Isothermal Transitions of a Thermosetting System

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Synopsis

A study of the curing reactions of a cycloaliphatic epoxy resin/anhydride system by torsional braid analysis showed the existence of two critical isothermal temperatures. These are $T'_{g\infty}$ (the maximum glass transition temperature of the thermoset system) and T_{gg} (the glass transition temperature of the material at its gel point). Two rheologically active kinetic transitions occur during isothermal cure which correspond to gelation and vitrification. Three types of isothermal behavior occur: if $T_{cure} > T_{g\infty}$, only gelation is observed; if $T_{g\infty} > T_{cure} > T_{gg}$, both gelation and vitrification are observed; if $T_{cure} < T_{gg}$, only vitrification is observed. T_{gg} corresponds to the isothermal cure temperature at which gelation and vitrification occur simultaneously. Methods for determining the time to gel and the time to vitrify, and also $T_{g\infty}$ and T_{gg}, have been developed. The time to gel obeyed the Arrhenius relationship, whereas the time to vitrify passed through a minimum. Application of these results to thermosetting systems in general is discussed in terms of the influence of molecular structure on the values of $T_{g\infty}$ and T_{gg}.
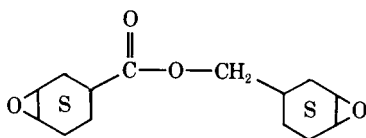
INTRODUCTION

A previous study[1] of the thermosetting reactions of the diglycidyl ether of bisphenol A with four aromatic diamines led to conclusions which appeared to be generalizations not limited to the specific systems studied. In particular, it was demonstrated that three types of rheological behavior occur on isothermal cure depending on the temperature of cure relative to two critical transition temperatures which were designated T_{gg} and $T_{g\infty}$. To test the generalizations further, the present investigation examined another type of thermosetting system, i.e., a cycloaliphatic epoxy resin/anhydride formulation. Since the results of the present work fitted the earlier generalizations which are summarized in the present conclusions, they are not repeated in this introduction. The technique which permitted the monitoring of the rheological changes which occur during the complete cure of a reactive system as it changes from liquid to solid was torsional braid analysis.[2]

EXPERIMENTAL

Reactants and Chemistry

The components used in the cure reaction of the epoxy resin/anhydride system were: (1) the epoxy resin 3,4-epoxycyclohexylmethyl-3,4-epoxy-

cyclohexane carboxylate (Bakelite Resin ERL-4211), (2) the hardener hexa-
hydrophthalic anhydride, (3) the initiator ethylene glycol, and (4) the
catalyst benzyldimethylamine.   The names, codes, formulae, molecular
weights, boiling points, and formulation of these chemicals are listed in
Table I.   All chemicals were obtained from the Union Carbide Corporation.

   A summary of the mechanism and cure chemistry of the cycloaliphatic
epoxy resin/hexahydrophthalic anhydride system appears in a technical
bulletin which was published by the manufacturer.[3]   The principal reaction
between the epoxy resin and hardener leads to the following polyester
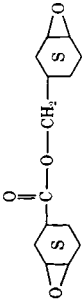structure:
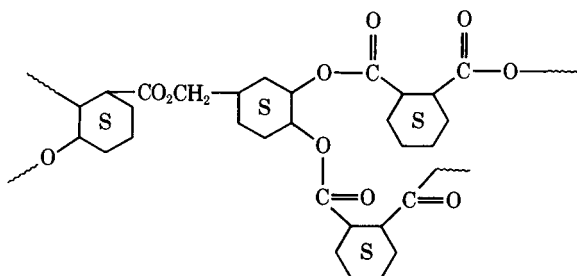
A certain amount of epoxide homopolymerization occurs in competition
with the formation of polyester linkages and leads to a polyether structure:
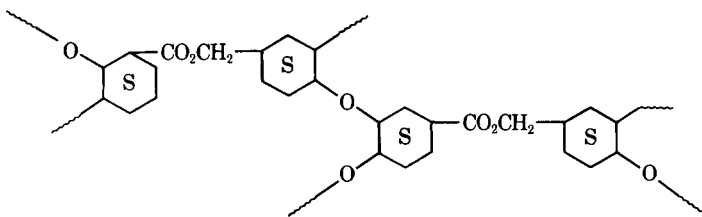
In both structures, the crosslinks of the molecular network are provided by
the tetrafunctional epoxide.   The anhydride reaction is initiated by active
hydrogen which is provided by ethylene glycol, and is catalyzed by base
which is provided by benzyldimethylamine.   The mole ratios of epoxide
and hexahydrophthalic anhydride components used in formulations reflect
the relative amounts of the competing reactions which occur for the given
amounts of initiator and catalyst and give rise to optimum thermophysical
properties in the cured resins.

