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Contributions of the network structure to the cure kinetics of epoxy resin systems according to the change of hardeners

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Abstract

The cure kinetics of epoxy resin systems was investigated according to the change of curing agents, and analyzed in respect of the network structure. An autocatalytic cure reaction can be shown in the epoxy resin systems with phenol novolac hardener regardless of the kinds of epoxy resin and the epoxy resin systems using Xylok and dicyclopentadiene type phenol resin curing agents follow *n*th-order kinetic mechanism. The conversion rates of novolac epoxy resins with phenyl and DCPD (dicyclopentadiene) moiety are higher than biphenyl epoxy resin (YX-4000H) and *o*-cresol novolac epoxy resin (EOCN-1020) systems. All kinetic parameters of each epoxy resin systems were reported in terms of generalized kinetic equation that considered diffusion term, and the network structure of each epoxy resin systems with different curing agents were analyzed using DiBenedetto equation. These kinetic data were interpreted in terms of network structure model in which a curing agent can act as a spacer and control the distances between epoxy resin units. © 2002 Published by Elsevier Science Ltd.

Keywords: Epoxy resin; Cure kinetics; Network structure

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1. Introduction

Since the requirements of the high-density integration and thin packaging technique of semiconductor have been increasing, a remarkable progress in plastic packaging materials has been shown [1]. However, there are serious problems due to the moisture absorption and thermal properties of epoxy molding compound (EMC) for semiconductor encapsulation according to the environmental requirements such as Pb free soldering. Some studies on the failure of plastic packages for semiconductors were reported during storage in a humid environment and reflow soldering process [2–5]. Water would condense in micro-pores of inner packages; especially in the die pad-die attach interface, which is absorbed through the package exterior, and interfaces between lead frame and EMC. This condensed moisture is vaporized during reflow soldering and caused in delamination and popcorn crack. Various methods to solve them have been presented, however, an important technique is the modification of epoxy resins and hardeners.

The most general epoxy resin system for this application is *o*-cresol novolac epoxy resin and phenol novolac hardener, of which the curing kinetics according to the changes of hardeners was reported [6]. Low viscosity epoxy resin, especially biphenyl type epoxy resin is introduced which makes high filler loading easy, and curing characteristics of these systems were investigated in previous articles [7,8].

Recently, new epoxy resins are developed for high thermal and moisture resistance packaging materials, which included aromatic and dicyclopentadiene (DCPD) moiety. This epoxy resin shows low viscosity, low water absorption, high adhesives, and high toughness [9]. In this study, the curing characteristics of such new epoxy resins were investigated according to the change of kinds of curing agents. They were compared with the cure kinetics of conventional biphenyl epoxy resin (YX-4000H) and *o*-cresol novolac epoxy resin (EOCN-1020) in order to perform the systematic study. The contributions of network structure to these kinetic data were investigated using curing model in which a hardener can act as a spacer [10].

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2. Experimental

2.1. Materials

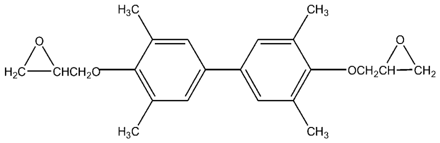
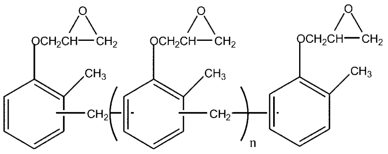
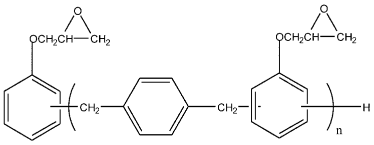
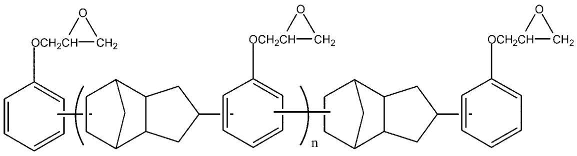
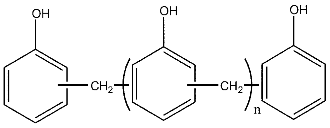
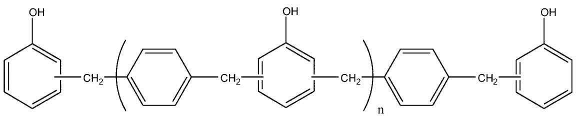
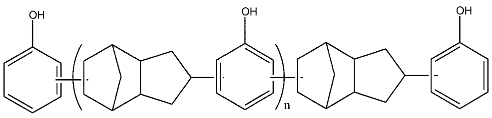
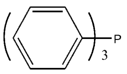
The new epoxy resins including phenyl group and DCPD moiety used in this experiment are XP-2030 and XD-1000 grade, respectively, which are obtained from Nippon Kayaku Co. YX-4000H as received from Yuka Shell Co., and EOCN-1020 supplied by Nippon Kayaku Co. were used as reference state of biphenyl epoxy resin and *o*-cresol novolac epoxy resin.

