

# Cure Kinetics of Biphenyl Epoxy Resin System Using Latent Catalysts

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Received 24 May 2000; accepted 2 December 2000

**ABSTRACT:** The investigation of the cure kinetics of a biphenyl epoxy–phenol resin system with different kinds of latent catalysts was performed by differential scanning calorimetry using an isothermal approach. All kinetic parameters of the curing reaction including the reaction order, activation energy, and rate constant were calculated and reported. The results indicated that the curing reaction of the biphenyl epoxy resin system in this experiment proceeded through an autocatalytic kinetic mechanism, irrespective of the kind of catalyst. The epoxy resin system with acid/diazabicycloundecene (DBU) salt as the latent catalyst showed a second overall reaction order; however, a third reaction order was represented for microencapsulated triphenylphosphine (TPP). The storage stability tests for these systems were performed, and a good shelf life was observed in the epoxy resin system with pyromellitic acid/DBU salt, trimellitic acid/DBU salt, and microencapsulated TPP as the latent catalyst. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2711–2720, 2001

**Key words:** biphenyl epoxy resin; phenol resin; latent catalyst; shelf life; cure kinetics

## INTRODUCTION

A catalyst should be used to control the cure reaction of epoxy molding compounds (EMC) for semiconductor encapsulation in molding and postcuring processes. The problems of low fluidity in the molding process and the shelf life of the EMC under normal cure and storage conditions can be solved by the use of a latent catalyst. Although the biphenyl type epoxy resins are of

great advantage for highly reliable EMC with good adhesion and high toughness and for use of high filler loadings,<sup>1–3</sup> this low molecular weight epoxy resin system has low storage stability at room temperature. Therefore, latent catalysts for these systems need to be developed to improve the shelf life at room temperature, as well as the cure reaction at high temperature.

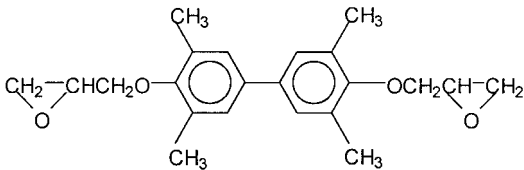
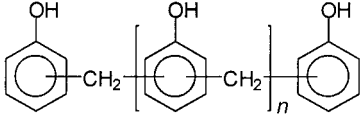
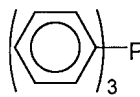
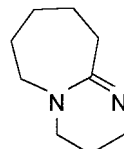
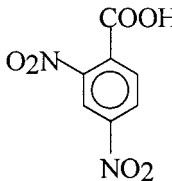
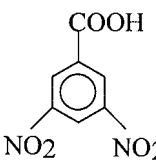
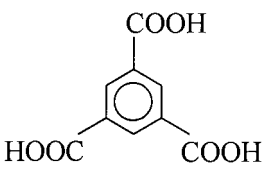
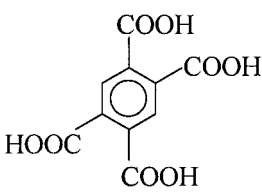
The development of efficient latent catalysts is desirable for the enhancement of both the storage stability and handling of thermosetting resins. Latent catalysts in an epoxy resin system can be classified into two groups: ionic and nonionic structure type groups. Several onium salts,<sup>4,5</sup> metal–imidazole complexes,<sup>6,7</sup> and imidazolium salts<sup>8</sup> were reported to be quite effective as ionic-

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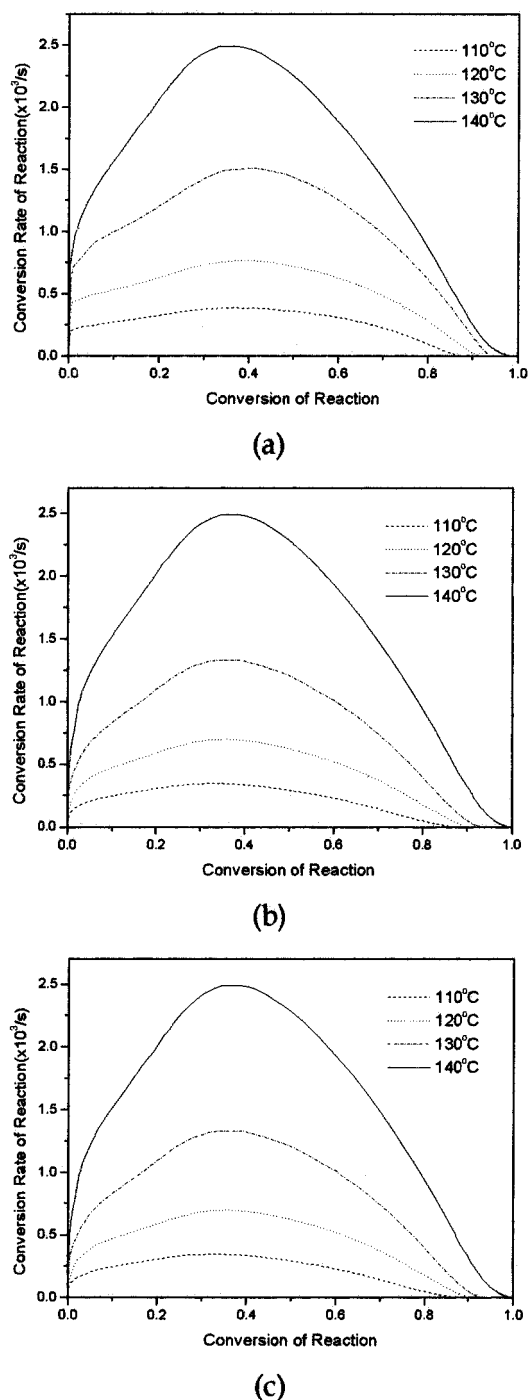
Contract grant sponsor: Basic Research Program, Korea Science & Engineering Foundation; contract grant number: 2000-1-30800-001-3.

