Kinetic Approach for Epoxy Resins Cured with Diaminodiphenyl Sulfone Under Non-isothermal Conditions

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ABSTRACT: The curing reactions of epoxy resin basing on diglycidyl ether bisphenol A (DGEBA) with 4,4′-diaminodiphenyl sulfone (DDS) were investigated with a differential scanning calorimeter and gel permeation chromatography. Based on the generating function method and the Monte Carlo simulation procedure, kinetic models for both isothermal and nonisothermal curing conditions were proposed. The apparent activation energy of curing reactions was found to be 14.9 Kcal/mol by the thermal analysis. According to our kinetic models, gel points, the profiles of epoxy conversion, and the molecular weights of polymers were calculated. Good agreement is obtained between the model predictions and experimental data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 721–728, 1999

Key words: epoxy; kinetics; molecular weight; nonisothermal condition

INTRODUCTION

Many researchers have developed various methods to analyze the network formation of epoxy resins cured with amines by various combined models, kinetic theory, and statistical model under isothermal conditions.[1–8] Because the kinetic method directly accounts for the history of network formation, we have developed the following 2 generalized kinetic methods: the generating function method and the Monte Carlo simulation procedure.[9–11]

By the first method, the infinite rate equations of curing system can be transformed into finite ordinary differential equations (ODE) for moments by a generating function. Then this set of equations can be solved by numerical methods, and the average molecular weight of polymers, which changed with reaction time, and the gel time of the systems can be analyzed by this generalized kinetic method.[9,10] On the other hand, the strategy of the Monte Carlo simulation is divided into 2 steps, as follows: selecting the type of the reaction mechanism, then choosing the reacting molecules. Upon reaction, 2 smaller molecules become a larger one, or a cyclization forms. This makes the simulation possible to be accomplished in a reasonable computer time, and the changes of the structure, such as molecular weight distribution of polymers, and gel fraction can be calculated.[11] These generalized kinetic models have been successfully used to simulate the complicated systems, such as nonlinear polymerization with multistage process, and epoxy resins cured with mixed amines under isothermal conditions in our previous work.[9–11]

Because most of the industrial curing processes are under nonisothermal conditions, in this work, we extended the kinetic methods, both the generating function method and the Monte Carlo simulation, to the nonisothermal system and applied these methods to the curing system of epoxy resins based

on diglycidyl ether bisphenol A (DGEBA) with 4,4′-diaminodiphenyl sulfone (DDS). The conversion profiles and average molecular weight of polymers calculated were compared with the experimental data determined by both differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) at various rising rates of temperature.

KINETIC MODEL OF EPOXIDES CURED WITH AMINES

According to the literature,[12,13] the 3 main elementary reactions for the epoxy cured with primary amine system are as follows.

$$H_2C \!-\! CH\!\sim\! + RNH_2 \rightarrow RNHCH_2 \underset{OH}{CH}\!\sim\! \quad (1)$$

$$H_2C \!-\! CH\!\sim\! + RNHCH_2 \underset{OH}{CH}\!\sim\! \rightarrow$$

$$\sim\!\underset{OH}{C}HCH_2\!-\!\underset{R}{N}\!-\!CH_2 \underset{OH}{C}H\!\sim\! \quad (2)$$

$$H_2C \!-\! CH\!\sim\! + \sim\!\underset{R'}{C}HOH\!\sim\! \rightarrow$$

$$\sim\!\underset{R'}{C}H\!-\!O\!-\!CH_2 \underset{OH}{C}H\!\sim\! \quad (3)$$

The reaction of an epoxy group with a primary amine affords a hydroxyl group and a secondary amine, of which the secondary amine will react with another epoxide and result in a tertiary amine and a hydroxyl group. The third reaction is a etherification, which is thought to occur by base-catalyzed mechanism or at high temperature.[13,14] Therefore, the reaction mechanism of an epoxide with an amine includes both stepwise [eq. (1) or (2)], and chain polymerization [eq. (3)]. In terms of the reacting and resultant groups, eqs. (1), (2), and (3) can be written as follows.

