

Curing Characteristics of Epoxy Resin Systems That Include a Biphenyl Moiety

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ABSTRACT: The curing characteristics of epoxy resin systems that include a biphenyl moiety were investigated according to the change of curing agents. Their curing kinetics mainly depend on the type of hardener. An autocatalytic kinetic reaction occurs in epoxy resin systems with phenol novolac hardener, regardless of the kinds of epoxy resin and the epoxy resin systems using Xylok and DCPDP (dicyclopentadiene-type phenol resin) curing agents following an n th-order kinetic mechanism. The kinetic parameters of all epoxy resin systems were reported in terms of a generalized kinetic equation that considered the diffusion term. The fastest reaction conversion rate among the epoxy resin sys-

tems with a phenol novolac curing agent was obtained in the EOCN-C epoxy resin system, and for systems with Xylok and DCPDP hardeners, the highest reaction rate values were obtained in NC-3000P and EOCN-C epoxy resin systems, respectively. The system constants in DiBenedetto's equation of each epoxy resin system with different curing agents were obtained, and their curing characteristics can be interpreted by the curing model using a curing agent as a spacer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1942–1952, 2002

Key words: biphenyl epoxy resin; curing agent; curing mechanism; cure kinetics

INTRODUCTION

Because of the growing need for high-density integration and thin-packaging technique of semiconductors, the performance improvement of packaging materials is progressing fast.¹ In particular, the most significant challenges have been in the area of improving the thermal resistance and moisture resistance of epoxy molding compound (EMC) for semiconductor encapsulation, both to overcome the thermal stress that occurs at reflow soldering and to prevent popcorn crack and warpage of package.^{2–5} Various methods to solve these problems have been presented, although to date the most economical and effective method has been the high filler loading technique. If this technique were used, however, there should be a concomitantly high viscosity of EMC with the increase of filler content, which causes moldability problems in packaging. Therefore, it is necessary to use the epoxy resin system to ensure low viscosity when this technique is applied.⁶

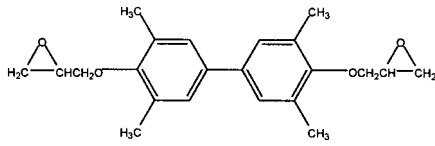
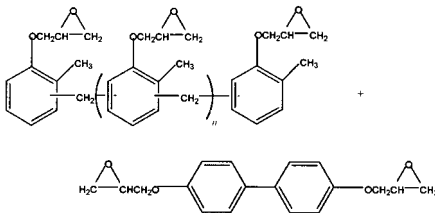
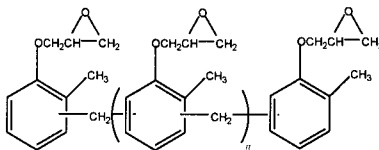
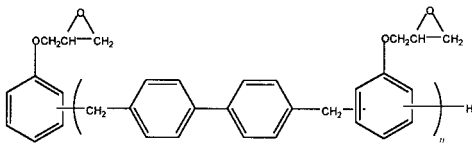
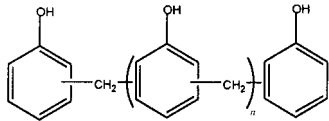
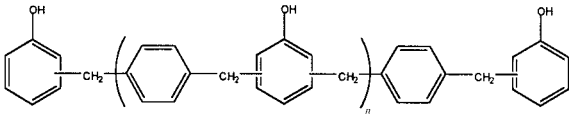
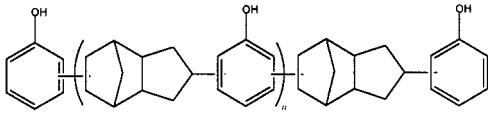
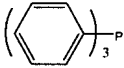
The most efficient epoxy resin for this application is a biphenyl-type epoxy resin, which is characterized by low viscosity, liquid crystalline properties, and good adhesion and mechanical properties.⁷ The most popular biphenyl-type epoxy resin is YX-4000H, developed by Yuka Shell Co. (Tokyo, Japan), and studies of cure kinetics and catalyst effect on this resin have been performed.^{8–10} However, the heat resistance and moisture resistance in this simple biphenyl-type epoxy resin system are insufficient, compared to those of the *o*-cresol novolac epoxy resin system, because the epoxy resin of this epoxy resin system is of low molecular weight and shows low glass-transition temperature. The new biphenyl-type epoxy resins have been developed recently to overcome such disadvantages.

In this study, the curing characteristics of such new biphenyl-type epoxy resins were investigated that would show the advantages of a typical biphenyl epoxy resin and *o*-cresol novolac epoxy resin. The cure kinetics of epoxy resin systems should change from an autocatalytic cure reaction to an n th-order cure reaction according to the kind of curing agent used¹¹; therefore, the cure kinetics of new epoxy resin systems that include a biphenyl moiety with the change of kind of curing agents are reported in this study. They were compared with the cure characteristics of both the conventional biphenyl epoxy resin (YX-4000H) and the *o*-cresol novolac epoxy resin (EOCN-1020) systems to perform the systematic study.

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TABLE I
Description of Raw Materials Used in This Study

Component	Grade name	Structure	Remarks ^a
Epoxy resin	YX-4000H		EEW = 193
	EOCN-C		EEW = 192
	EOCN-1020		EEW = 198
	NC-3000P		EEW = 286
Hardeners	PSM-4261		HEW = 104
	Xylok		HEW = 178
	DCPDP		HEW = 170
Catalyst	TPP		

^a EEW, epoxy equivalent weight (g/equiv); HEW, hydroxy equivalent weight (g/equiv).

EXPERIMENTAL

Materials

The new biphenyl epoxy resins used in this experiment are EOCN-C and NC-3000P grade obtained from Nippon Kayaku Co. (Japan). As shown in Table I, EOCN-C is an epoxy resin used to blend biphenyl epoxy resin with *o*-cresol novolac epoxy resin and

NC-3000P is synthesized from monomer with these two functional groups. YX-4000H (Yuka Shell Co., Japan) was used as a reference grade of biphenyl epoxy resin and EOCN-1020 (Nippon Kayaku Co.) was used as a reference state of *o*-cresol novolac epoxy resin.

