system. Similarly, correcting the time of cure would be expected to reduce the difference between the test values of T_g and the average value of $T_{g\infty}$ (Figures 1 and 2). As a quantitative example, a sample of the DER331/TMAB system was cured at 165°C for 39 minutes which according to equation 2 should give full cure. The observed T_g of 117°C was much lower than $T_{g\infty}$ (168°C). However, the observed T_g was 167°C when cure at 165°C was for the time to vitrification (351 minutes) plus 39 minutes.

CONCLUSIONS

Analysis of the relationships between the time and temperature of cure for two epoxy systems has led to the following conclusions for both systems.

1. A linear T_g - T_{cure} relationship for isochronal cure was observed.

2. The cure temperature for full cure to occur in a given cure time can be determined by extrapolation of the appropriate T_g - T_{cure} line to $T_{g\infty}$. A plot of T_{cure} versus log time of cure to full cure yields a new line, the full cure line, on the time-temperature-transformation (TTT) cure diagram.

3. The apparent activation energies for full cure, and for gelation and vitrification, were obtained from their Arrhenius relationships. The activation energy for full cure is much higher than those for gelation and vitrification as a consequence of the cure reactions being controlled by physical relaxations in the glassy state.

4. An empirical T_g - T_{cure} -time equation for cure in the vitrified state has been developed which permits computation of the glass transition temperature from the temperature and time of cure.

ACKNOWLEDGMENTS

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TABLE CAPTIONS

1. T_g vs. T_{cure} for Specified Times of Cure for the DER 331/TMAB System.
2. T_g vs. T_{cure} for Specified Times of Cure for the XD/TMAB System.
3. $T_g = A + B\ T_{cure}$: Values of A and B for the DER 331/TMAB System.
4. $T_g = A + B\ T_{cure}$: Values of A and B for the XD/TMAB System.
5. Time to Full Cure versus Cure Temperature for the DER 331/TMAB and XD/TMAB Systems.
6. $T_x = a + b \log t_x$: Full Cure Line Parameters for the DER 331/TMAB and the XD/TMAB Systems.
7. Apparent Activation Energies for the Isothermal Transformations of the DER 331/TMAB and the XD/TMAB Systems.

FIGURE CAPTIONS

1. T_g vs. T_{cure} for the DER 331/TMAB System for Preselected Times of Cure (Solid Lines):
(▽) 720 min, (■) 1440 min; (□) 2880 min; (⬡) 5760 min; (▲) 8640 min; (o) 23040 min. Extrapolated values to $T_{g\infty}$ of T_g vs. T_{cure} (•). Also: experimental test values of T_g (■, □, and ▲) from the extrapolated values of T_{cure} (see text). Also included is the line for the average value of $T_{g\infty}$, and the $T_g = T_{cure}$ line (which is not for constant time).

2. T_g vs. T_{cure} for the XD/TMAB System for Preselected Times of Cure (Solid Lines):
(▽) 60 min; (■) 300 min; (□) 1440 min; (⬡) 2880 min; (Δ) 5760 min; (o) 14440 min. Extrapolated values to $T_{g\infty}$ of T_g vs. T_{cure} (•). Also: experimental test values of T_g (□ and ⬡) from the extrapolated values of T_{cure} (see text). Also included is the line for the average value of $T_{g\infty}$ and the $T_g = T_{cure}$ line (which is not for constant time).

3. Schematic Isothermal Time-Temperature-Transformation (TTT) Cure Diagram Displaying Temperature of Cure, T_{cure}, vs. Times to Gelation, Vitrification, Full Cure and Char Formation. The full cure line ($T_g = T_{g\infty}$) is constructed so as to connect the physically controlled relationship in the glassy state with the chemically controlled relationship above $T_{g\infty}$.

4. TTT Cure Diagram for the DER 331/TMAB System: (■) Gelation (experimental); (o) Vitrification (experimental); (▲) Full Cure (calculated, see text).

5. TTT Cure Diagram for the XD/TMAB System: (■) Gelation (experimental); (o) Vitrification (experimental); (▲) Full Cure (calculated, see text).

6. Ln Time (min) vs. 1/T(K) for the DER 331/TMAB System: (∇) Gelation; (■) Vitrification; (□) Full Cure. Also Ln Time (min) vs. 1/T(K) for the XD/TMAB System: (O) Gelation; (▲) Vitrification; (o) Full Cure. Activation energies were obtained from the regions of linear data (solid lines).