*Journal of Applied Polymer Science*, Vol. 81, 2711–2720 (2001)  
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**Table I** Description of Raw Materials Used in Study

Materials	Structure
YX-4000H	
PSM 4261	
TPP	
MCE-9957	TPP coated with PMMA (TPP content; 20 wt %)
DBU	
2,4-DNBA	
3,5-DNBA	
TMA	
PMA	

PMMA, poly(methyl methacrylate).



**Figure 1** The isothermal conversion rate as a function of the conversion of the biphenyl epoxy resin system with (a) DBU, (b) 2,4-dinitrobenzoic acid/DBU, and (c) 3,5-dinitrobenzoic acid/DBU.

type latent catalysts. Phosphonium ylides,<sup>9</sup> carboxylates,<sup>10</sup> and microencapsulated catalysts<sup>11</sup> were used as nonionic-type latent catalysts. However, the investigation of the effect of a latent

catalyst on the cure properties for a biphenyl epoxy resin system was not performed to date.

In this study the effects of latent catalysts on the curing characteristics of epoxy resin compositions containing biphenyl type epoxy resin and phenol novolac hardener were investigated using a DSC technique. The curing mechanism of these systems with different latent catalysts was interpreted by means of an *n*th order and an autocatalytic mechanism,<sup>12,13</sup> and the curing kinetics in the overall conversion region were analyzed using the kinetic and diffusion model.<sup>14</sup> Acid/diazabicycloundecene (DBU) salt as the salt-type latent catalyst and microencapsulated triphenylphosphine (TPP) as the nonsalt type were used in this experiment.

