Cure Kinetics of Biphenyl Epoxy-Phenol Novolac Resin System Using Triphenylphosphine as Catalyst

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ABSTRACT: The effects of the concentration of triphenylphosphine as a catalyst on the cure reaction of the biphenyl epoxy/phenol novolac resin system were studied. The kinetic study was carried out by means of the analysis of isothermal experiments using a differential scanning calorimeter. All kinetic parameters including the reaction orders, activation energy and kinetic rate constants were evaluated. To describe the cure reaction with the catalyst concentration, the normalized kinetic model was developed. The suggested kinetic model with a diffusion term was successfully able to describe and predict the cure reaction of epoxy resin compositions as functions of the catalyst content and temperature. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 713–720, 1999

Keywords: biphenyl epoxy resin; phenol novolac resin; triphenylphosphine; concentration of catalyst; cure kinetics

INTRODUCTION

Epoxy/novolac resins have been widely used as the base material of epoxy molding compounds for integrated circuit packaging, since the 1970s.[1] Because the uncatalyzed epoxy-phenol reaction is very slow, catalysts are used in most molding compound formulations to reduce the in-mold time and thus improve productivity. Hence, the key to the development of the proper epoxy molding compounds is the catalyst in the formulation.[2]

Many studies have been done to clarify the reaction between epoxides and phenols in the presence of catalyst. Shechter and Wynstra[3] and Sorokin and Shodé[4] studied the base-catalyzed reaction between epoxides and phenols under dilute conditions in solvents. Banthia and McGrath[5] proposed a mechanism for the triphenylphosphine (TPP) catalysis of the reactions between epoxy resins and phenols and concluded that little or no side reaction of epoxy
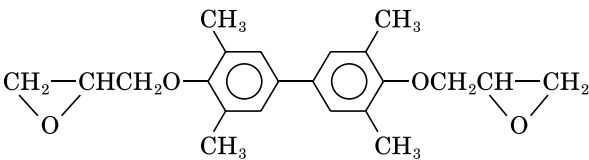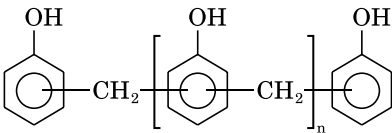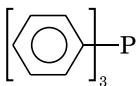
with secondary hydroxyls took place. Biernath and Soane[6] developed a semiempirical rate law that describes the epoxy-phenol reaction catalyzed by TPP and proposed a reaction mechanism for the catalyzed epoxy-phenol reaction. In the previous study,[7] we reported the curing reactions between biphenyl-type epoxy resin and three different phenolic-functional hardeners, such as phenol novolac, xylok, and dicyclopentadiene type phenolic resin, in the presence of TPP. Hale and Macosko[8] studied the imidazole-catalyzed reaction and reported that the selectivity of the catalyst is strongly dependent on its concentration. In the other previous studies,[9,10] the influences of the catalyst types on the curing reactions between biphenyl-type epoxy and the derivatives of phenol novolac were investigated.

The curing reaction rate, however, could be modified with the amount of catalyst as well as the type of catalyst added. Hence, to obtain the optimum curing reaction, not only the effect of the catalyst type but also the effect of the catalyst concentration on the cure reaction should be investigated. Despite the importance of its concentration in catalytic systems, the studies mainly

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Table I. Description of Raw Materials Used in This Study

Materials	Structure	Epoxy/Hydroxy Equivalent (g/eq)
Biphenyl Epoxy Resin		193
Phenol Novolac		104
Triphenylphosphine (TPP)		

focus on the selectivity of the catalyst, time to gelation, and the physical properties of the cured epoxy resin.[8,11–14] There is hardly any study about the detailed kinetic model that can predict the advance of cure of epoxy resin with the catalyst concentration. In this study, therefore, the kinetic model was developed that could describe and predict the curing reaction of epoxy resin compositions with the catalyst content.

