

Latent Catalyst Effects in Halogen-Free Epoxy Molding Compounds for Semiconductor Encapsulation

Je Hong Ryu,¹ Ki Seop Choi,² Whan Gun Kim³

¹Department of Electronic Materials, Cheil Industries, 332-2, Gochun-Dong, Euiwang-Shi, Kyunggi-Do 437-010, Korea

²Department of Chemical Engineering, Korea Polytechnic University, 101, 3-Ga, Jeongwang-Dong, Siheung, Kyunggi-Do, Korea

³Department of Applied Chemistry, Seokyeong University, 16-1 Jeongneung-Dong, Seongbuk-Ku, Seoul 136-704, Korea

Received 19 February 2004; accepted 31 May 2004

DOI 10.1002/app.21001

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Latent catalyst effects were investigated to improve the physical properties of halogen-free epoxy molding compounds (EMCs) for semiconductor encapsulation. In this study, biphenyl-type resins were used as the epoxy and hardener resin for halogen-free EMCs to obtain high flame-retardant properties and high filler contents. Latent catalyst effects were examined with two kinds of EMC compositions, halogen-free EMCs and conventional EMC compositions. We used triphenylphosphine-benzoquinone salt (TPP-BQ) as a latent catalyst. Spiral flow and gel time were measured to investigate the change in moldability with the latent catalyst. We measured package fail, moisture absorption, and delamination for reliability evaluation and flexural strength, flexural modulus, and adhesion for mechanical properties to examine latent catalyst effects. An

improvement in moldability, reliability, and the mechanical properties were observed in two types of halogen-free EMCs with TPP-BQ as a latent catalyst. These phenomena were seen in conventional EMCs, including *o*-cresol novolac epoxy resin. The cure kinetics of these systems were investigated by differential scanning calorimetry with an isothermal approach to explain these phenomena. The results indicate that the improvement in moldability in halogen-free EMCs with TPP-BQ was due to the low conversion rate of this system, and the increase in mechanical properties was attributed to the high conversion of curing reaction. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2287–2299, 2005

Key words: flame retardance; curing of polymers; catalysts

INTRODUCTION

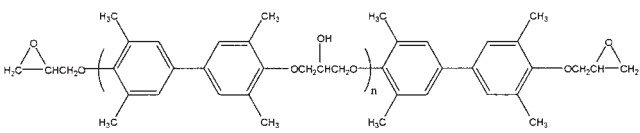
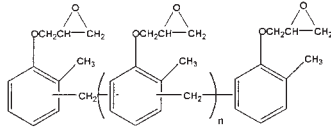
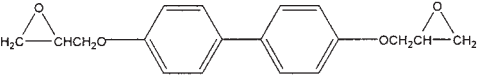
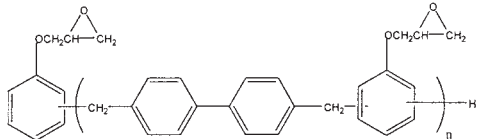
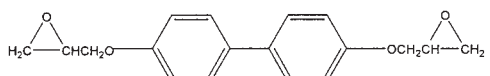
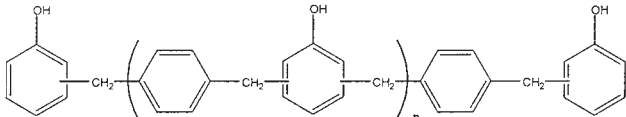
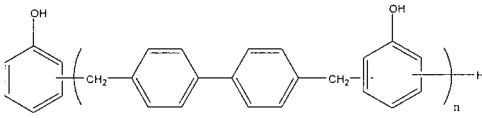
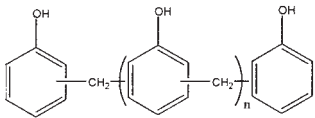
Organic and inorganic flame-retardant agents are used to make the epoxy molding compounds (EMCs) for semiconductor encapsulation inflammable for the safety of electronic devices. It is widely known that organic compounds containing Br as an organic flame retardant and Sb₂O₃ as an inorganic flame retardant are mainly used in EMCs.¹ Although these materials are excellent flame-retardant agents, it is postulated that these materials, including halogen compounds such as Br, would be difficult to use in the production of dioxane derivatives because they are harmful to the environment when combusted. Because of these circumstances, the development of green EMCs that do not contain the very toxic halogen and Sb is required. This course of research can be summarized in three ways. First, the improvement of these inflammable properties has been achieved through the development of epoxy resins and hardeners, including aromatic groups, which contain these properties.^{2,3} Second, an increase in filler content is needed. Silica in

EMC compositions is one such filler, and it is being used to improve low thermal expansion coefficients, thermal resistance, and reliability. This filler improves inflammability because this inorganic material is very difficult to combust. By this method, to increase the inflammability of EMC, a filler content of 90 wt % or higher is needed so that the UL-94/V-0 standard for electronic devices can be matched. However, when the filler content is increased, the viscosity of EMCs also increases in this case. This results in a disadvantage in the productivity and moldability of EMCs.^{4,5} Finally, the last course of research has been to develop a new type of flame retardant. In other words, the most extensive research has been performed to develop flame-retardant agents that do not contain halogen or Sb. In general, phosphorous-type flame retardants have been commercialized in thermoplastic polymers. Therefore, phosphorous-type flame retardants have been applied to EMCs for semiconductor encapsulation. This has resulted in low reliability of the semiconductor, which has caused serious problems; thus, phosphorous-type flame retardants cannot be used.^{6,7}

In this study, we studied the physical and curing properties of new epoxy resin systems with inflammable properties and good moldability for nonhalogen-type EMCs. Two formulations of halogen-free EMCs

Correspondence to: W. G. Kim.

