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Registry No. (propylene glycol)(tris(4-isocyanatophenyl)-thiophosphate) (copolymer), 124687-67-8.

Mechanistic Reaction Kinetics of 4,4′-Diaminodiphenyl Sulfone Cured Tetraglycidyl-4,4′-diaminodiphenylmethane Epoxy Resins[†]

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ABSTRACT: A mechanistic kinetic model of 4,4′-diaminodiphenyl sulfone cured tetraglycidyl-4,4′-diaminodiphenylmethane epoxides is developed, which accurately describes experimental data published in the literature. The model is based on an accepted reaction mechanism, which consists of three main reactions. Other efforts to quantitatively model epoxy cure generally focus on empirical rate laws, which apply only to the conditions to which they are fit. It is demonstrated that a mechanistic approach results in a model that can predict the effects of moderate variations in the resin formulation, without being cumbersome or impractical. Moreover, the mechanistic model, unlike the empirical ones, is capable of estimating the relative amounts of linkages formed during the cure reactions. These data offer some insight into the cured resin morphology, which determines the mechanical properties of the material.

Introduction

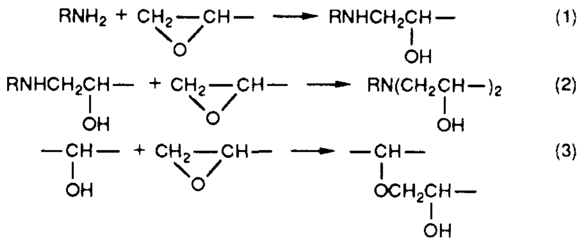
Epoxy resins based on 4,4′-diaminodiphenyl sulfone (DDS) cured tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) are currently the most commonly used matrix material for advanced fiber composites. It is desirable to understand the reaction kinetics of these epoxies for processing purposes. In this work, mechanistic rate expressions are written for the main reactions according to an accepted reaction mechanism. The resulting kinetic model is compared to published literature data.

There have been a number of experimental studies on the cure of DDS/TGDDM resins published in the literature. Most of these efforts utilize differential scanning calorimetry (DSC) to estimate overall degree of cure as the reactions proceed.[1–4] The disadvantage of this method is that the contributions of the individual reactions are not elucidated. Moreover, the method assumes implicitly that the reaction enthalpies of the important reactions are similar, which may not be true.[5] Recently, Morgan and Mones[6] performed an extensive Fourier-transform infrared (FTIR) spectroscopy analysis of DDS/TGDDM epoxies, which yielded cure data on the individual species involved.

To date, virtually all thermoset polymer kinetic models that appear in the literature are based on empirical rate laws.[1–4,7,8] These empirical rate laws have been used successfully in modeling studies.[9–15] However, there are advantages to using mechanistic kinetic models: (1) Unlike empirical models, moderate changes in the resin formulation that do not change the reaction mechanism would not require recharacterization, because the contributions of the individual chemical components are described. (2) Extrapolated behavior of the resin system outside of the envelope from which the kinetic parameters were fitted is more predictable, since the temperature dependencies of the individual reactions involved are known. With empirical models, the resin behavior is only predictable over the temperature range used to characterize it. (3) Unlike empirical models, which can only estimate relative degree of cure, mechanistic models account for individual chemical species. Thus, they offer some insight into the cured resin morphology, which determines the material mechanical properties.[6,16]

Model Development

The structures of the TGDDM and DDS monomers are shown in Figure 1. It is generally agreed that there are three main reactions that occur for amine-cured epoxies:[3,6,17,18] Reactions 1 and 2 are the primary and



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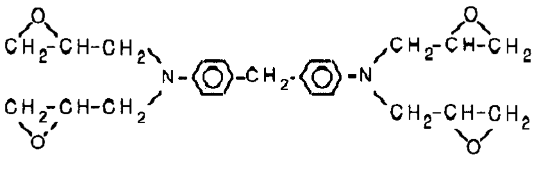
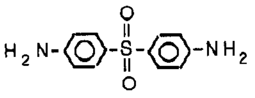


Tetraglycidyl 4,4' diaminodiphenyl methane (TGDDM)



4,4' diaminodiphenyl sulfone (DDS)

Figure 1. Structures of TGDDM and DDS monomers.

secondary amine reactions with the glycidyl ether and reaction 3 is an etherification reaction of the glycidyl ether by a pendant hydroxyl group.