   The chemicals were combined at room temperature as liquids in the order
epoxy (first), anhydride (at 55°C), ethylene glycol, and benzyldimethyl-
amine (last).   No solvent was required since the viscosity was low.   The
reactive mixture was stored under nitrogen in a freezer.   The mixture

TABLE I
Cycloaliphatic Epoxy Resin System: Chemicals and Formulation

Chemical	Molecular weight	Boiling point at 760 mm Hg, °C	Formulation	
			Wt. used, g	Equivalents used
3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL-4221)	252.3 (theoretical) specification equivalent weight (per epoxy group) = 137 (average)	354	10.0002	0.073
Hexahydrophthalic anhydride	154.2	284 (at 750 mm Hg)	10.0065	0.0649
Ethylene glycol	62.1	198	0.2989	0.00964(OH)
Benzyldimethylamine	135.2	178–180	0.1002	0.00074

was used to prepare specimens for torsional braid analyses by intermittently warming to room temperature.

Torsional Braid Analysis

The low strain isothermal dynamic mechanical data were obtained at about 1 cps by the technique of torsional braid analysis (TBA).[2] This adaptation of the torsional pendulum involves a free-hanging composite specimen consisting of a multifilamented ($\sim$3600) glass braid and the polymer system which is the subject of investigation. A specimen was prepared in a dry box by impregnating a glass fiber braid with the reactive mixture for 30 min at room temperature. The specimen was then mounted in the TBA apparatus which was being maintained at a predetermined constant temperature ($\pm0.5°C$). The remainder of the reactive mixture was saved for successive experiments. Monitoring of changes in dynamic mechanical behavior began within 2 min after introducing the specimen into the TBA specimen chamber. The same specimen could be used for determination of transitions in the cured polymer (while cooling to $-180°C$ and then heating) and for observing the effects of additional cure (by heating to 300°C followed by cooling). Flowing dry nitrogen gas was used as the environment in all experiments.

Details of the theory, technique, methods of data reduction, and conventions for presentation of data for torsional braid analysis have been published.[2]

Results and Discussion*

Dynamic mechanical behavior of the epoxy resin/anhydride system during isothermal cure at different temperatures is presented in Figure 1. The curves are arranged in order of increasing cure temperature for the purpose of easy comparison. Stacking the curves in this manner on a logarithmic scale does not alter the shapes of the curves (since $\Delta \log [(\text{constant})X] = \Delta \log X$).

Analysis of the results presented in Figure 1 reveals the occurrence of three different types of dynamic mechanical behavior. The first type of behavior occurs at low temperatures and is characterized by the occurrence of a single damping peak, B, which is accompanied by a one-step increase in rigidity. As the temperature of cure is increased, a second damping peak, A, becomes resolvable as shown by the 80°C cure isotherm. The relative rigidity curves then show a two-step increase in rigidity corresponding to damping peaks A and B. This represents the second type of behavior on isothermal cure. Increasing the temperature further results in a broadening of damping peak B, and the first step of the two-step increase in rigidity becomes relatively more dominant. Above a certain temperature, only a single damping peak, A, and a corresponding one-step increase in rigidity

