

## Epoxy Thermosetting Systems: Dynamic Mechanical Analysis of the Reactions of Aromatic Diamines with the Diglycidyl Ether of Bisphenol A

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### Synopsis

Dynamic mechanical behavior during the reactions of four aromatic diamines (*m*-phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone, and benzidine) with the diglycidyl ether of bisphenol A was studied by torsional braid analysis under isothermal conditions. Depending on the cure temperature, three types of behavior were observed: (I) below  $T_{gg}$  (the glass transition temperature of the reactive systems at the gel point); (II) between  $T_{gg}$  and  $T_{g\infty}$  (the glass transition temperature of the ultimately cured polymers); (III) above  $T_{g\infty}$ . Overall activation energies and apparent overall rate constants of the cure reactions based on third-order overall kinetics were determined before gelation, after gelation but before vitrification, and after vitrification, using gelation time, relative rigidity, and glass transition temperature  $T_g(t)$  of the polymers as kinetic terms. The influence of cure temperature and structure of the diamines on the kinetic parameters is discussed.

### INTRODUCTION

The cure of a reactive thermosetting prepolymer usually involves transformation of low molecular weight monomers or oligomers from the liquid to solid state as a result of the formation of a polymer network by chemical reactions of the reactive groups in the system. Two stages, which are divided by a gel point, are usually distinguished in this process. It is accepted that growth and branching of the polymer chains occur in the liquid state where the reactive system is soluble and fusible. An infinite network of polymer chains appears and develops only after the gel point. The reactive system then loses its solubility and fusibility, and the final reactions take place in the solid state.

Traditionally, studies of the cure of reactive prepolymers have used a chemical approach which consists in analysis of the degree of conversion of reactive groups by methods such as chemical analysis, infrared spectroscopy, and calorimetry. Although the chemical approach is useful for

studying the kinetics of curing reactions and for deducing details of molecular architecture on the basis of stoichiometric relationships, it reveals little about the bulk properties of the curing polymers. Furthermore, the sensitivity and capabilities of the techniques decrease sharply in the late stages of cure which usually significantly determine the optimal properties of a crosslinked polymer.

Another approach consists in monitoring physical behavior by, for example, measurements of changes in density, viscosity, refractive index, swelling characteristics, and mechanical and electrical properties. In general, these suffer from the theoretical disadvantage of not knowing the relationships between the physical properties and chemical composition. However, some theories relating mechanical behavior to chemical conversion are available and, since criteria of cure are often expressed in mechanical terms, also have practical relevance. Nevertheless, the total range of cure has been difficult to monitor mechanically by a single experiment because of the extreme rheological changes which occur during conversion of the liquid prepolymer to the solid crosslinked polymer.

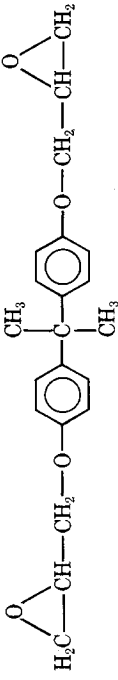
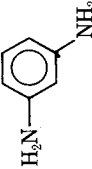

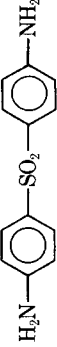
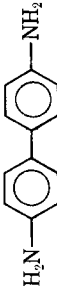
Dynamic mechanical techniques that use a supported sample as the specimen, such as torsional braid analysis (TBA),<sup>1,2,3</sup> flexural braid analysis,<sup>4</sup> and a rebound relaxation technique,<sup>5</sup> have been applied to the study of reactive systems *throughout* the thermosetting liquid-to-solid change in state. Recent advances in instrumentation and technique of TBA make it a convenient method for monitoring changes in rigidity and damping in a reactive prepolymer system. The experiments are monitored intermittently during exposure to various environmental conditions at different but constant temperatures, or at constant rates of increase or decrease of temperature.

The objective of this work was to analyze the cure transitions and cure kinetics of some epoxy/aromatic diamine systems through their dynamic mechanical behavior under isothermal conditions using TBA data. These systems were chosen because they are typical reactive prepolymers and are commercially important. The chemistry of cure and the structure-properties relationships of epoxy/diamines have been investigated by more conventional methods,<sup>6-16</sup> which together aid the understanding and interpretation of some of the experimental results presented herein.

## EXPERIMENTAL

Stoichiometric mixtures (1 mole epoxy with 1 mole amine hydrogen) of the epoxy monomer (the crystalline diglycidyl ether of bisphenol A) and four aromatic diamines (see Table I) were used as reactive systems in this investigation. All chemicals were stored in the dark in a dry nitrogen atmosphere before use. Solutions of the reactive mixtures (60% in acetone, weight/volume) were used after being stored in a freezer for not more than a week, during which time their viscosity at room temperature did not appear to change.

TABLE I  
Chemicals

Name, code and formula	Source and purification
Diglycidyl ether of bisphenol A (DGEBA)	Dow Chemical, crystalline (used without further purification)
	Matheson, Coleman & Bell, practical (distilled twice at 280–281 °C)
<i>m</i> -Phenylenediamine (mPDA)	
	
4,4'-Diaminodiphenylmethane (DDM)	Eastman Kodak, practical (recrystallized twice from benzene)
	
4,4'-Diaminodiphenyl sulfone (DDS)	Polychemical Lab. (recrystallized from ethanol)
	
Benzidine	Baker, crystalline (used without further purification)
	

The dynamic mechanical measurements were carried out with a torsional braid apparatus using a temperature controller for maintaining constant temperature. A glass fiber braid, after having been impregnated with the acetone solution and dried in vacuum at room temperature for 60 min, was mounted in the apparatus at the chosen constant temperature. The intermittent monitoring of changes in dynamic mechanical behavior (relative rigidity =  $1/P^2$ , mechanical damping index =  $1/n$ )<sup>2,3</sup> usually began within 2 min after lowering the specimen into the TBA specimen chamber. The same specimen could be used for other experiments, such as determination of the transitions in the cured polymer by cooling to  $-150^\circ\text{C}$  and heating again. Flowing dried nitrogen was used as the environment in all experiments.

## RESULTS AND DISCUSSION

### Transitions during Isothermal Cure

Analysis of the isothermal cure of the epoxy/aromatic diamine systems (Figs. 1-4) shows that, depending on the temperature of cure, there are three different types of dynamic mechanical behavior.

The first type of behavior is observed at relatively low temperatures where the sigmoidal increase in rigidity is accompanied by a single damping peak, A, and at higher temperatures, by a damping shoulder which precedes peak A (Figs. 1-4, curve 1). The shoulder becomes more apparent at higher isothermal temperatures (results not shown), and above a certain temperature becomes resolved as a second damping peak, B. This is the onset of the second type of behavior (Figs. 1-4, curves 2-5). The relative rigidity curves show two distinct increases which correspond to the B and A damping peaks. Further increase in the cure temperature is accompanied by changes in the shapes of the curves and in the times of occurrence of the damping peak maxima. The width of the A peak increases and its intensity decreases. Damping peak A disappears by a certain temperature which represents the onset of the third type of behavior (Figs. 1-4, curve 6).

A study<sup>4</sup> of the cure of an epoxy/aliphatic amine system, by flexural braid analysis, examined behavior of the second type. It was recognized that the first (and smaller) peak in damping was associated with the gel point of the reactive system, while the second was associated with vitrification (i.e., transition to the glassy state).