TABLE I
Description of the Raw Materials Used in This Study

Grade name	Structure	Remarks
YX-4000H		EEW = 193
EOCN-C	 + 	EEW = 188
CER-3000L	 + 	EEW = 241
MEH-7800SS		HEW = 175
MEH-7851SS		HEW = 203
HF-1		HEW = 106

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

were introduced in this experiment, and these data were compared with EMCs for high-memory devices. Generally, biphenyl-type epoxy resins are used in these applications for high filler-loading requirements in EMCs. However, these biphenyl epoxy resins with low molecular weights have low crosslinking densities for fast reactions with crystallinity and low storage stability at room temperature. Recently, the development of new ionic-type latent catalysts for these epoxy resin systems has been reported, and we investigated the effects of these catalysts on the curing characteristics of halogen-free EMCs. The curing characteristics of such epoxy resin compositions were investigated with differential scanning calorimetry.^{8,9}

EXPERIMENTAL

Materials

The epoxy resins used in this experiment were commercially available epoxy resins YX-4000H (Yuka

Shell Co., Tokyo, Japan), EOCN-C (Nippon Kayaku Co., Tokyo, Japan), and CER-3000L (Nippon Kayaku Co.). The hardeners used were a phenol type (HF-1, Meihwa Co., Tokyo, Japan), a xylok type (HEH-7800SS, Meihwa Co.), and a biphenyl type phenol resin (MEH-7851SS, Meihwa Co.) Triphenylphosphine (TPP; Aldrich Chemical Co., St. Louis, MO) and benzoquinone (BQ; Aldrich Chemical Co.) were used as received. Other materials in the EMC compositions, including filler, coupling agent, releasing agent, carbon black, and so on, were same grades as shown in previous articles.¹⁰ Detailed descriptions of the chemical structures of the epoxy and hardener resins used in this study are summarized in Table I.

Triphenylphosphine-benzoquinone salt (TPP-BQ) was synthesized as an ionic-type latent catalyst. TPP was dissolved in acetone at room temperature, and a BQ weight equivalent to that of the TPP dissolved in acetone was dropped into it. This solution was mixed

TABLE II
Basic Formulations of EMC in This Study

Sample No.	Epoxy resin	Hardener	Catalyst (mol/kg)		Coupling agent	Releasing agent	Filler (wt %)	EEW/HEW	UL-94/V-0
			TPP	TPP-BQ					
1	YX-4000H	MEH-7800SS	0.02	0.02	4.26	1.66	88.2	1.0	○
2	CER-3000L	MEH-7851SS	0.02	0.02	2.89	2.12	84.3	1.0	○
3	EOCN-C	HF-1	0.02	0.02	4.15	1.62	85.6	1.0	×

well for 2 h, and the precipitate (TPP-BQ) was filtered out and dried.¹¹

Sample preparation

Detailed recipes from this experiment are shown in Table II. The compositions of samples 1 and 2 in Table II were halogen-free recipes, which UL-94/V-0 standard properties represent, and that of sample 3 was a standard recipe that was designed for this experiment. The formulation of sample 3 could not be satisfied with the UL-94/V-0 standard without a flame-retardant agent. With these formulations, an EMC sample was prepared through a premixing, melt mixing, cooling, crushing, tableting, and molding process as shown in Figure 1.^{12,13}

Measurements

Flame-retardance test

Sample specimens 1/8 in. thick for a flame-retardance test were molded with a transfer molding press under a molding pressure 70 Kgf/cm² at 180°C and were cured at 180°C for 4 h. They were measured in accordance with the UL-94/V-0 standard.

Spiral flow

We measured the length of molding compound with a spiral flow mold in accordance with EMMI-1-66 under a molding temperature of 180°C, a molding pressure of 70 Kgf/m², and a molding time of 90 s.

Gel time

We measured the time elapsed until the viscosity of the EMC did not increase any more with the flow tester (CFT-500, Shimatsu Co., Tokyo, Japan).

Package fail

We checked package fail, such as a void, weld line void, crack, and flaw, with a microscope. The model package used in this experiment was 32 units of thin small outline package (TSOP)-type 54T2.

Moisture absorption

After specimens were left as they were in the pressure cooker test chamber (Hirayama Co., Tokyo, Japan) at 120.6 ± 5°C, 2 atm, and 100% relative humidity for 48 h, the moisture absorption was calculated by the following equation:

$$M_{\infty} = \frac{(W_{\infty} - W_0)}{W_0} \times 100 \quad (1)$$

where M_{∞} is the saturated moisture absorption, W_{∞} is the weight of the specimen after 48 h in the pressure cooker test chamber, and W_0 is the initial weight of the specimen.

Delamination

Sample specimens were manufactured with the TSOP mold, and these specimens were stored in a chamber

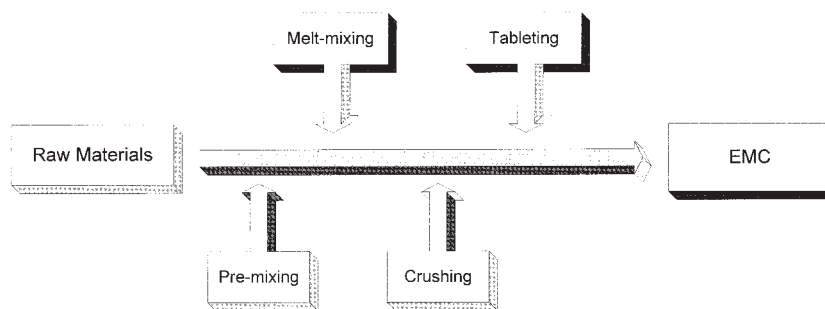
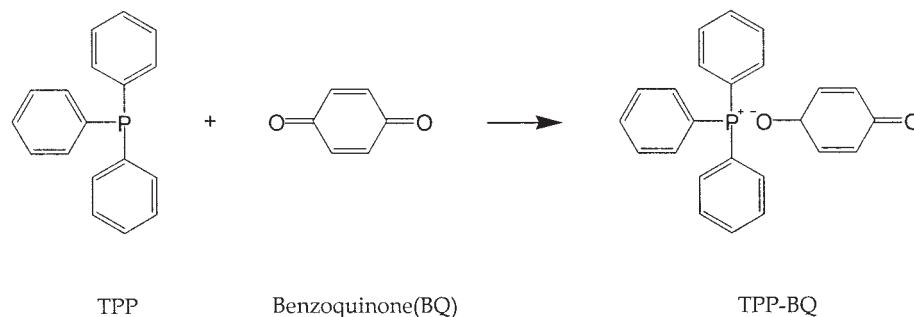


Figure 1 EMC preparation process.



Scheme 1

under at 85°C and 85% relative humidity for 168 h. Then, the delamination of the TSOP was observed after they were soaked in IR reflow chamber at 260°C. The internal images for delamination evaluation were observed by Scanning Acoustic Microscopy (C-SAM, Sonoscan Inc., Elk Grove Village, IL) before and after soaking in the IR reflow chamber.

Flexural strength and modulus

Specimens 6.4 × 12.7 × 127 mm in size were measured at a span width of 100 mm and a test speed of 2.8 mm/min at 25 and 260°C with a universal testing machine (Zwick Co., Ulm, Germany) in accordance with ASTM D-790.