Phenol novolac resin (PSM 4261; Gunnei Chemical Co., Japan), Xylok (Mitsui Tohatsu Chemical, Japan),

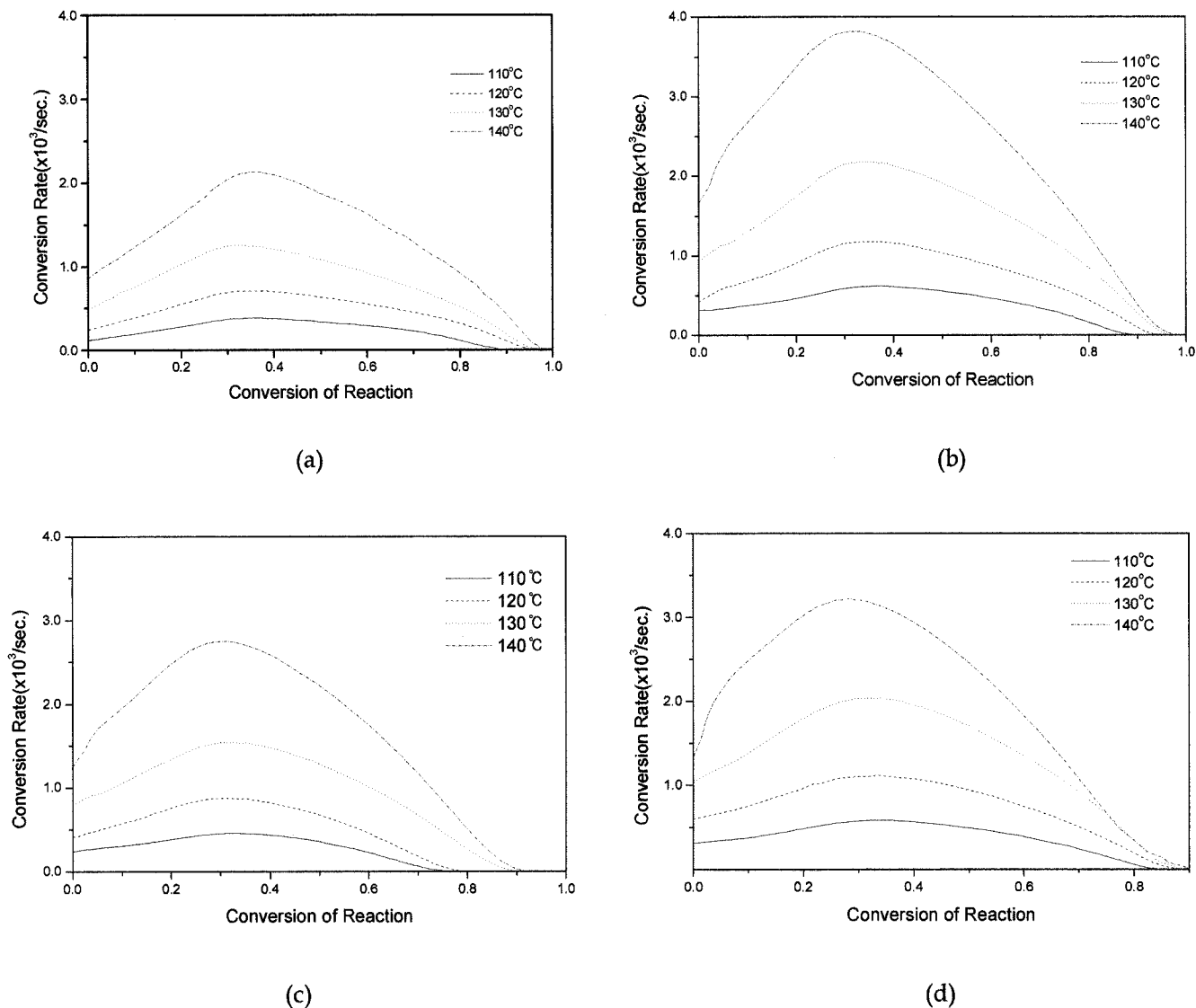


Figure 1 Isothermal conversion rate as a function of the conversion of epoxy resin systems with phenol novolac hardener: (a) YX-4000H, (b) EOCN-C, (c) EOCN-1020, (d) NC-3000P.

and dicyclopentadiene-type phenol resin (DCPDP; Nippon Petrochemicals Co., Japan) were used as hardeners. The catalyst used was triphenylphosphine (TPP; Hokko Chemical Co., Japan). Detailed descriptions of chemical structures used in this study are summarized in Table I.

Sample preparation

All epoxy resin compositions in this study were composed of the same equivalent weight ratio (1 : 1) of epoxy and hydroxyl group with 0.02M of TPP as catalyst. Epoxy resin and hardener were well mixed at 120°C until a homogeneous solution was obtained. After being cooled to 80°C, the catalyst was added and fully stirred for about 10 s. Each sample was immediately quenched and stored in a refrigerator at 4°C.

DSC measurement

Calorimetric measurements were performed using a TA-2020 differential scanning calorimeter (TA Instruments, New Castle, DE). This was calibrated in the region from -40 to about 450°C . 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 $5^{\circ}\text{C}/\text{min}$ from -10 to 300°C , beyond which decomposition was observed. A set of isothermal cure curves was obtained to evaluate the kinetic parameter for the curing reactions.

RESULTS AND DISCUSSION

The reaction conversion changes of each epoxy resin system, according to the hardener changes, were ex-

