비화학량론적 Biphenyl Epoxy-Dicyclopentadiene Type Phenolic Resin계의 경화특성에 관한 연구

최일중 · 한 승 · 윤호규† · 김환건*

고려대학교 재료공학과, *서경대학교 화학과

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A Kinetic Study of Off-Stoichiometric Biphenyl Epoxy-Dicyclopentadiene Type Phenolic Resin System

Il Jung Choi, Seung Han, Ho Gyu Yoon†, and Whan Gun Kim*

Department of Materials Science, Korea University, Anam-dong, Sungbuk-ku, Seoul 136-701, Korea
Department of Chemistry, Seokyeong University, 16-1 Jeongneung-dong, Sungbuk-ku, Seoul 136-704, Korea
†*e-mail : hgyoon@kuccnx.korea.ac.kr*

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요 약: 등온 differential scanning calorimetry (DSC)를 이용하여 biphenyl계 에폭시 수지 (4,4-diglycidyloxy-3,3′,5,5′-tetramethyl biphenyl)와 dicyclopentadiene type phenolic resin (DCPDP)와의 비화학량론적 에폭시 수지 조성물의 경화반응을 검토하였다. 에폭시와 경화제의 당량비 (epoxy/hydroxyl ratio)를 0.8, 1.0, 및 1.2로 변화시켰으며, 반응차수, 활성화에너지, 속도상수를 포함한 모든 반응속도 파라미터들을 계산하였다. 반응속도 모델과 Chern과 Pohlein이 제안한 반실험식을 이용하고 계산된 파라미터 값을 적용함으로써 유리화 이후 발생하는 확산에 의한 경화반응을 예측할 수 있었다. DiBenedetto 방정식으로부터, 측정된 유리전이온도와 전화량과는 경화온도에 무관한 일대일 관계가 성립함을 알 수 있었고, 확산을 고려한 반응속도식과 DiBenedetto 방정식을 이용하여 Time-Temperature-Transformation (TTT) 등온경화도표를 작성할 수 있었다.

ABSTRACT: The cure kinetics of off-stoichiometric biphenyl epoxy (4,4-diglycidyloxy-3,3′, 5,5′-tetramethyl biphenyl)-dicyclopentadiene type phenolic resin system by differential scanning calorimetry (DSC) using an isothermal approach were investigated. The epoxy/hydroxyl (E/H) ratios of stoichiometric (E/H=1), excess phenol off-stoichiometric (E/H=0.8) and excess epoxy off-stoichiometric (E/H=1.2) of epoxy and phenolic group were selected and all kinetic parameters of the cure reaction including the reaction order, activation energy and the rate constant were calculated and reported. To describe the curing reaction after the vitrification controlled by diffusion factor, the semiempirical relationship proposed by Chern and Poehlein and the calculated parameters were used. A one-to-one relationships, which is independent of the cure temperature, between the glass transition temperature and the fractional conversion were interpreted using DiBenedetto equation. Time-Temperature-Transformation (TTT) isothermal cure diagram has been established at each equivalent weight ratio using the kinetic model coupled with diffusion factor and the DiBenedetto equation.

Keywords: *biphenyl epoxy resin, dicyclopentadiene type phenolic resin, off-stoichiometry, cure kinetics, TTT isothermal cure diagram.*

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INTRODUCTION

Epoxy molding compound (EMC) has been used as the encapsulation material for the semiconductor in view of its cost and productivity. However, there are limitations to the development of high filler EMC using *o*-cresol novolac epoxy resin, which is widely used as the base material of EMC for large scale integrated circuits, due to the high viscosity. Therefore, low viscosity epoxy resin systems such as biphenyl type epoxy resin are required. Biphenyl type epoxy resin has several advantages such as good adhesion, high toughness and feasibility of high filler loading, but it has very low reaction rate and thus the difficulty of control of cure reaction.

In the previous work,[1] we investigated the cure characteristics of biphenyl type epoxy resin with different phenolic-functional hardeners using differential scanning calorimetry (DSC) technique, and reported that the cure reaction of the formulation using phenol novolac with triphenylphosphine (TPP) catalyst proceeds through an autocatalytic kinetic mechanism and the cure reaction of the formulations with xylok or dicyclopentadiene type phenolic resin (DCPDP) under the same catalyst proceeds by a first order kinetic mechanism.