TABLE 1. T_g vs. T_{cure} for Specified Times of Cure for the DER 331/TMAB System

Cure Time	720 min					1440 min					2880 min			
T_{cure}, °C	110	120	135	140	150	100	110	120	135	140	100	110	120	135
T_g, °C[1]	123	137	151	156	164	119	131	143	155	159	126	135	145	158
T_g cal, °C[2]	127	137	151	156	166	120	130	140	154	159	123	133	143	158

Cure Time	5760 min				8640 min				23040 min		
T_{cure}, °C	80	100	120	135	80	100	120	135	80	100	120
T_g, °C[1]	105	128	147	160	107	130	148	161	113	134	152
T_g cal, °C[2]	107	126	146	161	109	128	148	162	113	132	152

[1] Measured values

[2] Calculated values

TABLE 2. T_g vs. T_{cure} for Specified Times of Cure for the XD/TMAB System

Cure Time	60 min			300 min				1440 min				
T_{cure}, °C	180	200	220	150	180	195	200	90	120	150	180	195
T_g, °C[1]	213	238	261	184	219	241	245	119	158	191	229	249
T_g cal, °C[2]	211	236	261	184	221	240	246	119	157	194	231	250

Cure Time	2880 min						5760 min					14400 min		
T_{cure}, °C	90	120	150	180	195	200	90	120	150	180	195	80	150	190
T_g, °C[1]	123	162	195	234	254	261	127	167	198	239	259	119	203	260
T_g cal, °C[2]	124	161	198	235	254	260	128	165	202	240	258	121	208	258

[1] Measured values

[2] Calculated values

TABLE 3. $T_g = A + B\ T_{cure}$: Values of A and B for the DER 331/TMAB System

Cure Time	720 min	1440 min	2880 min	5760 min	8640 min	23040 min
A	13.40	21.70	34.09	26.49	30.36	35.50
B^a	1.01	0.99	0.92	1.00	0.98	0.98
r^b	0.99	0.99	1.00	1.00	1.00	1.00

a Average value of B = 0.98

b Correlation coefficient

TABLE 4. $T_g = A + B\ T_{cure}$: Values of A and B for the XD/TMAB System

Cure Time	60 min	300 min	1440 min	2880 min	5760 min	14400 min
A	-2.67	-2.56	9.27	11.01	15.45	15.84
B^c	1.20	1.24	1.22	1.24	1.24	1.27
r^d	1.00	1.00	1.00	1.00	1.00	1.00

c Average value of B = 1.24

d Correlation coefficient

TABLE 5. Time to Full Cure versus Cure Temperature for the DER 331/TMAB and XD/TMAB Systems.

System	DER 331/TMAB ($T_{g\infty}$ = 168°C)						XD/TMAB ($T_{g\infty}$ = 268°C)					
T_{cure}, °C	152	148	146	142	141	136	226	218	211	207	203	198
1/Tx1000,°K	2.35	2.38	2.39	2.41	2.42	2.45	2.00	2.04	2.07	2.08	2.10	2.12
t_x, min	720	1440	2880	5760	8640	23040	60	300	1440	2880	5760	14400

TABLE 6. $T_x = a + b \log t_x$: Full Cure Line Parameters for the DER 331/TMAB and the XD/TMAB Systems