## EXPERIMENTAL

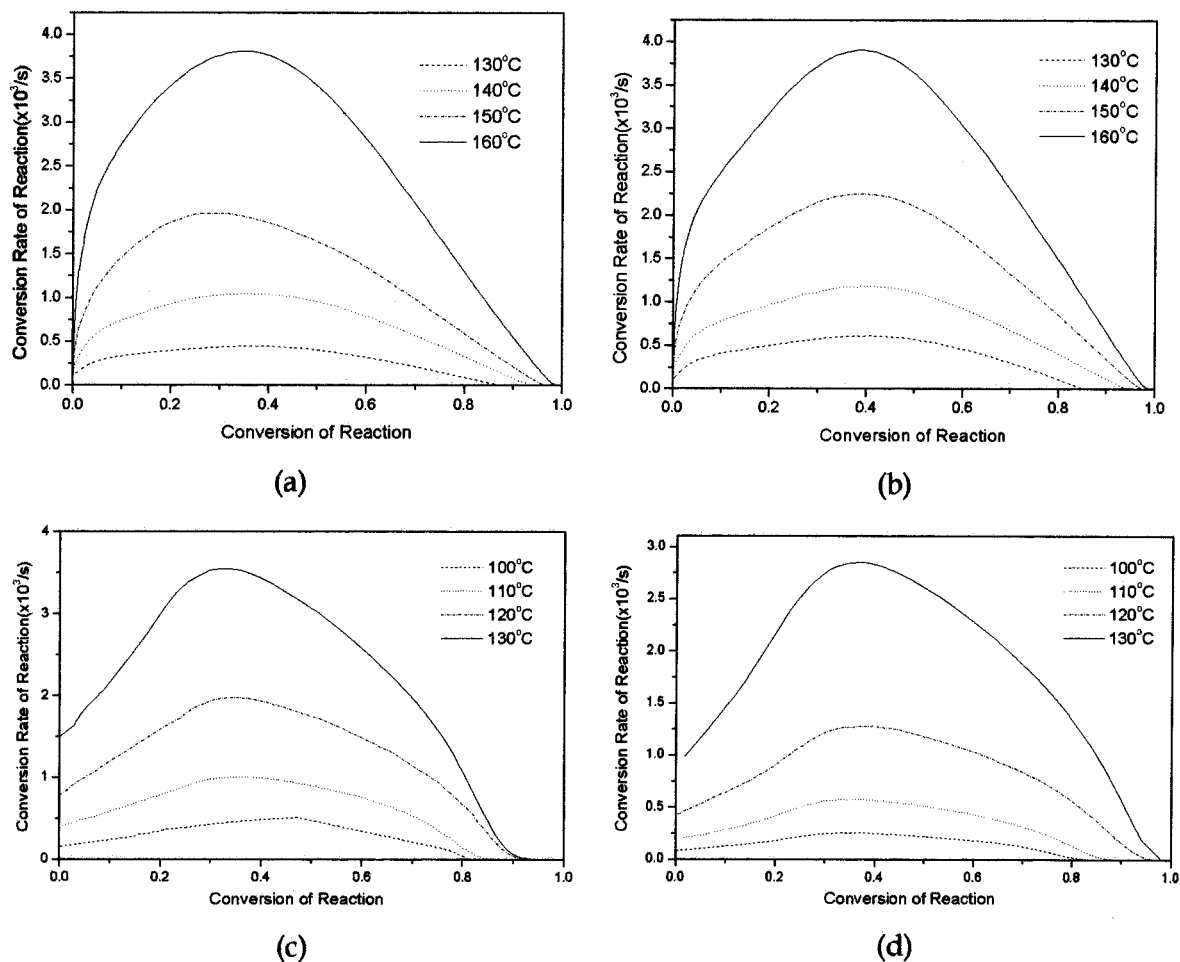
### Materials

The epoxy resin used in this study was commercially available biphenyl epoxy resin (YX-4000H) obtained from Yuka Shell Co. The hardener used was phenol novolac resin (PSM 4261) obtained from Gunnei Chemical Co. Microencapsulated TPP (MCE-9957, Nippon Kayaku Co.) as the nonsalt latent catalyst, TPP (Hokko Chemical Co.), and DBU (SAN-APRO Chemical Co.) were used as received. As the carbonic acid to make a salt-type latent catalyst, 2,4-dinitrobenzoic acid (2,4-DNBA, Aldrich Chemical Co.), 3,5-dinitrobenzoic acid (3,5-DNBA, Aldrich Chemical Co.), trimellitic acid (TMA, Aldrich Chemical Co.), and pyromellitic acid (PMA, Aldrich Chemical Co.) were used as received. Detailed descriptions of the chemical structures are summarized in Table I.

Carbonic acid/DBU salts were synthesized as salt-type latent catalysts. Carbonic acid was dissolved in tetrahydrofuran (THF) at room temperature, and a DBU weight equivalent to that of the carbonic acid was dropped into them. This solution was mixed well for 2 h, and a precipitate (acid/DBU salt) was filtered out and dried. The melting points of these acid/DBU salts were measured using DSC, and they agreed with previous data.<sup>15</sup>

### Sample Preparation

All the epoxy resin compositions in this study were composed of the same equivalent weight ratio (1:1) of epoxy and hydroxyl groups with



**Figure 2** The isothermal conversion rate as a function of the conversion of the biphenyl epoxy resin system with (a) TMA/DBU, (b) PMA/DBU, (c) TPP, and (d) MCE-9957.

0.07*m* of each catalyst. The concentration of MCE-9957 was fixed on the basis of the net content of TPP (20 wt %). The epoxy resin and hardener were well mixed at 120°C until a homogeneous solution was obtained. After cooling 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 instruments differential scanning calorimeter (TA-2020), which was calibrated in the -40 to 450°C region. Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 60 mL/min. For the dynamic cure the sample was heated at a rate of 5°C/min from

-10 to 300°C, beyond which decomposition was observed. A set of isothermal cure curves was obtained in order to evaluate the kinetic parameters for the curing reactions. To perform the shelf life test, each sample was stored at 30 and 50°C. Then it was taken out of the thermostat oven at proper intervals for 0–500 h, and it was scanned at a heating rate of 5°C/min up to 300°C so that its reaction conversion at that time could be determined.

#### RESULTS AND DISCUSSION

The reaction conversion rates of biphenyl epoxy-phenol novolac resin systems with different kinds of catalysts are plotted as a function of conversion in Figures 1 and 2. It can be seen that the curing

**Table II Kinetic Parameters of Epoxy Resin Compositions Using DBU, 2,4-DNBA/DBU, and 3,5-DNBA/DBU as Catalyst**

Catalyst	Temp. (°C)	$k_1$ (/s)	$k_2$ (/s)	$m$	$n$	Temp. Dependence of Rate Constant	Average $m + n$ Value
DBU	110	$0.20 \times 10^{-5}$	$1.95 \times 10^{-3}$	1.2	1.5		
	120	$0.40 \times 10^{-3}$	$4.00 \times 10^{-3}$	1.3	1.5	$k_1 = 5.44 \times 10^3 \exp(-5.41 \times 10^4/RT)$	2.6
	130	$0.56 \times 10^{-3}$	$6.57 \times 10^{-3}$	1.1	1.4	$k_2 = 6.00 \times 10^6 \exp(-6.93 \times 10^4/RT)$	
	140	$0.70 \times 10^{-3}$	$9.53 \times 10^{-3}$	0.9	1.4		
2,4-DNBA/ DBU	110	$0.10 \times 10^{-3}$	$1.35 \times 10^{-3}$	0.8	1.6		
2,4-DNBA/ DBU	120	$0.10 \times 10^{-3}$	$2.05 \times 10^{-3}$	0.7	1.2	$k_1 = 2.10 \times 10^4 \exp(-6.89 \times 10^4/RT)$	2.2
	130	$0.30 \times 10^{-3}$	$5.63 \times 10^{-3}$	0.9	1.5	$k_2 = 3.11 \times 10^9 \exp(-9.10 \times 10^4/RT)$	
	140	$0.40 \times 10^{-3}$	$9.70 \times 10^{-3}$	0.8	1.4		
	3,5-DNBA/ DBU	110	$0.12 \times 10^{-3}$	$1.30 \times 10^{-3}$	0.9	1.4	
3,5-DNBA/ DBU	120	$0.26 \times 10^{-3}$	$2.54 \times 10^{-3}$	1.0	1.4	$k_1 = 3.19 \times 10^5 \exp(-6.88 \times 10^4/RT)$	2.4
	130	$0.38 \times 10^{-3}$	$3.84 \times 10^{-3}$	1.0	1.4	$k_2 = 1.20 \times 10^6 \exp(-6.56 \times 10^4/RT)$	
	140	$0.60 \times 10^{-3}$	$5.95 \times 10^{-3}$	1.2	1.4		