Reactions 1 and 2 are also catalyzed by the presence of hydroxyl groups, which are created by the amine reactions themselves and sometimes added in the formulation as an accelerator. Water and other impurities can also contribute to this effect. Shechter et al.[17] suggest that the mechanism of this catalytic effect is via hydrogen bonding of the hydroxyl group to the oxygen of the glycidyl ether in the transition state. These autocatalytic reactions must also be included in the kinetic model.

The empirical rate law shown in eq 4, or slight variations of it, is widely used for modeling the cure of epoxies:[1,2,8,9,14]

$$d\alpha/dt = (k_a + k_b\alpha^m)(1-\alpha)^n \tag{4}$$

The variable α represents the degree of cure of the resin and ranges from zero to unity. The constants m and n are empirical power law exponents. The rate constants k are assumed to be of the Arrhenius form:

$$k = Ae^{-E_a/RT} \tag{5}$$

The constant A is the Arrhenius preexponential factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. While eq 4 has been used successfully, it is generally applicable only to the specific formulation analyzed, within the experimental temperature range.

Alternatively, a fundamental approach[18] offers more flexibility to changes in formulation, since the dependence of the reaction rates on species concentrations is described. Moreover, the Arrhenius form should hold over a wide temperature range, if the correct reaction mechanism is used. Mechanistic kinetic rate expressions may be written for reactions 1–3, assuming that they proceed as elementary steps:

$$r_1 = k_1(\mathrm{E})(\mathrm{PA}) \tag{6a}$$

$$r_1' = k_1'(\mathrm{E})(\mathrm{PA})(\mathrm{OH}) \tag{6b}$$

$$r_2 = k_2(\mathrm{E})(\mathrm{SA}) \tag{7a}$$

$$r_2' = k_2'(\mathrm{E})(\mathrm{SA})(\mathrm{OH}) \tag{7b}$$

$$r_3 = k_3(\mathrm{E})(\mathrm{OH}) \tag{8}$$

The variable r represents the reaction rate, where (E), (PA), (SA), and (OH) are defined as the concentrations of glycidyl ether (epoxide), primary amine, secondary amine, and hydroxyl containing molecules, and the rate constants k are of the Arrhenius form. Care must be taken when applying eqs 6–8 to kinetic data. They are valid only when the reactions are not occurring in the diffusion limited region; i.e., they apply when the cure temperature is above the glass transition temperature.

Table I
Arrhenius Correlations for a Commercial DDS/TGDDM Resin System[a]

	k_1'	k_2'	k_3
ln (A)	10.64	12.26	20.50
E/R, K	6622	8608	11694
r^2	0.93	0.99	0.99

[a] Rate constants fitted to 22 wt % experimental data from Mijovic et al., 1984. $k_i = Ae^{-E_i/RT}$, units of A are in molar concentrations (M) and minutes; $i = 1$, primary amine reaction; $i = 2$, secondary amine reaction; $i = 3$, etherification reaction. $k_1'/k_1 = 20.92$ from Chiao and Lyon, 1989; $k_2'/k_2 = 16.09$ from Chiao and Lyon, 1989.

Transient balance equations can be written for the reactive species, as shown below:

$$d(\mathrm{E})/dt = -(r_1 + r_1' + r_2 + r_2' + r_3) \tag{9a}$$

$$d(\mathrm{PA})/dt = -(r_1 + r_1') \tag{9b}$$

$$d(\mathrm{SA})/dt = -(r_2 + r_2') \tag{9c}$$

$$d(\mathrm{OH})/dt = r_1 + r_1' + r_2 + r_2' \tag{9d}$$

Equation 9d can be eliminated by a species balance on the hydroxyl containing molecules. Assuming that there are no secondary amines present initially

$$(\mathrm{OH}) = (\mathrm{OH})_0 + 2[(\mathrm{PA})_0 - (\mathrm{PA})] - (\mathrm{SA}) \tag{10}$$