Phenol novolac resin (PSM 4261) obtained from Gunnei Chemical Co., Xylok made by Mitsui Tohatsu Chemical, and dicyclopentadiene type phenol resin (DCPDP) supplied by Nippon Petrochemicals Co. were used as hardeners. A catalyst used was triphenylphosphine (TPP, Hokko Chemical Co.). Detailed descriptions of chemical structures used in this study are summarized in Table 1.

2.2. Sample preparation

All epoxy resin compositions in this study are composed

Table 1
Description of raw materials used in this study

Component	Grade name	Structure	Remarks
Epoxy resin	YX-4000H		EEW = 193[a]
	EOCN-1020		EEW = 198
	XP-2030		EEW = 236
	XD-1000		EEW = 240
Hardeners	PSM-4261		HEW = 104[b]
	Xylok		HEW = 178
	DCPDP		HEW = 170
Catalyst	TPP		

[a] EEW, epoxy equivalent weight (g/equiv.).

[b] HEW, hydroxy equivalent weight (g/equiv.).

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

2.3. DSC measurement

Calorimetric measurements were performed using a TA instruments differential scanning calorimeter (TA-2020). This was calibrated in the −40–450 °C 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 °C/min from −10 to 300 °C, beyond which the decomposition was observed. A set of isothermal cure curves has been obtained in order to evaluate the kinetic parameter for the curing reactions.

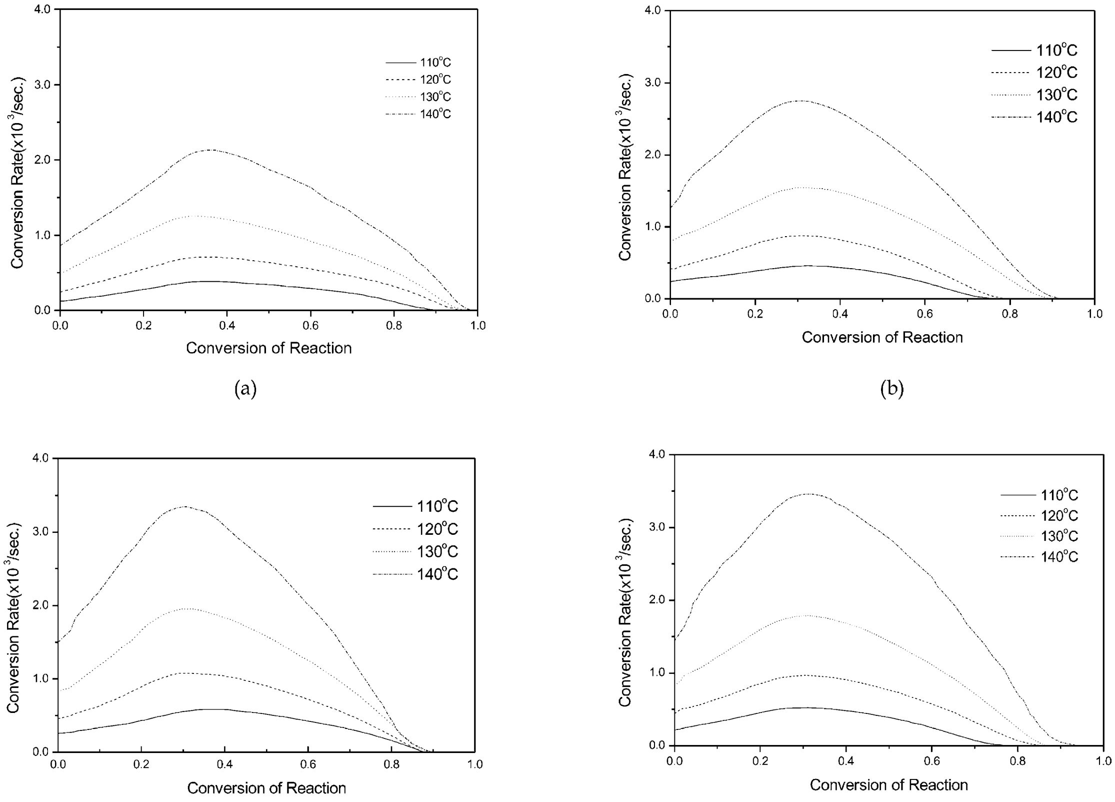
3. Results and discussion

The reaction conversion changes of new novolac epoxy resin systems with phenyl and DCPD moiety were examined according to the hardener changes, and compared with biphenyl and *o*-cresol novolac epoxy resin systems. The reaction conversion rate changes of each epoxy resin system with phenol novolac hardener are plotted as a function of reaction conversion in Fig. 1. The reaction conversion rates of these epoxy resin systems with Xylok hardener are represented in Fig. 2 and they are shown for the DCPDP hardener in Fig. 3. As seen in these figures, it can be found that epoxy resin systems with phenol novolac hardener follow autocatalytic kinetic reaction and *n*th-order kinetic reaction is observed in epoxy resin systems using Xylok and DCPDP hardeners [11,12]. It can be thought that a curing reaction mechanism of epoxy resin system is dependent on the kind of a curing agent rather than an epoxy resin from these experimental results.