Among those epoxy-hardener systems, the formulation with DCPDP is most expected to give high reliable EMC because of the characteristics of low moisture adsorption and good adhesion. In order to obtain the optimum curing condition of such epoxy resin composition, we investigated the curing characteristics of the compositions with different catalysts using DSC technique.[2] However, the study on the off-stoichiometric cure kinetics of biphenyl type epoxy compositions has not been examined.

In this work, the cure kinetics of off-stoichiometric biphenyl epoxy resin/DCPDP compositions with TPP as a catalyst using DSC technique were investigated. The cure mechanism of those systems was interpreted by *n*th order cure mechanism, and the cure kinetics in the overall conversion region have been analyzed using the kinetic model and diffusion model. The glass transition temperature change during cure reaction was also measured, and the relationships between glass transition temperature and fractional conversion were interpreted using DiBenedetto equation. Using the kinetic model with diffusion factor and the DiBenedetto equation, Time-Temperature-Transformation (TTT) isothermal cure diagram[3,4] has been constructed.

EXPERIMENTAL

Materials. Epoxy resin used in this study was the commercially available biphenyl epoxy resin (YX-4000H) obtained from Yuka Shell Co. Hardener used was dicyclopentadiene type phenol resin (DCPDP) obtained from Nippon Petrochemicals Co. Triphenylphosphine (TPP, Hokko Chemical Co.) as a catalyst was used as received. Detailed descriptions of chemical structures are summarized in Table 1.

Sample Preparation. Epoxy resin compositions contain stoichiometric (E/H=1), excess phenol off-stoichiometric (E/H=0.8), and excess epoxy off-stoichiometric (E/H=1.2) of epoxy and phenolic group. The content of each catalyst is fixed to 1.5 parts per hundred of resin (phr) to epoxy resin. Epoxy resin and hardener were well mixed at 120 ℃ until a homogeneous solution was obtained. This mixture being cooled down to 80 ℃, the catalyst was added and fully stirred for about 20 seconds. Each sample was immediately quenched and stored at 4 ℃.

DSC Measurement. All experimental data

Table 1. Description of Raw Materials Used in This Study

materials	structure
biphenyl epoxy resin (YX4000H)	
dicyclopentadiene type phenolic resin (DCPDP)	
triphenylphosphine (TPP)	

reported in this work were obtained from differential scanning calorimetry (DSC) studies using a TA Instruments DSC (TA-2020). This was calibrated in the -40 ℃ ~ 450 ℃ region. Isothermal and dynamic heating experiments were conducted under a nitrogen flow of 60 mL/min. For dynamic cure, the sample was heated at a rate of 5 ℃/min from 0 ℃ to 260 ℃. A set of isothermal cure curves has been obtained in order to evaluate the kinetic parameters. To measure the glass transition temperature during cure reaction and residual heat, each sample was quenched to -40 ℃ after isothermal curing at each temperature in the range from 1 to 60 min, and subsequently scanned at a heating rate of 5 ℃/min up to 250 ℃.

RESULTS AND DISCUSSION

Fig. 1 shows the DSC thermograms for dynamic cure of the biphenyl epoxy-DCPDP composition with the change of equivalent weight ratio at a heating rate of 5 ℃/min. The total heat of reaction, ΔH_{tot}, has been determined as the total area under the thermogram based on the extrapolated base line at the end of reaction. Each experiment has been performed five times, and the average corresponding values of
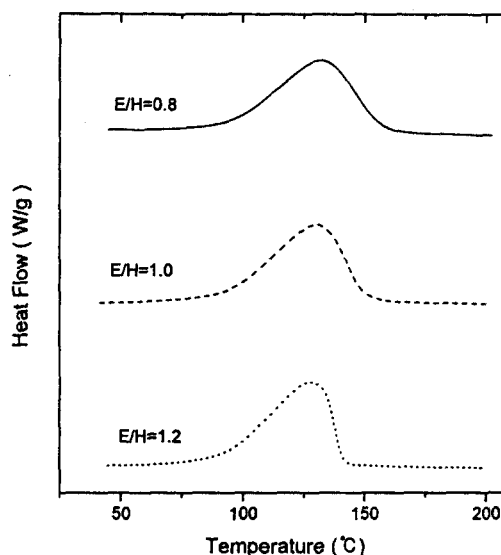
Figure 1. DSC thermodiagrams in the dynamic cure of biphenyl epoxy resin with the equivalent weight ratio.