EXPERIMENTAL

Materials

Epoxy resin used in this study was the commercially available biphenyl epoxy resin (YX-4000H) obtained from Yuka Shell Epoxy Co. Hardener used was phenol novolac received from Meiwa Kasei Co. Triphenylphosphine (TPP, Hokko Chemical Co.) as a catalyst was used as received. Detailed descriptions of chemical structures are summarized in Table I.

Sample Preparation

All epoxy resin compositions in this study contain the same equivalent weight ratio (1 : 1) of epoxy and phenolic group. The concentration of catalyst added are 2.3×10^{-2}, 4.6×10^{-2}, 6.9×10^{-2}, 9.2×10^{-2}, and 11.5×10^{-2} M. Epoxy resin and hardener were well mixed at 120°C until a homogeneous solution was obtained. This mixture was

cooled down to 80°C. The catalyst was added and the mixture was fully stirred for about 20 s. Each sample was immediately quenched and stored in a refrigerator at 4°C.

DSC Measurement

Calorimetric measurements were performed using a TA Instruments differential scanning calorimeter (TA-2020). 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°C/min from −10 to 280°C. A set of isothermal cure curves has been obtained in order to evaluate the kinetic parameters for the curing reactions. To measure glass transition temperature during curing reaction, each sample was quenched to −10°C after isothermal curing in the range from 1 to 120 min, and subsequently scanned at a heating rate of 5°C/min up to 280°C.

RESULTS AND DISCUSSION

Cure Kinetics

Figure 1 shows a series of isothermal reaction rate curves as a function of time for biphenyl epoxy resin compositions with different TPP concentration. For each composition, the peaks were found, and the value of the peak was increased and shifted to shorter time with temperature.
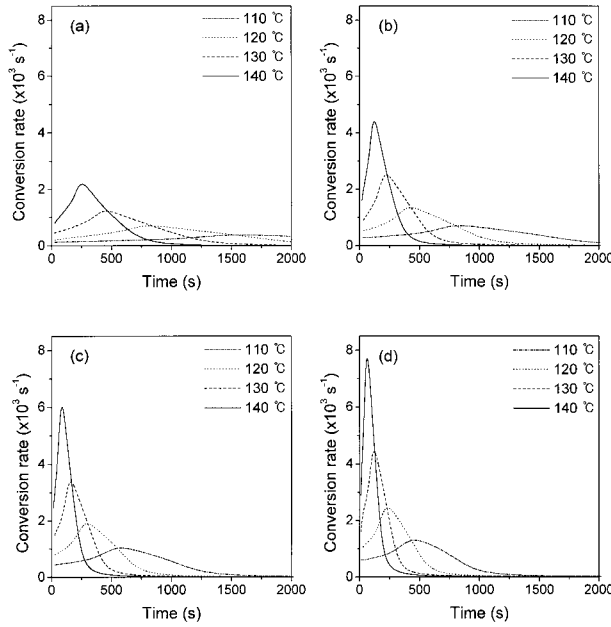
Figure 1. Conversion rate as a function of time at several isothermal temperatures of biphenyl epoxy resin composition; the concentrations of TPP are (a) 2.3 $\times$ 10^{-2}, (b) 4.6 $\times$ 10^{-2}, (c) 6.4 $\times$ 10^{-2}, and (d) 9.2 $\times$ 10^{-2} M.

With TPP concentration, an increase in the peak value of the reaction rate and its shift to shorter time were observed at the same curing temperature. Fractional conversions were calculated from Figure 1 and the conversion rate was plotted as a function of conversion in Figure 2. It can be seen that the curing reactions for all compositions proceed by an autocatalytic kinetic mechanism with maximum conversion rate in 30–40% in conversion region.

For thermosets following an autocatalytic cure reaction kinetics, the isothermal reaction rate is expressed as shown below:

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

where m and n are the reaction orders and k' is the kinetic rate constant.