An increase in the molecular weight of the prepolymer can cause its transition to the glassy state before the onset of gelation in the case of the DGEBA/aromatic diamine systems with the rigid diamine molecules. This explains the single damping peak at relatively low temperatures (type I behavior). If gelation occurs in the vicinity of the process of vitrification, its contribution to the increase in rigidity will be very small compared with that due to vitrification and produces only a small increase in rigidity and a corresponding shoulder on the damping curve. This be-

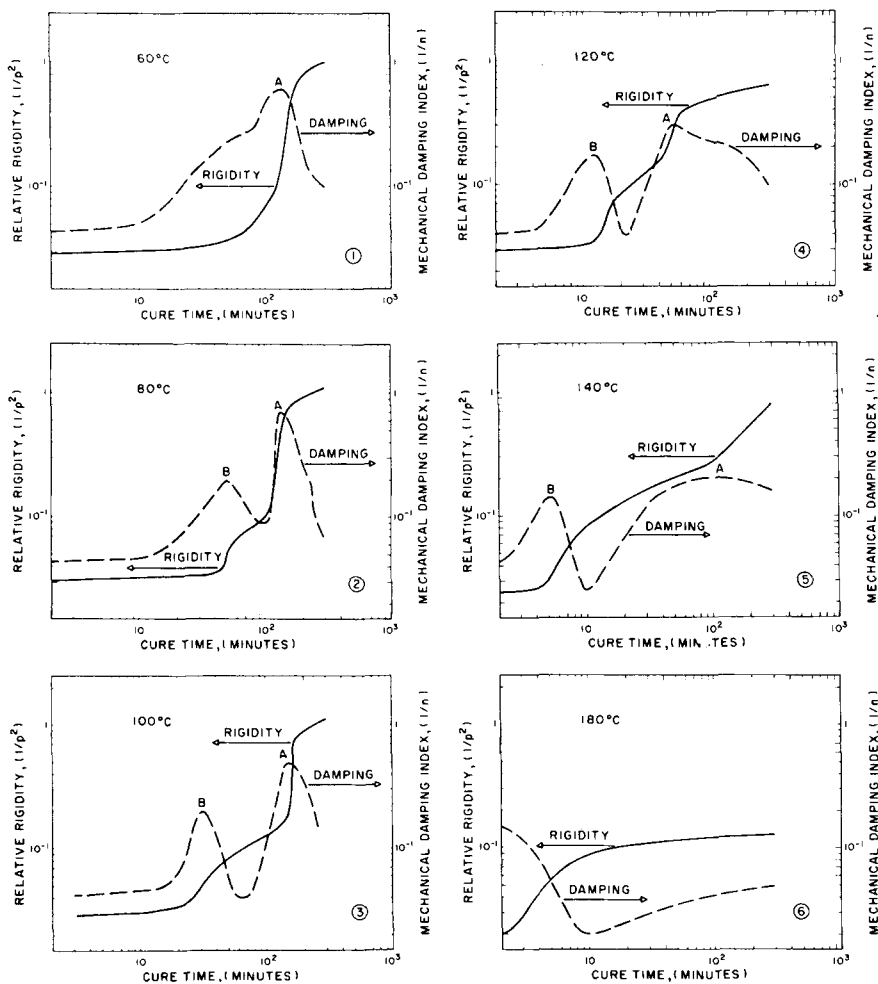
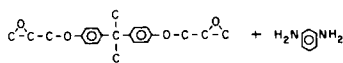


Fig. 1. Relative rigidity and damping curves vs. time for the reaction of the diglycidyl ether of bisphenol A with *m*-phenylenediamine under isothermal conditions.

havior is expected until the temperature of isothermal cure is equal to the glass transition temperature of the reactive system at the gel point, which is designated  $T_{gg}$ , when 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. If the temperature of cure exceeds  $T_{gg}$ , the reactive system passes through gelation to give damping peak B and can then pass through vitrification, which in this case is mostly due to the increase in crosslink density of the network after gelation, to give damping peak A.

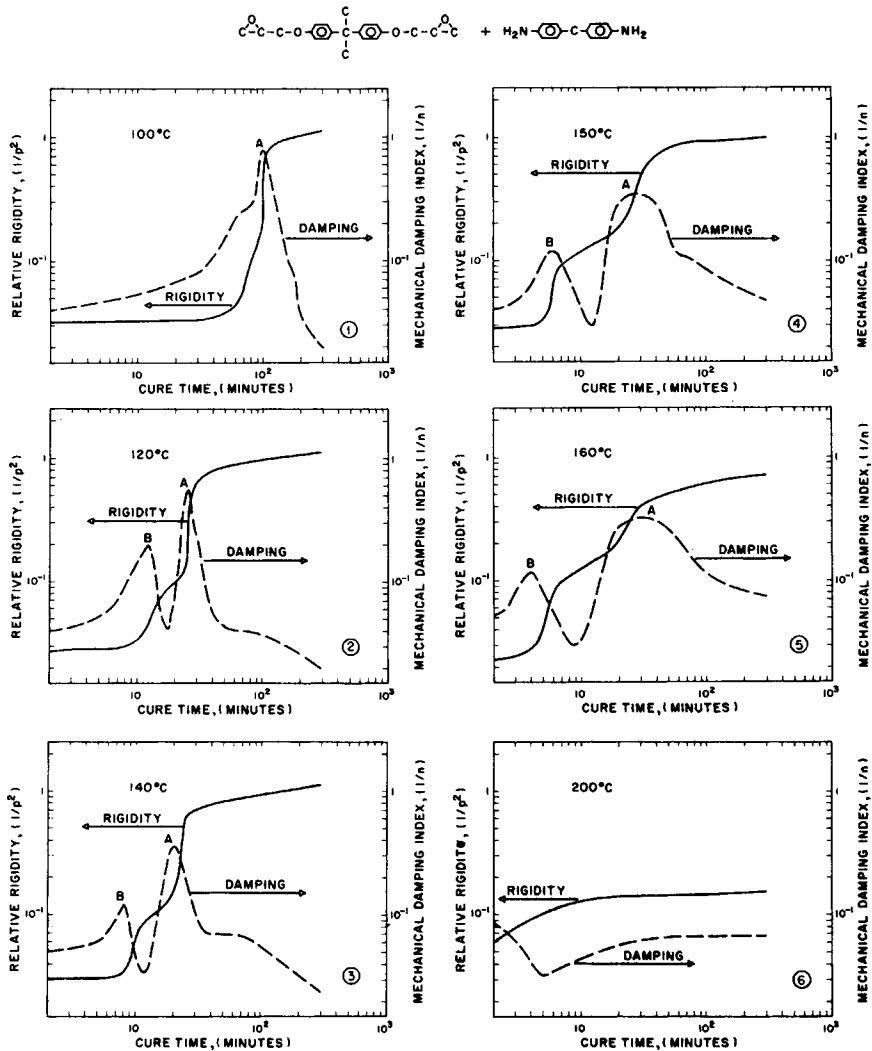


Fig. 2. Relative rigidity and damping curves vs. time for the reaction of the diglycidyl ether of bisphenol A with 4,4'-diaminodiphenylmethane.

This gives rise to the two-step increase in rigidity—the first (and smaller) during gelation and the second (and larger) during vitrification (Figs. 1–4, curves 2–5). This corresponds to the type II dynamic mechanical behavior of the reactive systems. After peak A, the cure reaction will continue in the transition region between the rubbery and the glassy states of the reactive systems.