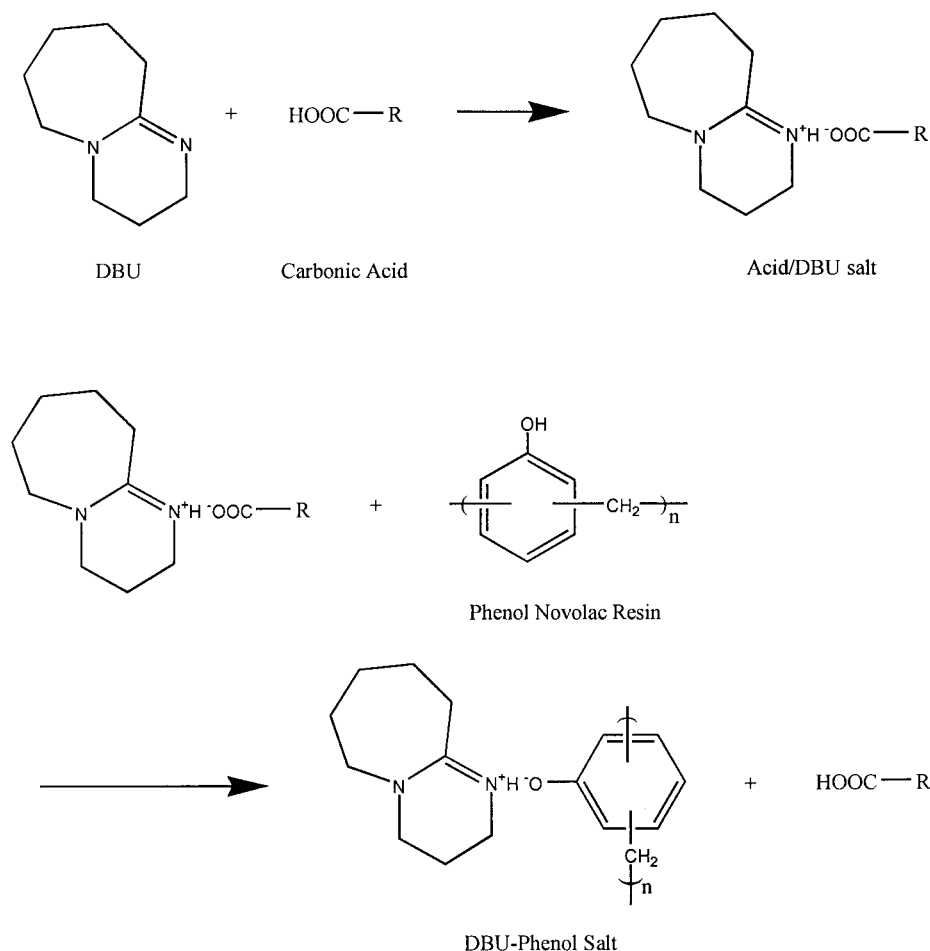
reactions in all systems proceeded through an autocatalytic kinetic mechanism with maximum conversion rates in the 30–40% conversion region. It is possible that these phenomena were due to the use of the phenol novolac resin as the

hardener, which was shown to proceed by an autocatalytic kinetic mechanism, irrespective of the types of epoxy resin used.<sup>2,12</sup>

For the thermosetting resin following an autocatalytic curing reaction, Kamal<sup>16</sup> proposed a