To precisely predict the cure kinetics over the whole range of conversion, the autocatalytic and *n*th-order model can be generalized in terms of the introduction of a diffusion term [13]. A generalized autocatalytic kinetic equation is represented in Eq. (1), and a generalized *n*th-order kinetic equation is shown in Eq. (2), respectively [14]

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

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{2}$$



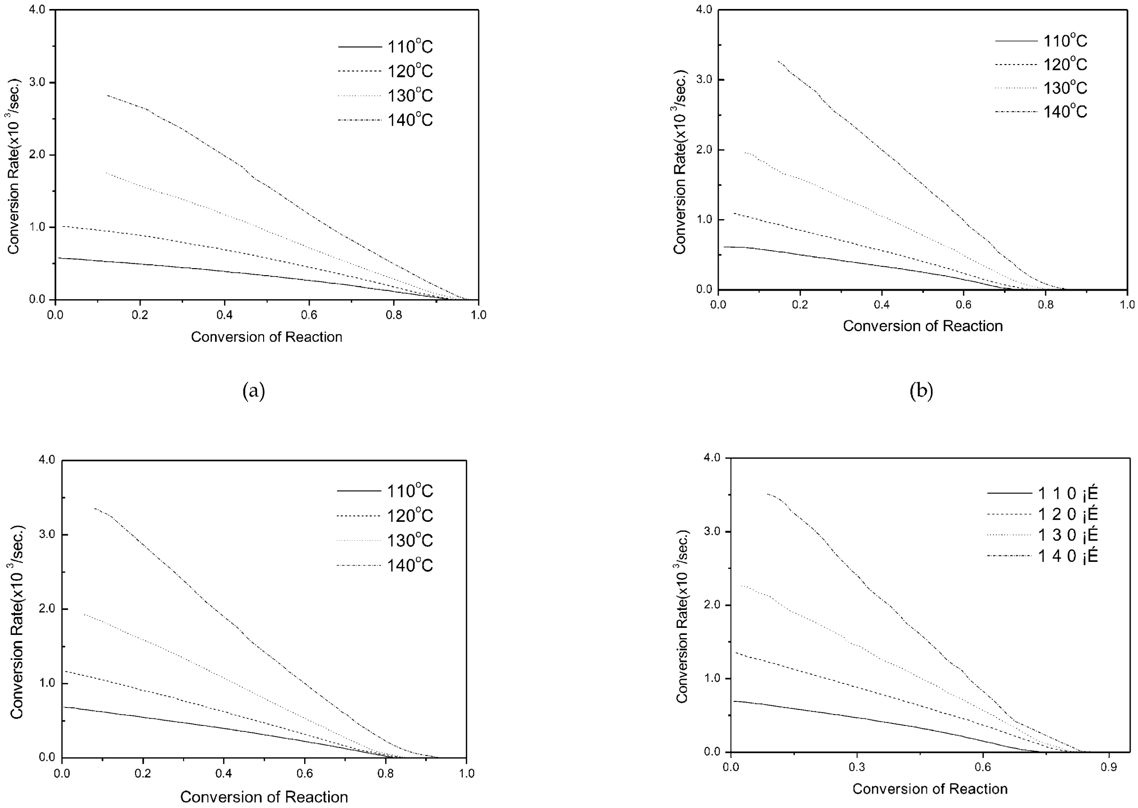
(a)

(b)

(c)

(d)

Fig. 1. The isothermal conversion rate as a function of the conversion of epoxy resin systems with phenol novolac hardener: (a) YX-4000H, (b) EOCN-1020, (c) XP-2030, and (d) XD-1000.