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* Complications due to volatility of constituents of the reaction mixture have been neglected in this analysis. Stoichiometry can be upset by selective volatilization of components from specimens with large surface to volume ratios.
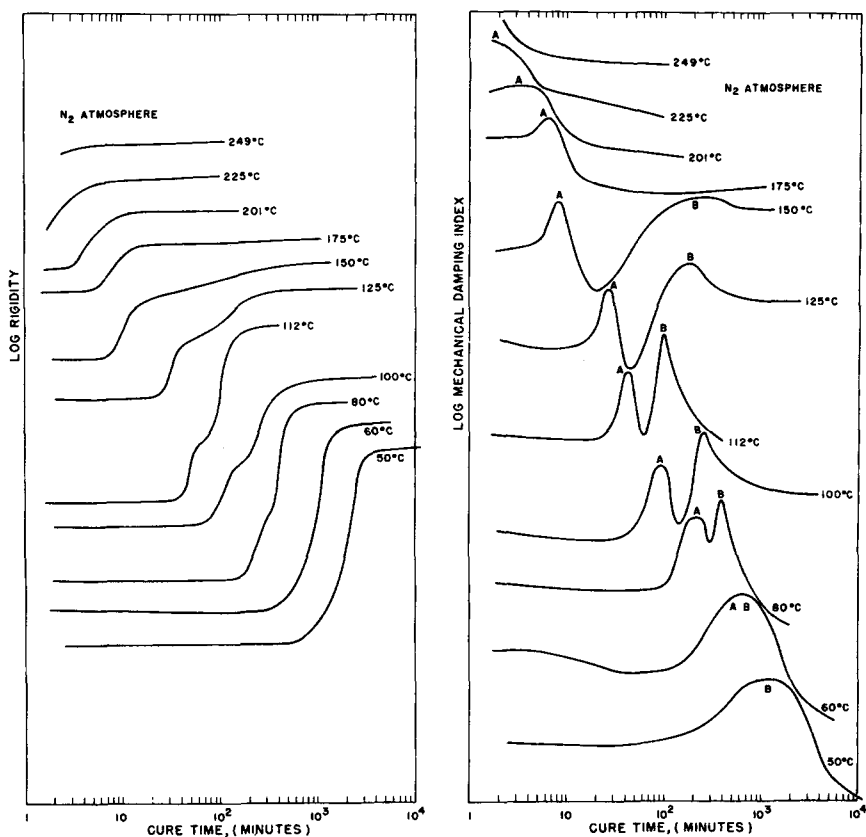
Fig. 1. Rigidity and mechanical damping vs. time during isothermal cure of the cyclo-aliphatic epoxy system in the temperature range of 50° to 249°C.

are observed. This corresponds to the third type of behavior on isothermal cure. At still higher cure temperatures, damping peak A is not completely definable owing to the high rate of reaction (i.e., when peak A occurs at a time less than 1 min after lowering the specimen into the TBA apparatus).

Damping peak A and its corresponding increase in rigidity are associated with the gel point of the reactive system, whereas damping peak B and its corresponding increase in rigidity are associated with vitrification (transition to the glassy state).

The first type of behavior is a result of an increase in molecular weight of the prepolymer which causes its transformation from the fluid to the glassy state before the onset of gelation. This behavior is apparent until the temperature of isothermal cure is equal to the glass transition temperature of the reactive system at its gel point, T_{gg}. At this point, the processes of vitrification and gelation occur together. This follows since vitrification occurs when the glass transition $T_g(t)$ of the reacting system equals the temperature of cure and since (for a given reactive system) gelation occurs at a constant conversion which is independent of temperature.

TABLE II
Gelation and Vitrification Times Versus Isothermal Cure
Temperatures as Determined by Three Methods

Cure temp., °C	Gelation time, min			Vitrification time, min		
	Rigidity intercept	$^1/_2\Delta$ (log rigidity)	Damping peak	Rigidity intercept	$^1/_2\Delta$ (log rigidity)	Damping peak
50	n.a.	n.a.	n.a.	—[b]	1,950	1,250
60	n.a.	n.a.	n.a.	—[b]	950	650
80	175	230	215	350	420	395
100	73	102	91	205	275	255
112	42	47	43	90	106	100
125	25	31	27	95	160	180
150	7.4	9.6	8.4	105	650	245
175	5.5	8.4	6.5	n.a.	n.a.	n.a.
201	3.1	4.7	3.8	n.a.	n.a.	n.a.
225	—[a]	2.6	—[a]	n.a.	n.a.	n.a.
249	—[a]	—[a]	—[a]	n.a.	n.a.	n.a.