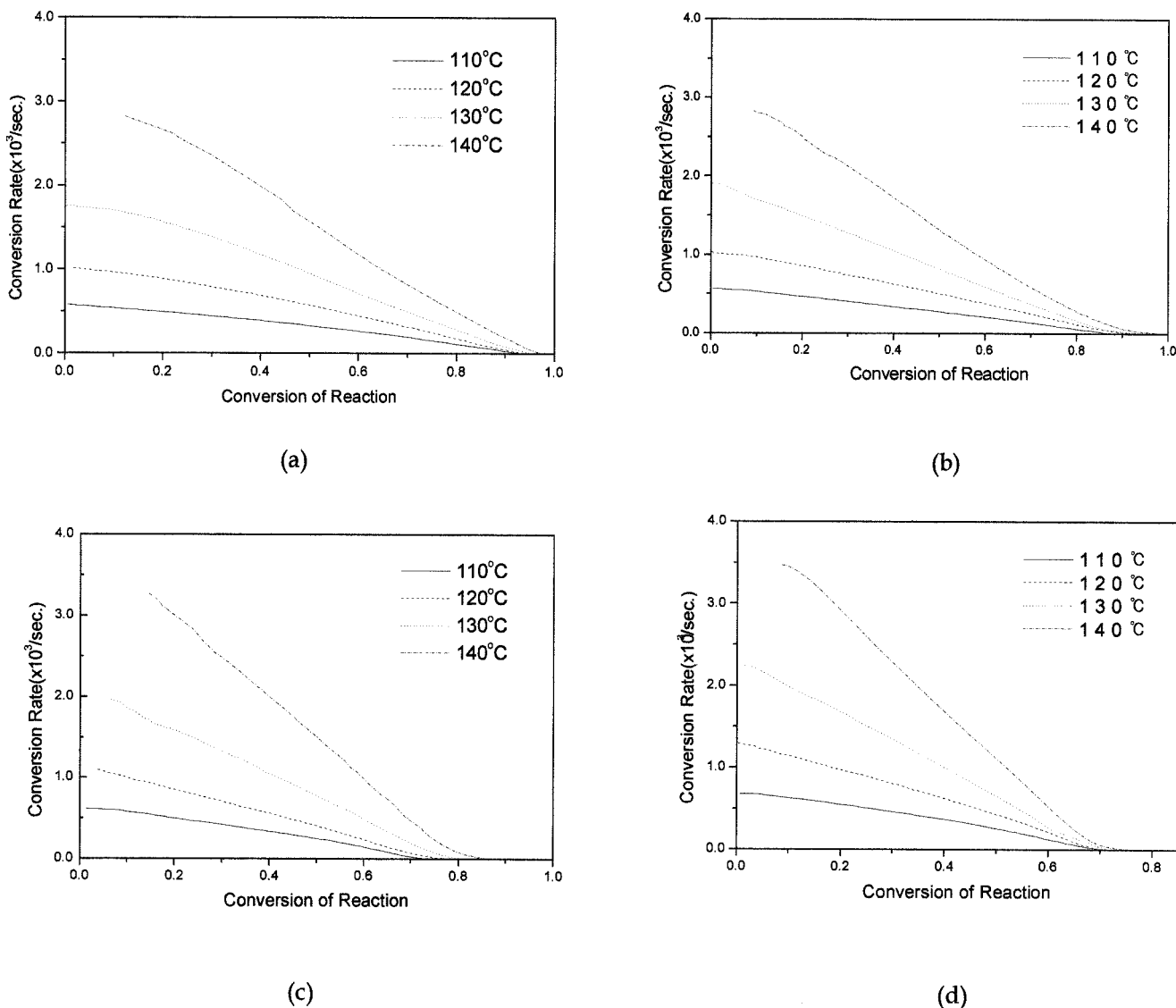


Figure 2 Isothermal conversion rate as a function of the conversion of epoxy resin systems with Xylok hardener: (a) YX-4000H, (b) EOCN-C, (c) EOCN-1020, (d) NC-3000P.

amined to investigate the curing characteristics of each of the above-mentioned epoxy resins. The reaction conversion rate changes of each epoxy resin system with phenol novolac hardener are plotted as a function of reaction conversion in Figure 1. Figure 2 represents them for the Xylok hardener system and Figure 3 shows them using DCPDP hardener. As seen in these figures, it can be found that epoxy resin systems with phenol novolac hardener follow an autocatalytic cure reaction as described in eq. (1); an *n*th-order cure reaction, as shown in eq. (2), is observed in epoxy resin systems using Xylok and DCPDP hardeners. From these experimental results, it is postulated that the curing reaction mechanism of an epoxy resin system is dependent on the kind of curing agent rather than on the epoxy resin.

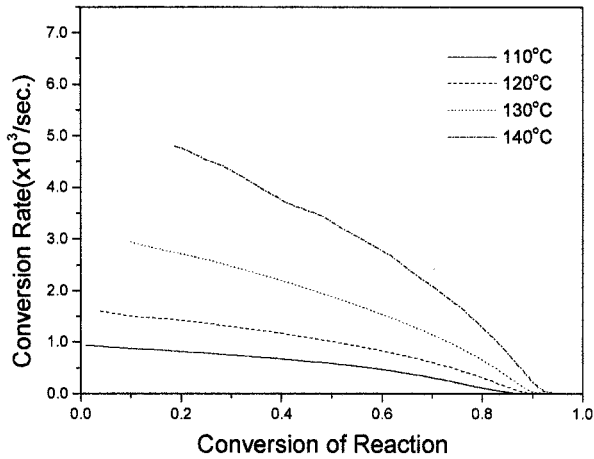
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

where α is the reaction conversion, t is time, m and n are the reaction orders of the system, and k_1 and k_2 are kinetic rate constants of the system.

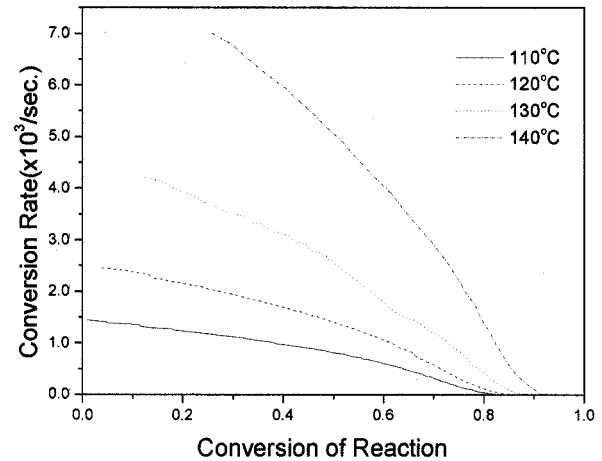
$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

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

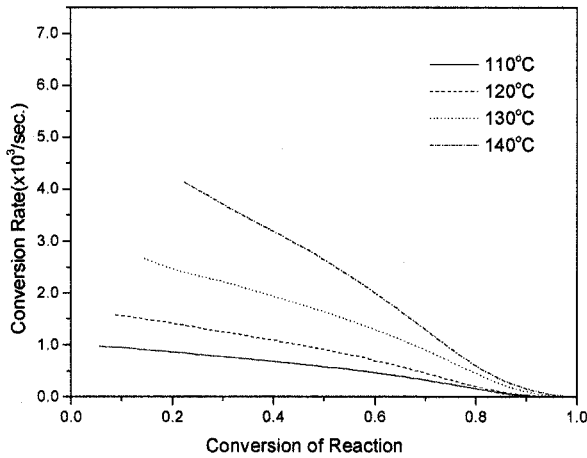
To precisely predict the cure kinetics over the whole range of conversion, the autocatalytic and *n*th-order models were modified in terms of the introduction of a diffusion term, as represented in eq. (3)¹²:



