Cure Properties of Self-Extinguishing Epoxy Resin Systems with Microencapsulated Latent Catalysts for Halogen-Free Semiconductor Packaging Materials

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ABSTRACT: The cure properties of self-extinguishing epoxy resin systems with different microencapsulated latent catalysts were investigated, which are composed of YX4000H and NC3000H as a biphenyl epoxy resin, MEH-7800SS as a hardener, and triphenylphosphine (TPP) microencapsulated with various polymers as a latent catalyst. The cure kinetics of these systems were analyzed by differential scanning calorimetry using an isothermal approach, and the kinetic parameters of all systems were reported in generalized kinetic equations with diffusion effects. Both the epoxy resin systems with microencapsulated latent catalysts showed lower cure conversion rate and higher critical cure reaction conversion than those with TPP. These different cure conversion rates could be explained by the decrease of crystallinity of the biphenyl epoxy resin and the activation energy of these epoxy resin systems. The cure conversion rates of the epoxy resin systems with the micro-encapsulated latent catalyst would be dependent on the activation energy of these systems. The storage stability tests for these systems were performed, and a good shelf-life was observed in both the epoxy resin systems with EPCAT-PAM, a core–shell-type latent catalyst. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 408–417, 2009

Key words: curing of polymers; thermosets; kinetics (polym.); catalysts
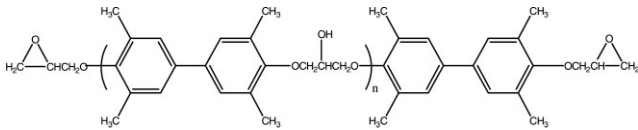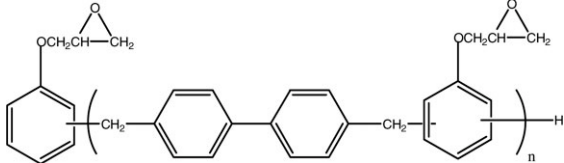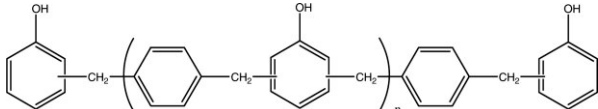
INTRODUCTION

A self-extinguishing epoxy resin system that does not have any flame-retarding additives, such as a halogen compound, has been developed for green epoxy molding compound (EMC) for semiconductor packaging materials. This resin system contains biphenyl and xylene moieties with high aromaticity.[1,2] This epoxy resin system forms a self-extinguishing network of structures after crosslinking reaction, which can form stable foam layers during ignition.[3] These foam layers effectively retard the transfer of heat to the insides of the compound and the flames are thus extinguished. The improvement of these inflammable properties has been achieved through an increase in filler content and it is also being used to improve low thermal expansion coefficients, thermal resistance, and reliability.[4] When the filler content is increased, however, the viscosity of EMC also increases. This results in a disadvantage in the productivity and moldability of EMC, and therefore low-viscosity epoxy resin such as a biphenyl type is required.[5,6]

Generally, these biphenyl epoxy resins with low molecular weights have low crosslinking density for fast reactions with crystallinity and low storage stability at room temperature. Therefore, latent catalysts for these systems should 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. In a previous work, the effects of carbonic acid/diazabicycloundecene salt and triphenylphosphine/benzoquinone (TPP/BQ) charge transfer complex as an ionic type latent catalyst on the curing characteristics of epoxy resin compositions containing biphenyl-type epoxy resin systems were investigated.[7,8]

This study investigated the curing properties of self-extinguishing epoxy resin systems with a micro-encapsulation-type latent catalyst as nonionic structure type. The curing characteristics of these systems with TPP coated with different encapsulation materials and types as a latent catalyst were examined with differential scanning calorimetry (DSC). The curing kinetics in the overall conversion region has been interpreted by means of the kinetic and diffusion model.[9,10]