Adhesion strength

After the EMC sample was molded on a lead frame, we measured the peel strength of the lead frame with the universal testing machine. An Alloy 42 and copper lead frame were used in this experiment.

Differential scanning calorimetry measurements

Calorimetric measurements were performed with a TA-2020 differential scanning calorimeter (TA Instruments, New Castle, DE). This was calibrated in the

−40 to 450°C range. 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 to evaluate the kinetic parameters for the curing reactions.

RESULTS AND DISCUSSION

As shown in Table II, we postulated that the epoxy resin and hardener modifications, such as the introduction of a biphenyl group and an aromatic group to conventional *o*-creosol novolac epoxy resin and phenol novolac hardener, are needed to meet the requirements of the flame-retardance standard UL-94/V-0. In general, an introduction of a biphenyl group can decrease shelf lifetime and crosslinking density because of the crystallinity of the biphenyl group. Therefore, the development of an efficient latent catalyst is needed for the enhancement of both the storage stability and the physical properties of EMCs. In this study, we used TPP-BQ as the latent catalyst and investigated the physical properties and curing characteristics of halogen-free EMCs with TPP-BQ.

The basic idea behind the use of TPP-BQ salt as a latent catalyst was to block the unshared electron pair of the phosphine in TPP, as shown in Scheme 1, which

TABLE III
Kinetic Parameters of the YX-4000H/MEH-7800SS Epoxy Resin System (Sample 1 in Table II)

Catalyst	Temperature (°C)	k_1 (s ⁻¹)	n	C	α_c	Temperature dependency of the rate constant	Average n value
TPP	110	0.57×10^{-3}	1.0	23.03	0.74	$k_1 = 1.35 \times 10^8 \exp(-8.36 \times 10^4/RT)$	1.2
	120	0.99×10^{-3}	1.2	19.84	0.73		
	130	1.86×10^{-3}	1.1	18.48	0.80		
	140	3.82×10^{-3}	1.4	28.79	0.84		
TPP-BQ	110	0.35×10^{-3}	0.8	28.43	0.91	$k_1 = 3.70 \times 10^8 \exp(-8.81 \times 10^4/RT)$	1.0
	120	0.70×10^{-3}	1.0	23.40	0.90		
	130	1.28×10^{-3}	1.1	15.69	0.88		
	140	2.72×10^{-3}	1.1	29.33	0.93		

R: gas constant; T: temperature (K).

TABLE IV
Kinetic Parameters of the CER-3000L/MEH-7851SS Epoxy Resin System (Sample 2 in Table II)

Catalyst	Temperature (°C)	k_1 (s ⁻¹)	n	C	α_c	Temperature dependency of the rate constant	Average n value
TPP	110	0.72×10^{-3}	1.3	22.62	0.71	$k_1 = 8.76 \times 10^8 \exp(-8.87 \times 10^4/RT)$	1.5
	120	1.36×10^{-3}	1.5	21.22	0.72		
	130	2.71×10^{-3}	1.5	18.72	0.83		
	140	5.43×10^{-3}	1.7	45.37	0.89		
TPP-BQ	110	0.38×10^{-3}	0.9	29.31	0.86	$k_1 = 6.85 \times 10^8 \exp(-8.98 \times 10^4/RT)$	1.1
	120	0.81×10^{-3}	1.1	22.21	0.89		
	130	1.60×10^{-3}	1.1	31.45	0.94		
	140	2.93×10^{-3}	1.2	38.32	0.96		

plays an important role in the cure reaction. The blocking of the phosphine moiety in TPP would impede the formation of TPP/epoxy/phenol intermediate,¹⁴ and a lower reaction order (n) should be obtained in a system with TPP-BQ salt compared to one with TPP only, as shown in Tables III–V.

The moldability, reliability, and mechanical properties of the YX-4000H/MEH-7800SS EMC (sample 1 in Table II) according to the change in catalyst are shown in Figure 2. The spiral flow and gel time for the YX-4000H/MEH-7800SS EMC with TPP-BQ as a catalyst were longer than those of the system with TPP as a catalyst. This increase in the flowability of the EMC with TPP-BQ as a catalyst was attributed to the increase in the system's moldability. This resulted in a decrease in the package fail of the system, as shown in Figure 2(a). There were few differences between TPP-BQ and TPP as catalysts in the properties of moisture absorption and delamination before and after soaking. The increases in the mechanical strength of the system with TPP-BQ as a catalyst were observed with respect to flexural strength at 25°C. There were few differences in other mechanical properties, such as the flexural modulus and adhesion properties, with TPP-BQ and TPP as catalysts. To explain these phenomena, the reaction conversion (α) rate changes of this EMC system with TPP and TPP-BQ as catalysts are plotted as a function of α in Figure 3(a,b). As shown in Figure 3,

these resin systems followed a n th-order curing reaction, as described in eq. (2):

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

where t is time, n is the reaction order of the system, and k is the rate constant of the system. To precisely predict the curing kinetics over the whole range of conversion, the n th-order model was modified in terms of the introduction of a diffusion term, as represented in eq. (3):¹⁵

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

where 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 the reaction is kinetically controlled. When the diffusion effect is considered, eq. (2) can be rewritten as eq. (4):

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

All kinetic constants in this equation for each resin system were obtained with a previous method.^{16,17}

TABLE V
Kinetic Parameters of the EOCN-C/HF-1 Epoxy Resin System (Sample 3 in Table II)

Catalyst	Temperature (°C)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	m	n	Temperature dependency of the rate constant	Average $m + n$ value
TPP	110	0.16×10^{-3}	0.84×10^{-2}	1.9	2.7	$k_1 = 1.45 \times 10^7 \exp(-8.04 \times 10^4/RT)$ $k_2 = 1.01 \times 10^4 \exp(-4.43 \times 10^4/RT)$	4.2
	120	0.28×10^{-3}	1.30×10^{-2}	1.7	2.7		
	130	0.32×10^{-3}	1.79×10^{-2}	1.6	2.5		
	140	1.01×10^{-3}	2.15×10^{-2}	1.4	2.2		
TPP-BQ	110	0.08×10^{-3}	0.10×10^{-2}	1.3	1.8	$k_1 = 2.25 \times 10^9 \exp(-9.87 \times 10^4/RT)$ $k_2 = 4.73 \times 10^{12} \exp(-1.15 \times 10^5/RT)$	3.6
	120	0.16×10^{-3}	0.27×10^{-2}	1.4	2.2		
	130	0.32×10^{-3}	0.88×10^{-2}	1.6	2.5		
	140	0.78×10^{-3}	1.25×10^{-2}	1.5	2.1		