**Table 2. Summary of Results Obtained from Dynamic-Heating Experiments**

E/H	ΔH_{tot}	T_{g0}	$T_{g\infty}$
0.8	198 (0.8)	27 (1.2)	124 (0.9)[a]
1.0	210 (0.6)	22 (0.7)	118 (0.8)
1.2	185 (0.7)	19 (0.6)	108 (1.2)

[a] The value in ( ) is the standard deviation.

ΔH_{tot} and the glass transition temperature of unreacted sample ($T_{g\infty}$) were summarized in Table 2. This dynamically cured sample was quenched and rescanned at the same heating rate to give the glass transition temperature of fully cured sample ($T_{g\infty}$). This values were compared with the glass transition temperature of sample cured at 160 ℃ drying oven for 6h. The discrepancy was little. The results were also summarized in Table 2. The glass transition temperature of uncured epoxy system decreases from 27 ℃ to 19 ℃ with the increase of equivalent weight ratio. The glass transition temperature of fully cured epoxy system also decreases from 124 ℃ to 108 ℃. Generally when the reac

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(a)

(b)

(c)
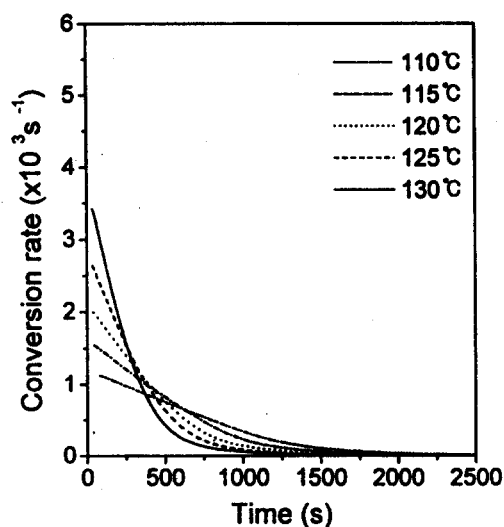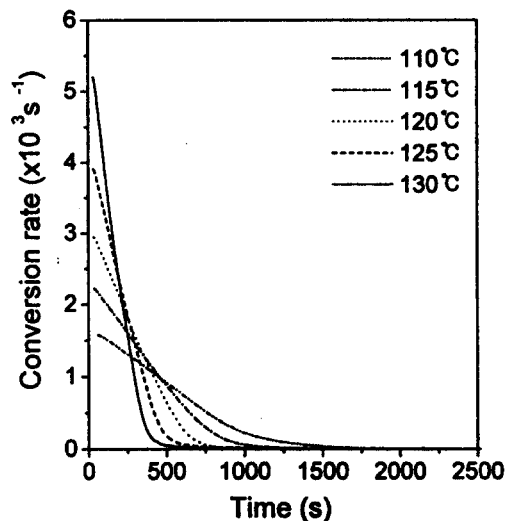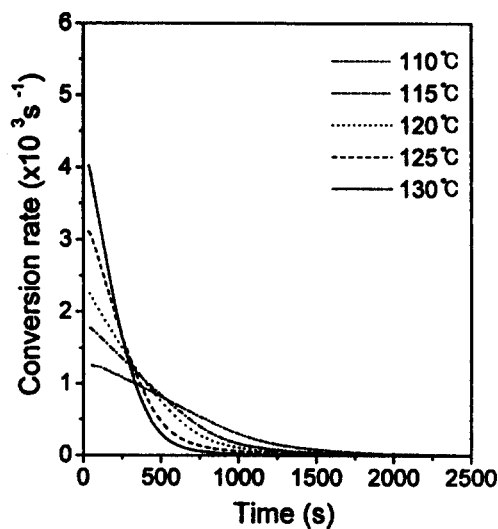
Figure 2. Conversion rate as a function of time at several isothermal temperatures of biphenyl epoxy resin system; (a) E/H=0.8, (b) E/H=1.0, and (c) E/H =1.2.