To take into account the autocatalytic reaction where initial reaction rate of an autocatalytic reaction is not zero, Kamal[15] proposed generalized expression:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (2)$$

where k_1 and k_2 are the kinetic rate constants. The kinetic rate constants are assumed to be constant at a given temperature and to follow an Arrhenius temperature dependence: This relationship can be described mathematically as

$$k_i = A_i\exp\left(\frac{Q_i}{RT}\right) \qquad i = 1, 2 \qquad (3)$$

where A_i is the pre-exponential constant, Q_i the activation energy, R the gas constant, and T the absolute temperature. To compute kinetic parameters in equation (2), several methods have been proposed.[16–19] In this study, k_1 was graphically calculated as the initial reaction rate at time = 0, given by the intercept of Figure 1. Then, without any constraints on the other kinetic parameters, k_2, m, and n were calculated by fitting the experimental data to equation (2) in the first portion of cure up to 60–80% depending on the composition and the curing temperature. Table II shows the resulting data obtained from this method for all isothermal experiments. Temperature dependence of the kinetic rate constants was determined with Arrhenius equation form and also listed in Table II. The reaction orders were determined by averaging the values of all isothermal experiments. As

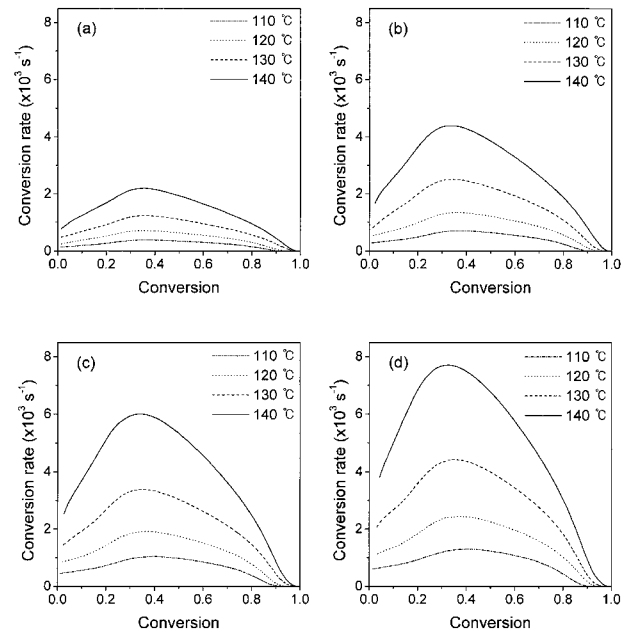**Figure 2.** Isothermal conversion rate as a function of conversion of biphenyl epoxy resin composition; the concentrations of TPP are (a) 2.3 $\times$ 10^{-2}, (b) 4.6 $\times$ 10^{-2}, (c) 6.4 $\times$ 10^{-2}, and (d) 9.2 $\times$ 10^{-2} M.

Table II. Kinetic Parameters of Biphenyl Epoxy/Phenol Novolac/TPP Systems with the Different TPP Concentration

Concentration of TPP (M)	Temp. (°C)	k_1 ($\times 10^{-3}$ s^{-1})	k_2 ($\times 10^{-2}$ s^{-1})	m	n	Temperature Dependence of the Rate Constant		Average m value	Average n value
						k_1 (s^{-1})	k_2 (s^{-1})		
2.3×10^{-2}	110	0.15	0.18	1.40	1.62	4.85×10^5	1.77×10^8	1.22	1.45
	120	0.25	0.36	1.22	1.48	$\exp(-70^a/RT)$	$\exp(-81/RT)$		
	130	0.45	0.63	1.19	1.35				
	140	0.73	1.15	1.07	1.35				
4.6×10^{-2}	110	0.23	0.36	1.55	1.74	9.52×10^5	1.66×10^9	1.26	1.53
	120	0.51	0.71	1.30	1.53	$\exp(-70/RT)$	$\exp(-86/RT)$		
	130	0.82	1.38	1.11	1.46				
	140	1.39	2.52	1.07	1.39				
6.9×10^{-2}	110	0.45	0.53	1.64	1.74	6.64×10^5	2.53×10^9	1.30	1.55
	120	0.80	0.99	1.40	1.62	$\exp(-67/RT)$	$\exp(-86/RT)$		
	130	1.31	1.85	1.19	1.47				
	140	2.09	3.79	0.96	1.38				
9.2×10^{-2}	110	0.59	0.73	1.64	1.78	2.29×10^6	6.46×10^8	1.35	1.61
	120	1.05	1.41	1.45	1.63	$\exp(-70/RT)$	$\exp(-80/RT)$		
	130	1.78	2.51	1.20	1.57				
	140	2.93	4.61	1.10	1.45				