$$EP + PA \xrightarrow{k_1} SA + OH \quad (4)$$

$$EP + SA \xrightarrow{k_2} TA + OH \quad (5)$$

$$EP + OH \xrightarrow{k_3} ET + OH \quad (6)$$

where EP, PA, SA, TA, ET, and OH are defined as the epoxy, primary amine, secondary amine, tertiary amine, ether, and hydroxyl-containing groups, respectively, and

$$k_i = k_i' + k_i''[OH] \quad i = 1, 2, 3 \quad (7)$$

where k_i' and k_i'' denote noncatalytic and catalytic rate constants, respectively, and [OH] is the concentration of hydroxyl group. The ratios of rate constants are assumed, as follows[5,14]:

$$k_2/k_1 = k_2'/k_1' = k_2''/k_1'' = a \quad (8)$$

$$k_3/k_1 = k_3'/k_1' = k_3''/k_1'' = b \quad (9)$$

where a and b are assumed as constants and are independent of the extent of reaction and curing temperature. Then the rate equation of the epoxy groups can be described as follows:

$$-d[EP]/dt = k_1[EP][PA]$$
$$+ k_2[EP][SA] + k_3[EP][OH] \quad (10)$$

And let

$$K_i'' = k_i''[EP]_0^2 \quad (11)$$

$$K_i' = k_i'[EP]_0^2 \quad (12)$$

$$\mu = K_i''/K_i', \quad i = 1, 2, 3 \quad (13)$$

where μ is assumed as a constant and is independent of the extent of reaction and curing temperature. Equation (10) becomes

$$d\alpha(EP)/dt = K_1''(1/\mu + [OH]^*)(2[EP]^*[PA]^*$$
$$+ a[EP]^*[SA]^* + b[EP]^*[OH]^*) \quad (14)$$

where $\alpha(EP)$ is the epoxy conversion, t is the reaction time, and [EP]*, [PA]*, [SA]*, [TA]*, [ET]*, and [OH]* are defined as the dimensionless concentrations of epoxy, primary amine, secondary amine, tertiary amine, ether and hydroxyl-containing groups, respectively; that is

$$[Gr]^* = [Gr]/[EP]_0 \tag{15}$$

where $[Gr]$ is the concentration of group Gr, and $[EP]_0$ is the initial concentration of epoxy group.

Furthermore, the value of K_1' of eq. (14) can be described in Arrhenius form, as follows:

$$K_1'' = k_1''[EP]_0^2 = K_{10}''\exp[-E_a/RT(t)] \tag{16}$$

where K_{10}'' is the frequency factor, E_a is the activation energy, R is the gas constant, and $T(t)$ is the absolute temperature, which will be changed with time under nonisothermal conditions. In our previous works,[9–11] under an isothermal condition, the value of K_1'' of eq. (11) is kept constant for a modeling calculation. However, in this study, the rate of curing reaction is not only dependent on the concentrations of reactive functional groups but also the temperature during nonisothermal cure; that is, the value of K_1'' will be changed for each step of calculation.

According to the kinetic model mentioned above, the profiles of epoxy conversion and the molecular weight of polymers can be calculated by the generating function and the Monte Carlo methods developed in our previous works.[9–11]

EXPERIMENTAL

Materials

The resin used in this study was diglycidyl ether of a bisphenol A (DGEBA) type epoxide (DER 331, EEW = 188, Dow Chemical Co.), which was cured with 4,4'-diaminodiphenyl sulfone (DDS, $\bar{M}_w$ = 248, Wakayama Seika Kogyo Co.). The chemical formulas are shown in Figure 1. The epoxy resin was heated to about 60°C and agitated under vacuum for degassing overnight before curing.