(functionalities of biphenyl epoxy and DCPDP are 2 and 2.3, respectively) and antiplasticization of the structure by excess phenolic hardener,[4] excess phenol off-stoichiometric system shows a little higher glass transition temperature.

Fig. 2 shows a series of isothermal reaction rate curve as a function of time for biphenyl epoxy resin with different equivalent weight ratios. Fractional conversion was calculated from Fig. 2 by integration and conversion rate was plotted as a function of conversion in Fig. 3. The maximum reaction rate of stoichiometric mixture and all off-stoichiometric mixtures occurs at time zero. Hence, it can be seen that the curing process of all compositions proceeds by an nth order kinetic mechanism.

For thermosets that follow an nth order kinetic mechanism, isothermal reaction conversion rate is proportional to the fraction of material unreacted $(1-\alpha)$, as expressed in the following equation (1):[5-8]

tants are in stoichiometric ratio, the cross-link density shows the maximum value, so the glass transition temperature also reaches the maximum value. In this study, excess phenol off-stoichiometric system shows slightly higher glass transition temperature than stoichiometric system. For biphenyl epoxy-DCPDP composition, due to the low cross-link density

(a)

(b)

(c)
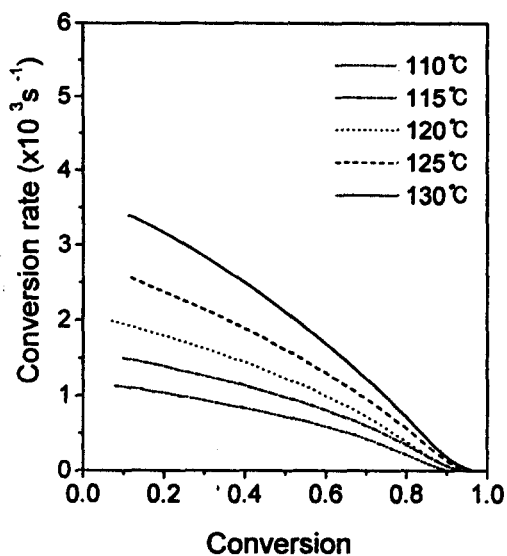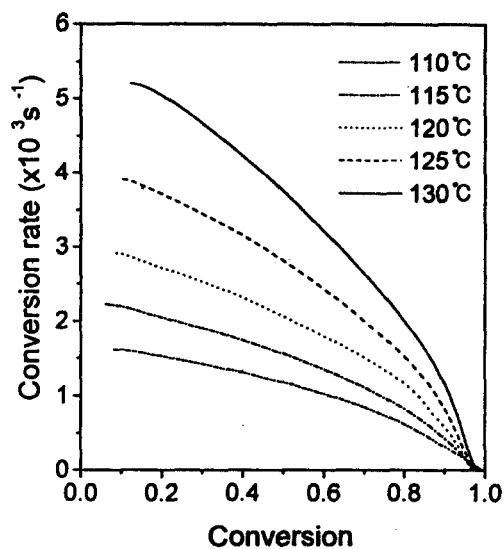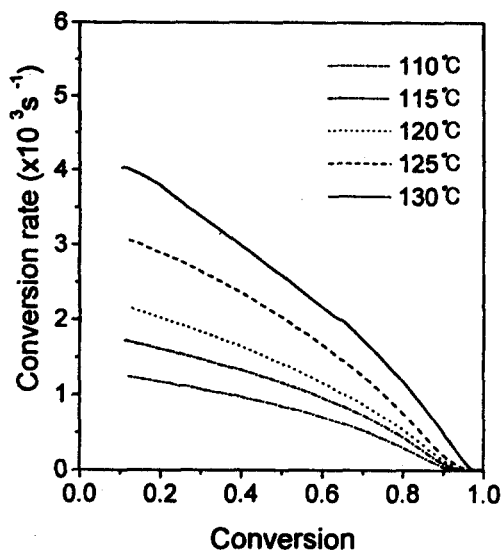
Figure 3. Conversion rate vs. conversion at several isothermal temperatures of biphenyl epoxy resin system; (a) E/H=0.8, (b) E/H=1.0, and (c) E/H=1.2.