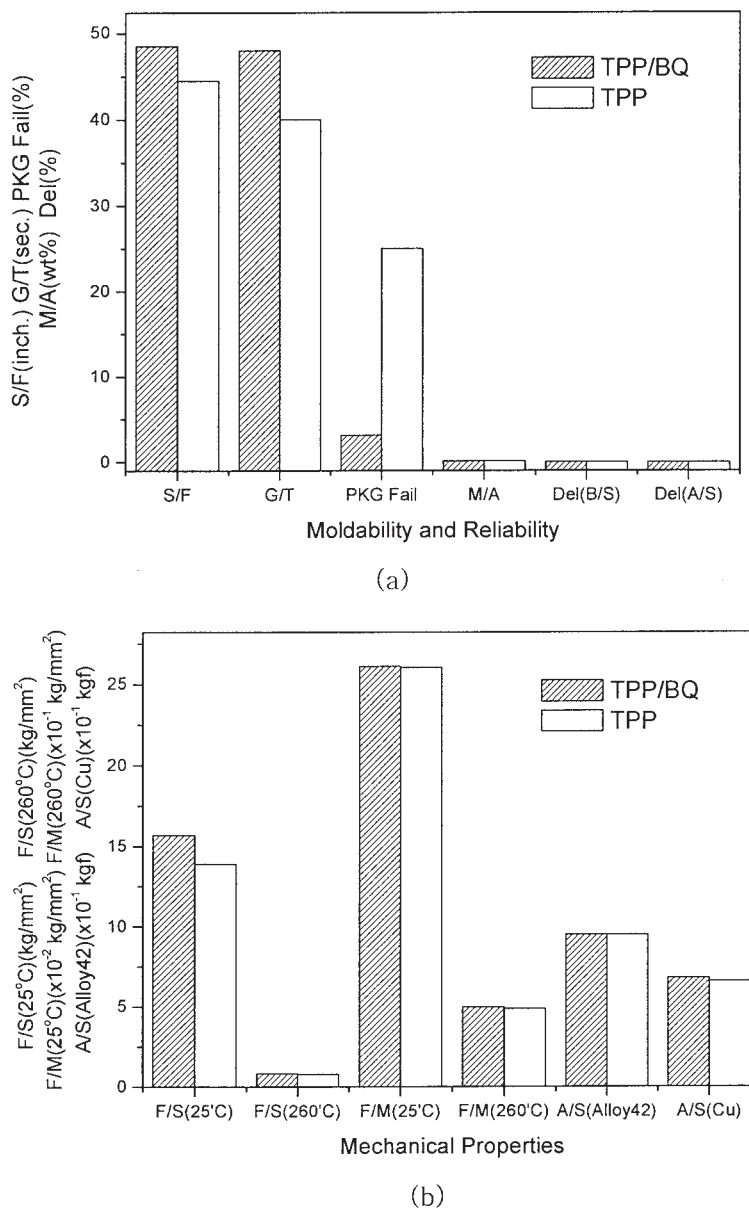


Figure 2 Physical properties of the YX-4000H/MEH-7800SS EMC (sample 1 in Table II): (a) moldability and reliability and (b) mechanical properties.

Figure 3(c,d) shows the comparisons between the experimental values of α and the values calculated with a generalized n th-order model for the YX-4000H/MEH-7800SS EMC systems with TPP and TPP-BQ as catalysts. Good agreements were found over the whole curing temperature range for all of the resin systems. The kinetic parameters are reported in Table III for the systems with TPP and TPP-BQ as catalysts that followed the n th-order curing reaction.

The reaction rate of the YX-4000H/MEH-7800SS EMC system with TPP was faster than that with TPP-BQ as a catalyst, as shown in Figure 3. We postulated that the increase in the spiral flow and gel time in this system with TPP-BQ was attributable to a low viscos-

ity because of its lower cure reaction rate. However, a notable increase in flexural strength at 25°C in this system with TPP-BQ as a catalyst was observed, as shown in Figure 2. These phenomena were caused by the increase in α with temperature in this system with TPP-BQ as a catalyst compared with that of the system with TPP. Therefore, the increase in crosslinking density due to the increase in α could cause an increase in the mechanical strength of this system with TPP-BQ.

In Figure 4, the moldability, reliability, and mechanical properties of the CER-3000L/MEH-7851SS EMC are shown. Both CER-3000L and MEH-7851SS have a biphenyl group in their chemical structures, as shown in Table I, so this system could meet the requirements