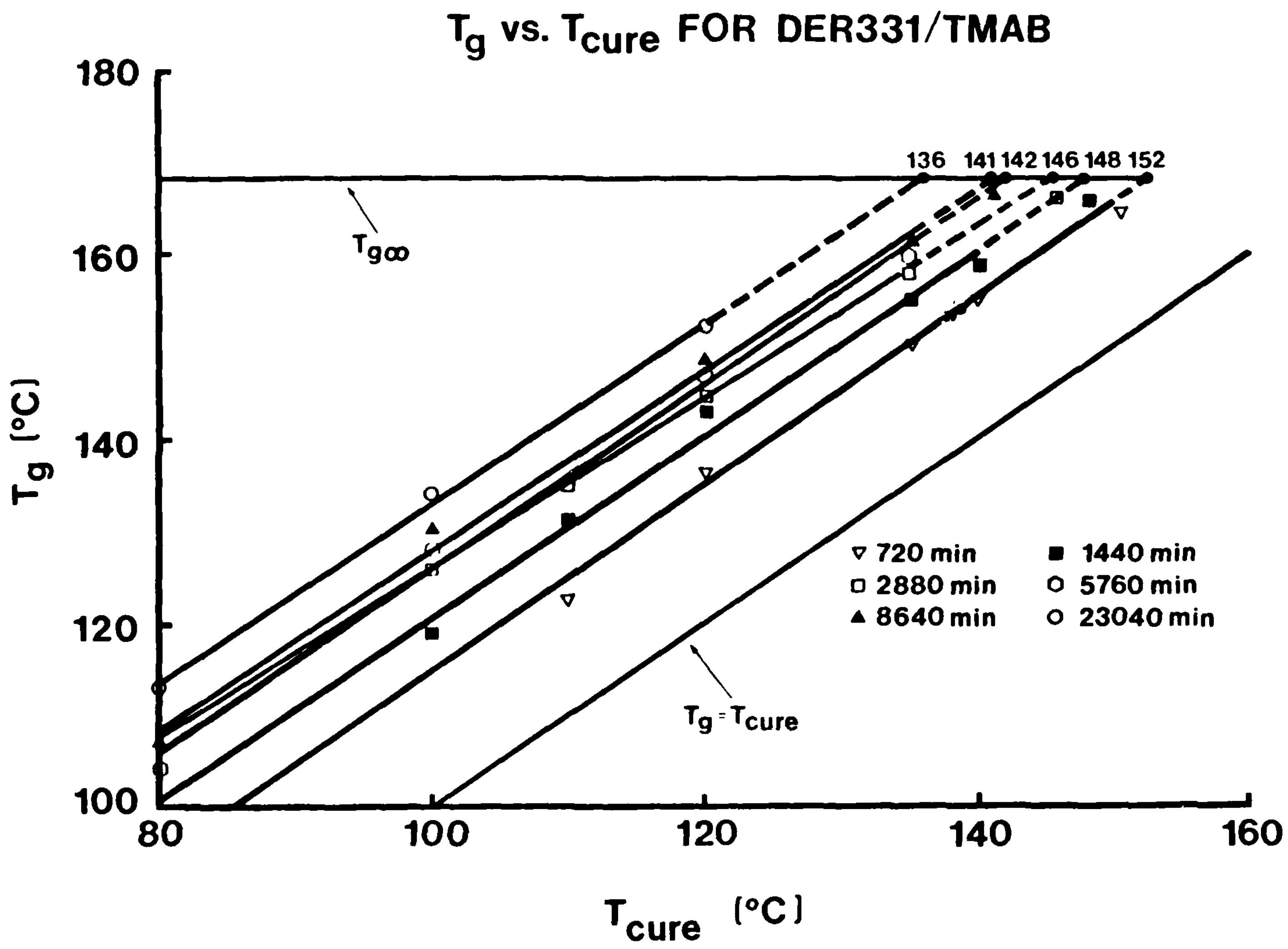
System	Intercept (a)	Slope (b)	Correlation Coefficient
DER 331/TMAB	181.47	-10.39	0.99
XD/TMAB	247.11	-11.68	1.00

TABLE 7. Apparent Activation Energies for Isothermal Transformations for DER331/TMAB and the XD/TMAB Systems

System	ΔE[1] Gelation	ΔE[1,2] Vitrification	ΔE[1] Full Cure
DER331/TMAB	13.6	9.2	71.6
XD/TMAB	13.7	10.9	92.7

1) ΔE in kcal/mole.

2) ΔE for vitrification determined from the linear region of vitrification curve (Fig. 6).