An increase in cure temperature increases the rate of reactions and so decreases the time to reach the gel point. Damping peak B corresponds to a rheological state which is determined by both the composition of the system at the gel point and the temperature dependence of rheological

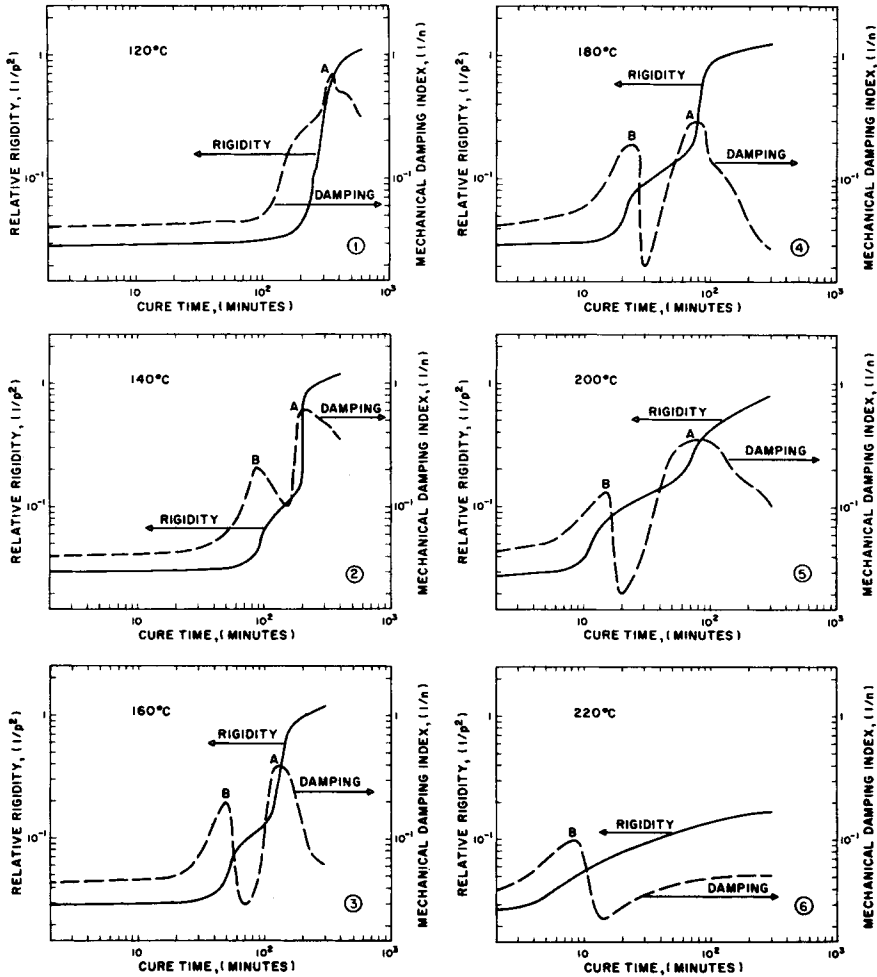
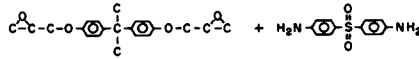


Fig. 3. Relative rigidity and damping curves vs. time for the reaction of the diglycidyl ether of bisphenol A with 4,4'-diaminodiphenyl sulfone.

behavior of the material in the vicinity of the gel point. Although the latter would be expected to prolong the *apparent* onset of gelation with increasing temperature, the time of occurrence of damping peak B is observed to decrease with increasing temperature, thus paralleling the effect of temperature on the time to gel. In contrast, the time of occurrence of damping peak A (i.e., vitrification time) is observed to depend on the cure temperature in a more complicated way and reflects the competition between the increased rate of cure with increased temperature and the degree of cure (the crosslink density) that is necessary for vitrification at higher temperatures.

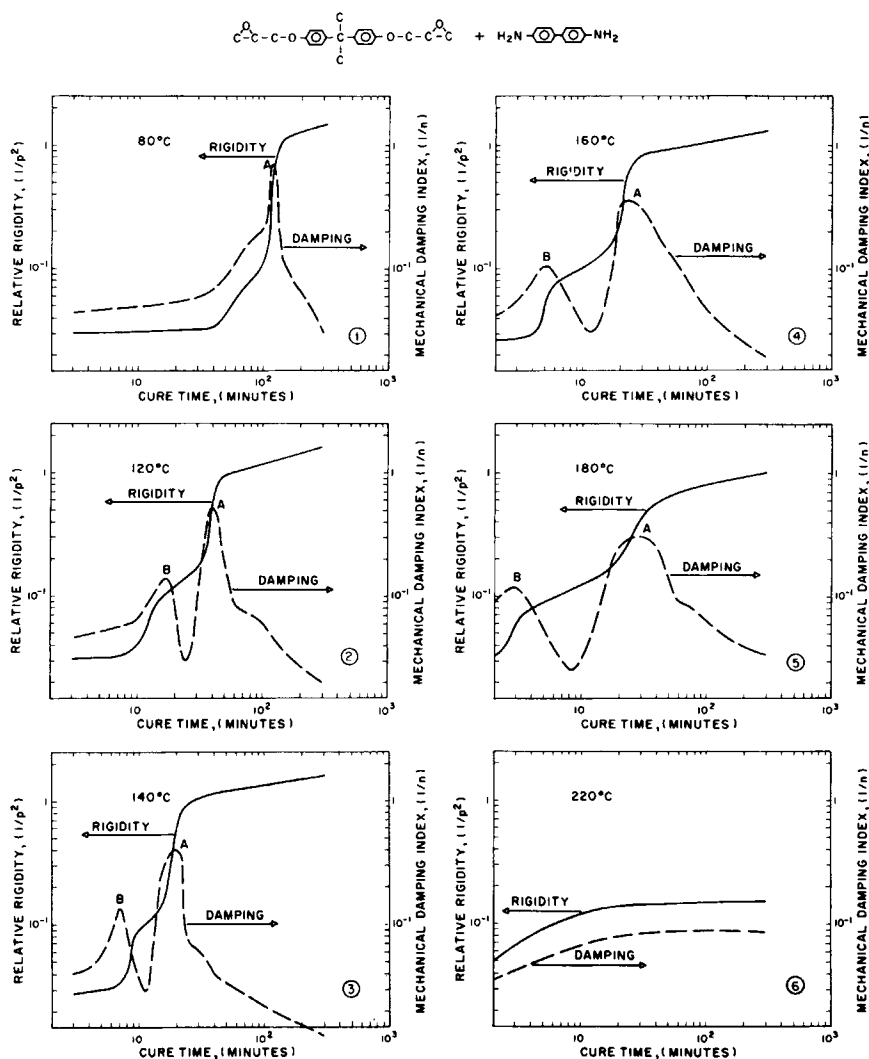


Fig. 4. Relative rigidity and damping curves vs. time for the reaction of the diglycidyl ether of bisphenol A with benzidine.

If the cure temperature exceeds the glass transition temperature of the ultimately cured polymer (designated as  $T_{g\infty}$ ), vitrification cannot occur, and peak A on the damping curves disappears (Figs. 1-4, curve 6). Peak B on the damping curves was not observed in all of the experiments with the epoxy/diamine systems because of the high rate of cure at temperatures above  $T_{g\infty}$ , where the gelation time is less than 2 min.