[a] The unit of the activation energy is kJ mole^{-1}.

shown in Table II, the kinetic rate constants, k_1 and k_2 increased with the concentration of TPP at the same curing temperature. The averages of each reaction order, m and n, also increased but their increments were relatively small. The total reaction order ($m + n$) converged to 3 as shown in typical autocatalytic reaction system such as epoxy/phenolic-functional hardener.[7,20]

Typical comparisons between the experimental and the autocatalytic model with previously determined model parameters are shown in Figure 3. Good agreements are observed up to 80–90%, but beyond that region deviations are observed. The deviations observed are attributed to the vitrification where the mobility of the reacting groups is hindered and the rate of conversion is controlled by diffusion rather than by kinetic factors.[21] To consider the diffusion effect more precisely, semiempirical relationships, based on the free volume considerations proposed by Chern and Poehlein,[22] have been widely used. In this relationship, a diffusion factor, $f(\alpha)$, has been defined with two empirical parameters as follows:

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (4)$$

where C is the material constant for a given epoxy resin composition and α_c is the critical conversion

depending on the curing temperature. For $\alpha \ll \alpha_c$, $f(\alpha)$ approximately equals unity and the effect of diffusion is negligible, so that the reaction is ki-
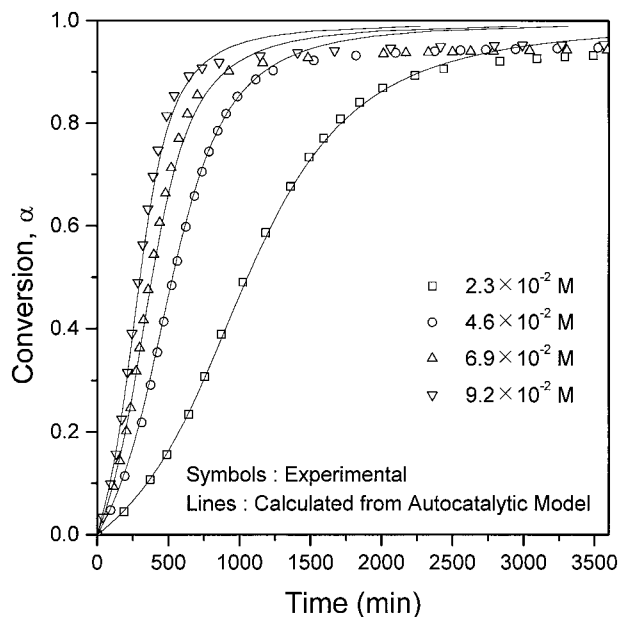

Figure 3. Comparisons of experimental data with autocatalytic cure model for biphenyl epoxy resin composition with the different TPP concentration; the concentrations of TPP are (□) 2.3×10^{-2}, (○) 4.6×10^{-2}, (△) 6.9×10^{-2}, (▽) 9.2×10^{-2} M.