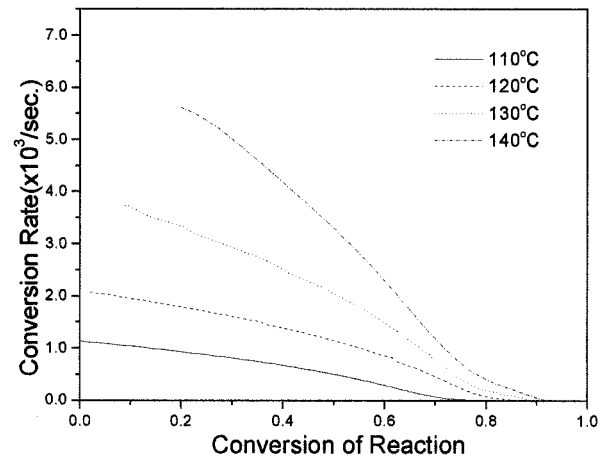
(a)



(b)



(c)



(d)

Figure 3 Isothermal conversion rate as a function of the conversion of epoxy resin systems with DCPDP hardener: (a) YX-4000H, (b) EOCN-C, (c) EOCN-1020, (d) NC-3000P.

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (3)$$

In this equation, C is a constant and α_c is the critical conversion. For $\alpha \ll \alpha_c$, $f(\alpha)$ is approximately equal to unity and the effect of diffusion is negligible, so that the reaction is kinetically controlled. Considering the diffusion effect, eqs. (1) and (2) can be rewritten as eqs. (4) and (5), respectively¹³:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (4)$$

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (5)$$

All kinetic constants in these equations of each epoxy resin system were obtained by taking advantage of a previous method.¹⁴ Figure 4 shows the comparison between the experimental values of reaction conversion and the values calculated using a generalized autocatalytic model for epoxy resin systems with phenol novolac hardener. The comparisons between the experimental and theoretical values in terms of a generalized n th-order model for epoxy resin systems with Xylok hardener are represented in Figure 5 and for the epoxy resin systems using DCPDP hardener in Figure 6. Good agreements were found over the whole curing temperature range for all epoxy resin systems.

The kinetic parameters are reported in Tables II and III for the epoxy resin systems with phenol novolac hardener that follow the autocatalytic curing reaction.

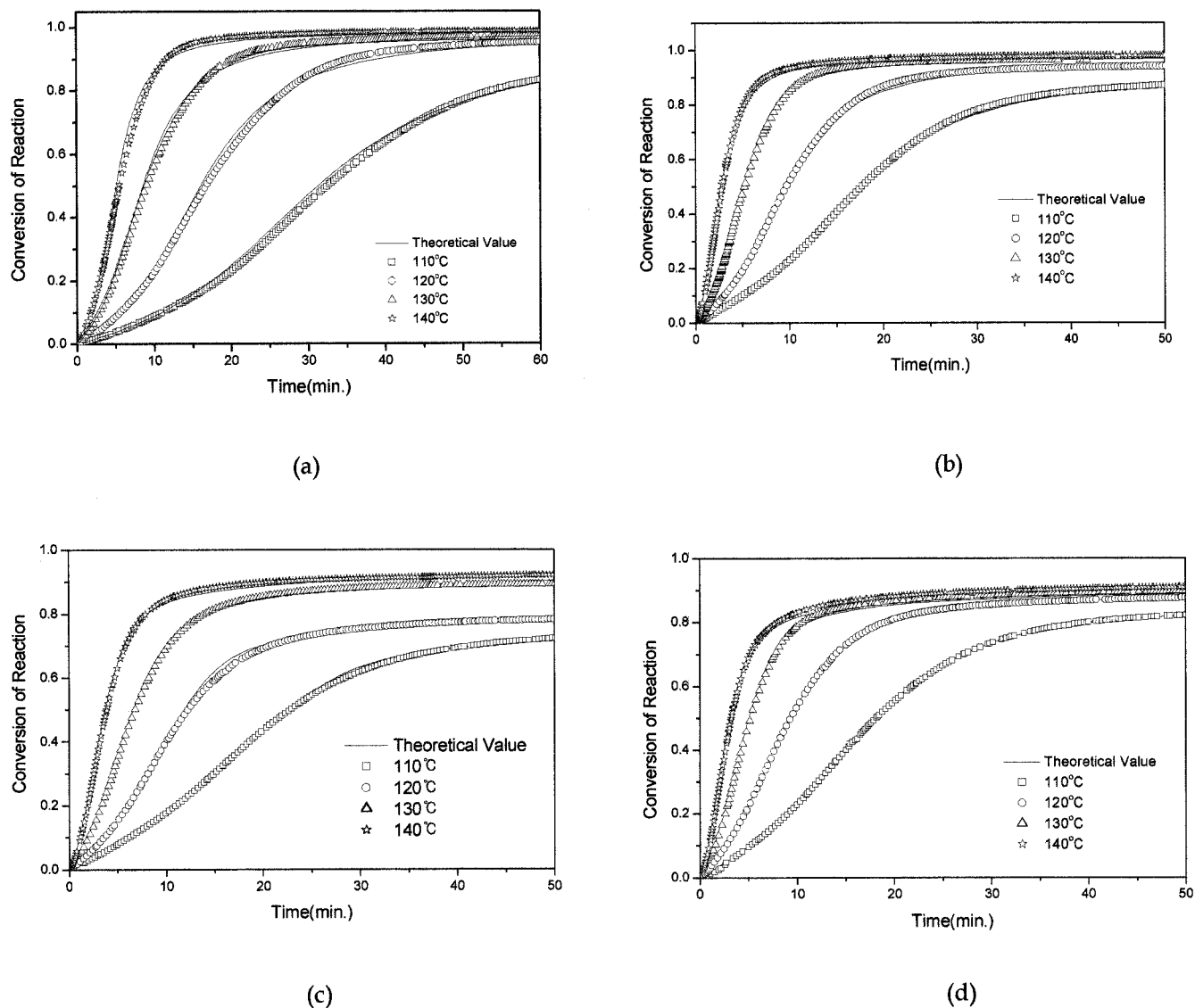


Figure 4 Comparisons between the experimental values of α and theoretical values obtained from the generalized autocatalytic model for the epoxy resin systems with phenol novolac hardener: (a) YX-4000H, (b) EOCN-C, (c) EOCN-1020, (d) NC-3000P.