Values of  $T_{g0}$  and  $T_{g\infty}$  of the DGEBA/aromatic diamine systems are presented in Table II. Approximate values for  $T_{g0}$  were obtained by locating the temperatures where damping peaks B appeared to be just not resolvable. Values for  $T_{g\infty}$  were obtained from thermomechanical spectra



TABLE II  
Glass Transition Temperatures ( $T_{g0}$ ) at the Gel Points and of the Ultimately Cured Epoxy/Diamine Systems ( $T_{g\infty}$ )

Reactive system	$T_{g0}$ , °C	Temperature of ultimate cure	$T_{g\infty}$ , °C
DGEBA/mPDA	70	180	150
DGEBA/DDM	110	200	180
DGEBA/DDS	130	220	210
DGEBA/Benzidine	90	220	200

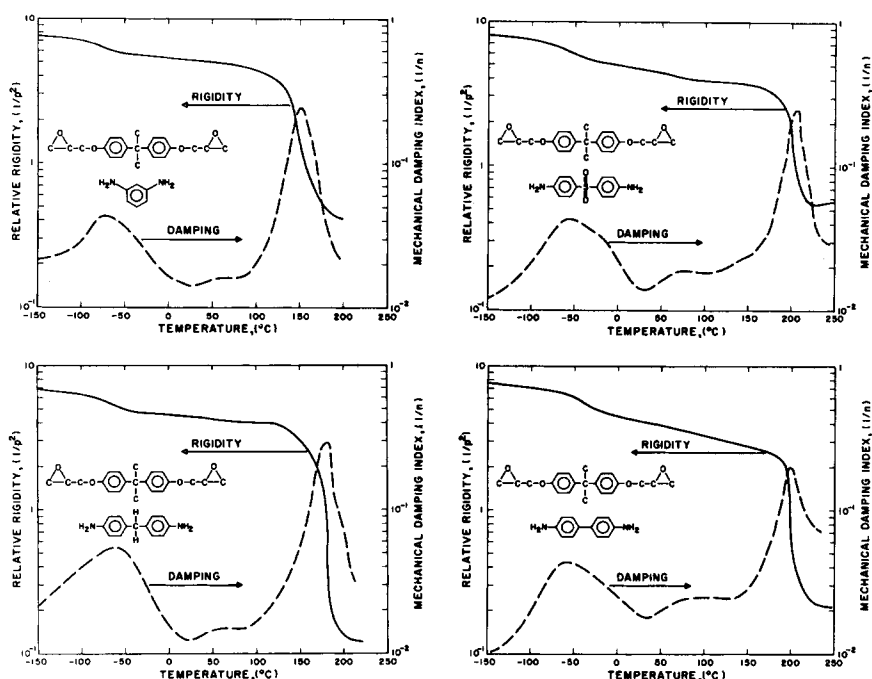


Fig. 5. Thermomechanical behavior of the ultimately cured epoxy/diamine systems.

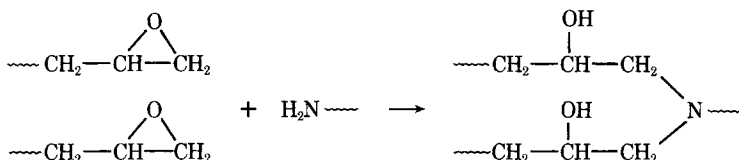
of polymers cured for 5 hr at about 20°C above  $T_{g\infty}$  (Fig. 5 and Table II). [The thermomechanical spectra revealed also two distinct transitions in the glassy state (at about -60° and +60°C) for each cured polymer.]

It is apparent, then, that there are two main structural transitions of a reactive prepolymer system that converts into a highly crosslinked network. The first, gelation, results from the structural transition from linear and branched molecules into the macromolecular network. The second, vitrification, involves a transition from the liquid or rubbery state into the glassy state as a consequence of an increase in molecular weight before gelation and in crosslink density after gelation. Using dynamic mechanical analysis of the isothermal cure of reactive prepolymer systems, one or both of these main transitions can be determined depending on the cure

temperature and the values of  $T_{gg}$  and  $T_{g\infty}$ . If  $T < T_{gg}$ , only vitrification can be observed (type I behavior). If  $T_{gg} < T < T_{g\infty}$ , both gelation and vitrification can be observed (type II behavior). If  $T_{g\infty} < T < T_{\text{decomposition}}$ , only gelation can be observed by dynamic mechanical analysis (type III behavior). For more highly crosslinked polymers or with polymer chains more rigid than those in the DGEBA/aromatic diamine systems,  $T_{g\infty}$  or even  $T_{gg}$  can be above  $T_{\text{decomposition}}$ , and then only type I and type II, or only type I, behavior would be observed. Only type III behavior can be observed at  $T \geq$  room temperature for reactive prepolymer systems with very flexible chains and low ultimate density of crosslinks if  $T_{g\infty}$  is less than room temperature. It may well be that other types of transitions occur as a result of changes in polymer chain structure during network formation by chemical reactions in reactive systems.

### Dynamic Mechanical Analysis of Cure Kinetics

The results of dynamic mechanical monitoring of the isothermal cure of stoichiometric mixtures of the epoxy/aromatic diamines were used to determine kinetic parameters of the reactions. It is known that the uncatalyzed reaction of a primary amine with an epoxide usually affords a secondary amine, which reacts with another epoxy group to form a tertiary amine, and that the reactions are autocatalyzed by hydroxyl groups which are formed in the reactions



The elemental reactions occur sequentially for aromatic amines, and so the network forms essentially by crosslinking of linear macromolecules.<sup>11</sup> Overall activation energies for cure of aliphatic and aromatic amines/epoxy systems lie in the range of 8–16 kcal/mole. The elementary reactions for aliphatic amine/epoxy systems are considered<sup>14</sup> to be third order (one each in epoxy, amine, and hydroxyl concentration). Internal consistency appears to be obtained for the results of this present paper by taking the overall reactions to be third order in concentration of epoxy group.

If a physical property of a reactive system is changing in direct proportion to the extent of reaction, it can be used as a kinetic parameter. In principle, three characteristics of reactive polymer systems undergoing crosslinking reactions can be used as kinetic terms in isothermal dynamic mechanical analysis—gel point, modulus, and glass transition temperature of the systems.

In any system in the process of forming a three-dimensional polymer network, the extent of reaction at the gel point is an intrinsic property of

the system and is not a function of the experimental conditions. The extent of reaction

$$\alpha = (C_0 - C_t)/C_0$$

where  $C_0$  = concentration of reactive groups at the reference state corresponding to time =  $t_0$ , and  $C_t$  = concentration of the groups at time ( $t - t_0$ ) from the reference state. At the gel point, the extent of reaction from the beginning of the reaction of a system containing tetrafunctional groups of equal reactivity on branching units is about 0.33, according to the theory<sup>17</sup> for step-growth polymerization. Even if there is some deviation from the theory due to a nonstep-growth mechanism, intramolecular reactions, and unequal reactivity of functional groups, it is considered that the gel point occurs at a constant extent of reaction for a given system, which is independent of temperature. (The conversion at the gel point for the DGEBA/DDM and DGEBA/mPDA systems is reported to be greater than 55%<sup>11</sup> and 67%<sup>16</sup> respectively.) On this basis, gelation time,  $t_g$ , can be used as a kinetic parameter.

The second property which can be used as a kinetic parameter is the modulus in the rubbery state after the gel point. It has been shown that the equation of rubber elasticity can be applied to epoxy/diamine networks in the rubbery state<sup>10,12,13</sup> where the elastic modulus is directly proportional to the density of crosslinks at constant temperature ( $T$ , °K):

$$G = \phi nRT$$

where  $G$  = elastic modulus of elasticity,  $\phi$  = front factor,  $n$  = density of crosslinks, and  $R$  = gas constant. (A correction term for chain ends becomes negligible when crosslinking involves branching from essentially linear molecules<sup>12</sup> and has therefore not been included.)