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TABLE I
Description of Epoxy Resins and a Hardener Used in This Study

Grade name	Structure	Remarks
YX-4000H		EEW = 193[a]
NC-3000H		EEW = 288[a]
MEH-7800SS		HEW = 175[b]

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

EXPERIMENTAL

Materials

The epoxy resins used in this experiment were commercially available biphenyl epoxy resins YX-4000H (Japan Epoxy Resin, Tokyo, Japan) and NC-3000H (Nippon Kayaku, Tokyo, Japan). The hardener used was a xylok type (MEH-7800SS, Meihwa, Tokyo, Japan). Detailed descriptions of the chemical structures of the epoxy resins and hardener resin are summarized in Table I. EPCAT-P (Nippon Kayaku), EPCAT-PS (Nippon Kayaku), EPCAT-PE (Nippon Kayaku), and EPCAT-PAM (Nippon Kayaku) as latent catalysts and TPP (Aldrich Chemical, St. Louis, MO) were used as received. Figure 1 shows the shapes of microencapsulated latent catalysts, and detailed descriptions of the catalysts used in this study are represented in Table II.

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 $0.02M$ of each catalyst. The concentration of microencapsulated latent catalysts was fixed on the basis of the net content of TPP. The 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.

Measurements

Calorimetric measurements were performed using a TA-2020 DSC (TA Instruments, New Castle, DE). This was calibrated in the range of −40 to 450°C.

Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 60 mL/min. For a 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 parameter 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 the heating rate of 5°C/min up to 300°C so that its reaction conversion at that time could be determined.

The surface morphology of the microencapsulated latent catalysts was investigated using a scanning electron microscope (S-3000H, Hitachi, Japan).

RESULTS AND DISCUSSION

The series of isothermal reaction conversion rates of YX-4000H/MEH-7800SS resin systems with different kinds of microencapsulated latent catalysts and TPP as reference are plotted as a function of reaction conversion (α) in Figure 2. It can be seen that the curing reactions in all systems proceeded through an nth-order kinetic mechanism,[11] irrespective of catalysts employed. The reaction conversion rates of these resin systems with microencapsulated latent catalysts were lower than those with TPP only as a catalyst. Among the resin systems with microencapsulated latent catalysts, the reaction rate of YX-4000H/MEH-7800SS with EPCAT-PS as a latent catalyst was the fastest as shown in Figure 2.