Tg vs. Tcure FOR DER331/TMAB
180
160
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Tg [°C]
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Tg∞
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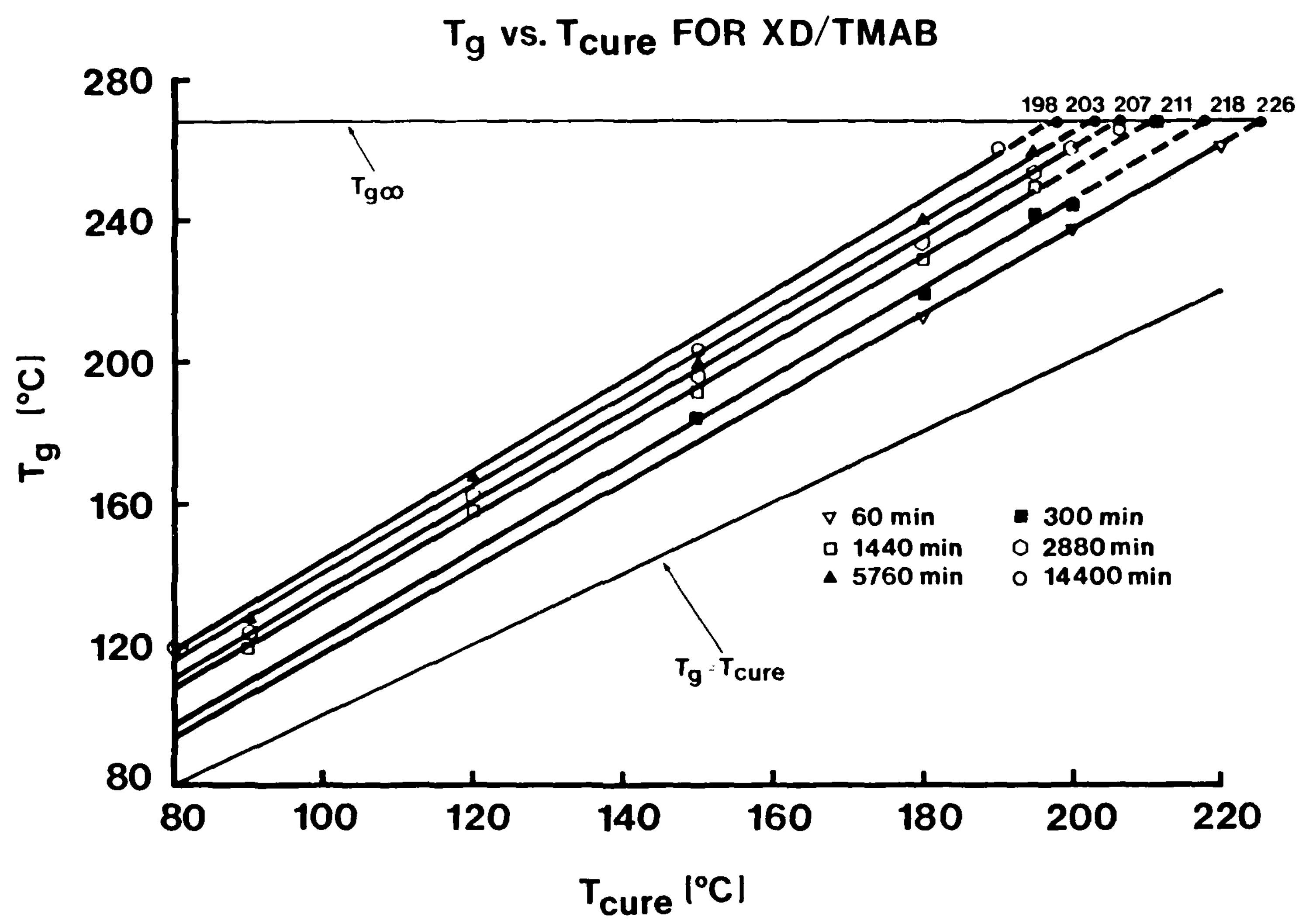
Fig. 1



T_g vs. T_{cure} FOR XD/TMAB
280
240
200
160
120
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T_g [°C]
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220
T_{cure} [°C]
198 203 207 211 218 226
$T_{g\infty}$
$T_g = T_{cure}$
60 min
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5760 min
300 min
2880 min
14400 min