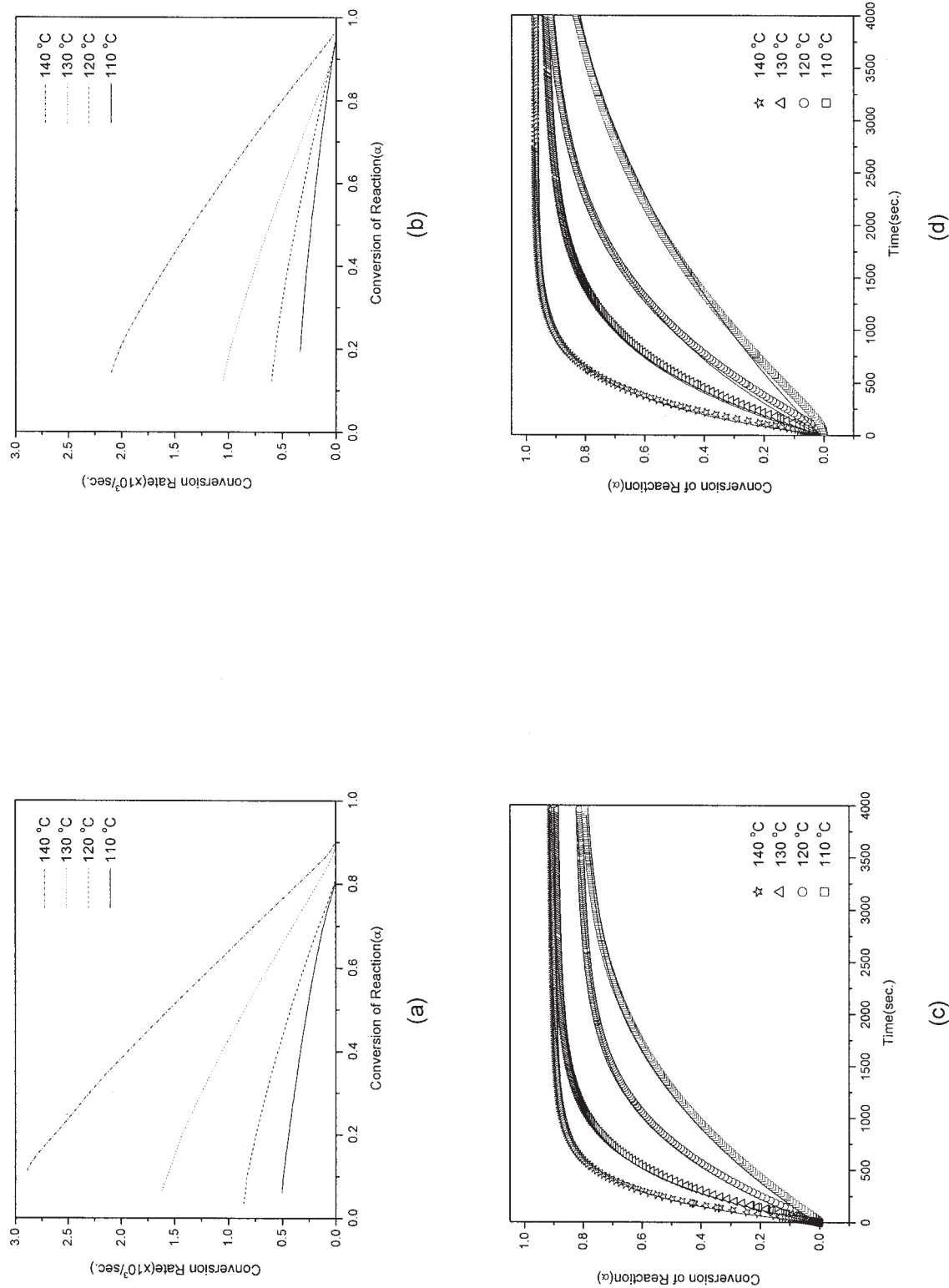


Figure 3 Curing properties of the YX-4000H/MEH-7800SS epoxy resin systems (sample 1 in Table II) according to the change in catalyst: isothermal conversion rate as a function of the conversion of the resin systems with (a) TPP and (b) TPP-BQ as the catalysts and comparisons between the experimental values of α and theoretical values obtained from the generalized n th-order kinetic model for the resin systems with (c) TPP and (d) TPP-BQ as the catalysts.

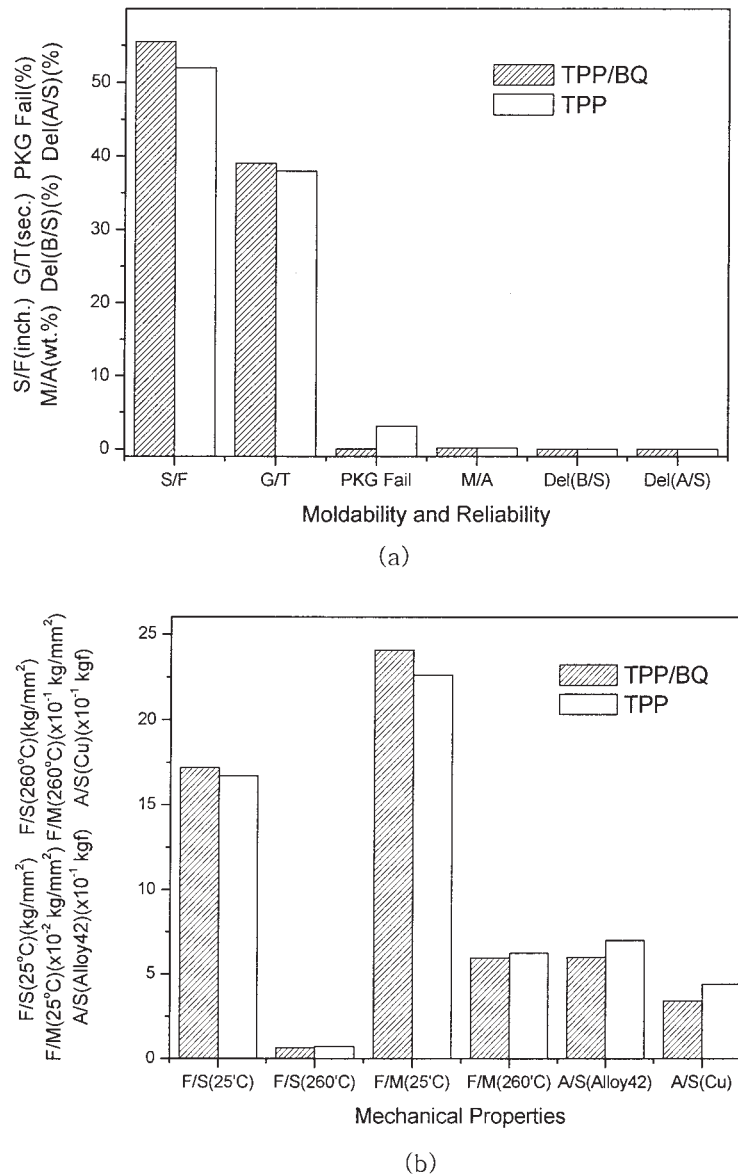


Figure 4 Physical properties of the CER-3000L/MEH-7851SS EMC (sample 2 in Table II): (a) moldability and reliability and (b) mechanical properties.

of a UL-94/V-0 flammability test with the lowest filler content. As shown in Figure 4, the CER-3000L/MEH-7851SS EMC system with TPP-BQ as a catalyst showed better results with respect of moldability and reliability compared with that of the system with TPP. The decrease in package fail was attributed to the decrease in viscosity according to the improvement in moldability, including spiral flow and gel time. The increase in the flexural strength and modulus at 25°C was observed in this system with TPP-BQ; however, the adhesion strength of this system showed a lower value than did the system with TPP as a catalyst.