Thermal Analysis

Epoxy resin and DDS at the stoichiometric ratio (DDS: 33 phr) were mixed at 130°C with a stirrer, and the mixtures were quenched in ice water. Samples of about 10–20 mg were sealed in aluminum pans. The thermal data, that is, the heat released during cure, were determined by DSC (Perkin–Elmer DSC-7) under either isothermal or nonisothermal conditions.

Figure 1 Structure formula of (a) DGEBA-based epoxy resin and (b) DDS.

Determination of Molecular Weight of Polymers

Mixed samples were cured in the DSC. After given time intervals, the samples were quickly quenched and removed from the DSC. The quenched samples were dissolved in a spectroscopic grade tetrahydrofuran (THF), and the molecular weights of polymers in the sol phase were measured by GPC with 5 separation columns in series (100, 100, 500, 1000, and $10000_{\text{Å}}$; Waters).

RESULTS AND DISCUSSION

Parameters of Kinetic Model of Epoxides Cured with Amines

The parameters in eq. (14) were assumed, as follows[10,11,14]: $a = 0.4$, $b = 0.1$, and $\mu = 20$.

The molecular weight distribution of the epoxide, DER 331, was found using the GPC, as follows: molecular weight of epoxide ($n = 0$) = 340, 92.14 mol %; epoxide ($n = 1$) = 624, 3.96 mol %; epoxide ($n = 2$) = 908, 3.87 mol %; and epoxide ($n = 3$) = 1192, 0.03 mol %.

Relationship Between Conversion and Reaction Time

The extent of reaction, epoxy conversion $\alpha(EP)$, could be calculated from the heat generation up to the time t, $\Delta H(t)$, measured by DSC, and the total heat of reaction, ΔH_T, by the following equation[15]:

$$\alpha(EP) = \frac{\Delta H(t)}{\Delta H_T} \tag{17}$$

Figure 2 Comparison of epoxy conversion versus time by the generating function method over pregelation stages to the experimental data determined by DSC analysis.

In this study, the total heat was determined by integrating the reaction peak of the mixture from 70 to 270°C under dynamic scan at 1°C/min. It was found to be 450 J/g, that is, 112.5 kJ/ee, and the reported data of literature for epoxy–amine system were about 110 ± 10 kJ/ee.[12,16,17] Because it was difficult to retard the curing reaction occurring in mixing the epoxy resin with amine, DDS, before the thermal analysis of DSC, the extent of reaction just after mixing stage was measured by the chemical titration of the pyridinium chloride method.[18,19] About 7% of the epoxy groups was reacted during mixing at 130°C. Therefore, in this study, eq. (17) was modified as follows:

$$\alpha(\text{EP}) = 0.07 + 0.93\frac{\Delta H(t)}{\Delta H_T} \tag{18}$$

Based on the above equation, the conversion profiles of isothermal runs at 130, 140, 150, 160, and 170°C are shown in Figure 2. As the temperature increased, the rate of curing reaction in-

Figure 3 Arrhenius plot of the reaction rate constant versus temperature.

creased. Since a portion of epoxy groups, 7%, was consumed during the mixing stage, the data of epoxy conversion started at 0.07.

On the other hand, the conversion profiles could be calculated by the generating function method before gelation, based on the various values of parameter K_1'' at different temperatures in eq. (14). The critical epoxy conversion, 0.584, was determined by the divergence of the second moment of the molecular weight distribution,[9,10,20,21] at which the weight-average molecular weight of polymers approached an infinite value. Using the least-squares method, the best-fit values of K_1'' at various temperatures were obtained in Table I, and the calculated curves were shown in Figure 2 (solid lines). Figure 3 showed the Arrhenius plot of reaction rate parameters. The activation energy E_a was 14.9 kcal/mol and was nearly the same as 14.8 Kcal/mol determined by Riccardi and Williams[14] for the DGEBA GAY-250–DDS system. The value of K_{10}'' in eq. (16) was 3.16×10^6 min^{-1}. Therefore, eq. (16) became

$$K_1'' = 3.16 \times 10^6 \exp(-14.9/RT)$$
$$= 3.16 \times 10^6 \exp(-7498.4/T) \tag{19}$$