Fig. 2

THE THERMOSETTING PROCESS: TIME–TEMPERATURE–TRANSFORMATION CURE DIAGRAM

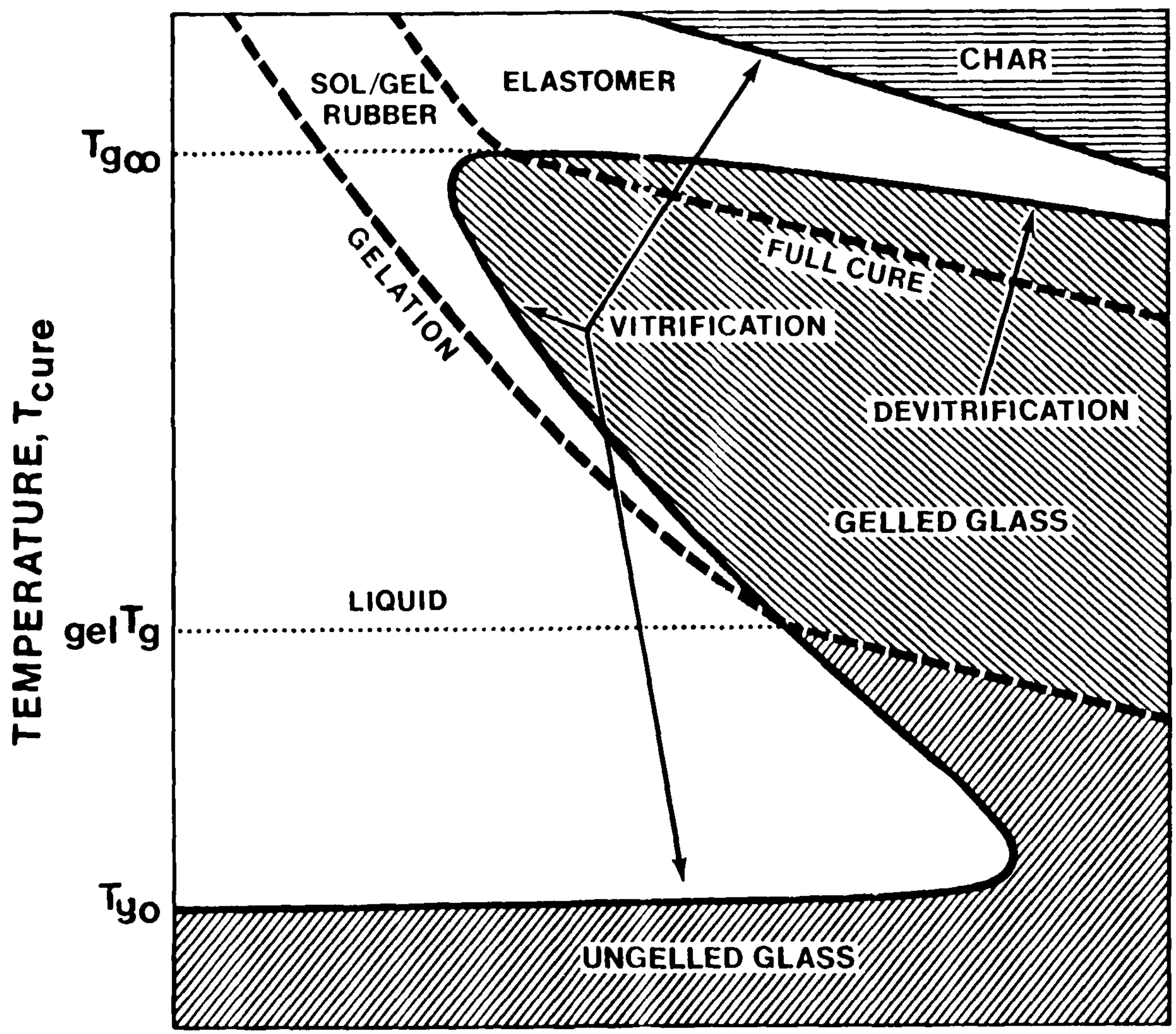

Fig. 3

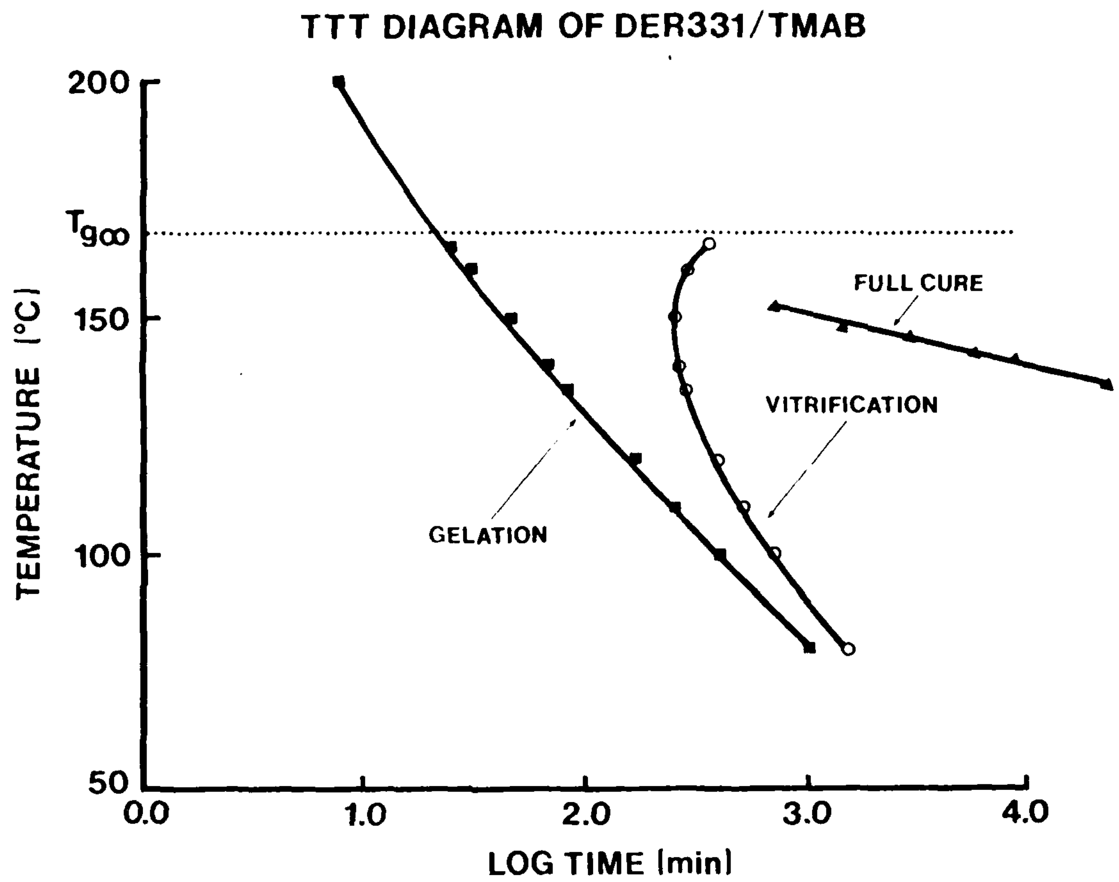
TTT DIAGRAM OF DER331/TMAB
200
$T_{g\infty}$
150
100
50
TEMPERATURE (°C)
0.0
1.0
2.0
3.0
4.0
LOG TIME (min)
GELATION
VITRIFICATION
FULL CURE