Figure 3 shows a series of isothermal reaction rate curves as a function of the reaction conversion for NC-3000H/MEH-7800SS resin compositions with different latent catalysts. It can also be shown that
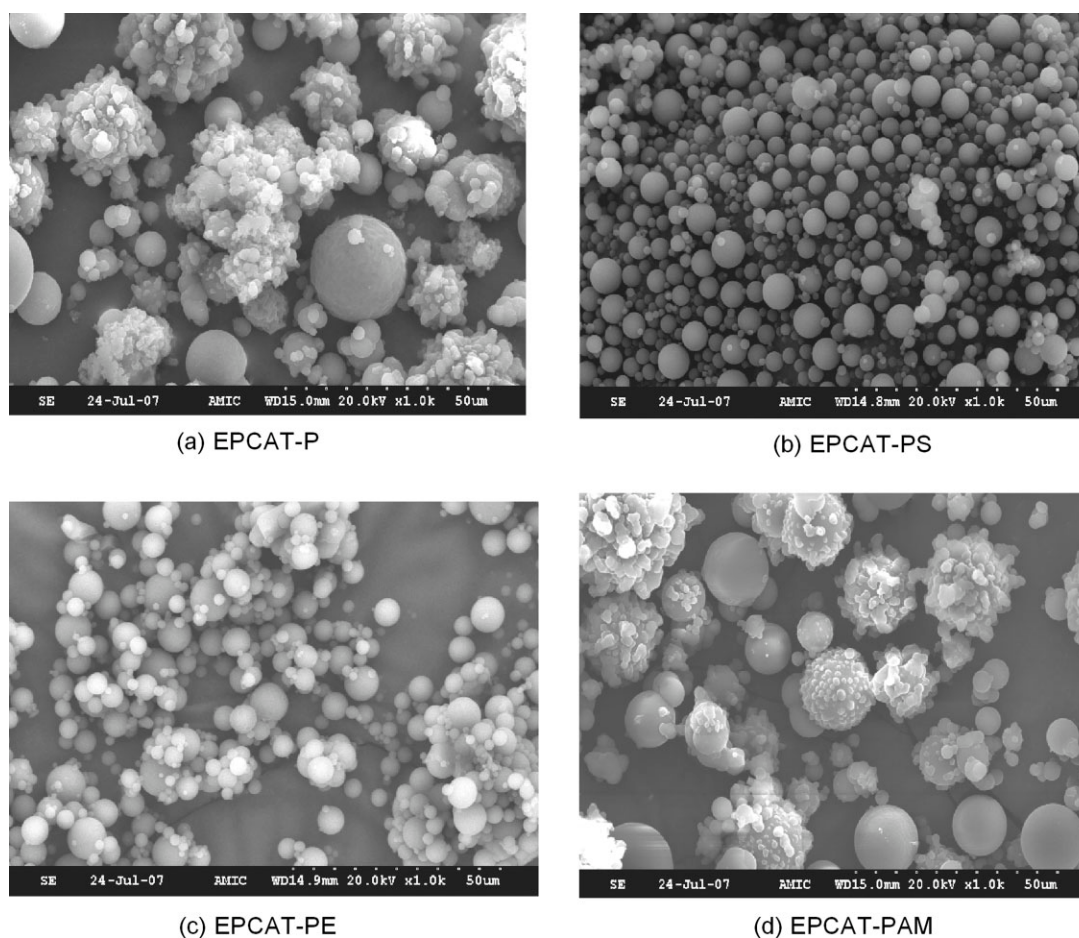
Figure 1 SEM images of encapsulated catalysts: (a) EPCAT-P, (b) EPCAT-PS, (c) EPCAT-PE, and (d) EPCAT-PAM.

the curing reactions in these systems proceed by an nth-order kinetic mechanism. The reaction conversion rates of these compositions were lower than those with TPP, and while the composition with the EPCAT-PE as a latent catalyst represented a faster reaction rate among the compositions with microencapsulated latent catalysts.

For thermosets that follow an nth-order curing reaction kinetics, the isothermal reaction conversion rate is proportional to the fraction of material unreacted $(1 - \alpha)$, as expressed in the form below:

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

where t is the time, n is the reaction order of the system, and k is the rate constant of the system. To precisely predict the cure kinetics over the whole range of conversion, the nth-order model was modified in terms of the introduction of a diffusion term as represented in eq. (2).[12,13] When the diffusion effect is considered, eq. (1) can be rewritten as eq. (2):

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

where C is a constant and α_c is the critical conversion.

All kinetic constants in this equation for each resin system were obtained by a previous method.[7,14]

TABLE II
Description of Microencapsulated Catalysts Used in This Study

| Grade name	Structure	CT (wt %)[a]	Remarks
EPCAT-P	Triphenyl phosphine microencapsulated with polymethylmethacrylate	20	Crosslinked type
EPCAT-PS	Triphenyl phosphine microencapsulated with polystyrene	20	Crosslinked type
EPCAT-PE	Triphenyl phosphine microencapsulated with polyethylacrylate	20	Crosslinked type
EPCAT-PAM	Triphenyl phosphine microencapsulated with polyamide 6 and polymethymethacryalte	13	Core–shell type