**Table III Kinetic Parameters of Epoxy Resin Compositions Using TMA/DBU, PMA/DBU, MCE-9957, and TPP as Catalyst**

Catalyst	Temp. (°C)	$k_1$ (/s)	$k_2$ (/s)	$m$	$n$	Temp. Dependence of Rate Constant	Average $m + n$ Value
TMA/ DBU	130	$0.12 \times 10^{-5}$	$1.56 \times 10^{-3}$	0.8	1.4		
	140	$0.17 \times 10^{-3}$	$3.44 \times 10^{-3}$	0.7	1.3	$k_1 = 8.28 \times 10^4 \exp(-7.63 \times 10^4/RT)$	2.0
	150	$0.28 \times 10^{-3}$	$6.50 \times 10^{-3}$	0.7	1.4	$k_2 = 9.17 \times 10^8 \exp(-9.06 \times 10^4/RT)$	
	160	$0.59 \times 10^{-3}$	$1.00 \times 10^{-3}$	0.6	1.1		
PMA/ DBU	130	$0.13 \times 10^{-3}$	$2.52 \times 10^{-3}$	0.9	1.5		
PMA/ DBU	140	$0.23 \times 10^{-3}$	$4.54 \times 10^{-3}$	0.8	1.4	$k_1 = 1.95 \times 10^6 \exp(-7.85 \times 10^4/RT)$	2.1
	150	$0.41 \times 10^{-3}$	$8.04 \times 10^{-3}$	0.8	1.3	$k_2 = 4.55 \times 10^6 \exp(-7.13 \times 10^4/RT)$	
	160	$0.65 \times 10^{-3}$	$1.06 \times 10^{-3}$	0.7	1.0		
	MCE- 9957	100	$0.90 \times 10^{-4}$	$3.90 \times 10^{-3}$	1.7	2.4	
MCE- 9957	110	$2.10 \times 10^{-4}$	$7.20 \times 10^{-3}$	1.7	2.2	$k_1 = 8.50 \times 10^9 \exp(-9.97 \times 10^4/RT)$	3.6
	120	$4.50 \times 10^{-4}$	$1.00 \times 10^{-2}$	1.5	1.7	$k_2 = 4.00 \times 10^6 \exp(-6.43 \times 10^4/RT)$	
	130	$1.00 \times 10^{-3}$	$2.00 \times 10^{-2}$	1.4	1.7		
	TPP	100	$1.60 \times 10^{-4}$	$5.70 \times 10^{-3}$	1.5	2.2	
TPP	110	$4.00 \times 10^{-4}$	$8.00 \times 10^{-3}$	1.4	1.9	$k_1 = 1.64 \times 10^9 \exp(-9.27 \times 10^4/RT)$	3.2
	120	$8.00 \times 10^{-4}$	$1.00 \times 10^{-2}$	1.2	1.7	$k_2 = 3.16 \times 10^5 \exp(-5.55 \times 10^4/RT)$	
	130	$1.50 \times 10^{-3}$	$2.20 \times 10^{-2}$	1.2	1.8		



**Scheme 1** The reaction scheme of acid/DBU salt.

generalized expression to consider that the initial rate of the autocatalytic reaction is not zero:

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

where  $\alpha$  is the reaction conversion,  $t$  is the time,  $m$  and  $n$  are the reaction order of the system, and  $k_1$  and  $k_2$  are kinetic rate constants of the system.

To compute the kinetic parameters in eq. (1) without any constraints on parameters  $m$ ,  $n$ ,  $k_1$ , and  $k_2$ , they were calculated by fitting the experimental data to eq. (1) in the first portion of cure up to 70–80% cure, depending on the composition and the curing temperature.<sup>14</sup> The resulting data obtained from this method are summarized in Tables II and III for all isothermal experiments of the biphenyl epoxy resin compositions with different latent catalysts. The temperature dependence of the rate constant of the epoxy resin composition

with different catalysts is also shown in Tables II and III using the Arrhenius equation. The reaction orders were determined by averaging the values of all isothermal experiments, and the total reaction order (average  $m + n$  value) is listed in Tables II and III. From these data it can be seen that the total reaction order of the biphenyl epoxy resin system with DBU and acid/DBU salt as the latent catalyst was about 2, and that with TPP and microencapsulated TPP was about 3. The total reactions orders for DBU and MCE-9957 were 2.6 and 3.6, respectively; however, it had to be considered with DBU and MCE-9957 of about 2 and 3, respectively, because they decreased with the curing temperature. The reaction order of this system with acid/DBU salt was lower than that with DBU only, and that with microencapsulated TPP was higher than TPP only.