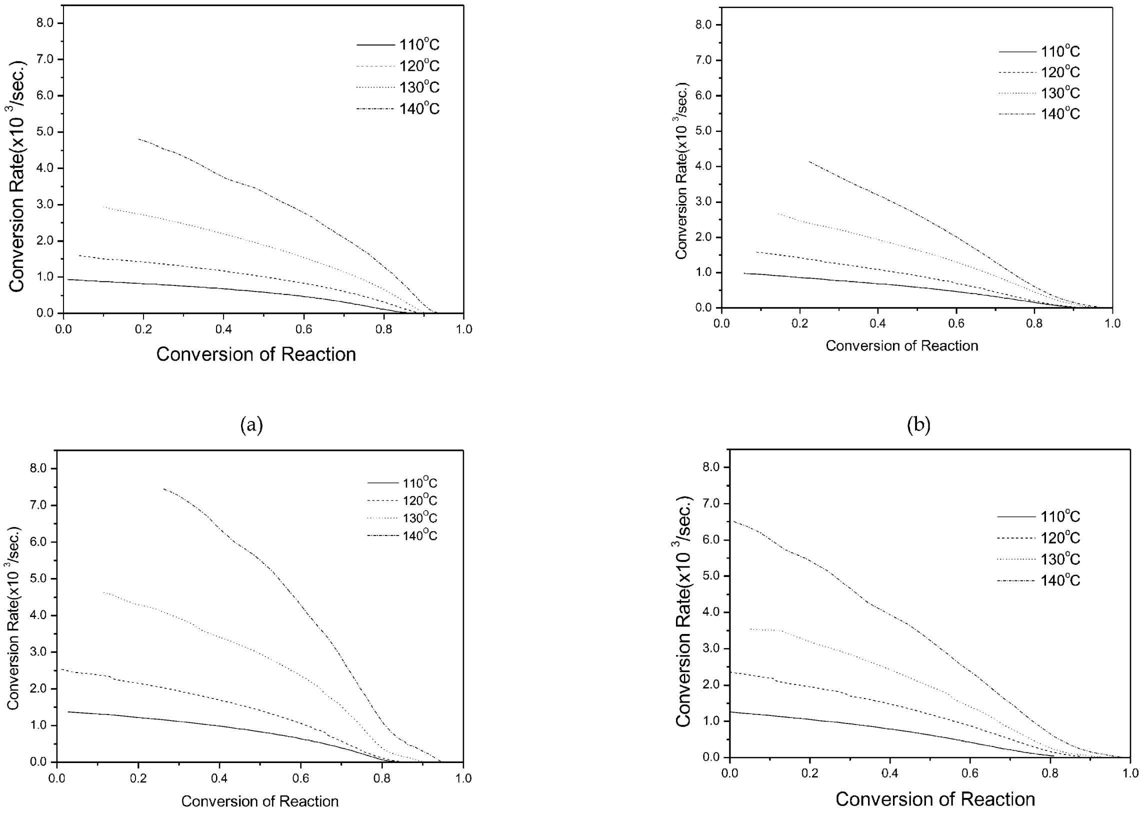
(a) (b) (c) (d)

Fig. 2. The isothermal conversion rate as a function of the conversion of epoxy resin systems with Xylok hardener: (a) YX-4000H, (b) EOCN-1020, (c) XP-2030, and (d) XD-1000.

All kinetic constants in these equations of each epoxy resin system were obtained by taking advantage of previous method [12]. Fig. 4 shows the comparison between the experimental values of reaction conversion and these values calculated using generalized autocatalytic model for epoxy resin systems with phenol novolac hardener. The comparisons between the experimental and theoretical values in terms of generalized *n*th-order model for epoxy resin systems with Xylok hardener were represented in Fig. 5 and they were shown in Fig. 6 for epoxy resin systems using

Table 2
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 dependence of the rate constant	Average $m+n$ value
YX-4000H	110	0.12×10^{-3}	0.34×10^{-2}	1.4	2.0	$k_1=9.36\times10^7\exp(-8.72\times10^4/RT)$	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	$k_2=3.56\times10^7\exp(-7.35\times10^4/RT)$	
	140	0.86×10^{-3}	1.85×10^{-2}	1.5	1.8		
EOCN-1020	110	0.24×10^{-3}	0.36×10^{-2}	1.4	2.0	$k_1=2.75\times10^6\exp(-7.37\times10^4/RT)$	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	$k_2=2.12\times10^6\exp(-6.40\times10^4/RT)$	
	140	1.26×10^{-3}	1.56×10^{-2}	1.1	1.9		
XP-2030	110	0.26×10^{-3}	0.82×10^{-2}	1.8	2.4	$k_1=9.08\times10^6\exp(-7.73\times10^4/RT)$	4.0
	120	0.46×10^{-3}	1.39×10^{-2}	1.6	2.5		
	130	0.83×10^{-3}	2.29×10^{-2}	1.5	2.5	$k_2=4.25\times10^6\exp(-6.38\times10^4/RT)$	
	140	1.50×10^{-3}	3.50×10^{-2}	1.4	2.4		
XD-1000	110	0.22×10^{-3}	0.68×10^{-2}	1.5	2.8	$k_1=4.04\times10^7\exp(-8.25\times10^4/RT)$	3.7
	120	0.44×10^{-3}	0.90×10^{-2}	1.4	2.4		
	130	0.83×10^{-3}	1.48×10^{-2}	1.3	2.2	$k_2=1.33\times10^6\exp(-5.36\times10^4/RT)$	
	140	1.44×10^{-3}	2.24×10^{-2}	1.2	2.0		



(a) (b) (c) (d)

Fig. 3. The isothermal conversion rate as a function of the conversion of epoxy resin systems with DCPDP hardener: (a) YX-4000H, (b) EOCN-1020, (c) XP-2030, and (d) XD-1000.