The α rates of the CER-3000L/MEH-7851SS system with catalyst change are plotted as a function of α in Figure 5(a,b). The curing reactions in this sys-

tem proceeded through an n th-order kinetic mechanism, and we analyzed this experimental data with a generalized n th-order kinetic equation [eq. (4)]. Figure 5(c,d) shows a comparison of the experimental values of α and the values calculated with the generalized n th-order kinetic model for these compositions. Good agreement was found over the whole curing temperature range. The kinetic parameters of these systems with TPP and TPP-BQ as catalysts are reported in Table IV. As described for the YX-4000H/MEH-7800SS EMC system, the improvement in moldability and reliability in the CER-3000L/MEH-7851SS EMC system with TPP-BQ as a catalyst were attributed to a lower viscosity due to its slower α rate. We postulated that the increase in

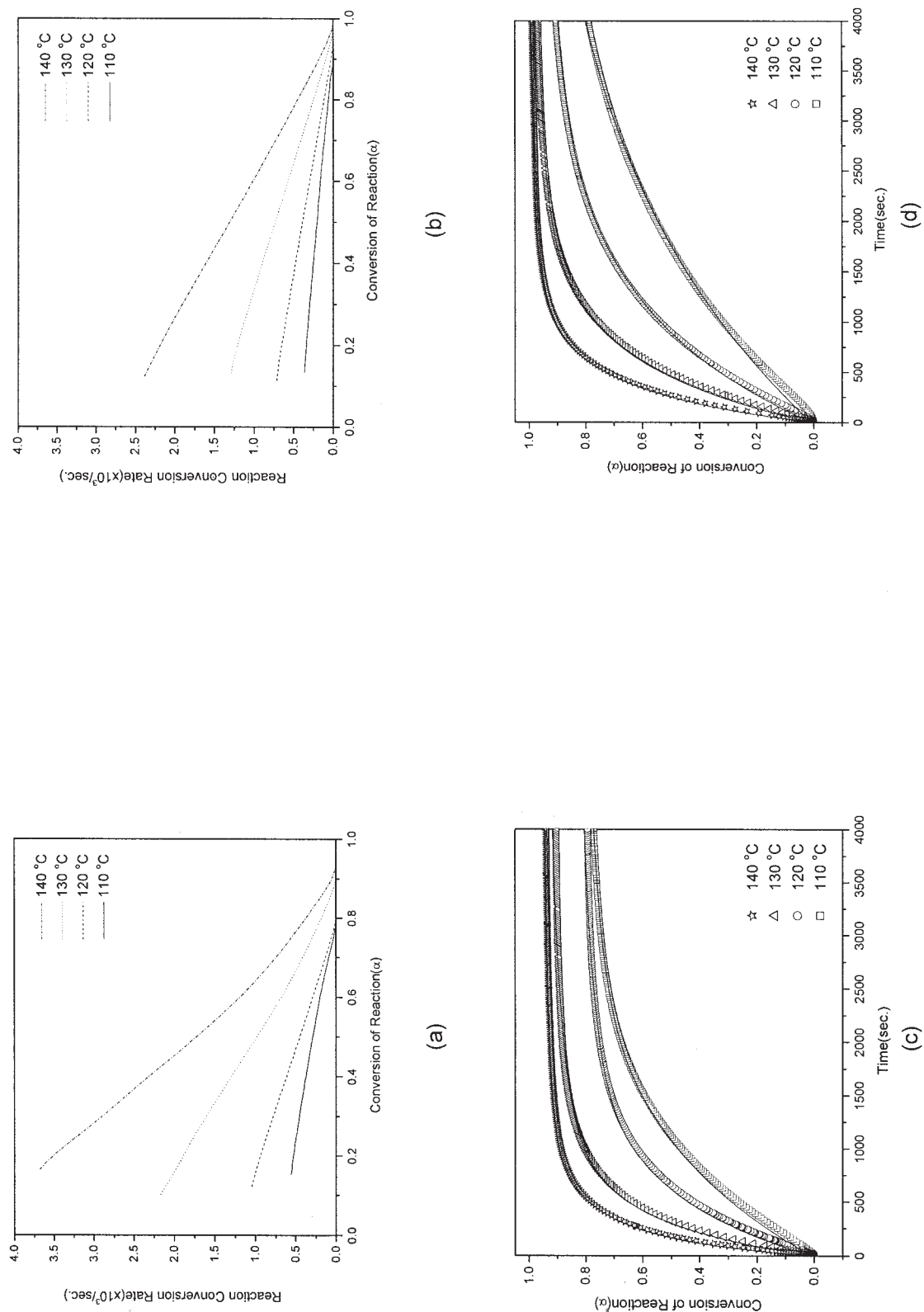
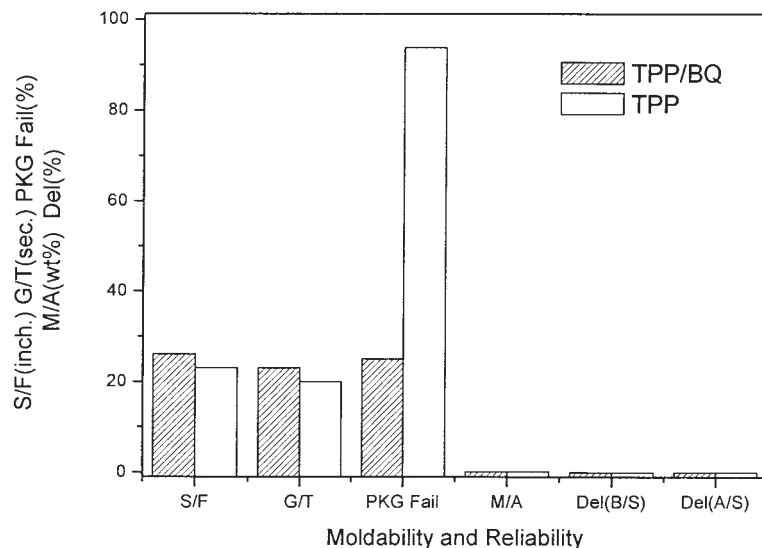
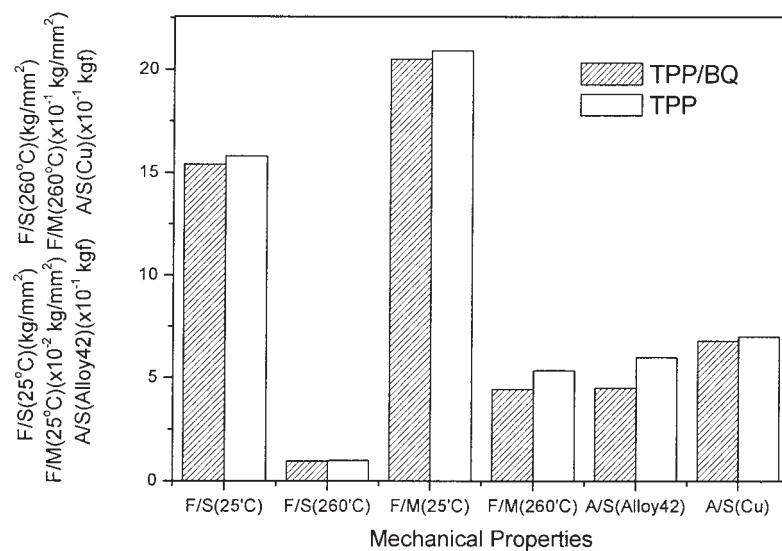


Figure 5 Curing properties of the CER-3000L/MEH-7851SS epoxy resin systems (sample 2 in Table II) according to the change in catalyst: isothermal conversion rate as a function of the conversion of the resin systems with (a) TPP and (b) TPP-BQ as the catalysts and comparisons between the experimental values of α and theoretical values obtained from the generalized n th-order kinetic model for the resin systems with (c) TPP and (d) TPP-BQ as the catalysts.