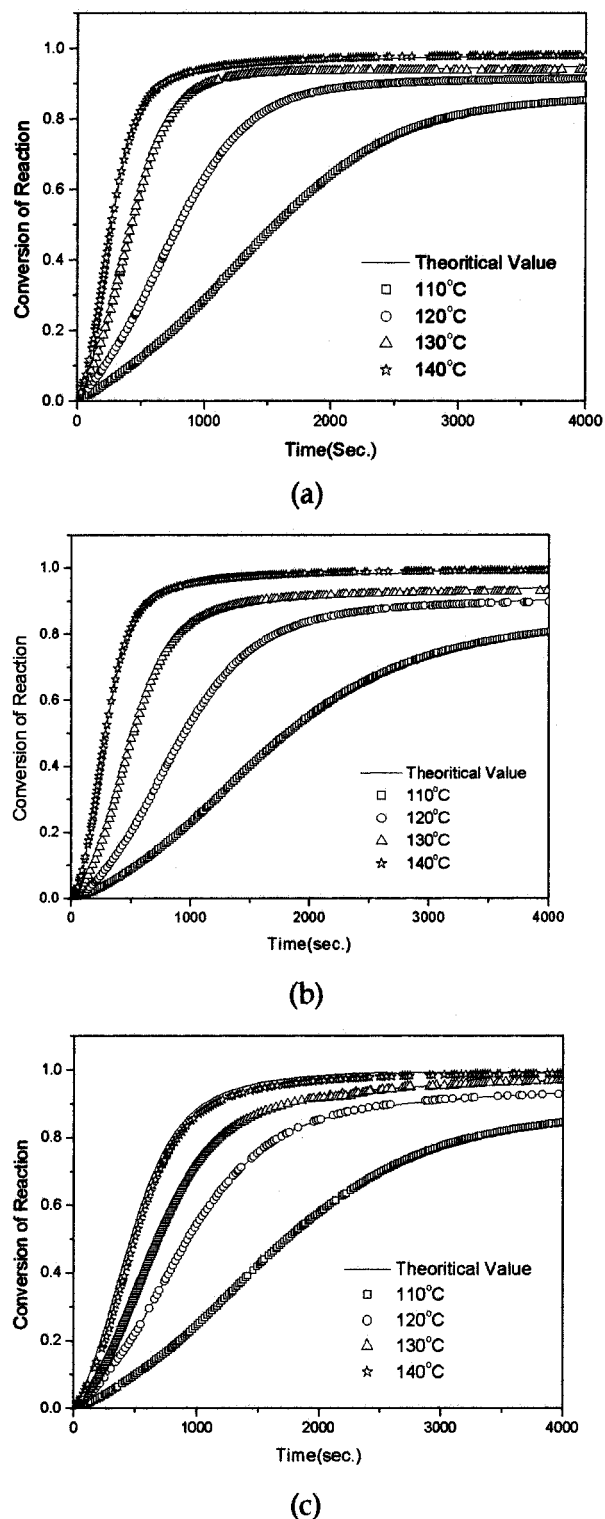
**Table IV** Values of Constant  $C$  and Critical Conversion at Different Temperature of Epoxy Resin Compositions Using DBU, 2,4-DNBA/DBU, and 3,5-DNBA/DBU as Catalyst

Catalyst	Temp. (°C)	$C$	$\alpha_c$
DBU	110	38.9	0.82
	120	42.0	0.87
	130	37.2	0.90
	140	24.2	0.92
2,4-DNBA/DBU	110	22.4	0.79
	120	25.1	0.82
	130	31.4	0.86
	140	27.7	0.93
3,5-DNBA/DBU	110	33.7	0.83
	120	23.3	0.87
	130	15.3	0.92
	140	18.8	0.99

The rate-determining step of the composition using DBU was the bimolecular reaction between DBU and the epoxy resin as in the epoxy resin system with imidazole.<sup>17</sup> However, for the phenol novolac hardener a DBU/phenol salt would be obtained because phenol is acid and DBU is base.

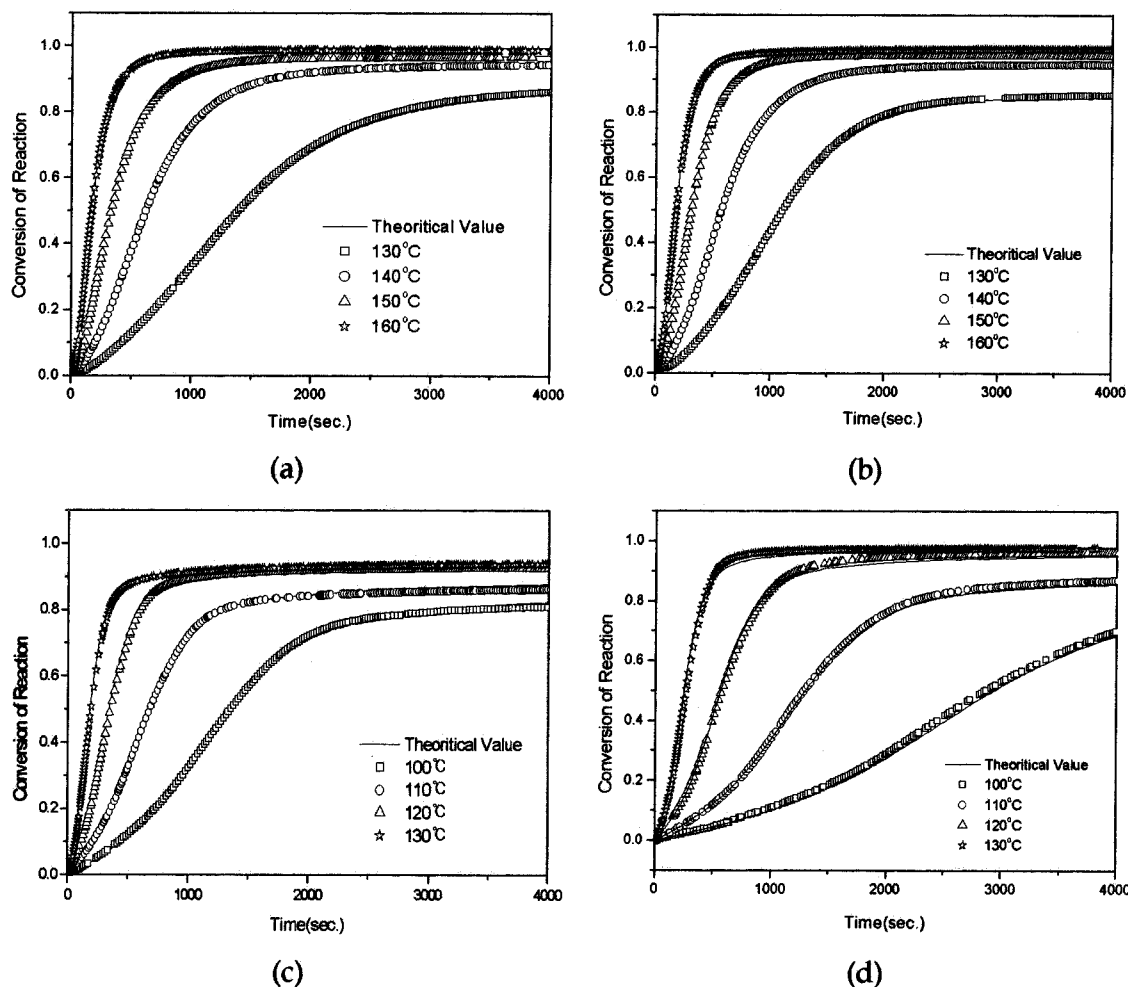
**Table V** Values of Constant  $C$  and Critical Conversion at Different Temperatures of Epoxy Resin Compositions Using TMA/DBU, PMA/DBU, MCE-9957, and TPP as Catalyst