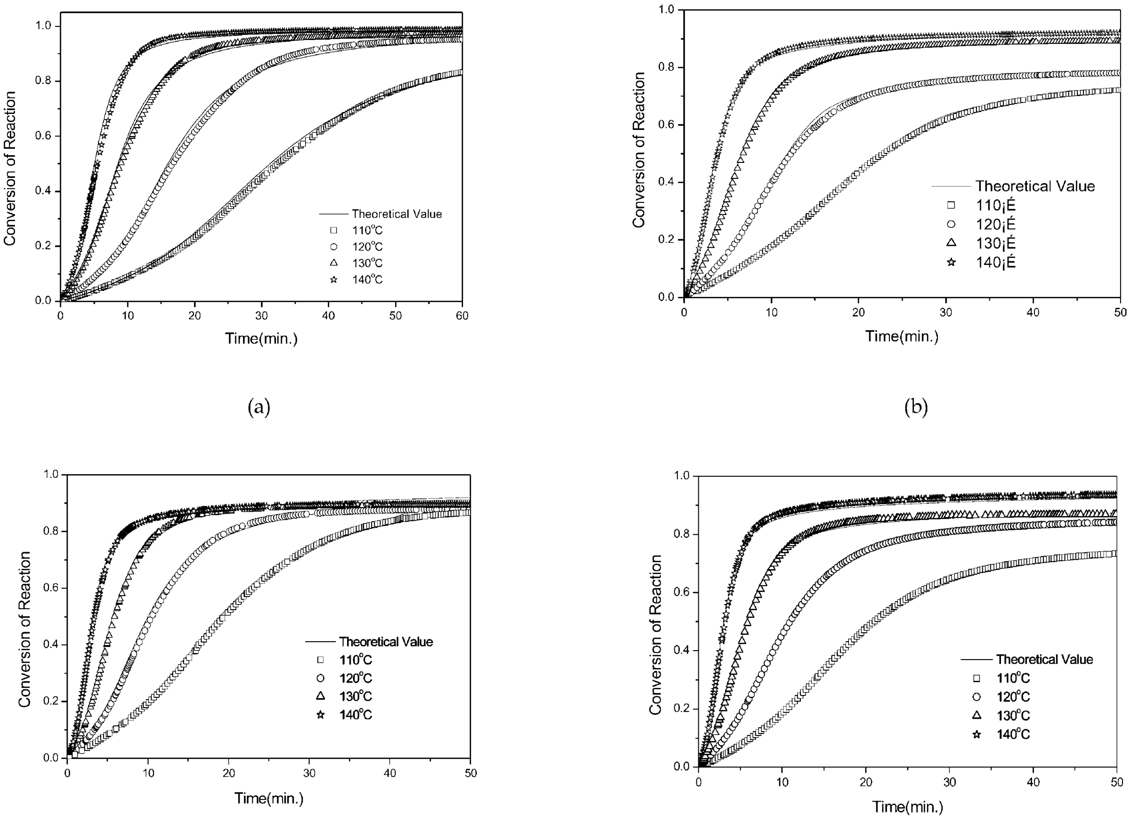
DCPDP hardener. Good agreements were found over the whole curing temperature range for all epoxy resin systems.

The kinetic parameters were summarized in Table 2, the epoxy resin systems with phenol novolac hardener. It can be seen that the reaction rate of XP-2030 and XD-1000 epoxy resin systems are faster than YX-4000H and EOCN-1020 system as shown in Fig. 1. It can be considered that the increase in the rate of XP-2030 and XD-1000 systems should be due to the higher values of the reaction rate constants k_1, k_2 and reaction order rather than other epoxy systems as reported in Table 2. The constant, C and the critical conversion of reaction, α_c in generalized autocatalytic kinetic equation (Eq. (1)) for epoxy resin systems with a phenol novolac hardener are reported in Table 3. Generally, the α_c increased with temperature, but C showed no discernible trend in these systems. It can be seen that values of α_c for high temperature in novolac type epoxy resin systems such as EOCN-1020, XP-2030, and XD-1000 epoxy resin with phenol novolac hardeners are similar and the lower values of α_c are also represented in novolac type epoxy resin systems than biphenyl epoxy resin system.

The kinetic parameters for epoxy resin systems with Xylok hardener were summarized in Table 4. As shown in Fig. 2, the reaction conversion rate of XP-2030 and XD-1000 epoxy resin system is faster than other epoxy resin systems, even if these differences were small. That is caused in the higher value of reaction rate constant of XP-2030 and XD-1000 system than other systems. Although XP-2030 and XD-1000 epoxy resin system shows as same value of reaction order as EOCN-1020 epoxy resin system, a lower activation energy of XP-2030 and XD-1000 system than

Table 3
Values of the constant C and critical conversion at different temperature 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-1020	110	29.9	0.65
	120	27.7	0.68
	130	23.6	0.83
	140	22.4	0.82
XP-2030	110	29.3	0.89
	120	37.1	0.89
	130	34.1	0.89
	140	28.9	0.84
XD-1000	110	18.0	0.65
	120	26.2	0.77
	130	32.9	0.80
	140	27.2	0.83



(a) (b) (c) (d)