Balances can also be written to describe the tertiary amine (TA) and ether linkage (ET) concentrations:

$$(\mathrm{TA}) = (\mathrm{TA})_0 + (\mathrm{PA})_0 - (\mathrm{PA}) - (\mathrm{SA}) \tag{11}$$

$$(\mathrm{ET}) = (\mathrm{ET})_0 + [(\mathrm{E})_0 - (\mathrm{E})] - 2[(\mathrm{PA})_0 + (\mathrm{PA})] + (\mathrm{SA}) \tag{12}$$

The subscript "0" denotes an initial value. Equations 9a–c and 10 can be easily solved numerically, with the initial concentrations of the reactive species.

Previous work[18] using published experimental data[17] suggests that the ratios of the hydroxyl-catalyzed to the uncatalyzed rate constants for reactions 1 and 2, given in Table I, may be treated as invariant. Thus, determination of k_1 and k_2 gives the values of k_1' and k_2' as well. Therefore, the kinetic model contains three independent rate constants.

Analysis of 177 °C FTIR Cure Data

Recently, Morgan and Mones[6] conducted a detailed FTIR analysis of the chemistry of TGDDM cure and degradation reactions, including the effects of DDS and $BF_3:NH_2C_2H_5$ catalyst concentrations. Since they report concentration data on all relevant species during reaction, the kinetic model was first evaluated by using their data.

Isothermal cure data at 177 °C were used in fitting the rate constants. The formulation analyzed consisted of 25 wt % DDS, 0.4 wt % $BF_3:NH_2C_2H_5$ catalyst, with the balance being a commercial TGDDM. In this analysis, the effects of the impurities and the 0.4 wt % catalyst are incorporated direcly into the rate constants. Unfortunately, there was not sufficient isothermal data available to investigate the effects of changing the catalyst concentration. The calculated rate constants appear in Table II, and the model fit can be seen in Figure 2. The relative magnitudes of the rate constants are consistent with observations by other workers, who claim

Table II
Comparison of Rate Constants at 177 °C

	fitted to commercial DDS/TGDDM/BF_3 cure data[a]	calcd from Arrhenius correlations[b]
k_1', M^{-2} min^{-1}	1.12×10^{-2}	1.71×10^{-2}
k_2', M^{-2} min^{-1}	4.74×10^{-4}	1.05×10^{-3}
k_3, M^{-1} min^{-1}	5.98×10^{-3}	4.17×10^{-3}

[a] From ref 6. [b] Which were fitted to commercial cure data from ref 1.

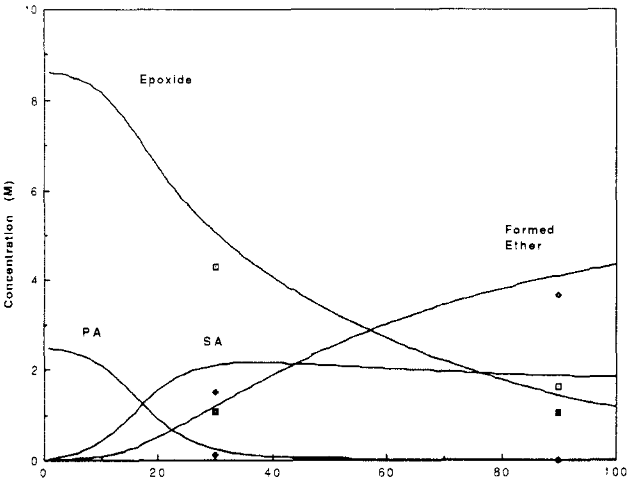


Figure 2. Kinetic model fit to the isothermal (177 °C) cure data of a commercial 25 wt % DDs/TGDDM, 0.4 wt % BF_3:$NH_2C_2H_5$ catalyst resin. Experimental data from ref 6.

that the primary amine reaction is generally 1 order of magnitude faster than the secondary amine and etherification reactions.[3,6,18,19]

Only data to 90 min of cure were used in the above analysis, since Morgan and Mones[6] state that the reactions becomes hindered after this point. Glass transition measurements on a TGDDM/DDS resin[20] show that at approximately 85–90% cure, the glass transition temperature reaches the cure temperature used, 177 °C. This causes the cure process to become limited by diffusion. By use of the kinetic model, it was calculated that 83% cure results from a 90-min cure at 177 °C.