It can be seen that the reaction rate of the EOCN-C system is the fastest and that of the YX-4000H system is the slowest, as shown in Figure 1. It is postulated that the increase of rate in the EOCN-C system should be attributable to higher values of the reaction rate constants k_1 , k_2 , and the reaction order than those of other epoxy systems, as summarized in Table II. In particular, the notable increase of reaction rate constant k_2 in the EOCN-C system can be observed, which would represent characteristics of an autocatalytic curing reaction. Even if the highest value of reaction order in the EOCN-C system and the lowest value of that in the NC-3000P system could be observed, it can be considered that the curing reactions of all these epoxy resin systems are close to a third-order kinetic mechanism, of which the rate-determining step would

be the termolecular reaction of epoxy resin, phenol novolac curing agent, and TPP for complex formation.¹⁵ A lower value of reaction order in the NC-3000P system was obtained compared to that of other epoxy systems, although the reaction conversion rate of the NC-3000P system is faster than that of either the YX-4000H or the EOCN-1020 system.

It is postulated that these phenomena are caused by the increase of reaction rate k_1 . The biphenyl epoxy resin used in EOCN-C is a biphenyl epoxy resin, excluding methyl groups in YX-4000H, and NC-3000P includes a novolac epoxy resin unit instead of *o*-cresol novolac epoxy resin of EOCN-1020. However, a large curing agent like the polymeric hardener used in this study can be considered to ignore steric interactions of the methyl groups as broadening the space between

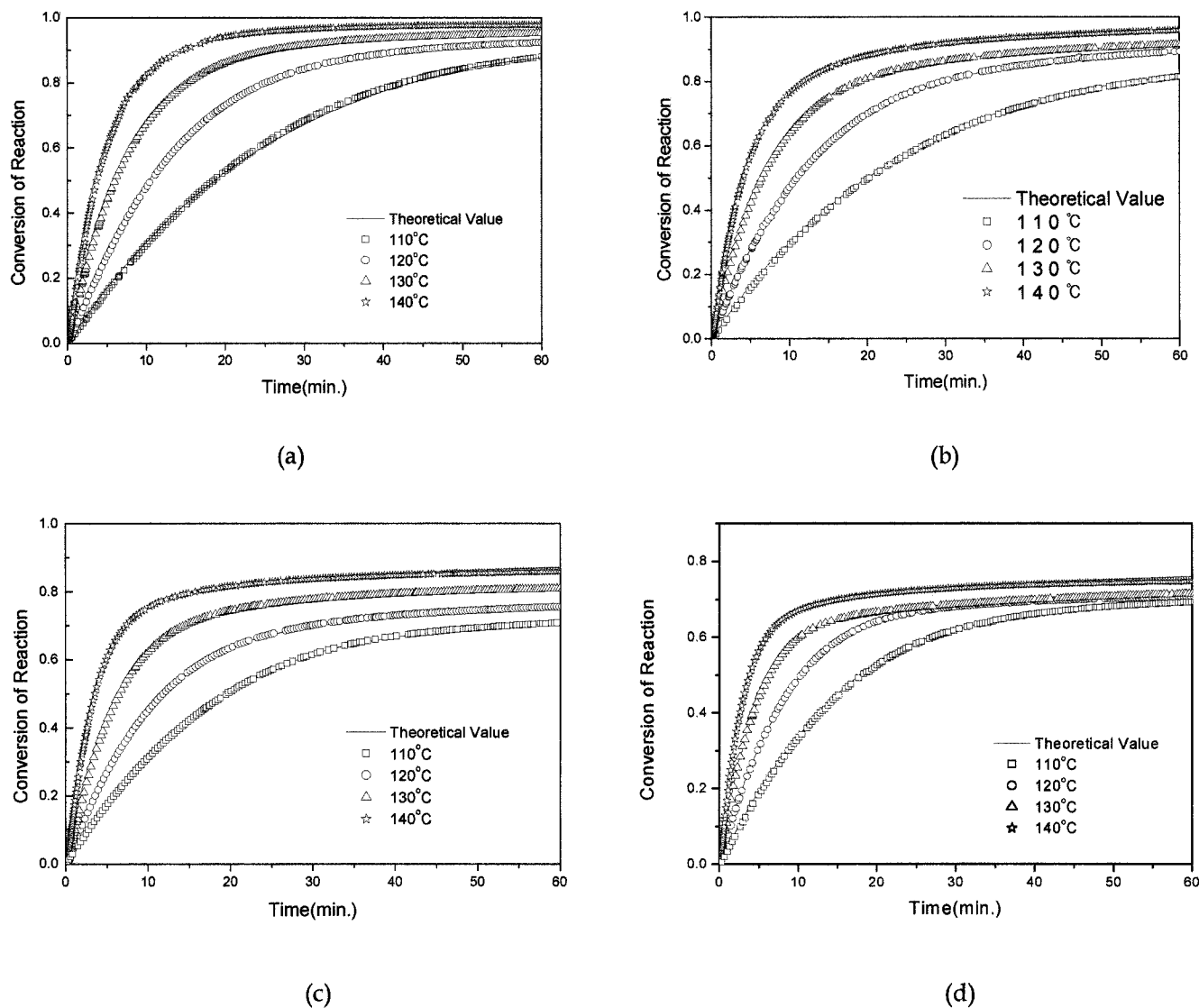


Figure 5 Comparisons between the experimental values of α and theoretical values obtained from the generalized n th-order model for the epoxy resin systems with Xylok hardener: (a) YX-4000H, (b) EOCN-C, (c) EOCN-1020, (d) NC-3000P.

biphenyl groups.¹⁶ If this methyl group effect could be ignored, it can be shown that the increases of reaction rate constants k_1 and k_2 were observed when biphenyl epoxy resin was simply mixed with *o*-cresol novolac epoxy resin, although the increase of reaction rate constant k_1 was seen only when it was introduced to novolac epoxy resin by chemical reaction. The increased reaction rate of EOCN-C is attributed to the higher reaction rate constant, reaction order, and lower activation energy than those of other epoxy resin systems, as shown in Table II. Therefore, it can be seen that, by physically mixing the system of biphenyl epoxy resin with *o*-cresol novolac epoxy resin, EOCN-C is more efficient with respect to the curing reaction rate than chemically mixing its system with novolac epoxy resin NC-3000P. The constant C and the critical conversion of reaction α_c in the generalized autocatalytic kinetic equation for epoxy resin systems with a

phenol novolac hardener are reported in Table III. Generally, the α_c increased with temperature but C showed no discernible trend in these systems.