[a] Difficult to measure experimentally.
[b] Rigidity intercept method ambiguous because unique linear extrapolation of log rigidity vs. log time not possible.
n.a. Not applicable.

The second type of behavior occurs when the temperatures of cure exceed T_{gg}, at which temperatures the reactive system can pass through gelation before vitrifying. Vitrification is due to an increase in crosslink density after gelation. In this region, the materials pass from the fluid to the rubbery and then to the glassy state.

The results also show (Table II) that the time of occurrence of gelation decreases with increasing temperature. This is due to the increased rate of reactions at higher temperatures. The time of occurrence of vitrification reflects the competition between the increased rate of cure with increased temperature and the increased degree of cure necessary for vitrification at higher temperatures. Vitrification time is observed to pass through a minimum value at 112°C. The occurrence of a minimum is presumably the consequence of a decrease in reaction rate at high conversion.

The gelation and vitrification times were measured in the three ways illustrated in Figure 2. These are designated rigidity intercept, $^1/_2\Delta$ (log rigidity), and damping peak maximum methods. The times for gelation and vitrification for each of the isothermal experiments as measured by the three methods are tabulated in Table II. It is noted for both gelation and vitrification at any isothermal temperature that the time of a transition depends on the method of measurement and that the value of the time generally increases thus: rigidity intercept time < damping peak time $<^1/_2\Delta$ (log rigidity) time.

Since the chemical conversion at the gel point is constant for a given reactive thermosetting system, it follows that the gelation time, t_g, is a
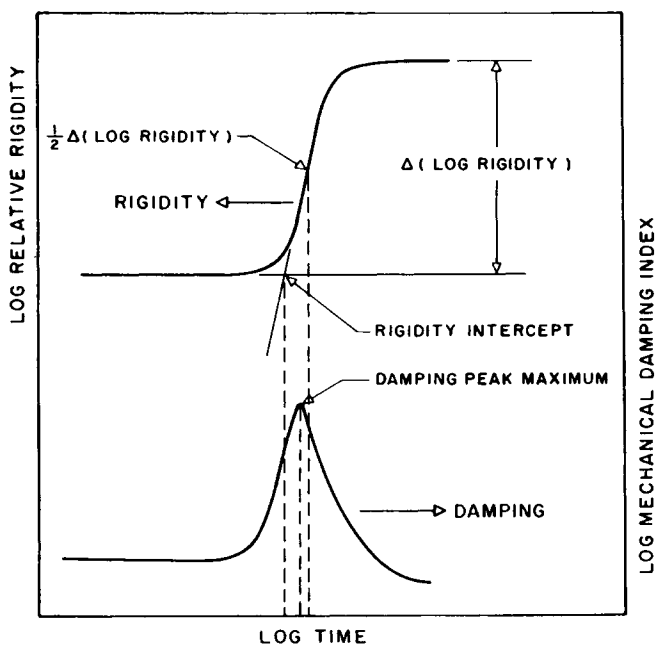
Fig. 2. Methods for determining time to gel and time to vitrify: top, rigidity inter-cept and $^1/_2\Delta$ (log rigidity) from relative rigidity curve; bottom, damping peak maxi-mum from damping curve.

direct inverse measure of the overall rate of the reaction. The Arrhenius relationship can be used to relate gelation time to temperature by plotting the logarithm of the gelation time versus the reciprocal of the absolute temperature since $t_g = $ constant $\times$ e$^{E/RT}$, where E is the activation energy. The plot of logarithm gelation time, measured by the three methods, versus $1/T°$K is displayed in Figure 3. Three lines with the same slope appear to fit the data. The apparent overall activation energy calculated from the slope is 12.2 kcal/mole, a value which agrees with those obtained for other epoxy systems.