Fig. 4

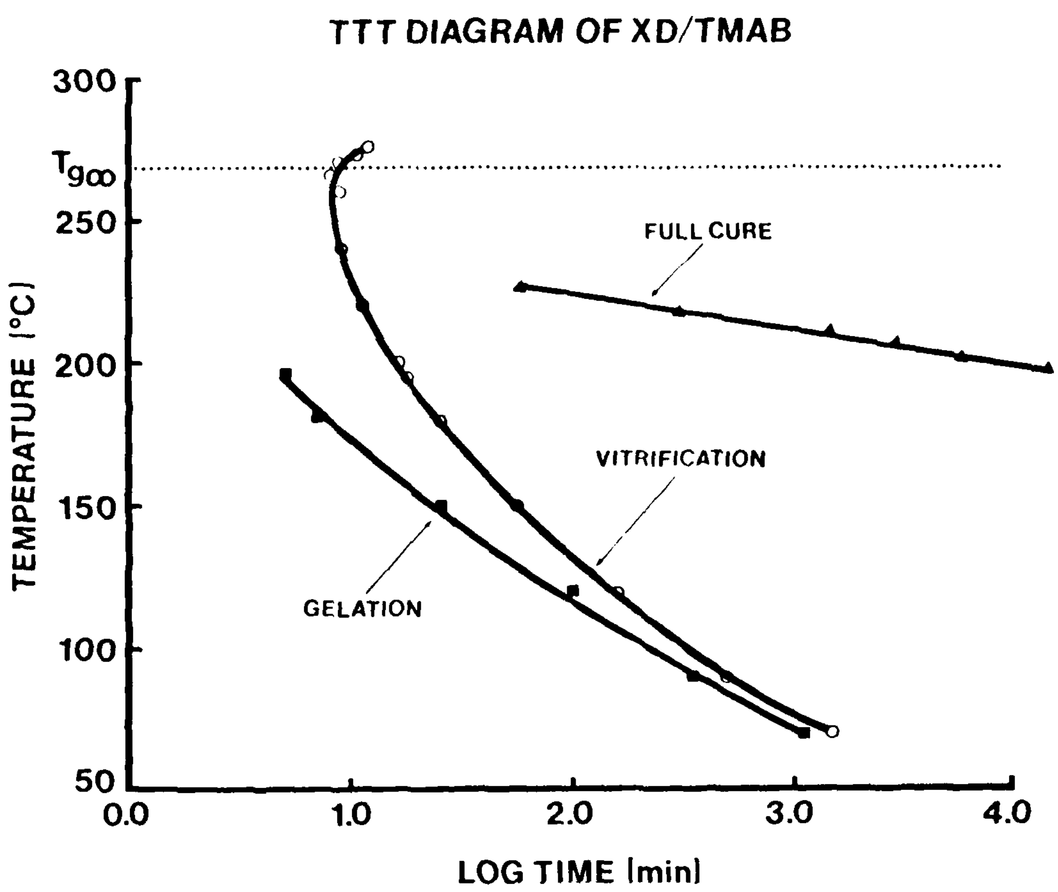
TTT DIAGRAM OF XD/TMAB
300
$T_{g\infty}$
250
200
150
100
50
TEMPERATURE (°C)
0.0
1.0
2.0
3.0
4.0
LOG TIME (min)
FULL CURE
VITRIFICATION
GELATION

Fig. 5