The kinetic parameters for epoxy resin systems with Xylok hardener are summarized in Table IV. As shown in Figure 2, the reaction conversion rate of the NC-3000P and EOCN-1020 system is faster than that of the YX-4000H and EOCN-C system. That is caused by the higher value of reaction rate constant k and reaction order of the NC-3000P and EOCN-1020 system than those of other systems. Similarly, with epoxy resin systems with phenol novolac hardener, the α_c in the generalized n th-order kinetic equation increased with temperature, although a unique tendency cannot be found in C of eq. (5) for these systems. However, it can be shown that the value of α_c in the NC-3000P and EOCN-1020 system with higher reaction rate is lower than that of the YX-4000H and EOCN-C system with

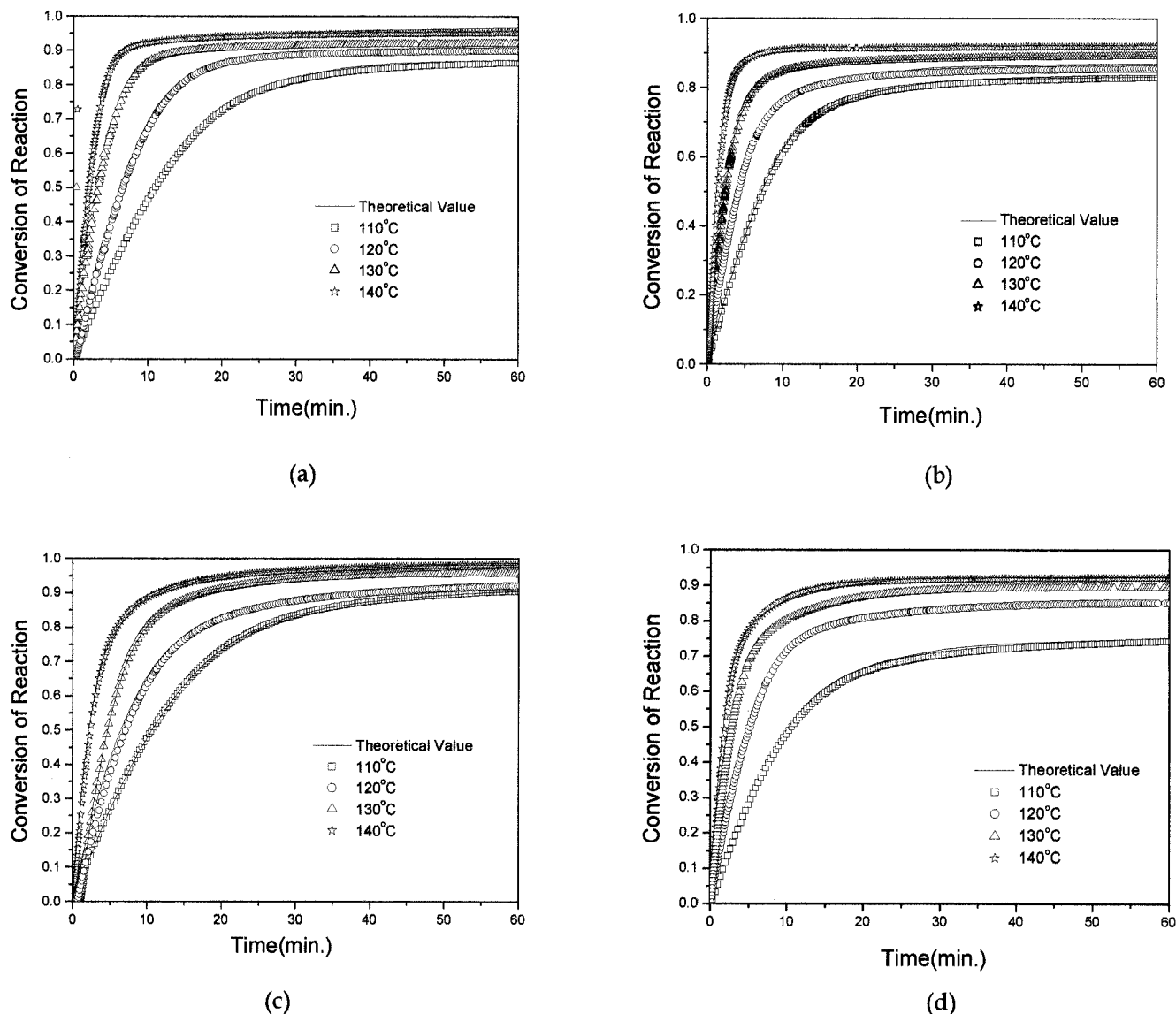


Figure 6 Comparisons between the experimental values of α and theoretical values obtained from the generalized n th-order model for the epoxy resin systems with DCPDP hardener: (a) YX-4000H, (b) EOCN-C, (c) EOCN-1020, (d) NC-3000P.

lower reaction rate, and is different in systems with phenol novolac hardener. It can be considered that the reaction of the YX-4000H and EOCN-1020 system with this curing agent is a first-order kinetic reaction mechanism, of which the rate-determining step could be the epoxide ring-opening reaction, whereas that of the EOCN-1020 and NC-3000P system seems to involve the presence of more than one type of kinetic mechanism.⁹

The reaction conversion rate of the EOCN-C and NC-3000P system with DCPDP hardener is faster than that of the YX-4000H and EOCN-1020 system, as represented in Figure 3. These increases of conversion rate are the result of the high values of reaction rate constant k , as shown in Table V. It can be seen that the curing process of all epoxy resin systems with DCPDP hardener is a first-order kinetic reaction mechanism,

and these systems show the same trend of C and α_c as that of other epoxy resin systems with different hardeners. It can also be shown that the α_c value of the EOCN-C and NC-3000P system, in which the reaction rate is fast, is smaller than that of the YX-4000H and EOCN-1020 system, in which the rate is slow. These phenomena, which cannot be observed in the autocatalytic kinetic reaction, but only in the n th-order reaction, can be interpreted to show that the diffusion-controlled reaction of epoxy resin systems can be observed at a lower reaction conversion because of their rapid reaction rate in the case of n th-order reaction.