Catalyst	Temp. (°C)	$C$	$\alpha_c$
TMA/DBU	130	20.0	0.80
	140	26.8	0.89
	150	43.7	0.94
	160	8.6	0.94
PMA/DBU	130	43.2	0.80
	140	50.6	0.90
	150	50.8	0.95
	160	9.4	0.93
MCE-9957	100	43.9	0.78
	110	40.7	0.82
	120	37.0	0.91
	130	36.8	0.93
TPP	100	50.6	0.77
	110	41.8	0.80
	120	40.1	0.85
	130	36.2	0.85



**Figure 3** Comparisons between the experimental values of  $\alpha$  and theoretical values obtained from the generalized autocatalytic model for the biphenyl epoxy resin system with (a) DBU, (b) 2,4-dinitrobenzoic acid/DBU, and (c) 3,5-dinitrobenzoic acid/DBU.





**Figure 4** Comparisons between the experimental values of  $\alpha$  and theoretical values obtained from the generalized autocatalytic model for the biphenyl epoxy resin system with (a) TMA/DBU, (b) PMA/DBU, (c) TPP, and (d) MCE-9957.

Therefore, the termolecular reaction between the DBU/phenol salt and the epoxy resin can be contributed to the rate-determining step, so that a reaction higher than second order could be obtained. The basic idea behind using the acid/DBU salt as a latent catalyst is to block the unshared electron pair of the nitrogen in DBU, which plays an important role in the cure reaction as in Scheme 1. The blocking of the imine group would impede the formation of the DBU/phenol salt and the rate-determining step of that would be the bimolecular reaction between the acid/DBU salt and the phenol novolac resin. Therefore, a lower reaction order should be obtained in the system with acid/DBU salt compared to DBU only.

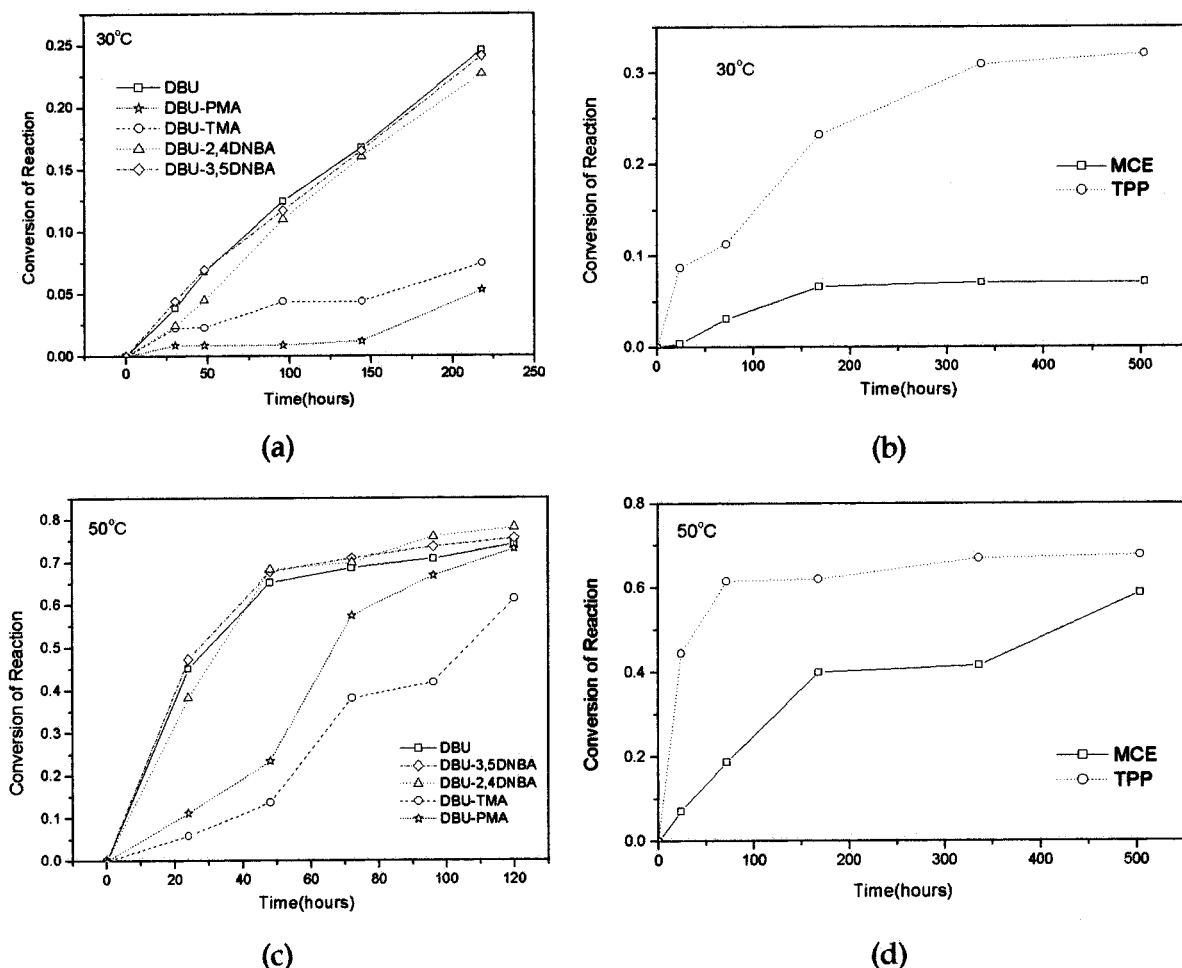
It is known that the rate-determining step of this system with TPP catalyst is the termolecular reaction between the TPP/epoxy resin salt and