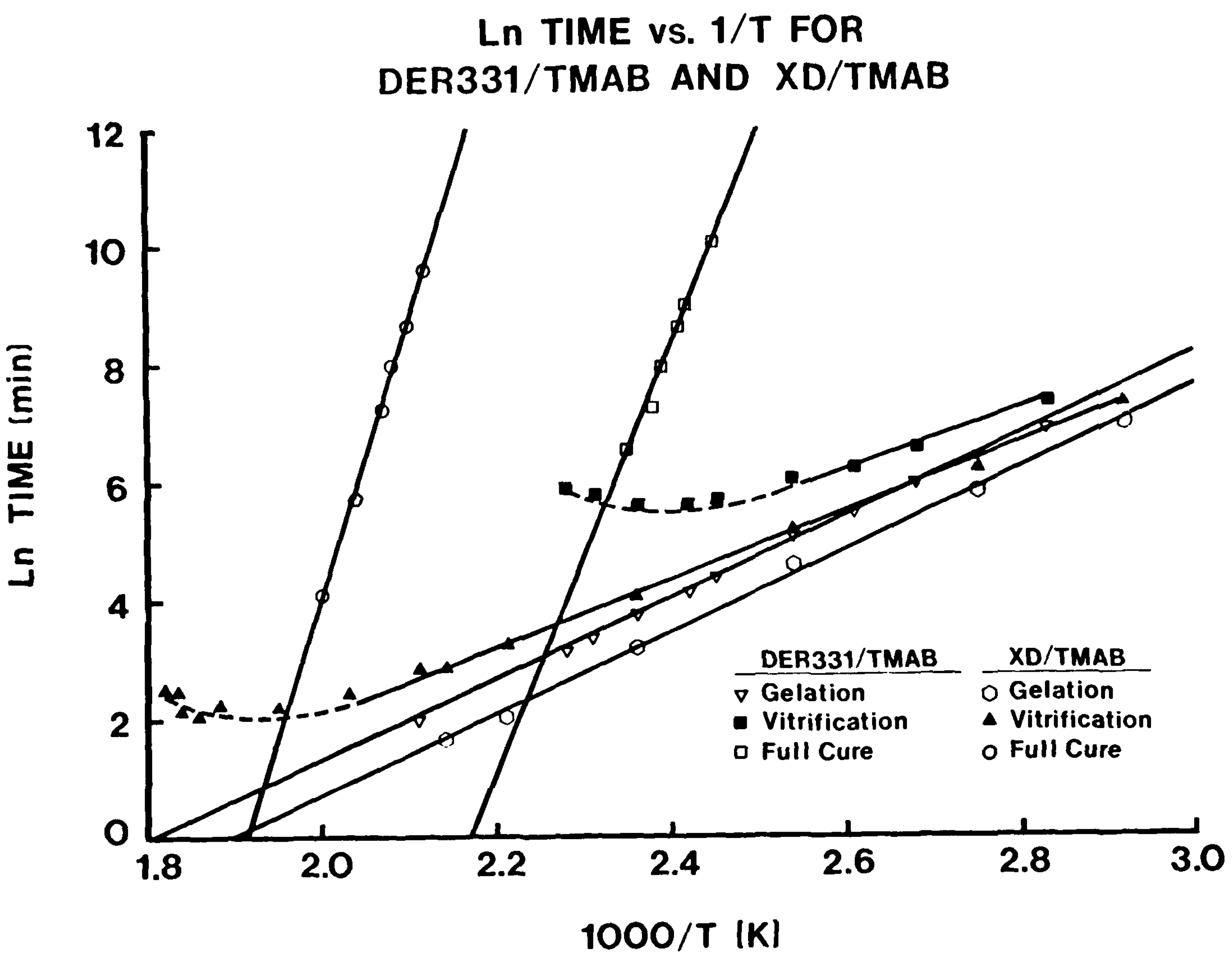
Ln TIME vs. 1/T FOR
DER331/TMAB AND XD/TMAB
Ln TIME (min)
12
10
8
6
4
2
0
1.8
2.0
2.2
2.4
2.6
2.8
3.0
1000/T (K)
DER331/TMAB
Gelation
Vitrification
Full Cure
XD/TMAB
Gelation
Vitrification
Full Cure