The glass-transition temperature (T_g), according to the reaction conversion change, was measured to understand the relationships between molecular characteristics and thermodynamic properties. These results were analyzed using the following equation, based on

TABLE II
Kinetic Parameters of Epoxy Resin Compositions Using Phenol Novolac Hardener According to the Change of Epoxy Resin

Epoxy resin	Temperature (°C)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	m	n	Temperature dependency of the rate constant	Average $m + n$ value
YX-4000H	110	0.12×10^{-3}	0.34×10^{-2}	1.4	2.0	$k_1 = 9.36 \times 10^7 \exp(-8.72 \times 10^4/RT)$ $k_2 = 3.56 \times 10^7 \exp(-7.35 \times 10^4/RT)$	3.3
	120	0.24×10^{-3}	0.60×10^{-2}	1.4	1.8		
	130	0.49×10^{-3}	1.00×10^{-2}	1.4	1.8		
	140	0.86×10^{-3}	1.85×10^{-2}	1.5	1.8		
EOCN-C	110	0.32×10^{-3}	0.84×10^{-2}	1.8	2.3	$k_1 = 2.34 \times 10^6 \exp(-7.24 \times 10^4/RT)$ $k_2 = 1.15 \times 10^3 \exp(-3.77 \times 10^4/RT)$	3.4
	120	0.54×10^{-3}	1.10×10^{-2}	1.5	2.0		
	130	0.94×10^{-3}	1.33×10^{-2}	1.3	1.7		
	140	1.67×10^{-3}	2.06×10^{-2}	1.1	1.8		
EOCN-1020	110	0.24×10^{-3}	0.36×10^{-2}	1.4	2.0	$k_1 = 2.75 \times 10^6 \exp(-7.37 \times 10^4/RT)$ $k_2 = 2.12 \times 10^6 \exp(-6.40 \times 10^4/RT)$	3.3
	120	0.42×10^{-3}	0.77×10^{-2}	1.4	2.1		
	130	0.79×10^{-3}	1.15×10^{-2}	1.3	2.0		
	140	1.26×10^{-3}	1.56×10^{-2}	1.1	1.9		
NC-3000P	110	0.31×10^{-3}	0.32×10^{-2}	1.3	1.7	$k_1 = 2.64 \times 10^6 \exp(-6.52 \times 10^4/RT)$ $k_2 = 1.46 \times 10^6 \exp(-6.32 \times 10^4/RT)$	2.9
	120	0.60×10^{-3}	0.62×10^{-2}	1.2	1.8		
	130	1.04×10^{-3}	0.93×10^{-2}	1.2	1.8		
	140	1.34×10^{-3}	1.40×10^{-2}	0.9	1.9		

the principle of corresponding states, proposed by DiBenedetto¹⁷:

$$\frac{(T_g)_{\alpha=0}}{T_g} = 1 + C_1\alpha + C_2\alpha^2 \quad (6)$$

where C_1 is a system constant and C_2 is the index of the change in average mobility of the repeating segment. The values of C_1 and C_2 that give a best fit of the experimental data are summarized in Table VI. In general, the system constant C_1 for these epoxy resin systems represents similar values, except for epoxy resin systems with DCPDP hardener, which contains a dicyclopentadiene moiety that distinguishes it from

the molecular structure of other hardeners. It can be seen that the absolute values of C_2 decrease with the bulky molecular structures of epoxy resins for the epoxy-phenol novolac hardener systems with the same system constant. However, for the epoxy-Xylok hardener systems, the decrease of chain mobility can be observed in the YX-4000H epoxy resin system, which has a relatively small molecular structure, and the change of system constant can be seen in the NC-3000P epoxy system with the most bulky structure among the epoxy resins. It can be shown that the deviation of the system constant according to the change of epoxy resin is obtained in the epoxy systems with DCPDP hardener, which has the most bulky structure among the hardeners. The curing characteristics of epoxy systems are mainly influenced by the kind of hardener, although they are more dependent on the epoxy resin than on the curing agent used for the epoxy systems with a hardener that include a bulky group moiety.

The curing model of the epoxy resins with different phenolic functional hardeners based on a cure system using a biphenyl epoxy resin-amine type curing agent¹⁶ is suggested in Figure 7. As seen in this figure, the curing agent can act as a spacer and control the distances between epoxy resin units. It is postulated that an autocatalytic cure reaction (in which a secondary hydroxyl group produced by a cure reaction between epoxy and the phenol group would participate in the cure reaction) occurs in epoxy resin systems with phenol novolac hardener, in which R_1 is a methylene group with short length.⁹ If R_1 were a bulky group like Xylok or DCPDP as a curing agent, it can be considered that an n th-order

TABLE III
Values of the Constant C and Critical Conversion at Different Temperatures of Epoxy Resin Compositions Using Phenol Novolac as Hardener

Epoxy resin	Temperature (°C)	C	α_c
YX-4000H	110	25.3	0.90
	120	29.4	0.98
	130	27.5	0.99
	140	33.1	0.98
EOCN-C	110	31.0	0.88
	120	38.2	0.94
	130	40.1	0.93
	140	23.6	0.98
EOCN-1020	110	29.9	0.65
	120	27.7	0.68
	130	23.6	0.83
	140	22.4	0.82
NC-3000P	110	25.1	0.80
	120	28.1	0.83
	130	29.4	0.82
	140	18.0	0.81

TABLE IV
Kinetic Parameters of Epoxy Resin Compositions Using Xylok Hardener According to the Change of Epoxy Resin

Epoxy resin	Temperature (°C)	k (s ⁻¹)	n	C	α_c	Temperature dependency of the rate constant	Average n value
YX-4000H	110	0.62×10^{-3}	1.0	36.4	0.89	$k = 4.84 \times 10^7 \exp(-7.99 \times 10^4/RT)$	1.2
	120	1.14×10^{-3}	1.0	20.1	0.86		
	130	2.22×10^{-3}	1.3	34.7	0.91		
	140	3.77×10^{-3}	1.3	40.0	0.96		
EOCN-C	110	0.62×10^{-3}	1.2	26.1	0.82	$k = 3.10 \times 10^7 \exp(-7.85 \times 10^4/RT)$	1.3
	120	1.14×10^{-3}	1.2	21.8	0.84		
	130	2.20×10^{-3}	1.3	20.0	0.84		
	140	3.74×10^{-3}	1.5	17.9	0.92		
EOCN-1020	110	0.68×10^{-3}	1.4	26.9	0.65	$k = 7.08 \times 10^7 \exp(-8.09 \times 10^4/RT)$	1.5
	120	1.17×10^{-3}	1.5	21.0	0.66		
	130	2.22×10^{-3}	1.5	22.1	0.70		
	140	4.25×10^{-3}	1.5	20.1	0.74		
NC-3000P	110	0.75×10^{-3}	1.4	20.7	0.61	$k = 1.17 \times 10^7 \exp(-7.47 \times 10^4/RT)$	1.6
	120	1.36×10^{-3}	1.5	24.3	0.62		
	130	2.43×10^{-3}	1.8	26.9	0.60		
	140	4.09×10^{-3}	1.8	26.0	0.63		