The rate constants form a unique set, because the individual species concentrations were used in their calculation. That is, no other combination of k_1, k_2, and k_3 can correctly describe the data. This fact lends physical credibility to their values. On the other hand, if only epoxide consumption data had been used (e.g., degree of cure data from DSC analysis), it is possible that more than one set of rate constants would describe the data. If this were the case, then the constants could be mere mathematical artifacts, with no physical basis.

Analysis of DSC Cure Data

Mijovic et al.[1] performed an experimental DSC study of a commercial DDS/TGDDM epoxy used for prepreg applications. The published DSC data are presented as isothermal degree of cure versus time curves. This requires the assumption that the enthalpy of reaction is the same for all relevant reactions, which is reasonable as a first approximation. Three DDS/TGDDM formulations were studied (19, 22, 27 wt % DDS), which corresponds to amine hydrogen/epoxide ratios of 0.44, 0.54, and 0.71. Data were obtained over 185–215 °C in 5 °C increments.

In their analysis, Mijovic et al.[1] fit eq 4, the empirical rate law, to the data. This yielded a rate law that was usable, but only for the specific formulations analyzed, and within the studied temperature range. Significant deviations from the Arrhenius form were observed. Changing the formulation ratio from 0.44 to 0.71 caused the preexponential factor for k_a and k_b to change by 4 and 2 orders of magnitude, respectively, with changes in activation energies of 25% and 50%. Moreover, the fitted power law exponents were found to be both temperature and formulation dependent. Because eq 4 is empirical, none of these parameter changes can be determined a priori. Thus, each new formulation would have to be recharacterized. The work required to repeat the characterization for every change could quickly become tiresome, if not impractical.

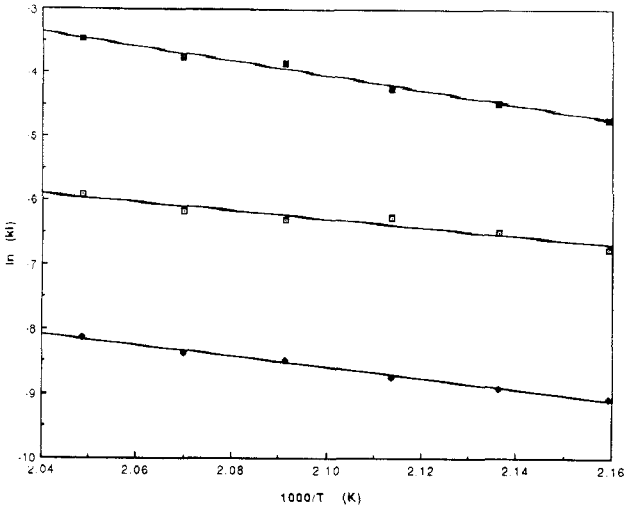


Figure 3. Arrhenius plots for a 22 wt % commercial DDS/TGDDM resin: ⊡, k_1; ◆, k_2; ◘, k_3. Rate constants fitted to experimental data from ref 1.

The mechanistic model offers more flexibility. However, as discussed in the previous section, the calculation of rate constants for these data is more difficult, since only degree of cure is presented. Fortunately, the rate constants determined previously from the FTIR data[6] (at 177 °C) can be used as the initial values in the present analysis. This set the initial relative magnitudes of the constants and allowed convergence to the correct solutions for the 22 wt %, 190 °C data. These rate constants were then used as the initial values to determine those for the 195 °C data. This process was performed successively, for each isothermal curve of the 22 wt % DDS resin. Excellent Arrhenius correlations resulted, as shown in Figure 3. By use of the Arrhenius parameters (Table I), the model was compared to the experimental data (Figure 4). As can be seen, there is good agreement. The calculated activation energies and preexponential factors are physically reasonable and consistent with previous work.[18]