In using the torsional pendulum, the elastic modulus of elasticity of a homogeneous specimen,  $G$ , is related to the natural period,  $P$ , of the freely oscillating system by the expression

$$G \approx (8\pi IL/r^4) \frac{1}{P^2} = K \frac{1}{P^2}$$

where  $K$  is a geometric factor which incorporates dimensional terms ( $r$  = radius,  $L$  = length) of the specimen and the moment of inertia ( $I$ ) of the oscillating system.

If the geometry factor is constant during the cure (epoxy systems usually shrink little after gelation), the modulus is directly proportional to the relative rigidity ( $1/P^2$ ) which can therefore be used as a kinetic parameter.

The composite structure of the specimens in the TBA technique would appear to complicate matters. However, to a first approximation, the modulus of elasticity of a unidirectional glass fiber/polymer matrix composite with good adhesion between fibers and matrix (as in the case of epoxy systems) obeys the rule of mixtures, and therefore

$$G_c = \frac{1}{V_f/G_f + V_m/G_m}$$

where  $G_c$ ,  $G_f$ ,  $G_m$  = transverse shear modulus of composite, fiber, and matrix, and  $V_f$ ,  $V_m$  = volume fraction of fiber and matrix, respectively.<sup>18</sup> At constant temperature,  $G_f$ ,  $V_f$ ,  $V_m$ , and even the influence of surface forces on the interface layer structure (which usually cause deviations from the rule) are constant, and therefore changes which occur in the modulus of the composite specimen on cure are determined only by changes in modulus of the polymer phase. Since the modulus of the rubbery matrix is much less than that of the inorganic glass,  $V_f/G_f$  is small in comparison with  $V_m/G_m$  and the increase in modulus of the composite specimen is directly proportional to the increase in the crosslink density of the matrix. Glass fibers in a specimen change only the absolute value of the modulus, and kinetic analyses can be performed using relative changes in the modulus.

A third property which can be used to monitor curing reactions is the glass transition temperature,  $T_g(t)$ . It has been shown experimentally and theoretically that the glass transition temperature can increase in direct proportion with crosslink density.<sup>12,14,19-21</sup>

At cure temperatures below  $T_{g0}$ , none of these three kinetic terms can be used in dynamic mechanical analysis of cure processes because it is not possible to determine the gel point, and an increase in modulus and  $T_g$  before the gel point is not directly proportional to the extent of reaction.

In the second region of cure temperature ( $T_{g0} < T < T_{g\infty}$ ), all three parameters can be used as kinetic terms.

The values of gelation time,  $t_g$ , which characterize the rate of cure before gelation, and the values of the overall activation energy,  $E$ , of these curing reactions, determined by plotting  $\log t_g$  versus  $1/T$  ( $^{\circ}\text{K}$ ) (Fig. 6), are summarized in Table III. The values of activation energy are approximately the same for all the epoxy/diamine systems studied, which indicates that the overall mechanisms are the same. The values do not deviate much from results obtained by other techniques.

Assuming that the isothermal relative rigidity is directly proportional to the crosslink density after the gel point in the rubbery state of the reactive systems, the extent of cure reactions from the gel point can be calculated for the temperature region  $T_{g0} < T < T_{g\infty}$  by using the equation

$$\alpha' = \frac{(1/P^2)_t - (1/P^2)_0}{(1/P^2)_\infty - (1/P^2)_0}$$

where  $\alpha'$  defines the extent of reaction from the gel point,  $(1/P^2)_t$  = relative rigidity of the specimen at time  $(t - t_g)$  from the gel point,  $(1/P^2)_0$  = relative rigidity of the specimen at the gel point, and  $(1/P^2)_\infty$  = relative rigidity of the ultimately cured specimen in the rubbery state. Then, if the reactions of the DGEBA/diamine systems obey overall third-order kinetics, the apparent overall rate constants ( $k'$ ) of the cures can be determined from the slopes of the plots of  $1/(1 - \alpha')^2$  versus  $(t - t_g)$ . The overall energy of activation for each system can be determined by plotting  $\log k'$  versus  $1/T$  ( $^{\circ}\text{K}$ ).

TABLE III  
Gelation Times and Overall Activation Energies of the Epoxy/Diamine Reactions for  $T_{60} < T < T_{\infty}$

Reactive system	Gelation time $t_g$ , min							$E$ , kcal/mole	
	80°C	100°C	120°C	140°C	150°C	160°C	180°C		200°C
DGEBA/mPDA	55	30	13	6					11
DGEBA/DDM			12	8	6	4			9
DGEBA/DDS				85		50	25	16	11
DGEBA/Benzidine			18	7		5	3		11

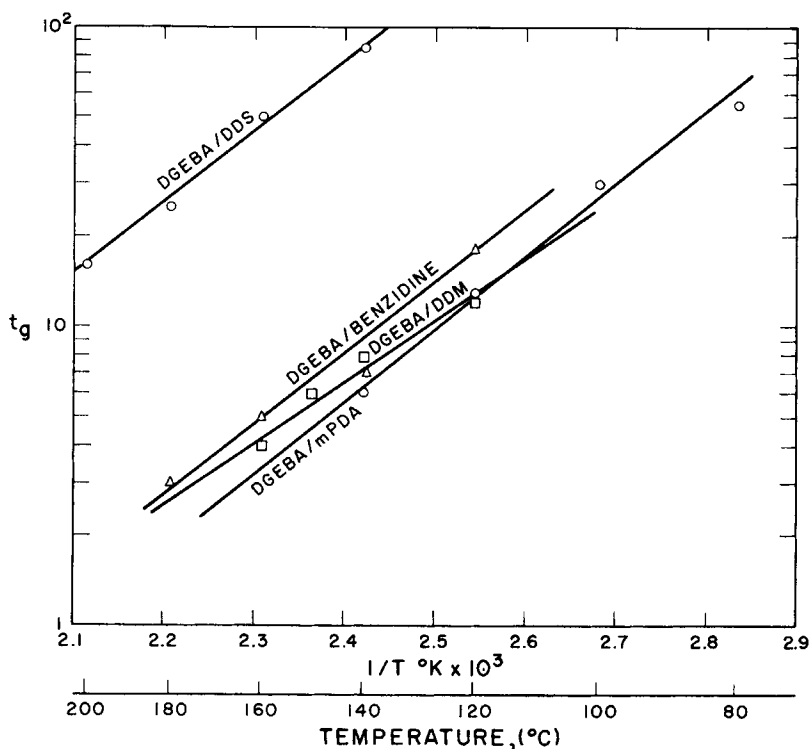


Fig. 6. Arrhenius plots.  $\text{Log}(t_g)$  vs.  $1/T$  ( $^\circ\text{K}$ ) for the epoxy/diamine reactions ( $T > T_{99}$ ).