netically controlled. As α approaches α_c, $f(\alpha)$ begins to decrease and approaches 0.5 when $\alpha = \alpha_c$. Beyond this point, it continues to decrease and approaches zero, which means that the reaction becomes very slow and effectively stops. With the introduction of the diffusion factor the effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$. In this study, $f(\alpha)$ was determined as the ratio of the experimental reaction rate to the reaction rate predicted on the basis of the autocatalytic cure kinetic model in equation (2). The values of C and α_c were obtained by fitting $f(\alpha)$ versus α at each temperature and composition. They are summarized in Table III. C has no discernible trend but α_c increases with temperature at a given composition, as in other studies.[9,10,23] Furthermore, it can be seen that α_c value is almost equivalent regardless of the content of TPP at the given temperature. It is worthwhile examining this result more closely. The glass transition temperatures (T_g) were measured at a certain fractional reaction conversion. Figure 4 displays the experimental results of T_g plotted as a function of fractional conversion. The fractional conversion was obtained from the residual exotherm of a partially cured specimen to the total reaction heat of an unreacted sample. Many authors have shown a one-to-one relationship between T_g and fractional conversion, independent of cure temperature.[24–26] Interestingly, a unique one-to-one relationship,
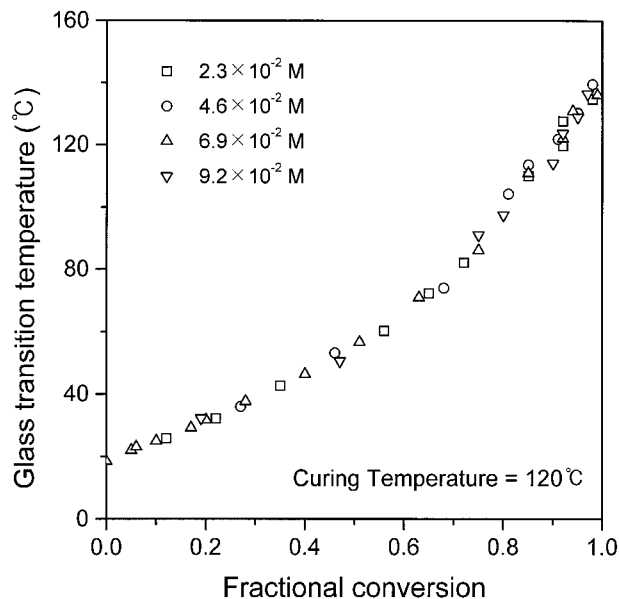

Figure 4. Relationships between T_g and reaction conversion of biphenyl epoxy resin composition with the different TPP concentration; the concentrations of TPP are (□) 2.3×10^{-2}, (○) 4.6×10^{-2}, (△) 6.9×10^{-2}, (▽) 9.2×10^{-2} M.

independent of the content of TPP, was observed as shown in Figure 4. Conventionally, the one-to-one relationship between T_g and conversion implies either that the molecular structure of the materials cured at different cure temperature is the same or that the difference in molecular structure for materials cured at different temperatures does not have a significant effect on the glass transition temperature.[24] Hence, it is reasonable to suppose that the glass transition temperatures and the network structures are not influenced by the TPP concentration. These results could lead to the conclusion that the TPP promotes only the cure reaction without causing significant changes in the crosslinking network of epoxy resin composition. Consequently, α_c could be taken as a material constant at a given curing temperature, independent of the TPP content.

Generalization of Cure Kinetic Model

The model represented by equation (2) has been successfully applied to the autocatalytic polymerization reactions where one of the products of the cure process acts as a catalyst as in the cure of epoxies with amines or phenols. However, since equation (2) does not contain any terms related to the catalyst concentration, it is impossible to pre-

Table III. Values of the Constant C and Critical Conversion at Different Temperature

Concentration of TPP (M)	Temperature (°C)	C	α_c
2.3×10^{-2}	110	53	0.88
	120	59	0.91
	130	57	0.95
	140	60	0.97
4.6×10^{-2}	110	57	0.87
	120	55	0.90
	130	59	0.94
	140	61	0.97
6.9×10^{-2}	110	53	0.87
	120	51	0.90
	130	52	0.93
	140	58	0.98
9.2×10^{-2}	110	52	0.87
	120	48	0.90
	130	55	0.93
	140	51	0.97

dict the isothermal reaction rate with its concentration.