The parameters listed in Table I were used to calculate rate constants for 177 °C. These constants appear in Table II, which shows a comparison for the constants fitted to the DSC data[1] and the FTIR data.[6] The constants for the two different systems are comparable and follow the observations that the primary amine reactions are an order of magnitude faster than the secondary amine and etherification reactions during the first part of the cure.[3,6,18,19] That the differences between the two sets of constants are small is surprising, since Morgan and Mones[6] found that even a small amount of BF_3:$NH_2C_2H_5$ catalyst significantly accelerates the reactions. However, examination of the cure data shows that the uncatalyzed resin formulations used by Mijovic et

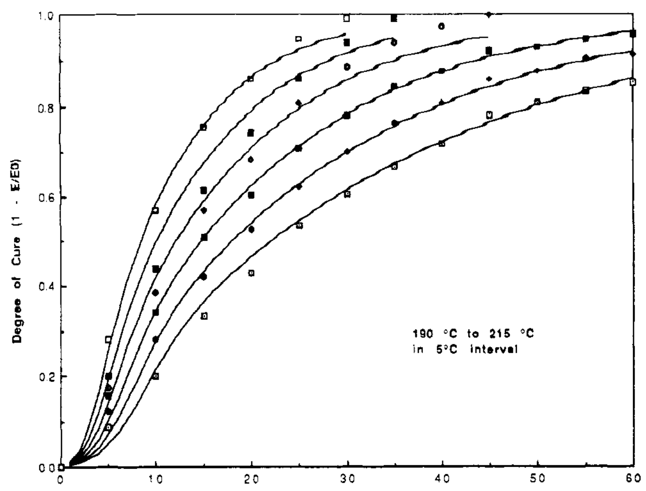


Figure 4. Kinetic model comparison to isothermal cure data of a 22 wt % commercial DDS/TGDDM resin. Rate constants calculated from Arrhenius parameters. Experimental data from ref 1.

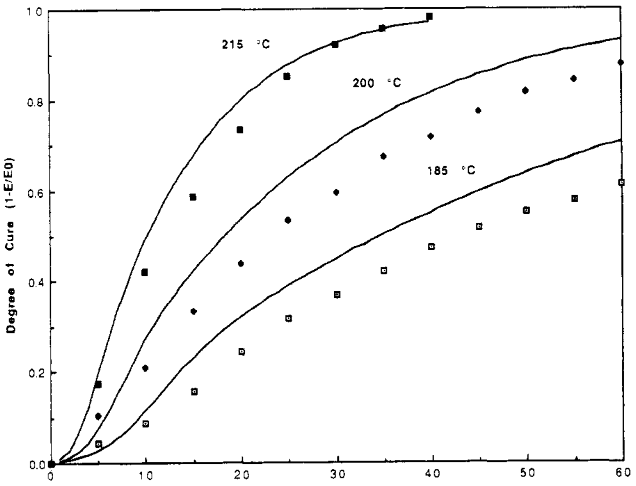


Figure 5. Kinetic model comparison to isothermal cure data of a 19 wt % commercial DDS/TGDDM resin. Rate constants calculated from Arrhenius parameters. Experimental data from ref 1.

al.[1] cured with similar reaction rates as the catalyzed formulation of Morgan and Mones,[6] no errors were made in fitting the constants. A possible explanation of these results is that the commerical TGDDM used by Mijovic et al.[1] was different enough (e.g., impurities, etc.) from that used by Morgan and Mones[6] that the effect of the catalyst in the latter formulation was compensated for.

Other studies[3,18] show evidence that the etherification reaction is insignificant at low temperatures, becoming important only above 150 °C. To investigate this assertion with the kinetic model, the Arrhenius parameters were used to calculate rate constants at 150 °C. These values, shown in Table III, support these claims. The etherification reaction rate constants is larger than that for the catalyzed secondary amine reaction but is still an order of magnitude smaller than that for the catalyzed primary amine reaction, as expected.[6]

One of the advantages to using a mechanistic kinetic model is that the effects of the individual species are described. Thus, in principle, reaction profiles after moderate formulation changes should be predictable a priori. That is, the rate constants should be invariant, as long as the same reaction mechanism applies. The kinetic model, with rate constants calculated for the 22 wt % DDS data, was compared to the 19 and 27 wt % data (Figures 5 and 6). Good general agreement was observed. These results were obtained without adjusting any kinetic parameters for the formulation changes.