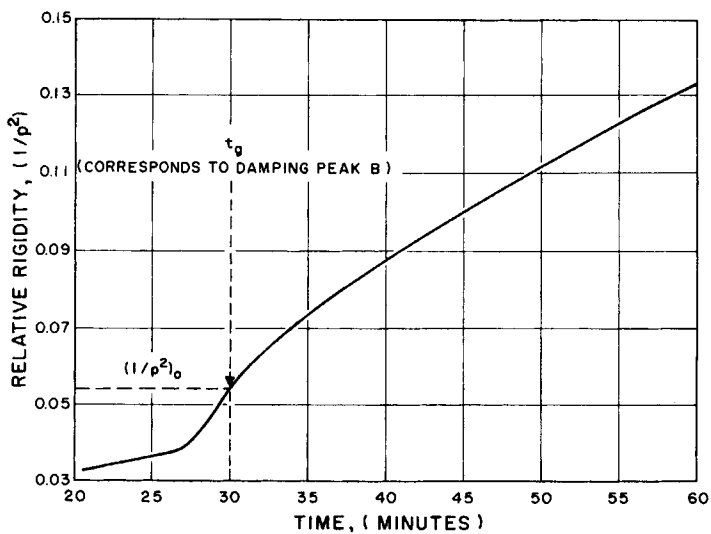


Fig. 7. Relative rigidity vs. time for the diglycidyl ether of bisphenol A/*m*-phenylenediamine reaction at  $100^\circ\text{C}$  (i.e.,  $T > T_{99}$ ).

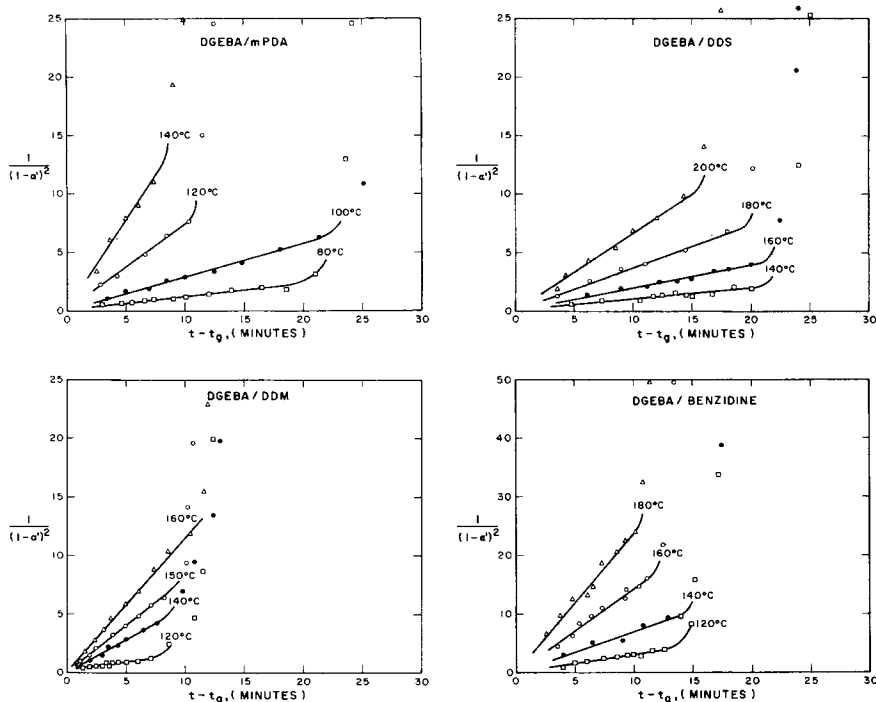


Fig. 8. Plots of  $1/(1 - \alpha')^2$  vs.  $(t - t_g)$  for the epoxy/diamine reactions in the second temperature region ( $T_{gg} < T < T_{g\infty}$ ).

Experimentally,  $(1/P^2)_0$  and  $(1/P^2)_t$  could be determined from the experimental curves of  $1/P^2$  versus time. As an example, the rigidity curve for the DGEBA/mPDA system at 100°C is presented in Figure 7. There,  $(1/P^2)_0$  corresponds to the gel point (peak B) and  $(1/P^2)_t$  to any point on the curve at  $(t - t_g)$  time after the gel point.  $(1/P^2)_\infty$  was determined after curing the same specimen at about 30°C above  $T_{g\infty}$  for 5 hr (see Table II) and extrapolating the values of the rubbery-state relative rigidity from above  $T_{g\infty}$  to the temperature  $T$ . Plots of  $1/(1 - \alpha')^2$  versus  $(t - t_g)$  for the epoxy/diamine systems at temperatures between  $T_{gg}$  and  $T_{g\infty}$  are displayed in Figure 8. The plots are linear only in the initial stages of the cure after the gel point. Sharp increases and deviation from linearity at later stages may be explained by the influence of vitrification.

The slope of the linear region of the plot  $1/(1 - \alpha')^2$  versus  $(t - t_g)$  gives the overall apparent rate constant  $k'$  of the cure after the gel point, and the slope of the plot  $\log k'$  versus  $1/T(^{\circ}\text{K})$  provides the overall activation energy of the reactions (Table IV, Fig. 9). These activation energies, when compared with the results obtained from gelation times (Table III), show that in the absence of vitrification the overall mechanism of the cure reaction after the gel point is apparently the same as before the gel point.

In applying TBA, it is experimentally difficult to use  $T_g$  as a kinetic parameter immediately after the gel point for the DGEBA/aromatic

TABLE IV  
Overall Apparent Rate Constants and Overall Activation Energies of the Epoxy/Diamine Reactions After Gelation for  
 $T_{gg} < T < T_{g\infty}$  and  $T_{g\infty} < T < T_{decomposition}$

Reactive system	Rate constant $k'$ after gel point, $\text{sec}^{-1} \times 10^3$										$E$ , kcal/mole
	80°C	100°C	120°C	140°C	150°C	160°C	180°C	200°C	220°C		
DGEBA/mPDA	0.9	2.4	6.0	13.3			41.0				11.8
DGEBA/DDM			1.9	4.6	6.6	8.8			42.0		12.2
DGEBA/DDS				0.9		1.7	3.0	5.6	11.0		11.6
DGEBA/Benzidine			2.8	5.8		12.0	23.0		48.0		12.4



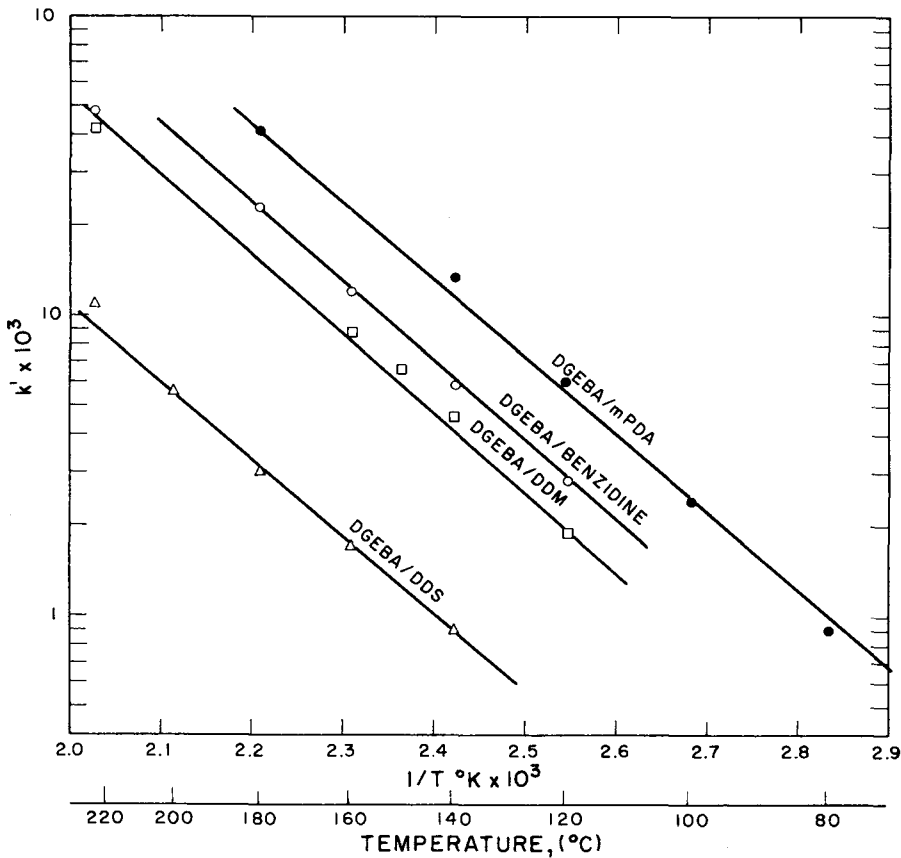


Fig. 9. Arrhenius plots.  $\text{Log}(k')$  vs.  $1/T$  ( $^{\circ}\text{K}$ ) for the epoxy/diamine reactions ( $T_{\infty} < T$ ).