(a)



(b)

Figure 6 Physical properties of the EOCN-C/HF-I EMC (sample 3 in Table II): (a) moldability and reliability and (b) mechanical properties.

the flexural strength in this system was a result of the increase in crosslinking density according to the increase in curing α with increasing temperature. However, these phenomena were remarkably observed in the YX-4000H/MEH-7800SS EMC system, which included epoxy resin with only a biphenyl moiety.

In Figure 6, we show the change in the physical properties with the change in catalyst for the EOCN-C/HF-1 EMC system. The EOCN-C epoxy resin was composed of *o*-cresol novolac epoxy resin (80 wt %)

and biphenyl epoxy resin (20 wt %), and the HF-1 hardener resin was phenol novolac resin without a biphenyl group. This system, with a low content of the biphenyl group, showed different results than other systems with a biphenyl group. Although an improvement in the moldability and reliability in EOCN-C/HF-1 EMC system with TPP-BQ as the catalyst were observed, the improvements in the mechanical properties, including flexural strength, modulus, and adhesion in this system with TPP-BQ could not be measured.

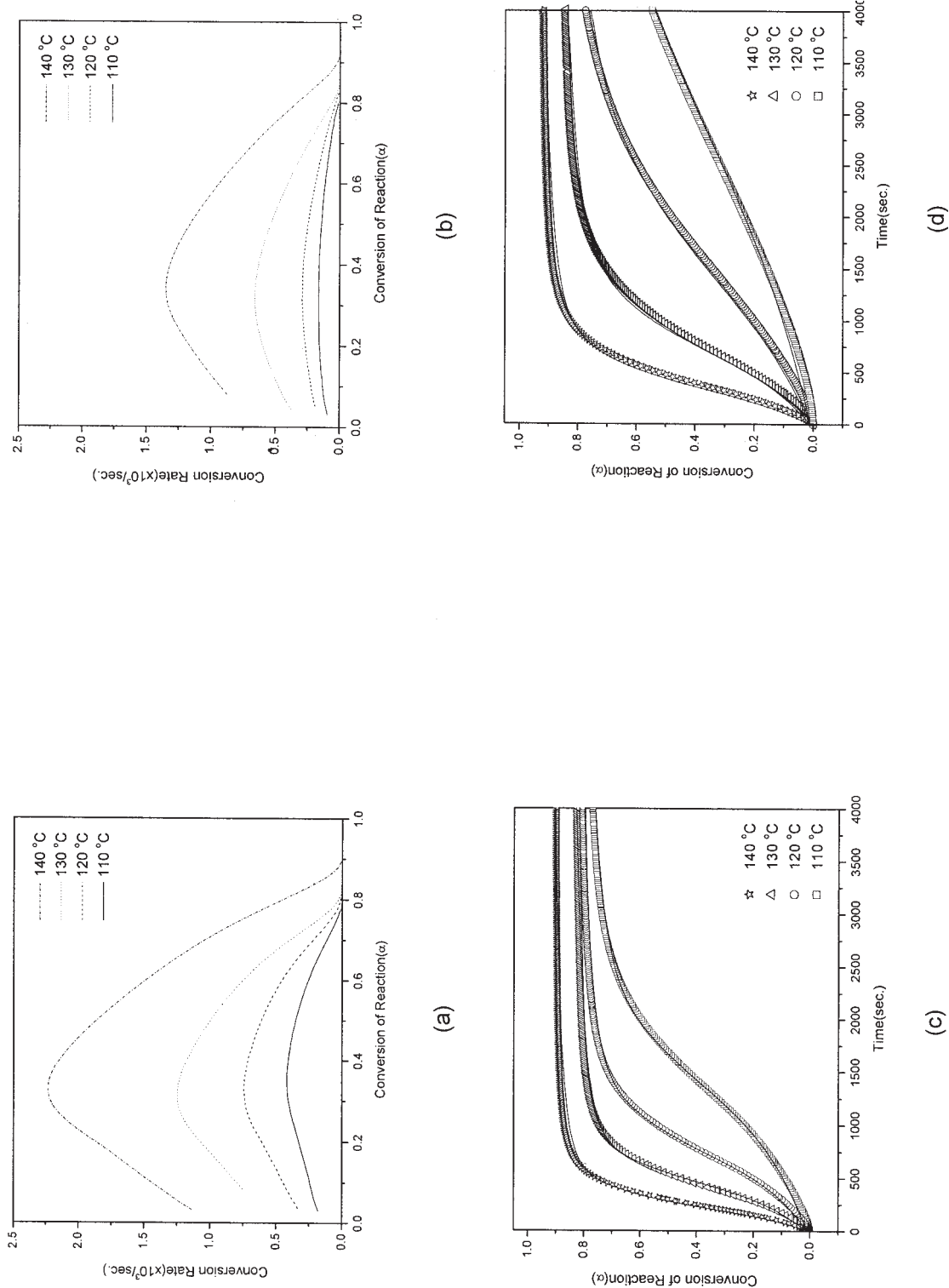


Figure 7 Curing properties of the EOCN-C/HF-1 epoxy resin systems (sample 3 in Table II) according to the change in catalyst: isothermal conversion rate as a function of the conversion of the resin systems with (a) TPP and (b) TPP-BQ as the catalysts and comparisons between the experimental values of α and theoretical values obtained from the generalized autocatalytic model for the resin systems with (c) TPP and (d) TPP-BQ as the catalysts.