Based on eq. (17), above, the profiles of epoxy conversion calculated by either the generating

Table I   Rate Constant K_1'' as a Function of Curing Temperature

Temperature (°C)	130	140	150	160	170
K_1'' (min^{-1})	0.0255	0.0408	0.0637	0.0979	0.160

Figure 4 Comparison of epoxy conversion versus time by the generating function method and the MC simulation to the experimental data determined by DSC analysis ($D_f = 0$; vitrification is described in the Appendix).

Figure 5 Comparison of epoxy conversion versus time by the generating function method and the MC simulation to the experimental data determined by DSC analysis ($D_f = 2.4$).

function method over pregelation stage or the Monte Carlo procedure over the whole stage are shown in Figure 4. We found that the experimental data were very consistent with both theoretical curves over pregelation stage, but a little lower than the calculated values after gelation. At the gel point, a crosslinked network is formed. Because most of the reactive functional groups are attached to the gel and their mobilities are very limited, the curing reaction becomes diffusion-controlled. According to the theory of free volume, Chern and Polhlein had derived a semi-experimental model to describe this diffusion-controlling effect,[22] as follows:

$$K''_{10} = K^*_{10}\exp[-D_f(\alpha(\mathrm{EP})-\alpha_\mathrm{C}(\mathrm{EP}))],$$
$$\text{when } \alpha(\mathrm{EP}) \geq \alpha_c(\mathrm{EP}) \quad (20)$$

where D_f is the parameter of diffusion control, which are dependent on the curing temperature, K^*_{10} is the value of K''_{10} before gel point, and $\alpha_c(\mathrm{EP})$ is the critical epoxy conversion upon which gelation occurred. After calculation, we found the value 2.4 was the best-fit value of D_f for the system under 150°C, the middle temperature among 5 temperatures. For simplification, the value of D_f was set to be 2.4 for all conditions, and the profiles of epoxy conversion modified by eq. (20) are shown in Figure 5.

Figures 6 and 7 showed the epoxy conversion versus reaction time at rising rates of 1 and 2.5°C/min, respectively, and the epoxy conversion rose slowly in the low-temperature region, whereas it increased rapidly with increasing temperature. The profiles predicted by the generating method and MC simulation agree fairly well with the experimental measurements.

Profiles of Average Molecular Weight of Polymers

The molecular weight of polymers in sol was measured by GPC. The chromatography of epoxy res-

Figure 6 Comparison of epoxy conversion versus time by the generating function method and the MC simulation to the experimental data determined by DSC at a heating rate of 1°C/min.

Figure 7 Comparison of epoxy conversion versus time by the generating function method and the MC simulation to the experimental data determined by DSC at a heating rate of 2.5°C/min.

ins cured with amine at early curing stage is plotted in Figure 8. There were 4 main peaks obtained just after the mixing stage, at 130°C. The first one, of which the elution time was the longest, was attributed to DGEBA ($n = 0$), the second one was attributed to DDS, the third one was attributed to dimers (DGEBA with DDS), and the last one was attributed to either trimers

Figure 9 Calibration curve of GPC for DER 331–DDS system.

or DER 331 ($n = 1$; see Fig. 1).[23] As reaction time increased, the intensity of DGEBA and DDS decreased, and the dimers and trimers increased due to reaction.

The calibration curve is shown in Figure 9. For the molecular weight of the dimer (588, DGEBA with DDS) was lower than the standard curve of polystyrene (PS); in this study, the molecular weight of polymer was calculated by a modified

Figure 8 GPC curves of epoxy resin, DER 331, and mixtures, DER 331 with DDS, during early curing stage.