diamine systems owing to the high rates of the cure reactions which do not permit the measurement of  $T_g$  (by TBA) without changing it. The  $T_g$  value can be conveniently measured by TBA and used as a kinetic term after the onset of vitrification. It was determined while heating the specimen, which had been cured for a known time, from its cure temperature  $T$  through its glass transition at the heating rate of  $3^{\circ}\text{C}/\text{min}$ . For another time of cure, another specimen was used. A measure of the extent of reaction from the occurrence of damping peak A can be calculated as follows:

$$\alpha'' = \frac{T_g(t) - T}{T_{g\infty} - T}$$

where  $T_g(t)$  = glass transition temperature at time  $(t - t_A)$  from damping peak A. In this case, the reference point is damping peak A and  $\alpha''$  defines the extent of the cure reactions after vitrification and was used for determining the kinetic parameters. The curves  $\alpha''$  versus  $(t - t_A)$  are shown in Figure 10 for two of the epoxy systems (with mPDA and DDM). The plots  $1/(1 - \alpha'')^2$  versus  $(t - t_A)$  are linear (Fig. 11) in the early stages,

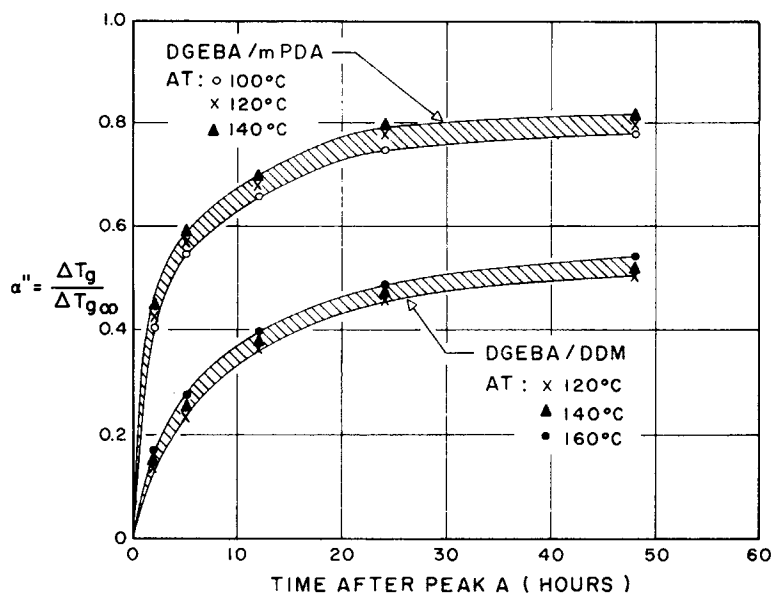


Fig. 10. Extent of reaction  $\alpha''$  vs. time from peak A for two epoxy/diamine reactions ( $T_{g0} < T < T_{g\infty}$ ).

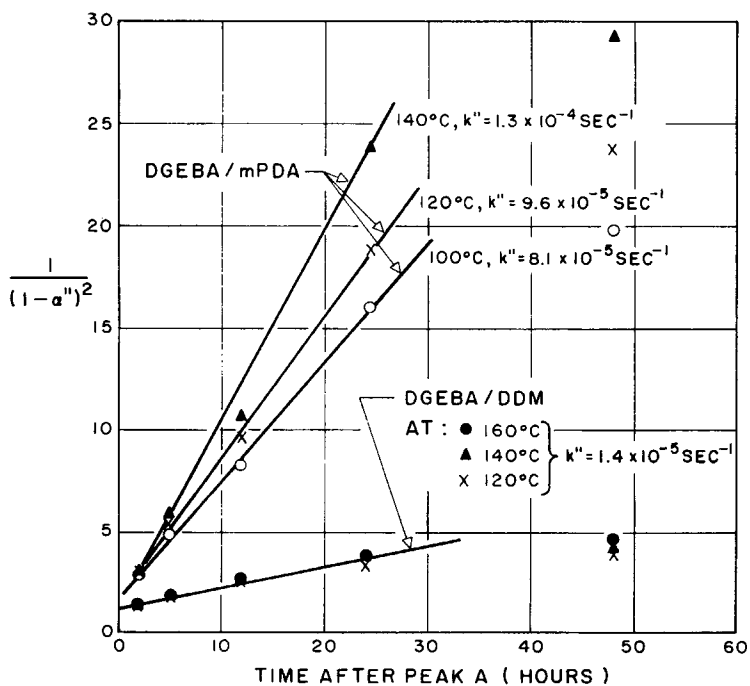


Fig. 11. Plots of  $1/(1 - \alpha'')^2$  vs. time from peak A for two epoxy/diamine reactions ( $T_{g0} < T < T_{g\infty}$ ).

and the apparent overall rate constants  $k''$  (Fig. 11) are much smaller than in the rubbery state (Table IV). Deviations from linearity at higher conversions may be attributed to decreases in reaction rates due to the increasing glassy character of the polymers on prolonged cure below  $T_{g\infty}$ .

All three kinetic terms (gel time, relative rigidity, and  $T_g$ ) can also in principle be used in the third cure temperature region ( $T_{g\infty} < T < T_{\text{decomposition}}$ ). However, in the case of applying TBA to the DGEBA/aromatic diamine systems, the gelation times are too short to be determined and  $T_g(t)$  is changing too rapidly during the cures to be determined properly. At later stages of the cures, when the processes become sterically hindered or diffusion controlled,  $T_g(t)$  may well be useful for analysis of the kinetics of crosslinking. The relative rigidity is a convenient

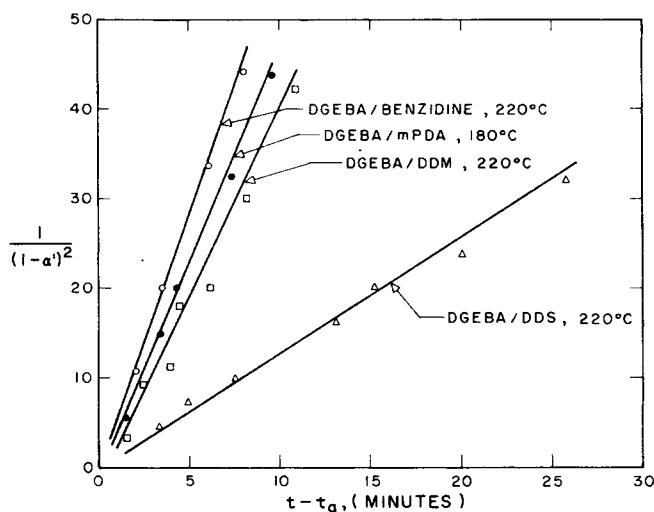


Fig. 12. Plots of  $1/(1 - \alpha')^2$  vs.  $(t - t_g)$  for the epoxy/diamine reactions in the third temperature region ( $T > T_{g\infty}$ ).

kinetic term for the range  $T_{g\infty} < T < T_{\text{decomposition}}$ . The extent of reaction can be calculated as in the case of  $T_{g0} < T < T_{g\infty}$ , and the plots  $1/(1 - \alpha')^2$  versus  $(t - t_g)$  are straight lines (Fig. 12) the slopes of which provide  $k'$  (Table IV). The latter values of  $k'$  lie on the plots  $\log k'$  versus  $1/T(^{\circ}\text{K})$  for the initial stage of the cure reactions after the gel point in the region  $T_{g0} < T < T_{g\infty}$  (Fig. 9).