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (1)$$

where n is the reaction order and k is the rate constant.

The kinetic parameters were obtained by fitting the experimental data in the first portion of cure to Eq. (1) and they are summarized in

Table 3. The temperature dependence in the rate constant are also shown in Table 3. It can be seen that the value of k increases with the increase of equivalent weight ratio at the same temperature and the average n value decreases from 0.81 to 0.59 with the increase of equivalent weight ratio. Comparisons between experimental data and predictions of the nth order kinetic model with the previously determined kinetic parameters are shown in Fig. 4. Good fits are obtained at the initial stage of reaction, beyond which deviations are observed. The deviation is attributed to the gelation or vitrification where the mobility of the reacting group is hindered and the rate of conversion is controlled by diffusion rather than by chemical factors.[9] To consider diffusion effect, we used a semiempirical relationship, based on free volume considerations, proposed by Chern and Poehlein.[10] In this relationship, a diffusion factor, $f(\alpha)$, has been defined with two empirical parameters as follows ;

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Table 3. Kinetic Parameters of Epoxy Resin Systems Obtained from Each Isothermal Test

E/H	temperature (℃)	k ($\times 10^{-3}$)	n	temperature dependence of the rate constant	average n value
0.8	110	1.22	0.76	$1.30 \times 10^7 \times$ $\exp(-73562/RT)$	0.81
	115	1.60	0.77		
	120	2.13	0.79		
	125	2.90	0.86		
	130	3.80	0.88		
1.0	110	1.37	0.69	$3.01 \times 10^7 \times$ $\exp(-75820/RT)$	0.76
	115	1.92	0.75		
	120	2.42	0.78		
	125	3.46	0.78		
	130	4.47	0.79		
1.2	110	1.73	0.56	$5.54 \times 10^7 \times$ $\exp(-77062/RT)$	0.59
	115	2.34	0.59		
	120	3.11	0.59		
	125	4.24	0.60		
	130	5.77	0.63		
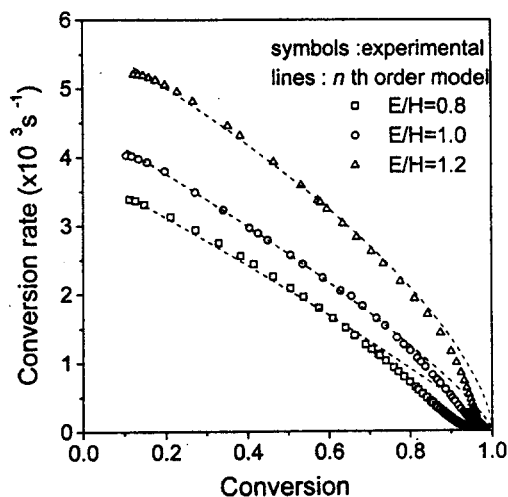
Figure 4. Comparisons of experimental data with n th order cure model at several isothermal cure temperature at 130 ℃ for (□) E/H=0.8, (○) E/H=1.0, and (△) E/H=1.2.

$$f(\alpha) = \frac{1}{1+\exp[C(\alpha - \alpha_c)]} \qquad (2)$$

where C is a constant and α_c is the critical value

of conversion at which the effect of diffusion takes place. For $\alpha \ll \alpha_c$, $f(\alpha)$ is approximately equal to 1, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$ becomes to decrease, and reaches a value of 0.5 at $\alpha = \alpha_c$. Beyond this point it continues to approach zero and the reaction effectively stops. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$.

In this work, $f(\alpha)$ is determined by dividing the experimental values of $d\alpha/dt$ by those from nth order model predicted in Eq. (1). The values of C and α_c obtained by ˈfitting $f(\alpha)$ versus α at various temperatures are summarized in Table 4. An increase in α_c was observed with the increase of curing temperature and equivalent weight ratio.