Plots displaying the times to gelation and times to vitrification, measured by the three methods, versus cure temperature are shown in Figure 4. The gelation curves were extrapolated (dashed lines) to low temperatures by using the Arrhenius relationship (see above). At cure temperatures below the minimum in the vitrification time, the vitrification curves were ex-trapolated linearly (dashed lines). The intersection of each pair of the extrapolated gelation and vitrification curves (paired according to the method used for determining the transitions) is designated T_{gg}. The values are tabulated in Table III. The values which result for T_{gg} differ but little, in part because of the steep slope of the exponential gelation time versus cure temperature relationship in the vicinity of T_{gg}. The procedure, therefore, results in an accurate method for determining T_{gg}.

TABLE III
Values of T_{gg} Determined by Intersection of Gelation and
Vitrification Times Versus Cure Temperature Curves

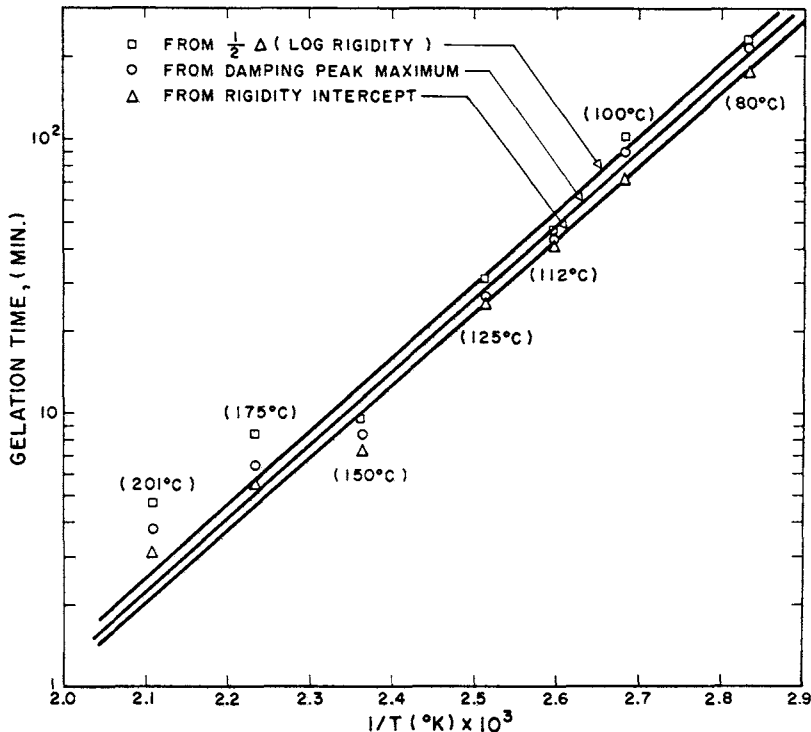| Method	T_{gg}, °C
Rigidity intercept	58
$^{1}/_{2}\Delta$ (log rigidity)	58
Damping peak	57

Fig. 3. Arrhenius plot of log (time to gel) vs. T^{-1} (°K). Gelation time was obtained by three methods: (1) rigidity intercept; (2) $^{1}/_{2}\Delta$ (log rigidity); (3) damping peak maximum.

The data points listed in Table II for vitrification times for isothermal cure temperatures of 60° and 50°C do not appear in Figure 4 and do not lie on the linear extrapolations of Figure 4. These data points are treated differently for the reason that above T_{gg} (and below $T_{g\infty}$) the measures of vitrification time involve measuring a change from a rubbery network to a glassy structure, whereas below T_{gg} measurements of vitrification time involve measuring a change from a liquid to glassy structure.