The influence of the structure of aromatic diamines on the kinetics of the epoxy cure in the liquid and rubbery states is determined mainly by the chemical reactivity of the  $\text{NH}_2$  groups and by the length, flexibility and geometry of the segments between these groups. The length, flexibility and geometry of the diamine segments determine the transition temperatures ( $T_{g0}$ ,  $T_g$ ,  $T_{g\infty}$ ) of the reactive systems during their cure and therefore the type (I, II, or III) of dynamic mechanical behavior in isothermal cure.

### Appendix

#### Interrelating the Time to Gel ( $t_g$ ), the Various Definitions of Extent of Reaction ( $\alpha, \alpha', \alpha''$ ), the Various Overall Rate Constants ( $k, k', k''$ ) and the Overall Activation Energy ( $E$ )

For an  $n$ th order reaction,

$$-\frac{dX}{dt} = kX^n$$

where  $X$  is the concentration of reacting groups and  $k$  is the overall rate constant,

$$-\frac{dX}{X^n} = kdt. \quad (I)$$

Integrating, we obtain

$$1/(n-1) \left[ \frac{1}{X^{n-1}} \right]_{X_0}^X = k[t]_{t_0}^t.$$

[Special cases:

If  $n = 0$ ,

$$[X]_{X_0}^{X_0} = k[t]_{t_0}^t \quad (Ia)$$

If  $n = 1$ ,

$$[\ln X]_{X_0}^{X_0} = k[t]_{t_0}^t \quad (Ib)]$$

i.e.,

$$\frac{1}{X^{n-1}} - \frac{1}{X_0^{n-1}} = (n-1)k(t-t_0). \quad (Ic)$$

The order of the reaction is found by finding the value of  $n$  which empirically gives a linear relationship between  $1/X^{n-1}$  and  $(t-t_0)$ .

The overall rate constant,  $k$ , can be obtained from the slopes of the lines defined by eqs. (Ia), (Ib), and (Ic), using any reference point in the reaction defined by  $X_0$  and  $t_0$ .

The activation energy is determined from the Arrhenius relationship ( $k = \text{constant} \times e^{-E/RT}$ ) by determining the slope of the plot of  $\ln k$  versus  $1/T$  ( $^{\circ}\text{K}$ ).

#### Determination<sup>22</sup> of the Activation Energy from the Time to Gel, $t_g$

The chemical conversion ( $X_0 - X_g$ ) at the gel point is a constant for a given system;  $\therefore$  from eq. (I),

$$\begin{aligned} \int_{X_0}^{X_g} \frac{dX}{X^n} &= \text{a constant, where } X_0 \text{ in this case is the initial value of } X \text{ at } t_0 = 0 \\ &= kt_g \\ t_g &= \text{a constant} \times 1/k. \end{aligned}$$

The activation energy is therefore determined from the Arrhenius relationship by determining the slope of the plot of  $\ln t_g$  versus  $1/T$  ( $^{\circ}\text{K}$ ).

### Determination of the Various Overall Rate Constants ( $k$ , $k'$ , $k''$ ) from Extent of Reaction ( $\alpha$ , $\alpha'$ , $\alpha''$ )

If  $\alpha$  is the extent of reaction, from reference  $X = X_0$  at  $t = t_0$ ,

$$\alpha = \frac{X - X_0}{X_\infty - X_0}$$

$$1 - \alpha = 1 - \frac{X - X_0}{X_\infty - X_0} = \frac{X_\infty - X}{X_\infty - X_0}$$

$$\therefore X_\infty - X = (1 - \alpha)(X_\infty - X_0)$$

$$X = X_\infty - (1 - \alpha)(X_\infty - X_0)$$

$$= X_0 - \alpha(X_0 - X_\infty)$$

$$= X_0 \left[ 1 - \alpha \left( \frac{X_0 - X_\infty}{X_0} \right) \right].$$

If  $X_\infty = 0$  (an assumption in practice when using an indirect measure of  $X$ ), then

$$X = X_0[1 - \alpha],$$

and, using eq. (Ic),

$$\frac{1}{X_0^{n-1}(1 - \alpha)^{n-1}} - \frac{1}{X_0^{n-1}} = (n - 1)k(t - t_0)$$

or

$$\frac{1}{(1 - \alpha)^{n-1}} = X_0^{n-1}(n - 1)k(t - t_0) + 1 \quad (\text{II})$$

From eq. (II), a plot of  $1/(1 - \alpha)^{n-1}$  versus  $(t - t_0)$  gives  $k$ , if  $X_0$  is known.

Most often,  $X_0$  is known at the beginning ( $t_0 = 0$ ) of the reaction. When the reference state is later in the reaction,  $X_0$  is often not directly known and the obtained slope will decrease directly with the value of  $X_0^{n-1}$ . If this decrease in  $X_0$  is not taken into account in determining the rate constant, then the term *apparent* overall rate constant is used herein in order to distinguish it from  $k$ . In the present work, the apparent overall rate constants  $k'$  and  $k''$  were calculated from the experimental slopes using values of  $X_0 = 1$  and  $n - 1 = 2$ .

Furthermore, in order to relate the same process as a function of temperature, it is necessary that  $X_0$  be the same for the different isothermal experiments. When  $X_0$  corresponds to gelation, the error in the procedure of identifying the damping peak B with a specific chemical conversion appears to be small. Similarly, since the results are consistent, it appears that the error is small in assuming that damping peak A corresponds with a particular conversion (probably because the time scale of the isothermal changes is large in comparison with the error of the assumed reference point).

### Determination of Overall Activation Energy ( $E$ ) from the Extent of Reaction

As above from eq. (II),

$$\begin{aligned} \text{the slope of the plot of } 1/(1 - \alpha)^{n-1} \text{ versus } (t - t_0) &= \text{constant} \times k \\ &= \text{constant}' \times e^{-E/RT} \text{ (Arrhenius),} \end{aligned}$$

and  $\ln$  [slope of  $1/(1 - \alpha)^{n-1}$  versus  $(t - t_0)$ ] versus  $1/T$  ( $^{\circ}\text{K}$ ) provides  $E$ .

Therefore, whereas the overall rate constant  $k$  cannot be obtained without knowledge of  $X_0$ , the overall activation energy can be obtained unequivocally.

These arguments are relevant to studying kinetics of cure since, in relating a change in some physical property (e.g.,  $\Delta G$ ,  $\Delta T_g$ ) to extent of reaction, the latter is often measured from some point (usually of unknown conversion) after the start of the chemical reaction. In particular, unless the reference points are the same, or values of the conversion at the reference points are known, values of  $k$ ,  $k'$ , and  $k''$  cannot be quantitatively compared because of the decrease in  $X_0$  with increased reference time  $t_0$  (which would make  $k < k' < k''$ , other things being equal).

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