This result would be due to the higher glass transition temperature of the excess phenol system than that of excess epoxy system. Hence, the mobility of reacting groups of excess phenol system is hindered at lower conversion compared to the excess epoxy system. But C has not discernable trend as in other studies.[10-12]

A more general model is necessary to predict the advance of cure at different temperatures. Considering diffusion effect, Eq. (1) can be rewritten as follows:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \times \frac{1}{1+\exp[C(\alpha - \alpha_c)]} \qquad (3)$$

In this study, based on the assumptions proposed by Barral et al.,[12] the generalized parameters in an nth order kinetic model of Eq. (3) were obtained and summarized in Table 5. Fig. 5 shows the comparisons of the experimental values of α with those calculated from the generalized nth order cure kinetic model at 120 ℃ for the composition with equivalent weight

Table 4. Values of the Constant C and Critical Conversion at Different Temperatures
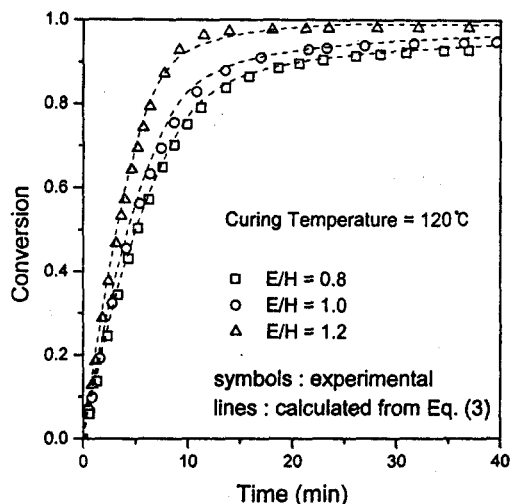
E/H	temperature (℃)	C	α_c
	110	20.4	0.82
	115	17.2	0.83
0.8	120	23.3	0.83
	125	29.1	0.86
	130	23.5	0.88
	110	18.9	0.83
	115	24.1	0.86
1.0	120	20.6	0.86
	125	21.4	0.89
	130	32.0	0.92
	110	20.9	0.91
	115	27.6	0.92
1.2	120	30.3	0.93
	125	30.2	0.94
	130	22.4	0.95

Table 5. Generalized Kinetic Parameters

E/H	kinetic parameter	value
	k	$1.30 \times 10^7 \exp(-73562/RT)$
0.8	n	0.81
	C	23
	α_c	$-0.414 + 0.0032T$
	k	$3.01 \times 10^7 \exp(-75820/RT)$
1.0	n	0.76
	C	23
	α_c	$-0.5776 + 0.0037T$
	k	$5.54 \times 10^7 \exp(-77062/RT)$
1.2	n	0.59
	C	26
	α_c	$0.1672 + 0.0019T$

Figure 5. Comparisons of experimental data with nth order cure model coupled with diffusion factor at 120 ℃ for (□) E/H=0.8, (○) E/H=1.0, and (△) E/H=1.2.

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1-\lambda)\alpha} \tag{4}$$

where λ is a structure-dependent parameter. The parameter λ is theoretically equated to $\Delta C_{p\infty}/\Delta C_{p0}$, where $\Delta C_{p\infty}$ and ΔC_{p0} are the differences in heat capacity between the glassy and rubbery state at T_g for the fully-cured network and monomer, respectively. However, many authors[14,15] took the parameter λ as an adjustable parameter due to the variation in the experimental values of heat capacity. In this study, λ was taken as an adjustable parameter.

Fig. 6 shows the fit of $(T_g - T_{g0})/(T_{g\infty} - T_{g0})$ vs. α at each equivalent weight ratio. The one-to-one relationship between T_g and conversion is observed at each system. The one-to-one relationship between T_g and conversion implies either that the molecular structure of the materials cured at different cure temperatures is the same or that the difference in molecular structure does not have a significant effect on the glass transition temperature.[15] Using the one-to-one relationship between T_g and conversion, α