the phenol novolac resin.<sup>2,18</sup> However, the reaction order of the system with microencapsulated TPP was higher than with TPP only. Although the data of our kinetic analysis in the system with microencapsulated TPP also represented an autocatalytic reaction, this reaction appeared to be complicated by more than one type of kinetic mechanism such as melting of the encapsulating material and diffusion of TPP.

To precisely predict the cure kinetics over the whole range of conversions, the modification of an autocatalytic model was performed by the introduction of a diffusion term as described in eq. (2).<sup>19</sup>

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





**Figure 5** The shelf life test for the biphenyl epoxy resin system with (a) DBU and DBU/acid salt at 30°C, (b) TPP and MCE-9957 at 30°C, (c) DBU and DBU/acid salt at 50°, and (d) TPP and MCE-9957 at 50°C.

where  $C$  is a constant and  $\alpha_c$  is the critical conversion. For  $\alpha \ll \alpha_c$ , the  $f(\alpha)$  is approximately equal to unity and the effect of the diffusion is negligible, so that the reaction is kinetically controlled. The  $f(\alpha)$  at different temperatures for the systems with different kinds of catalysts was obtained, and the values of  $C$  were obtained by fitting  $f(\alpha)$  versus  $\alpha$ . These results are summarized in Tables IV and V. The  $\alpha_c$  increased with temperature but  $C$  showed no discernible trend in these compositions.

A more general model was necessary to predict the advance of cure at different temperatures. Considering the diffusion effect, eq. (1) can be rewritten as follows<sup>3</sup>:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (3)$$

Figures 3 and 4 show a comparison of the experimental values of the reaction conversion and the values calculated using the generalized autocatalytic model for these compositions. Good agreement was found over the whole curing temperature range.

In order to test the shelf life the changes of the reaction conversion of these systems according to the storage time at 30 and 50°C were measured and these results are shown in Figure 5. It can be seen that the reaction conversion of systems with PMA/DBU and TMA/DBU salt were hardly changed at 30°C within 200 h and within 500 h for MCE-9957. Although the rapid increases of the reaction conversion were found at 50°C, irrespective of the kinds of latent catalysts used, the storage stabilities for the systems with PMA/DBU, TMA/DBU, and MCE-9957 were better

than those using DBU and TPP. The system with MCE-9957 showed especially good stability at 50° compared to acid/DBU salts. The nonionic-type latent catalyst should be better than the ionic type with respect to the shelf life.

## CONCLUSION

The curing reactions of a biphenyl epoxy-phenol novolac resin system with several latent catalysts proceeded through an autocatalytic kinetic mechanism, irrespective of the kinds of catalysts employed.

The curing kinetics in the overall conversion region were analyzed using kinetic and diffusion models and good agreement was found over the whole curing temperature range. The kinetic rate constants and total reaction order of the systems with TPP and microencapsulated TPP showed higher values than those with DBU and acid/DBU salt. The curing mechanism according to the kind of latent catalyst such as the ionic and nonionic types was investigated in terms of kinetic parameters obtained from this model. The rate-determining step of this system with acid/DBU salt was the bimolecular reaction between the acid/DBU salt and the phenol novolac resin. However, the system with microencapsulated TPP appeared to be complicated by other kinetic mechanisms.

The reaction conversions of these systems with the storage time at different temperatures were measured to evaluate the latent catalyst properties. It was shown that the nonionic-type latent catalyst should be better than the ionic type with respect to shelf life.

The authors would like to express their gratitude to Nippon Kayaku Co. for their generous supply of samples and fruitful discussions.

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