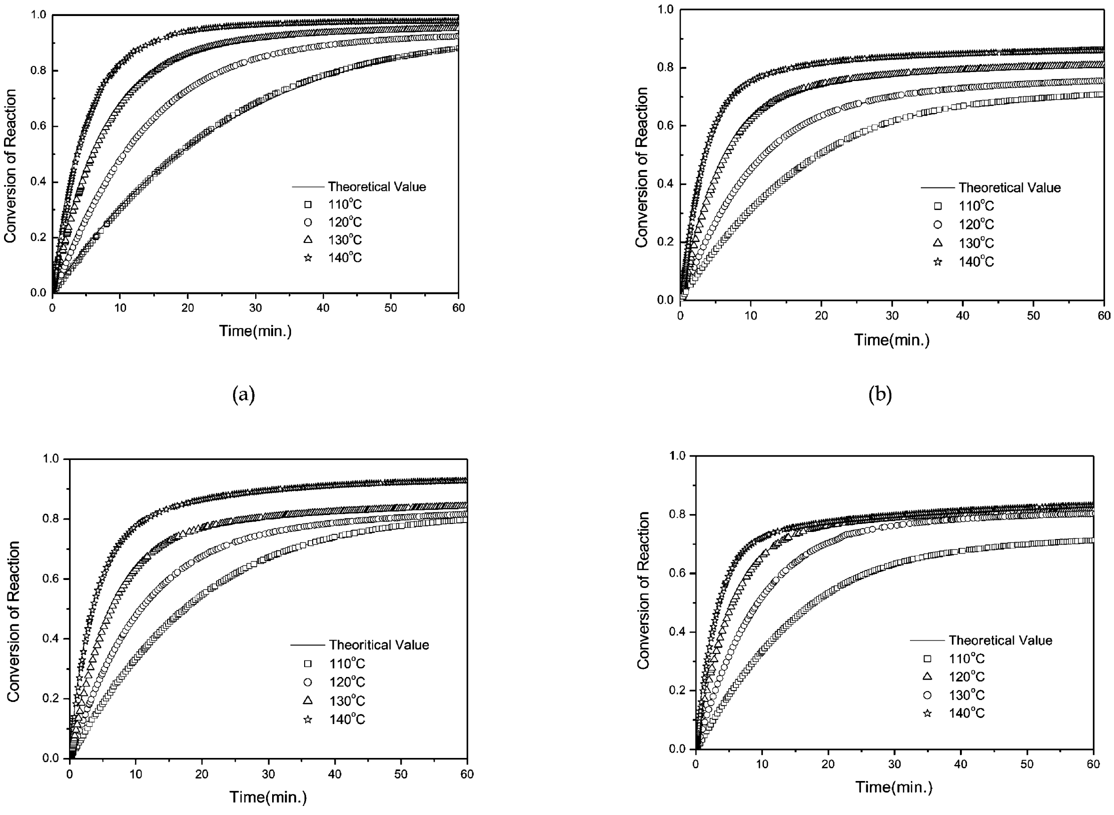
Fig. 4. Comparisons between the experimental values of α and theoretical values obtained from generalized autocatalytic model for the epoxy resin systems with phenol novolac hardener: (a) YX-4000H, (b) EOCN-1020, (c) XP-2030, and (d) XD-1000.

EOCN-1020 system can make the reaction conversion rate faster than EOCN-1020 system. Similarly in epoxy resin systems with phenol novolac hardener, the α_c in generalized nth-order kinetic equation (Eq. (2)) increased with temperature but a unique tendency cannot be found out in C of Eq. (2) for these systems. It can also be shown that the value of α_c in novolac type epoxy resin systems are lower than YX-4000H as shown in phenol novolac hardener systems.

The reaction conversion rates of XP-2030 and XD-1000 systems with DCPDP hardener are far faster than

Table 4
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 dependence of the rate constant	Average n value
YX-4000H	110	0.62×10^{-3}	1.0	36.4	0.89	$k = 4.84\times10^{7}\exp(-7.99\times10^{4}/RT)$	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-1020	110	0.68×10^{-3}	1.4	26.9	0.65	$k = 7.08\times10^{7}\exp(-8.09\times10^{4}/RT)$	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		
XP-2030	110	0.70×10^{-3}	1.1	18.7	0.74	$k = 5.06\times10^{7}\exp(-7.97\times10^{4}/RT)$	1.4
	120	1.23×10^{-3}	1.3	18.1	0.73		
	130	2.20×10^{-3}	1.5	20.2	0.74		
	140	4.34×10^{-3}	1.7	22.5	0.86		
XD-1000	110	0.73×10^{-3}	1.3	20.7	0.63	$k = 2.65\times10^{7}\exp(-7.74\times10^{4}/RT)$	1.5
	120	1.42×10^{-3}	1.4	23.5	0.72		
	130	2.43×10^{-3}	1.5	23.9	0.71		
	140	4.34×10^{-3}	1.7	22.5	0.70		



(a) (b)