ratio. Good agreement was found over the whole curing temperature at each equivalent weight ratio.
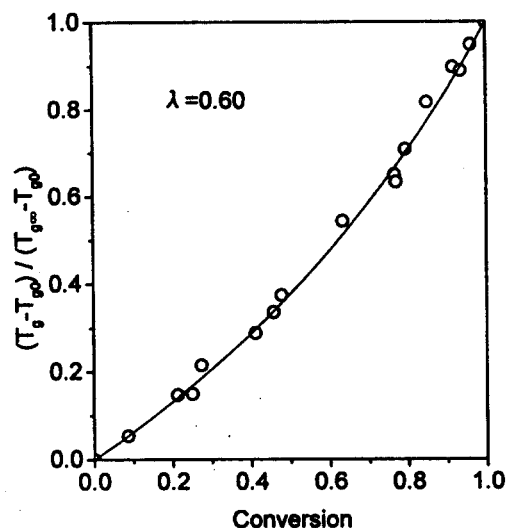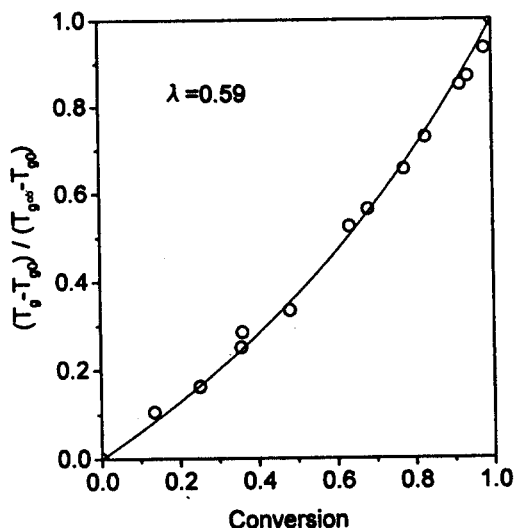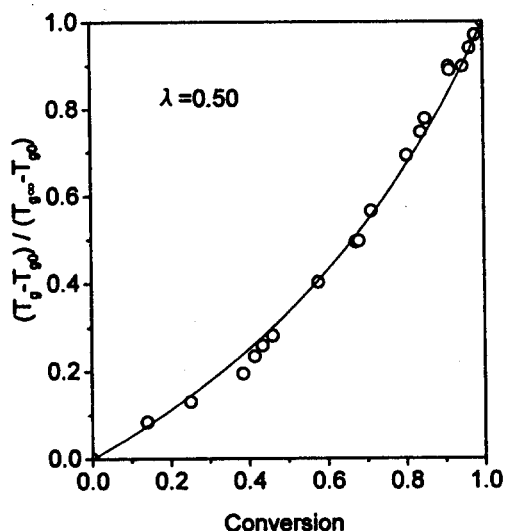
To present one-to-one relationship between glass transition temperature during cure reaction and conversion, DiBenedetto equation has been widely used to fit the experimental glass transition temperature vs. conversion.[14] In DiBenedetto equation, the glass transition temperature of partially cured thermoset with the advance of cure was expressed as follows:

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(a)

(b)


(c)

Figure 6. The fit of $(T_g - T_{g0})/(T_{g\infty} - T_{g0})$ vs. conversion for (a) E/H=0.8, (b) E/H=1.0, and (c) E/H=1.2.

values could be converted into T_g values and vice versa.

Time-Temperature-Transformation (TTT) isothermal cure diagram is a useful framework for analyzing cure processes of thermosetting systems. The TTT diagram exhibits the time to reach various states of materials during isother-

mal cure at different cure temperature, T_c. In this study, combining the generalized kinetic model and DiBenedetto equation, TTT diagram has been constructed. As previously described, the relationships between conversion and time and the relationships between conversion and T_g could be obtained from Eq. (3) and Eq. (4), respectively. When T_g equals the cure temperature, T_c, it is defined as vitrification. The vitrification corresponds to a transformation from a liquid or rubbery state to glassy state as a result of an increase in molecular weight. The vitrification curve was calculated by transforming conversion into T_g through Eq. (4). Iso-T_g contours were calculated from the generalized kinetic model as iso-conversion curves and then transformed into T_g by applying DiBenedetto equation. Fig. 7 shows the TTT diagrams for one stoichiometric and two off-stoichiometric biphenyl epoxy compositions (E/H=0.8, 1.0, 1.2) with iso-T_g contours and vitrification curve.