[a] CT, content of triphenyl phosphine.
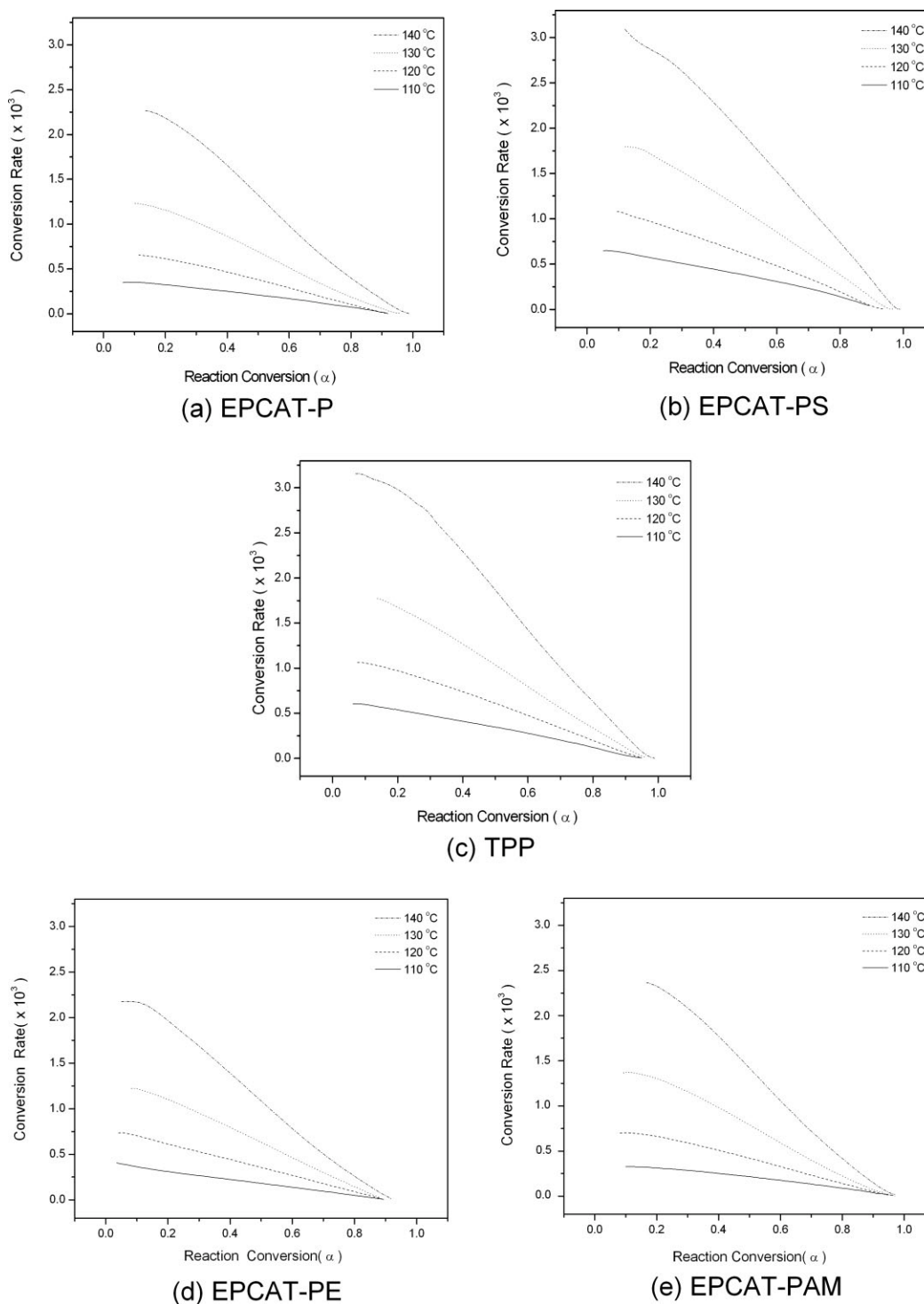
Figure 2 Isothermal conversion rate as a function of the conversion of the YX-4000H/MEH-7800SS resin systems with different catalysts: (a) EPCAT-P, (b) EPCAT-PS, (c) TPP, (d) EPCAT-PE, and (e) EPCAT-PAM.