Sorokin and Shodé[4] studied the reactions of epoxides with phenols in the presence of tertiary amines and suggested the following reaction mechanism:

$$E + P + B \xrightarrow{K_1} I \tag{5}$$

$$E + P + I \xrightarrow{K_2} PR + I \tag{6}$$

where E represents the epoxides, P the phenol, B the tertiary amine or catalyst, I an intermediate complex, PR the product of the addition of phenol to epoxide, and K_1 and K_2 are the kinetic constants. This reaction mechanism makes it clear that the isothermal reaction rate is proportional to the catalyst concentration. Additionally, since
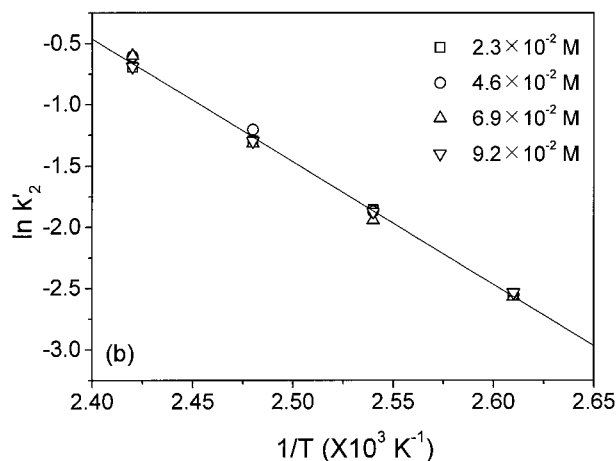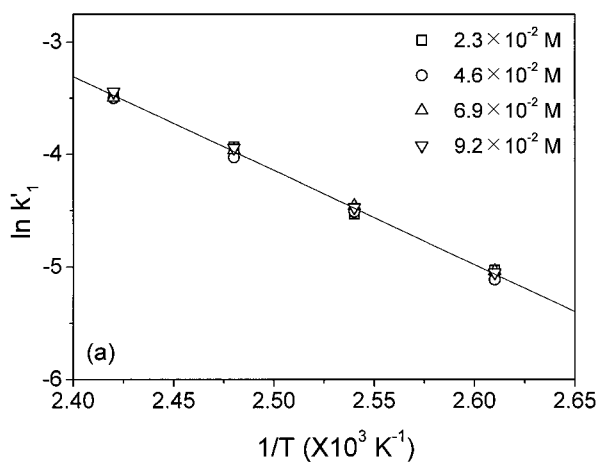

Figure 5. Temperature dependence of (a) k_1' and (b) k_2'.

Table IV. The Normalized Kinetic Constants, k_1' and k_2'

Kinetic Constant	Value (s^{-1})
k_1'	$1.86 \times 10^7 \exp(-69 \text{ kJ mole}^{-1}/RT)$
k_2'	$1.72 \times 10^{10} \exp(-83 \text{ kJ mole}^{-1}/RT)$

the reaction mechanism does not change with the TPP concentration, namely, the reaction orders are constants, and also the reaction rate constants increase with the catalyst concentration at the same temperature, the autocatalytic cure model can be simply modified by the introduction of the term related to the catalyst concentration. Then, equation (2) can be expressed as follows:

$$\frac{d\alpha}{dt} = (k_2' + k_2'\alpha^m)(1 - \alpha)^n[B] \tag{7}$$

where $[B]$ is the concentration of catalyst and k_1' and k_2' are the "normalized" kinetic rate constants which can be applied at any catalyst concentration.