TABLE VI
Values of C and α_c at Different Temperatures
for the EOCN-C/HF-1 Epoxy Resin System
(Sample 3 in Table II)

Catalyst	Temperature (°C)	C	α_c
TPP	110	23.18	0.70
	120	27.24	0.72
	130	27.21	0.72
	140	31.85	0.82
TPP-BQ	110	20.06	0.76
	120	21.96	0.77
	130	22.86	0.76
	140	27.45	0.84

The curing reaction of the EOCN-C/HF-1 system followed an autocatalytic cure reaction, as shown in Figure 7(a,b), which is a typical characteristic of an epoxy resin system with a phenol novolac hardener. The generalized autocatalytic kinetic equation with respect to the diffusion effect can be written as follows:¹⁸

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m) (1 - \alpha)^n \frac{1}{1 + \exp [C(\alpha - \alpha_c)]} \quad (5)$$

where m and n are the reaction order of the system, and k_1 and k_2 are kinetic rate constants of the system.

Figure 7(c,d) shows comparisons between the experimental values of α and the values calculated with the generalized autocatalytic model for the EOCN-C/HF-1 system with the change in catalyst. Good agreements were found over the whole curing temperature range for this system. The kinetic parameters are reported in Tables V and VI for this system with catalyst change that followed the autocatalytic curing reaction. As shown in Figure 7(a,b), the conversion rate of the EOCN-C/HF-1 EMC system with TPP-BQ as a cata-

lyst was lower than that with TPP. Therefore, we also postulated that the improvement in the moldability of this system was due to the low viscosity according to the low conversion rate, and the drop in the mechanical properties in this system was attributed to the decrease in crosslinking density in accordance with the low conversion of the curing reaction, as shown in Figure 7(c,d).

The final cure α 's of each EMC used in this experiment according to the change in temperature are summarized in Table VII. As shown in Table VII, the use of TPP-BQ as a latent catalyst in the YX-4000H/MEH-7800SS and CER-3000L/MEH-7851SS systems, which included mainly a biphenyl group in the epoxy resin, increased the cure α ; however, these phenomena could not be measured in the EOCN-C/HF-1 system with mainly a novolac-type epoxy resin. Therefore, we postulated that TPP-BQ as a latent catalyst improved the moldability, reliability, and mechanical properties for the epoxy resin systems that included a biphenyl moiety.

CONCLUSIONS

Latent catalyst effects were investigated to improve the physical properties of halogen-free EMCs for semiconductor encapsulation. An ionic-type latent catalyst, TPP-BQ, was used in this experiment, which was a salt of TPP, used in conventional EMCs as a catalyst, and BQ. The latent catalyst effects were examined on two kinds of halogen-free EMC formulations, and a typical EMC composition for a high-grade semiconductor, TSOP. The epoxy resin systems in halogen-free EMCs mainly include a biphenyl moiety, and the epoxy resin system in typical EMCs is mainly a cresol novolac-type epoxy resin. Improvements in the moldability, reliability, and mechanical properties were observed

TABLE VII
Summary of the Final Curing α According to the Change in Temperature
for Each EMC System Used in This Experiment

EMC	Temperature (°C)	Final curing α with TPP as a catalyst	Final curing α with TPP-BQ as a catalyst
YX4000H/MEH-7800SS	110	0.79	0.82
	120	0.81	0.91
	130	0.91	0.94
	140	0.92	0.98
CER-3000L/MEH-7851SS	110	0.77	0.80
	120	0.81	0.90
	130	0.90	0.97
	140	0.94	0.99
EOCN-C/HF-1	110	0.77	0.55
	120	0.81	0.77
	130	0.83	0.84
	140	0.90	0.90

in halogen-free EMCs with TPP-BQ as a catalyst, although they could not be measured in the conventional EMC with TPP-BQ. The curing kinetics of these systems was investigated to explain these phenomena. The improvement in moldability, including spiral flow and gel time, in the halogen-free EMC system with TPP-BQ over the halogen-free EMC system with TPP was due to its lower conversion reaction rate, and the increase in the mechanical strength in the system with TPP-BQ was attributed to its higher cure α than the system with TPP. Although the lower conversion reaction rate in a typical EMC system with TPP-BQ including a cresol novolac epoxy resin could be measured, a higher conversion reaction could not be observed. We postulated that TPP-BQ as a latent catalyst was very efficient in the epoxy resin system including a biphenyl group.

The authors thank Nippon Kayaku Co. for their generous supply of samples and for their fruitful discussions with us.

References

1. Yoon, H. G.; Kim, W. G. *Polymer for Electronics*; Mumindang: Seoul, Korea, 2001.
2. Ochi, M.; Takahashi, R. *J Polym Sci Part B: Polym Phys* 2001, 39, 1071.
3. Hsiue, G. H.; Liu, Y. L.; Liao, H. H. *J Polym Sci Part A: Polym Chem* 2001, 39, 986.
4. Shoji, K.; Nakamura, T.; Takahashi, T.; Miya, K.; Kimura, K. *NEC Res Dev* 2002, 43, 162.
5. Honda, S.; Tanaka, M.; Sawamura, Y.; Tokunaga, A.; Kayaba, K. *J Jpn Chem Soc* 2001, 9, 523.
6. La Losa, A. D.; Recca, A.; Carter, J. T.; McGrail, P. T. *Polymer* 1999, 40, 4093.
7. Li, X.; Ou, Y.; Shi, Y. *Polym Degrad Stab* 2002, 77, 383.
8. Han, S.; Yoon, H. G.; Kim, W. G.; Moon, T. J. *J Polym Sci Part A: Polym Chem* 1999, 37, 713.
9. Kim, W. G.; Lee, J. Y.; Park, K. Y. *J Polym Sci Part A: Polym Chem* 1993, 31, 633.
10. Kim, W. G.; Ryu, J. H. *J Appl Polym Sci* 1997, 65, 1975.
11. Masanobu, F.; Jiyunichi, C.; Takahiro, H. *Jpn Pat.* 11-035798 (1999).
12. Kim, W. G.; Nam, T. Y. *U.S. Pat.* 5,189,082 (1993); *U.S. Pat.* 5,266,612 (1993).
13. Kim, W. G.; Ryu, J. H. *Korean Chem Soc* 1996, 40, 81.
14. Kim, W. G.; Kim, H. S. *J Appl Polym Sci* 2000, 76, 1940.
15. Chem, C. S.; Poehlein, G. W. *Polym Eng Sci* 1987, 27, 782.
16. Kim, W. G.; Yoon, H. G.; Lee, J. Y. *J Appl Polym Sci* 2001, 81, 2711.
17. Han, S.; Yoon, H. G.; Kim, W. G.; Moon, T. J. *J Polym Sci Part A: Polym Chem* 1999, 37, 713.
18. Kim, W. G.; Lee, J. Y. *Polymer* 2002, 43, 5713.