Fig. 6

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$$T_x = a + b \log t_x \quad (2)$$

where T_x and t_x are the temperature and time to full cure, respectively. The intercepts (a) and slopes (b) for the two systems are provided in Table 6. The full cure line should be useful for designing cure processes which lead to full cure. Selection of the temperature or time of cure gives the time or temperature, respectively, to full cure.

The data for the extrapolated time to full cure versus temperature of isothermal cure for the two systems are plotted in an Arrhenius manner as the logarithmic time versus 1/T(K) in Figure 6, which also includes corresponding data for gelation and vitrification. The activation energies for full cure (after vitrification), gelation, and vitrification for the DER 331/TMAB and the XD/TMAB systems are presented in Table 7. That the activation energy for full cure is much higher than that for gelation is a result of the cure reactions being controlled by physical relaxations in the glassy state (which themselves have similarly high activation energies).

T_g - T_{cure} - Time Equation

An equation relating T_g, T_{cure} and time of cure can be derived from equations 1 and 2. From equation 1, with $T_g = T_{g\infty}$ and $T_{cure} = T_x$,

$$T_{g\infty} = A + B\,T_x \quad (3)$$

For cure in the same time period, subtracting equation 1 from equation 3 results in

$$T_{g\infty} - T_g = B(T_\infty - T_{cure}) \quad (4)$$

Substituting for T_x in equation 4 in terms of time using equation 2 gives

$$T_{g\infty} - T_g = B(a + b \log t_\infty - T_{cure}) \quad (5)$$

where t_x could be any time, t.

Therefore equation 5 can be rewritten as

$$T_g = T_{g\infty} - B(a + b \log t - T_{cure}) \quad (6)$$

The T_g of the material cured at temperature T_{cure} for time t can be calculated using this T_g - T_{cure} - time equation.

The particular equations for the DER 331/TMAB and the XD/TMAB systems were formulated by substituting values for $T_{g\infty}$, B, a, and b in equation 6 with the data in Tables 3-6. For the DER 331/TMAB system,

$$T_g = 10.18 \log t + 0.98\ T_{cure} - 10 \quad (7)$$

and for the XD/TMAB system,

$$T_g = 14.48 \log t + 1.24\ T_{cure} - 38 \quad (8)$$

where t is in minutes, and T_{cure} and T_g are in degrees centigrade.

For both systems, the T_g calculated (T_g cal) by equations 7 and 8 are included in Tables 1 and 2 together with the corresponding experimental values for T_g. The agreement is good.

For an approximate calculation of T_g from T_{cure} and cure time for the epoxy systems, only two T_g vs. T_{cure} lines for two specified cure times are

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