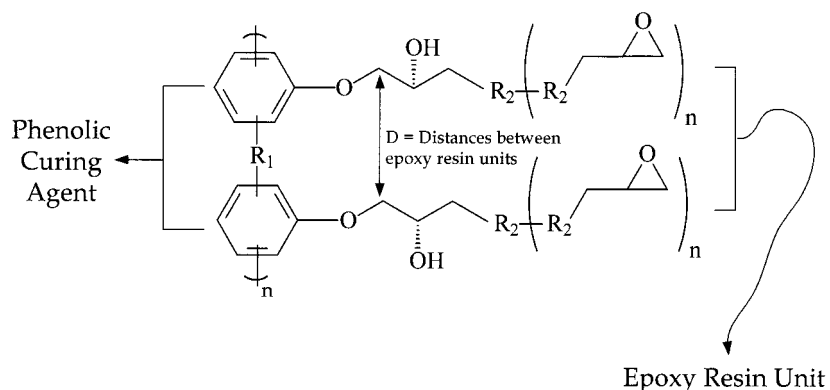
TABLE V
Kinetic Parameters of Epoxy Resin Compositions Using DCPDP Hardener According to the Change of Epoxy Resin

Epoxy resin	Temperature (°C)	k (s ⁻¹)	n	C	α_c	Temperature dependency of the rate constant	Average n value
YX-4000H	110	0.94×10^{-3}	0.6	14.5	0.76	$k = 1.44 \times 10^8 \exp(-8.28 \times 10^4/RT)$	0.7
	120	1.63×10^{-3}	0.7	20.0	0.80		
	130	3.41×10^{-3}	0.8	32.4	0.83		
	140	5.80×10^{-3}	0.8	42.1	0.87		
EOCN-C	110	1.46×10^{-3}	0.7	18.0	0.70	$k = 7.04 \times 10^7 \exp(-7.88 \times 10^4/RT)$	0.8
	120	3.06×10^{-3}	0.8	18.4	0.71		
	130	4.75×10^{-3}	0.8	14.7	0.74		
	140	9.00×10^{-3}	0.8	24.8	0.80		
EOCN-1020	110	1.76×10^{-3}	1.0	16.1	0.80	$k = 2.62 \times 10^7 \exp(-6.93 \times 10^4/RT)$	1.0
	120	2.11×10^{-3}	0.9	17.5	0.82		
	130	3.06×10^{-3}	0.9	16.6	0.84		
	140	5.46×10^{-3}	1.0	13.4	0.84		
NC-3000P	110	1.15×10^{-3}	1.0	17.7	0.63	$k = 1.93 \times 10^8 \exp(-8.30 \times 10^4/RT)$	1.0
	120	2.15×10^{-3}	0.9	21.5	0.72		
	130	4.30×10^{-3}	0.9	15.5	0.77		
	140	7.23×10^{-3}	1.1	13.2	0.73		

cure reaction (in which a secondary hydroxyl group cannot participate in cure reaction) can proceed because the reaction between the secondary hydroxyl group and the epoxy group in an epoxy resin unit is very difficult because of broadened distances between the groups. It can be shown that the cure characteristics of biphenyl-type epoxy resin systems are mainly dependent on the curing agent, although they can be more greatly influenced by the kinds of epoxy resin in epoxy resin systems with a very large group like DCPDP as a curing agent. This influence is a consequence of the emergence of a different cure system, which is attributed to the decrease of molecular interactions such as hydrophobic interaction between biphenyl groups of epoxy resins because of expanding distances between the groups.

TABLE VI
Values of C_1 and C_2 in the DiBenedetto Equation for Epoxy Resin Systems with Different Hardeners

Epoxy resin	Hardener	C_1	C_2
YX-4000H	Phenol novolac	-0.1	-0.18
EOCN-C		-0.1	-0.13
EOCN-1020		-0.1	-0.14
NC-3000P		-0.1	-0.09
YX-4000H	Xylok	-0.1	-0.10
EOCN-C		-0.1	-0.13
EOCN-1020		-0.1	-0.14
NC-3000P		-0.2	-0.05
YX-4000H	DCPDP	-0.1	-0.14
EOCN-C		0	-0.14
EOCN-1020		-0.2	-0.08
NC-3000P		-0.2	-0.01



R₁ = Functional Unit of Phenol Type Curing Agent (e.g., methylene, aromatic, DCPDP and so on)
 R₂ = Functional Unit of Epoxy Resin (e.g., biphenyl, novolac, o-cresol novolac and so on)

Figure 7 Curing model of the epoxy resin systems with different phenolic functional hardeners.

CONCLUSIONS

The curing characteristics of epoxy resin systems that include a biphenyl moiety with the change of hardeners were investigated by the thermal analysis method. It can be shown that the curing properties of each epoxy resin system are mainly dependent on the kind of hardener rather than the kind of epoxy resin, although an epoxy resin can influence the properties of the epoxy resin system with a bulky hardener group. The reaction conversion rate of the EOCN-C epoxy resin system, made by physically mixing biphenyl epoxy resin with *o*-cresol novolac epoxy resin, is the fastest among the epoxy resin systems, in which the phenol novolac hardener follows an autocatalytic kinetic mechanism, which is attributed to the higher reaction rate constant, the reaction order, and lower activation energy. In the epoxy resin systems with Xylok and DCPDP hardener following an *n*th-order kinetic reaction, high reaction conversion rate values of the NC-3000P epoxy resin system, synthesized by chemically reacting the biphenyl unit with the novolac epoxy group, were obtained. The cure model using a curing agent as a spacer was suggested, and the curing characteristics of these epoxy systems with different phenolic functional hardeners can be explained in terms of this model.

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