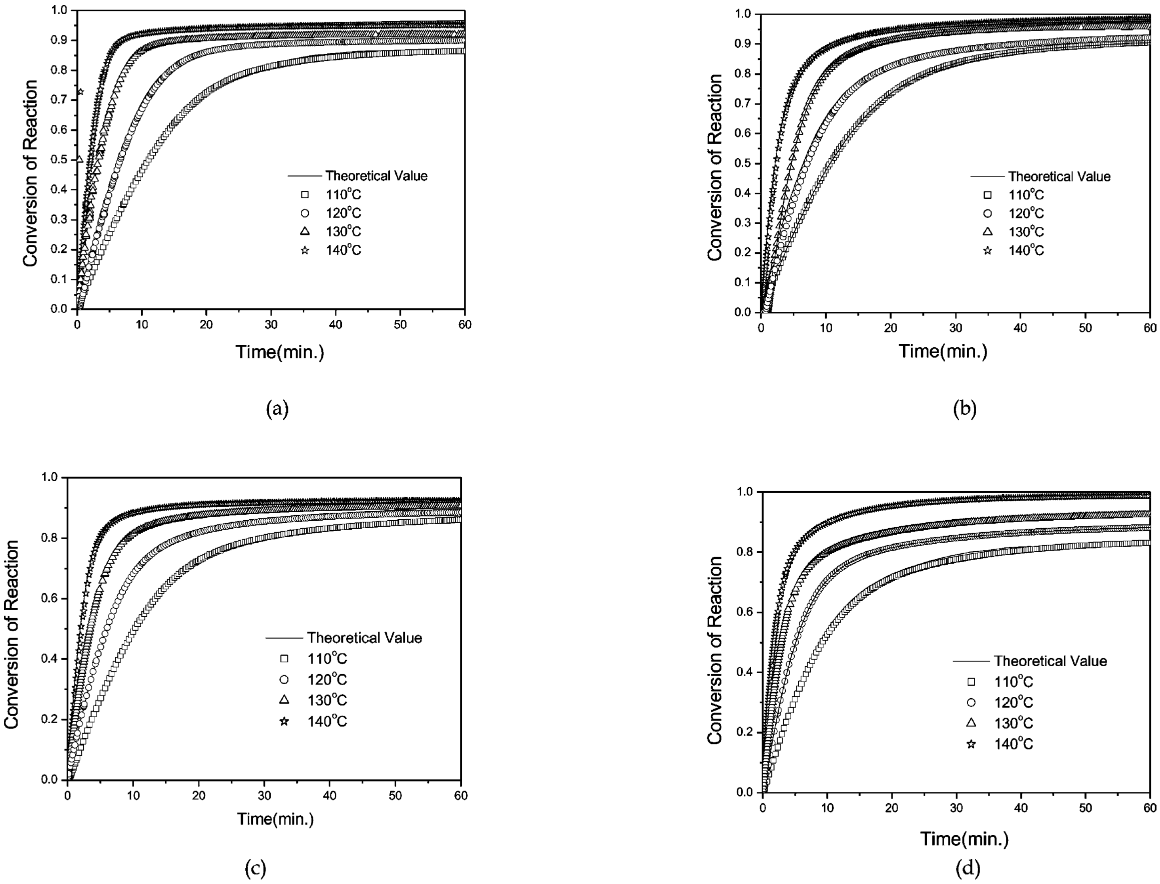
(c) (d)

Fig. 5. Comparisons between the experimental values of α and theoretical values obtained from generalized nth-order model for the epoxy resin systems with Xylok hardener: (a) YX-4000H, (b) EOCN-1020, (c) XP-2030, and (d) XD-1000.

YX-4000H and EOCN-1020 system as represented in Fig. 3. As shown in Table 5, these increases of conversion rate are due to the higher values of reaction rate constant in XP-2030 and XD-1000 epoxy resin systems. It can be seen that the values of α_c for high temperature in novolac type epoxy resin systems are lower than the YX-4000H system as shown in other curing agent systems, however, differences of α_c between these systems are smaller than epoxy resin systems with other hardeners. It can be considered that the contributions of epoxy resin to curing structures are reduced

Table 5
Kinetic parameters of epoxy resin compositions using DCPCP hardener according to the change of epoxy resin

Epoxy resin	Temperature (°C)	k (s^{-1})	n	C	α_c	Temperature dependence 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-1020	110	1.16×10^{-3}	1.0	16.1	0.80	$k = 2.62 \times 10^7 \exp(-6.93 \times 10^4/RT)$	1.0
	120	1.76×10^{-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		
XP-2030	110	1.43×10^{-3}	0.7	21.1	0.72	$k = 9.38 \times 10^8 \exp(-8.76 \times 10^4/RT)$	0.8
	120	2.29×10^{-3}	0.8	30.6	0.67		
	130	5.14×10^{-3}	0.8	20.4	0.75		
	140	9.75×10^{-3}	0.9	16.3	0.79		
XD-1000	110	1.27×10^{-3}	0.8	11.7	0.68	$k = 1.09 \times 10^7 \exp(-7.34 \times 10^4/RT)$	0.9
	120	2.38×10^{-3}	0.9	14.6	0.74		
	130	3.67×10^{-3}	1.0	13.9	0.74		
	140	6.67×10^{-3}	1.0	10.7	0.79		



(a) (b)

(c) (d)

Fig. 6. Comparisons between the experimental values of α and theoretical values obtained from generalized nth-order model for the epoxy resin systems with DCPDP hardener: (a) YX-4000H, (b) EOCN-1020, (c) XP-2030, and (d) XD-1000.

as a hardener including bulky group such as DCPDP is introduced.