(a)

(b)

(c)
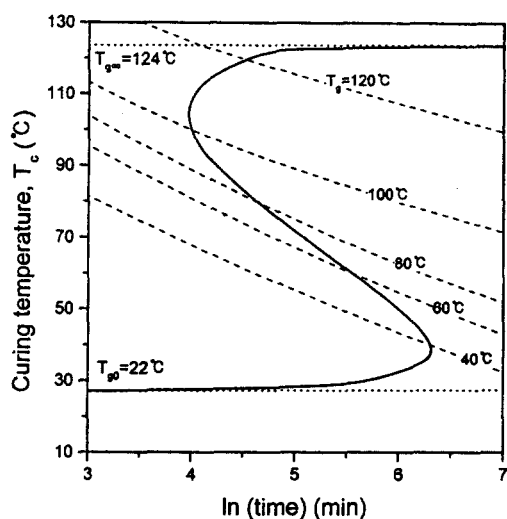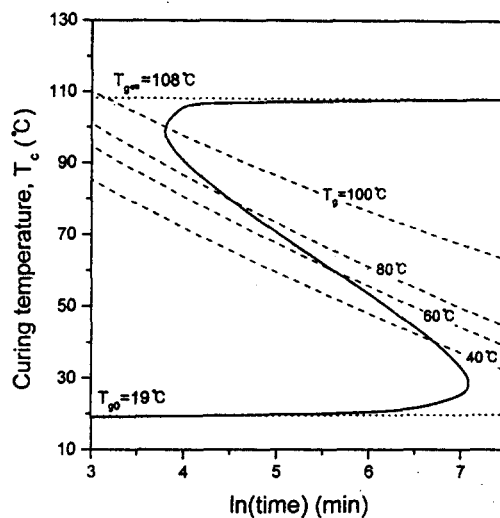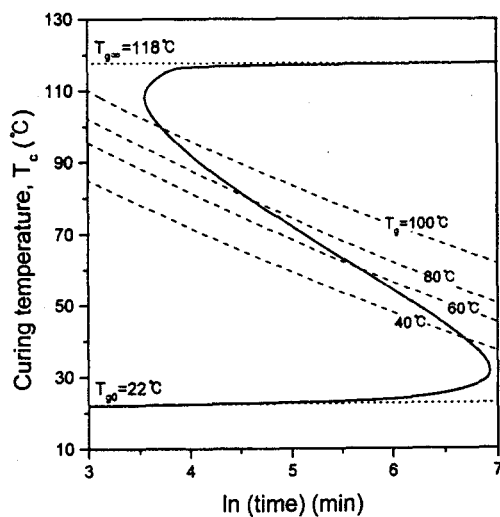
Figure 7. TTT isothermal cure diagram for (a) E/H =0.8, (b) E/H=1.0, and (c) E/H=1.2.

by an nth cure kinetic mechanism regardless of stoichiometry. However, with the increase of the equivalent weight ratio, the reaction order decreased, but activation energy and the rate constant increased at the same cure temperature. In the first stages of the cure, the nth order cure model obtained from the experimental data fits the experimental data well up to vitrification point, but beyond this point deviations are observed. In order to describe the cure in the latter stages of reaction, a diffusion factor has been introduced. With the introduction of this factor, we can predict the degree of conversion over the whole range of cure temperature. The comparisons between the experimental values and nth order cure kinetics model with the diffusion factor show good agreements over the whole temperature ranges at each equivalent weight ratio.

The relationships between glass transition temperature and fractional conversion were interpreted using DiBenedetto equation. There is a one-to-one relationship between glass transi-

CONCLUSIONS

The cure reactions of stoichiometric (E/H=1), excess phenol off-stoichiometric (E/H=0.8), and excess epoxy off-stoichiometric (E/H=1.2) systems have been studied by means of cure kinetic model and DiBenedetto equation. The results indicated that the cure reaction proceeds

tion temperature and conversion, which is independent of the cure temperature.

Using the generalized kinetic model and DiBenedetto equation, TTT isothermal cure diagram could be constructed.

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