Conversion rates were obtained by measuring isothermal and dynamic-heating experiments using DSC.[15] To compute the kinetic parameters in eq. (2) without any constraints on parameters, n, k, C, and α_c, they were calculated by fitting the experimental data to eq. (2). Figure 4 shows the comparisons

between the experimental values of reaction conversion and the values calculated using a generalized nth-order model for YX-4000H/MEH-7800SS resin system with different microencapsulated latent catalyst. Good agreements were found over the whole curing temperature range for all resin systems. The
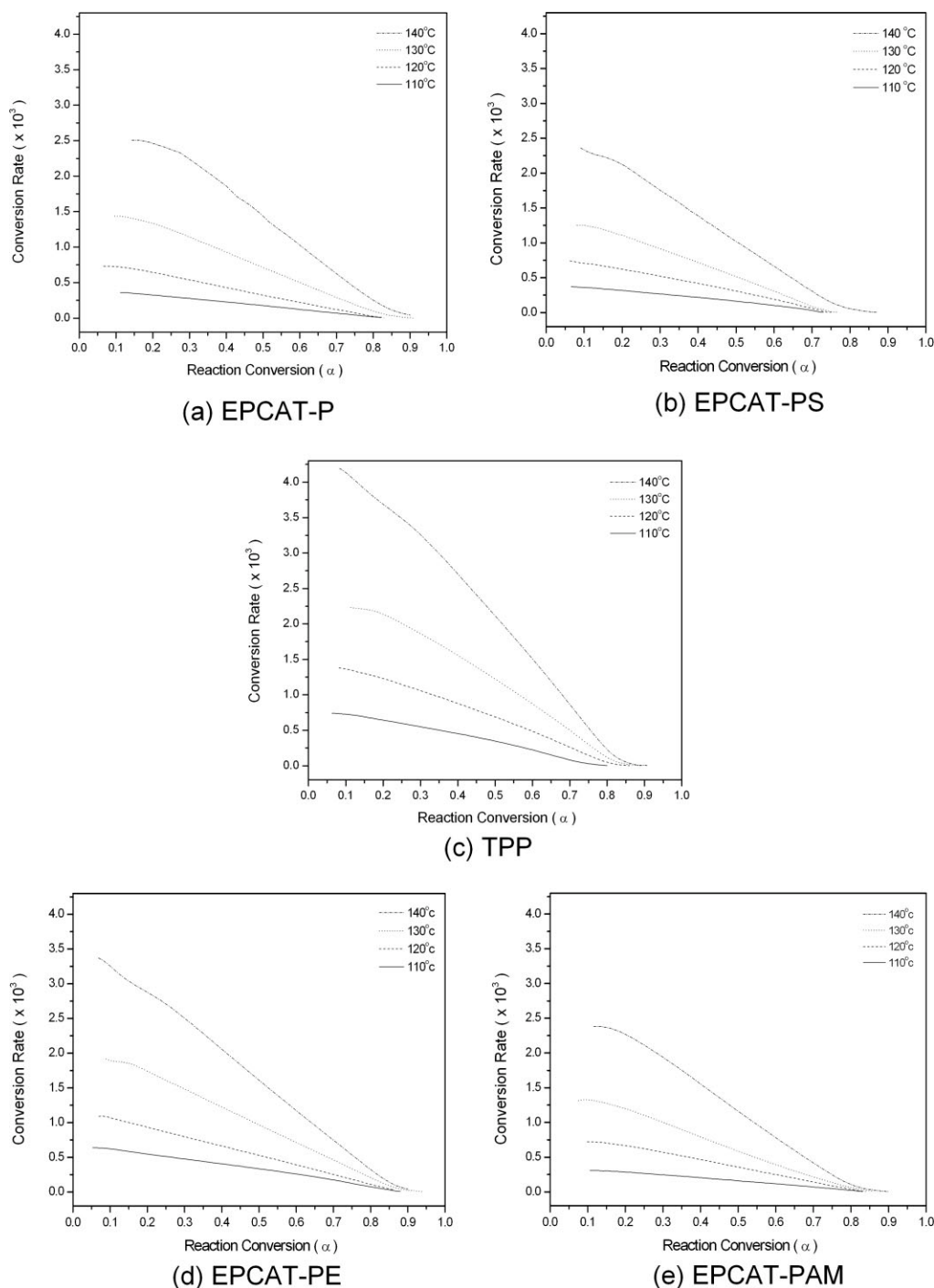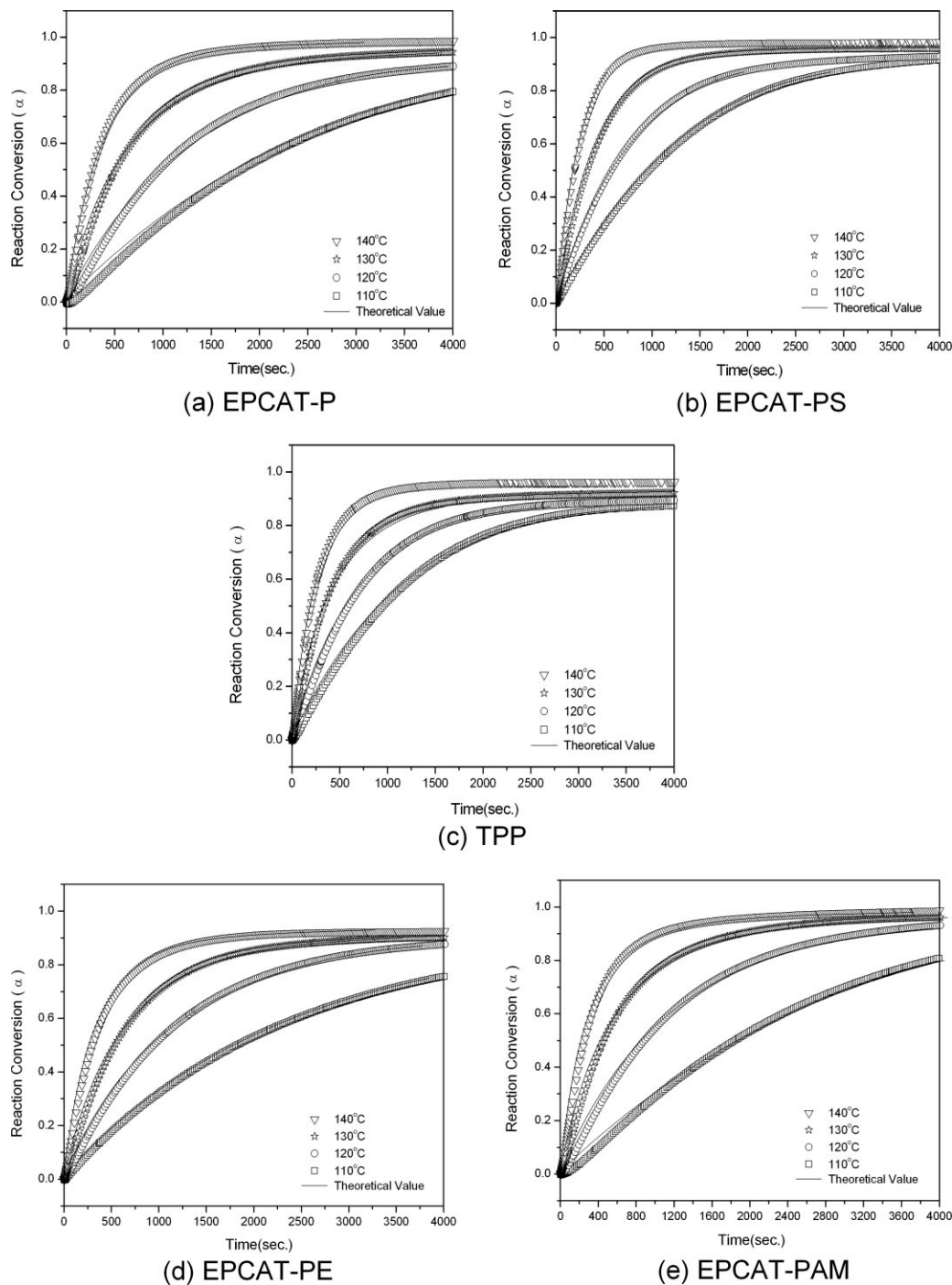
Figure 3 Isothermal conversion rate as a function of the conversion of the NC-3000H/MEH-7800SS resin systems with different catalysts: (a) EPCAT-P, (b) EPCAT-PS, (c) TPP, (d) EPCAT-PE, and (e) EPCAT-PAM.