The glass transition temperature (T_g) according to reaction conversion change was measured in order to understand the relationships between molecular characteristics and thermodynamic properties. These results were analyzed using DiBenedetto equation (Eq. (3)) that is based on the principle of corresponding states [15]

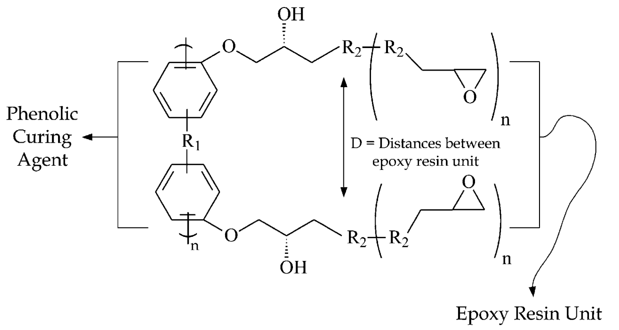
$$\frac{(T_g)_{\alpha=0}}{T_g} = 1 + C_1\alpha + C_2\alpha^2 \tag{3}$$

where C_1 is 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 6. Although YX-4000H epoxy systems with different phenolic hardeners showed a same value of system constant C_1 irrespective of hardeners, novolac type epoxy resin systems represented different values of it in accordance with hardener changes. It can be thought that novolac type epoxy resin systems are more influenced by hardener changes than biphenyl epoxy resin system, and these effects can be seen obviously in XD-1000 epoxy resin systems with bulky DCPD moiety. It can be seen in principle that absolute values of C_2 for each epoxy resin system with same system constant decrease with hardeners including bulky group moiety.

Ochi et al. suggested that curing model containing mesogenic groups such as biphenyl moiety [16,17]. A curing model with phenolic curing agent which can act as spacer and control the distances between epoxy resin was

Table 6
The 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
	Xylok	−0.1	−0.10
	DCPDP	−0.1	−0.14
EOCN-1020	Phenol novolac	−0.1	−0.14
	Xylok	−0.1	−0.14
	DCPDP	−0.2	−0.08
XP-2030	Phenol novolac	−0.2	−0.06
	Xylok	−0.1	−0.16
	DCPDP	−0.2	−0.01
XD-1000	Phenol novolac	−0.2	−0.04
	Xylok	−0.1	−0.09
	DCPDP	−0.3	−0.17



R$_1$ = Functional Unit of Phenol Type Curing Agent (e.g., methylene, aromatic, DCPDP and so on)
R$_2$ = Functional Unit of Epoxy Resin (e.g., biphenyl, novolac, o-cresol novolac and so on)

Fig. 7. The curing model of the epoxy resin systems with different phenolic functional hardeners.

shown in Fig. 7, which is based on this model. It can be thought that an autocatalytic cure reaction that a secondary hydroxyl group produced by a reaction between epoxy and phenol resin would participate in cure reaction can be occurred in epoxy resin systems with phenol novolac hardener, which has short distances between epoxy resin unit. However, if a curing agent had a bulky group such as phenyl or DCPDP moiety, an *n*th-order cure reaction that a secondary hydroxyl group cannot participate in cure reaction could proceed. This means that the reaction between secondary hydroxyl group and epoxy group should be very difficult as distances between epoxy resin unit expand. Although different three-dimensional structures of these epoxy resin systems can be represented due to the *ortho*- and *para*-positions of phenolic hardeners, the average distances between epoxy resin unit increase with bulky phenolic hardeners. It can be supposed that the considerable deviations of the system constant in the epoxy systems including DCPDP hardener is caused in steric hindrances and molecular interactions between bulky groups such as phenyl or DCPD moiety.

As shown in kinetic data of epoxy resin systems, it can be generally found that reaction conversion rate increased with molecular size of curing agents. This implies that there are wide reaction spaces according to the expansion of distances between epoxy resin unit, and these can make reaction conversion easy. These phenomena can be observed remarkably in *n*th-order cure reaction that a secondary hydroxyl group cannot participate in cure reaction. As shown in YX-4000H, differences of α_c between biphenyl epoxy resin system and novolac type epoxy resin decreased with a curing agent including bulky molecular structure such as DCPD moiety. This means that strong interactions between biphenyl groups [18] can decrease with distances between epoxy resin units. Therefore, considering these phenomena in respect of α_c which indicates critical conversion that diffusion controlled cure reaction begins, it can be seen that curing characteristics of biphenyl type epoxy resin system are resemble to novolac type epoxy systems. This implies that there are decreases of molecular interactions between biphenyl moieties in accordance with increase of distances between epoxy resin units.

4. Conclusions

The curing characteristics of new novolac type epoxy resin according to the change of hardeners were investigated in terms of thermal analysis method. It can be shown that the higher values of reaction conversion rate in epoxy resin systems with bulky molecular groups such as XP-2030 and XD-1000 epoxy resin are represented. These phenomena can be observed remarkably in epoxy resin systems with a bulky hardener, DCPDP, following *n*th-order cure reaction. The cure model using a curing agent as a spacer was suggested, and the cure reaction in these epoxy systems with different phenolic functional hardeners can be explained in terms of this model. These large molecule introductions can be contributed to the formation of optimum cure reaction space and reduction of molecular interactions between biphenyl moieties, therefore, it can be found out that reaction conversion rates increase with molecular size of network structures.

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