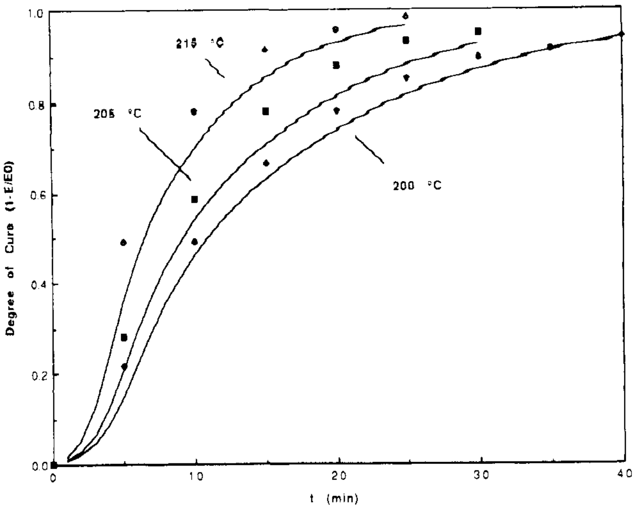


Figure 6. Kinetic model comparison to isothermal cure data of a 27 wt % commercial DDS/TGDDM resin. Rate constants calculated from Arrhenius parameters. Experimental data from ref 1.

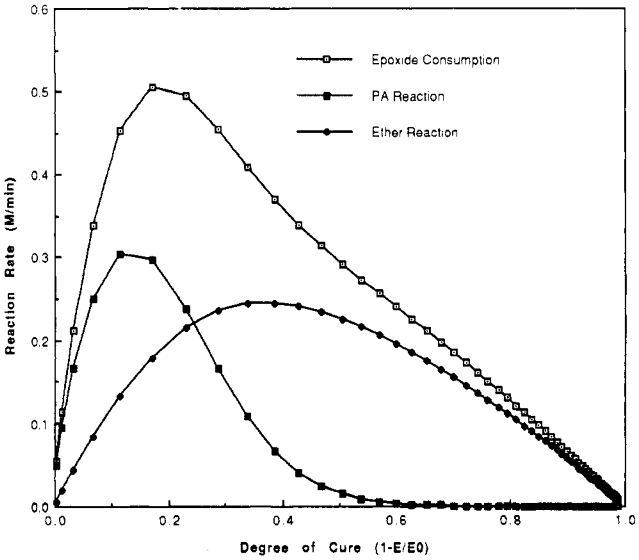


Figure 7. Reaction rate versus degree of cure for epoxide consumption, primary amine consumption, and ether linkage formation at 210 °C, as predicted by the kinetic model. The resin is a 19 wt % commercial DDS/TGDDM formulation. Note the "second exotherm" in the epoxide curve (due to ether reaction), which begins at 40% cure, as observed experimentally by Mijovic et al.[1]

In their work, Mijovic et al.[1] presented experimental reaction rate versus degree of cure data. They observed a second exotherm at approximately 40% cure and attributed it to a change in cure chemistry upon completion of the primary amine reaction. They also showed that the empirical rate law (eq 4) was unable to describe this phenomenon. Rate data for epoxide consumption, primary amine reaction, and etherification were calculated by using the kinetic model. These results, which appear in Figure 7, show evidence that the etherification reaction is the cause of the second exotherm. This appears as an inflection in the epoxide consumption curve at approximately 40% cure.