Figure 10 Comparison of number-average molecular weight of polymers versus time by the MC simulation ($N_0 = 100,000$) and the generating function method to the experimental data determined by GPC at heating rates of 1 and 2.5°C/min.

Figure 11 Comparison of weight-average molecular weight of polymers versus time by the MC simulation (N_0 = 100,000) and the generating function method to the experimental data determined by GPC at heating rates of 1 and 2.5°C/min.

calibration, which was shifted from the PS standard curve downward to the molecular weight of the dimer (see Fig. 9). Based on this calibration, the change of number-average and weight-average molecular weight, $\bar{M}_N$ and $\bar{M}_W$, of polymers measured by GPC under nonisothermal conditions are plotted in Figures 10 and 11, respectively. The average molecular weight of polymers increased slowly at the early curing stage, whereas they increased quickly near the gel point, about α(EP) = 0.6, at which insoluble fractions in THF were first detected.

On the other hand, the profiles of the average molecular weight of polymers were calculated by the generating function method and the Monte Carlo simulation under-nonisothermal conditions. As shown in Figures 10 and 11, the profiles of the number-average and weight-average molecular weight of polymers calculated by these 2 simulations agreed fairly well with the experimental measurements at heating rates of 1 and 2.5°C/min.

CONCLUSION

In this work, we have extended the kinetic models developed by us, the generating function method, and Monte Carlo simulation, to the nonisother-

Table A.I   The Glass Transition Temperatures of the Partially Cured Samples Under Various Curing Conditions

Isothermal Condition (°C)	Curing Time (min)	Epoxy Conversion (%)	T_g (°C)
120	465	64.4	118.3
130	421	71.7	140.1
140	384	83.2	155.1
150	342	84.3	161.8
160	208	87.4	172.8
170	183	91.2	184.6
180	175	93.1	185.8

mal system. Based on these models, the changes of the average molecular weights of polymers and the extent of reaction could be calculated under either isothermal or nonisothermal curing conditions.

We applied these methods to the curing system of epoxy resins, DER 331, with 4,4′-diaminodiphenyl sulfone (DDS). The curing system was investigated with DSC and GPC. The apparent activation energy of this curing reaction was found to be 14.9 Kcal/mol by DSC analysis and the proposed kinetic model. The critical epoxy conversion, about 0.6, detected by the gel fraction was close to the value of 0.584 determined by the generating function method. The profiles of epoxy conversion and the molecular weights of polymers were calculated by the kinetic models with con-

Figure A.1 Dependence of the T_g on the epoxy conversion [the solid line is the result of eq. (21)].

Table A.II   The Epoxy Conversions at Vitrification Points Under Various Curing Conditions Calculated by the Equation (21).

Isothermal Condition (°C)	Epoxy Conversion (%)
130	68
140	73
150	78
160	82
170	87

sideration of diffusion effect. Good agreement was obtained between the model predictions and experimental data at various rising rates of temperature.

APPENDIX

Dependence of the T_g on the Epoxy Conversion

The mixture of the DER 331 with DDS was cured in the DSC under isothermal mode for a long time, then quenched to give a partially cured sample. The epoxy conversion of the sample was determined by the heat generating in the DSC, and the glass transition temperature T_g of the partially cured sample was measured by the DSC rescanning under a heating rate 10°C/min. The results are listed in Table A.I. Figure A.1 shows the experimental data of the T_g dependent on the epoxy conversion, which can be approximated by the following equation[24]:

$$T_g(K) = 282.0\exp[0.521\alpha(EP)] \quad (A.1)$$

Vitrification Point

The vitrification point in Figure 4 was assigned to the time at which T_g became equal to the curing temperature. For example, for the mixture cured at 150°C, the vitrification occurs

when epoxy conversion equals 0.78, calculated by eq. A.1, and the epoxy conversions at the vitrification points for various isothermal conditions are shown in Table A.II.

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