As previously described, the reaction orders, m and n, could be taken as a constant, independent of curing temperature and the catalyst content. Therefore, they could be determined by averaging the values of all the isothermal experiments in Table II. The resulting m and n are 1.3 and 1.5, respectively. Comparing equation (2) and equation (7), the normalized kinetic rate constants could be evaluated from the equation as shown below:

$$\frac{k_i}{[B]} = k_i' \qquad i = 1, 2 \tag{8}$$

Taking the natural log of both sides of equation (8) gives

$$\ln\left(\frac{k_i}{[B]}\right) = \ln k_i' \qquad i = 1, 2 \tag{9}$$

Figure 5 shows the values of $\ln(k_i/[B])$ plotted as a function of reciprocal temperature using the data in Table II. Then, the pre-exponential constants and the activation energies of k_i' could be calculated from the intercepts and the slopes of the plot in Figure 5. Table IV gives the Arrhenius forms of k_i'.
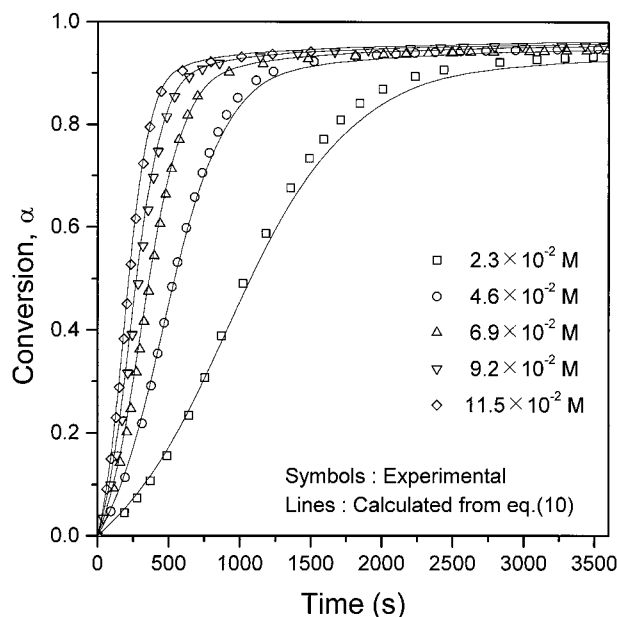
Figure 6. Comparisons between the experimental values of α with these values obtained from the equation (10) with the different concentration of TPP; the concentrations of TPP are ($\square$) 2.3 $\times$ 10^{-2}, ($\bigcirc$) 4.6 $\times$ 10^{-2}, ($\triangle$) 6.9 $\times$ 10^{-2}, ($\triangledown$) 9.2 $\times$ 10^{-2}, and ($\diamond$) 11.5 $\times$ 10^{-2} M.

Considering the diffusion effect, equation (7) could be generalized as follows:

$$\frac{d\alpha}{dt} = (k_1' + k_2'\alpha^m)(1 - \alpha)^n[B]$$

$$\times \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (10)$$

The constant C has been taken as a constant, as in other studies.[10,27] α_c has been taken as a material constant at a given curing temperature as previously described. Figure 6 shows the comparison between the experimental values of α with these values obtained from the equation (10). The calculated values agree very well with experimental data. Thus, we can employ the proposed generalized kinetic model to predict and describe the advance of cure of our epoxy resin systems as functions of the catalyst concentration and the curing temperature.

CONCLUSIONS

The effects of TPP concentration on the isothermal curing reactions of biphenyl epoxy/phenol novolac

system were investigated. The kinetic constants, k_1 and k_2, increase with the content of TPP but the reaction orders, m and n, slightly increase. Through the analysis of cure kinetics and the relationships between T_g and reaction conversion, it could be concluded that TPP promotes only the cure reaction without significantly changing the crosslinking network of epoxy resin compositions.

For determining the advance of cure of epoxy resin systems with the content of catalyst, the autocatalytic cure model has been simply modified by the introduction of the term related to the catalyst concentration. By combination of this proposed kinetic model with a diffusion term, it is possible to describe and predict the cure reaction of epoxy resin compositions as a function of the catalyst concentration.

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