kinetic parameters are reported in Table III for systems with different kinds of latent catalysts that follow the *n*th-order curing reaction.

As shown in Table III, it was postulated that the faster reaction rate of YX-4000H/MEH-7800SS resin system with EPCAT-PS was attributable to its lower activation energy. Generally, the microencapsulated catalyst can be classified into crosslinked type and core–shell type according to the encapsulation synthetic method.[16] EPCAT-P, EPCAT-PS, and EPCAT-PE are crosslinked-type microencapsulated latent catalyst manufactured by homopolymerization, and EPCAT-PAM is the core–shell-type microencapsulated latent catalyst composed of polymethylmethacrylate and polyamide double layer shell.[17] The highest value of the activation energy was obtained

Figure 4 Comparisons between the experimental values of α and theoretical values obtained from the generalized nth-order kinetic model for the YX-4000H/MEH-7800SS resin systems with different catalysts: (a) EPCAT-P, (b) EPCAT-PS, (c) TPP, (d) EPCAT-PE, and (e) EPCAT-PAM.

in YX-4000H/MEH-7800SS resin composition with EPCAT-PAM as represented in Table III, which is caused by the retardation of catalyst release with core–shell type EPCAT-PAM.

Figure 5 shows the comparisons between the experimental values of reaction conversion and the values calculated with a generalized nth-order

kinetic model for NC-3000H/MEH-7800SS resin system with various microencapsulated latent catalysts. Good agreements were found over the whole curing temperature range for all composition systems. The kinetic parameters of these systems with different kinds of latent catalysts are reported in Table IV.

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TABLE III
Kinetic Parameters of the YX-4000H/MEH-7800SS Resin Systems

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| Catalyst	T (°C)	k_1 (s^{-1})	n	C	α_c	Temperature dependency of the rate constant	n (Avg.)
TPP	110	0.79×10^{-3}	1.1	30.42	0.84	$k_1 = 3.76 \times 10^6 \exp(-7.09 \times 10^4/RT)$	1.3
	120	1.39×10^{-3}	1.4	32.98	0.85		
	130	2.50×10^{-3}	1.5	46.41	0.88		
	140	3.91×10^{-3}	1.2	47.88	0.93		
EPCAT-P	110	0.38×10^{-3}	0.9	19.05	0.87	$k_1 = 3.59 \times 10^8 \exp(-8.77 \times 10^4/RT)$	1.2
	120	0.75×10^{-3}	1.2	45.59	0.89		
	130	1.64×10^{-3}	1.4	56.45	0.93		
	140	2.69×10^{-3}	1.2	53.25	0.97		
EPCAT-PS	110	0.69×10^{-3}	0.9	17.54	0.88	$k_1 = 2.30 \times 10^7 \exp(-7.71 \times 10^4/RT)$	1.0
	120	1.25×10^{-3}	1.1	37.27	0.89		
	130	2.37×10^{-3}	1.1	41.43	0.92		
	140	3.94×10^{-3}	1.0	54.50	0.95		
EPCAT-PE	110	0.41×10^{-3}	1.2	20.15	0.86	$k_1 = 6.97 \times 10^8 \exp(-8.97 \times 10^4/RT)$	1.4
	120	0.85×10^{-3}	1.4	58.81	0.89		
	130	1.60×10^{-3}	1.5	36.49	0.88		
	140	3.19×10^{-3}	1.5	44.42	0.90		
EPCAT-PAM	110	0.34×10^{-3}	0.8	16.30	0.94	$k_1 = 7.16 \times 10^{10} \exp(-10.49 \times 10^4/RT)$	1.2
	120	0.84×10^{-3}	1.1	19.59	0.95		
	130	1.89×10^{-3}	1.4	75.97	0.96		
	140	3.71×10^{-3}	1.5	50.94	0.98		