Another feature of the mechanistic model is its ability to estimate the concentrations of the different linkages

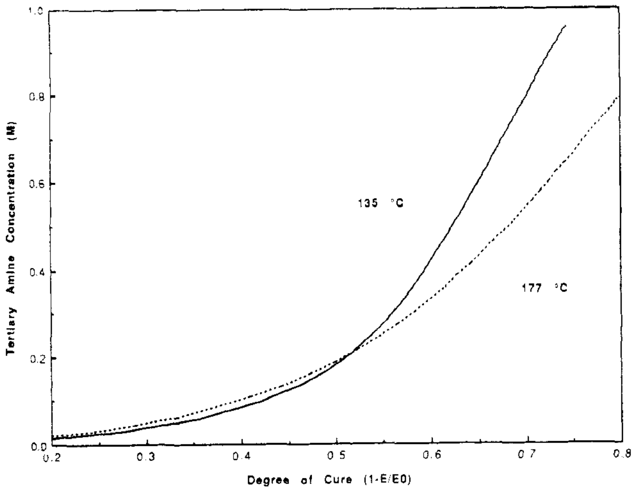


Figure 8. Effect of cure temperature on tertiary amine formation, as predicted by the kinetic model. The resin is a stoichiometric (34 wt %) commercial DDS/TGDDM formulation.

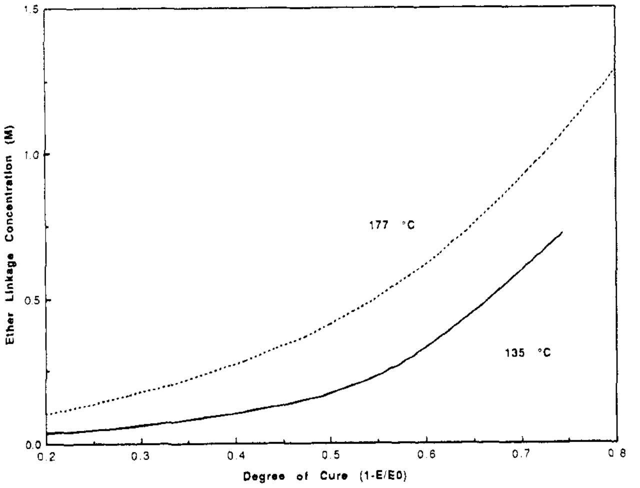


Figure 9. Effect of cure temperature on ether linkage formation, as predicted by the kinetic model. The resin is a stoichiometric (34 wt %) commercial DDS/TGDDM formulation.

Table III
Calculated Rate Constants at 150 °C

	calcd from Arrhenius correlations[a]
k_1', M^{-2} min^{-1}	6.71×10^{-3}
k_2', M^{-2} min^{-1}	3.09×10^{-4}
k_3, M^{-1} min^{-1}	7.95×10^{-4}

[a] Which were fitted to commercial DDS/TGDDM cure data from

formed. While these data are insufficient to differentiate between chain extensions and cross-links, they provide some insight into the resin morphology, which determines the material mechanical properties.[6,16] The cure conditions can alter the distribution of these linkages. Figures 8 and 9 show the differences in tertiary amine and ether linkages as a function of the degree of cure, as calculated by the model, for 135 and 177 °C. The relative amounts of the species are controllable, to a degree, by proper selection of the cure conditions.

Conclusions

In this work, fundamental kinetic rate expressions were written according to an accepted reaction mechanism for 4,4'-diaminodiphenyl sulfone cured tetraglycidyl-4,4'-diaminodiphenylmethane epoxy resins. The resulting kinetic model was applied to different formulations of DDS/TGDDM. Good agreement with experimental data was found over the temperature range 185–215 °C, and the rate constants were found to follow closely the Arrhenius form, with reasonable preexponential factors and activation energies. The relative values of the calculated rate constants were compared to observations published in the literature and found to be consistent: (1) The primary amine reaction is an order of magnitude faster than the others during the first phase of cure. (2) The etherification reaction becomes important above 150 °C.

The mechanistic model was shown to be more powerful than empirical rate laws: The fundamental kinetics correctly describe the effects of formulation ratio changes of epoxy/curing agent, without adjusting any kinetic parameters. Empirical rate laws have been shown to require recharacterization of new formulations to determine the appropriate parameters. Also, since the mechanistic model accounts for the individual species concentrations, it provides some insight into the cured resin morphology, which determines the material mechanical properties.

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Registry No. TGDDM, 28768-32-3; DDS, 80-08-0.