CONCLUSIONS

The significance of the presently reported and of the earlier research[1] lies in the generalities which appear to have been developed for reactive thermo-
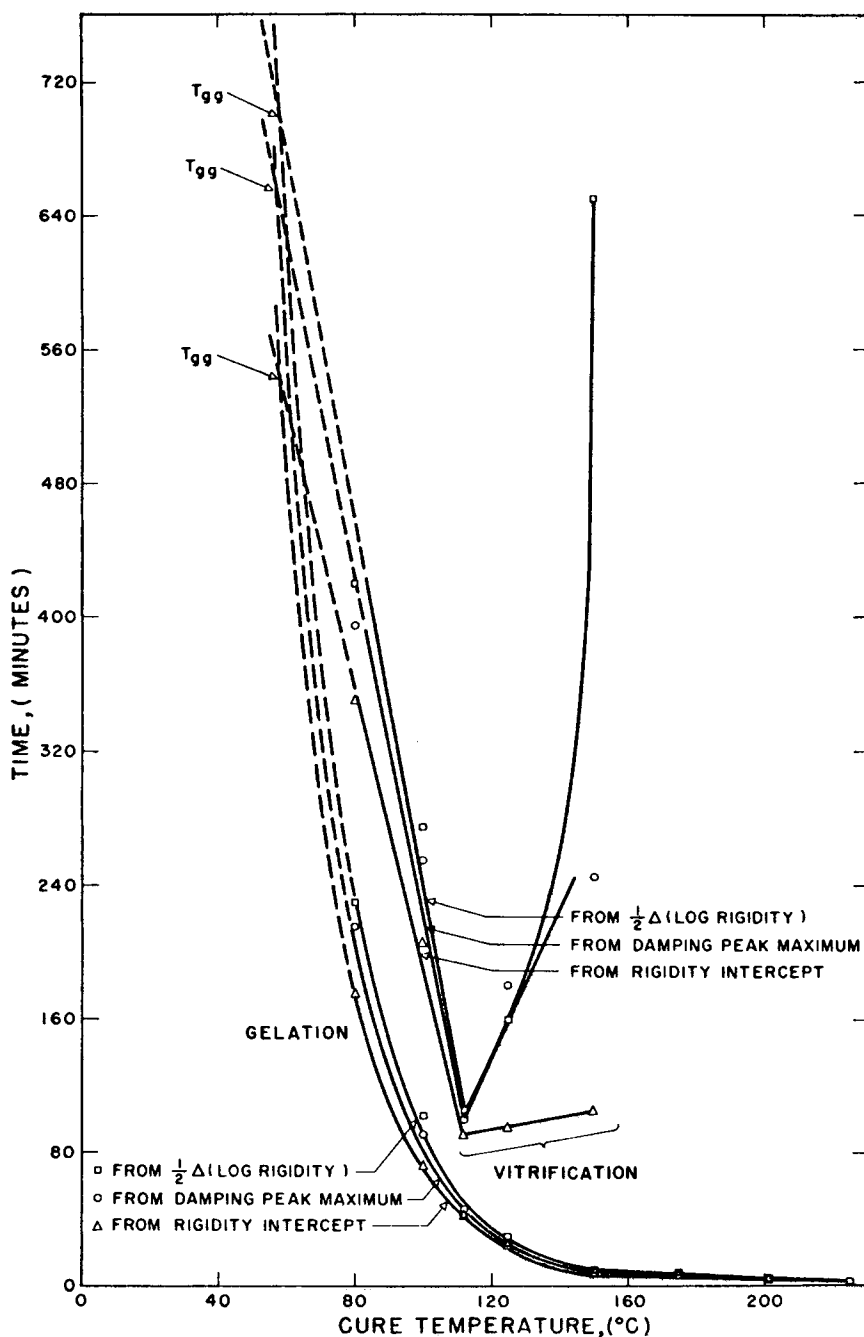
Fig. 4. Time to gelation and time to vitrification vs. temperature of isothermal cure of the cycloaliphatic epoxy system.   Gelation and vitrification times were obtained by three methods: (1) rigidity intercept; (2) $^1/_2\Delta$ (log ridigity); (3) damping peak maximum.

setting systems.   These depend on the existence of two critical tempera-
tures, T_{gg} and $T_{g\infty}$, for isothermal cure.   Three types of behavior can be
obtained on cure:

1. $T_{\mathrm{cure}} < T_{gg}$

Before the occurrence of vitrification, the rate of the reaction in the liquid
state presumably fits the Arrhenius relationship with the activation energy
which can be obtained by measuring times to gelation at isothermal tem-
peratures of cure above T_{gg}.   After vitrification, the rate of reaction is
essentially quenched.   A reactive thermosetting system should be stored
at temperatures well below T_{gg} so as to avoid gelation and provide a long
shelf-life.   This is presumably the basis of "B-stage" technology.

An accurate method for determining T_{gg} is reported which involves find-
ing the point of intersection of the vitrification and gelation times versus
temperature of cure curves (Fig. 4).   The method arose from the realization
that the vitrification and gelation times should coincide at an isothermal
temperature of cure which is equal to the glass transition temperature of the
reacting system at its gel point.

2. $T_{gg} < T_{\mathrm{cure}} < T_{g\infty}$

The rates of isothermal reaction are presumably the same before gelation
(in the fluid state) and up to the time of vitrification (in the rubbery state).
The reaction is essentially quenched on vitrification which occurs when the
glass transition temperature of the reactive system, $T_g(t)$, equals the tem-
perature of cure, T_{cure}.   A consequence of this is that the system can only be
fully cured by reacting above $T_{g\infty}$.   This is shown schematically in Figure
5, which shows the anticipated relation between the temperature of iso-
thermal cure, T_{cure}, and the resultant glass transition temperature, T_g.
The value for the glass transition temperature of the fully cured thermo-
setting system, $T_{g\infty}$, is obtained most easily after curing above $T_{g\infty}$.   A
convenient method for obtaining $T_{g\infty}$ is to obtain the thermomechanical
spectra after curing or postcuring above $T_{g\infty}$.

3. $T_{\mathrm{cure}} > T_{g\infty}$

The rates of reaction presumably obey the same Arrhenius relationship as
for $T_{\mathrm{cure}} < T_{g\infty}$ (before vitrification).   Gelation occurs, but there is no
vitrification process.

The influence of the reactants on the nature of the cure is determined
not only by the inherent reactivity of the functional groups, but also by
the geometry and polarity of the growing chain segments which determine
the transition temperatures $(T_{gg}, T_g, T_{g\infty})$ of the reactive systems and
therefore the type (1, 2, and 3) of dynamic mechanical behavior ex-
perienced in isothermal cure.   For example, for highly crosslinked or
rigid chain polymeric systems $T_{g\infty}$, or even T_{gg}, can be above the limits of
decomposition, and then only type 1 and type 2, or only type 1, behavior
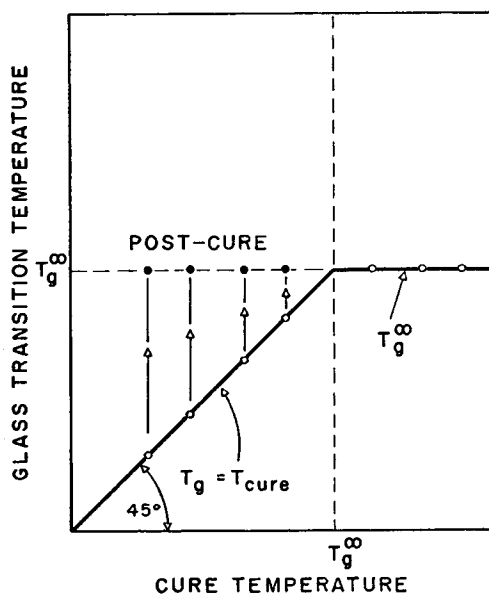would be observed.   Only type 3 behavior can be observed at $T \geq$ room

Fig. 5. Schematic diagram of glass transition temperature, T_g, to be expected from curing at isothermal temperature, T_{cure}. Note that the maximum value of the glass transition temperature, $T_{g\infty}$, is obtained only after heating to above $T_{g\infty}$.

temperature for reactive prepolymer systems if $T_{g\infty}$ is below room temperature (as for elastomers).

References

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