The reaction rate of NC-3000H/MEH-7800SS resin composition with EPCAT-PE as microencapsulated latent catalyst was faster than those with other latent catalysts as shown in Figure 3. As shown in Table IV, it was postulated that the increase in the reaction rate of this resin composition system with EPCAT-PE was the result of its lower activation energy. As described in the YX-4000H/MEH-7800SS resin composition systems, the highest activation energy of NC-3000H/MEH-7800SS resin composition systems can be seen in this resin composition with EPCAT-PAM, a core–shell-type microencapsulation latent catalyst.

The NC-3000H epoxy resin includes a benzene moiety over a biphenyl group in the repeating unit when compared with the YX-4000H epoxy resin, which decreases the crystallinity of the resin.[18] Thus, it can be seen that the reaction conversion rate of NC-3000H epoxy resin system with TPP as a catalyst is faster than that of YX-4000H epoxy resin system with TPP as shown in Figures 2 and 3, in spite of the lower activation energy of YX-4000H resin system than that of NC-3000H system as represented in Tables III and IV. It can also be seen that the pre-exponential factor in Arrhenius equation form of NC-3000H/MEH-7800SS with TPP resin composition is larger than that of YX-4000H/MEH-7800SS with TPP resin system. Therefore, the increase of reaction conversion rate in NC-3000H/MEH-7800SS with TPP was due to the orientation dominant effect for this reaction. However, it can be observed that the reaction conversion rates of both epoxy resin systems with the same microencapsulated latent catalyst are similar to each other. Especially, the epoxy resin system with lower activation energy in both epoxy resin systems with the same microencapsulated latent catalyst is faster as shown in epoxy resin compositions with EPCAT-PS and EPCAT-PE. Therefore, it can be assumed that the reaction conversion rates of these epoxy resin systems with TPP as a catalyst showed the orientation-dominant effect, and those with microencapsulated latent catalysts manifested the activation energy-dominant effect of these systems, kinetically.

The critical cure conversions of each resin composition used in this experiment according to the change in temperature are summarized in Table V. As shown in Table V, the use of microencapsulated TPP as a latent catalyst increased the cure conversion over the resin composition with TPP, irrespective of the kinds of epoxy resins. As shown in a previous study,[7] the halogen-free EMC system with TPP-BQ as a latent catalyst displayed better moldability in terms of spiral flow and gel time over the halogen-free EMC system with TPP because of its lower conversion reaction rate, and the increase in the mechanical strength of the system with TPP-BQ was attributed to its higher cure reaction conversion. As shown in Figures 2 and 3, all resin composition systems with microencapsulated latent catalysts showed their lower conversion reaction rate and more increase of critical cure conversion than those with TPP as summarized in Table V. Therefore, the improvement of mechanical properties and moldability can be expected in the halogen-free EMC with microencapsulated latent catalysts.

The changes of the reaction conversion of these systems according to the storage time at 30 and 50°C were measured to test their shelf-life. These results
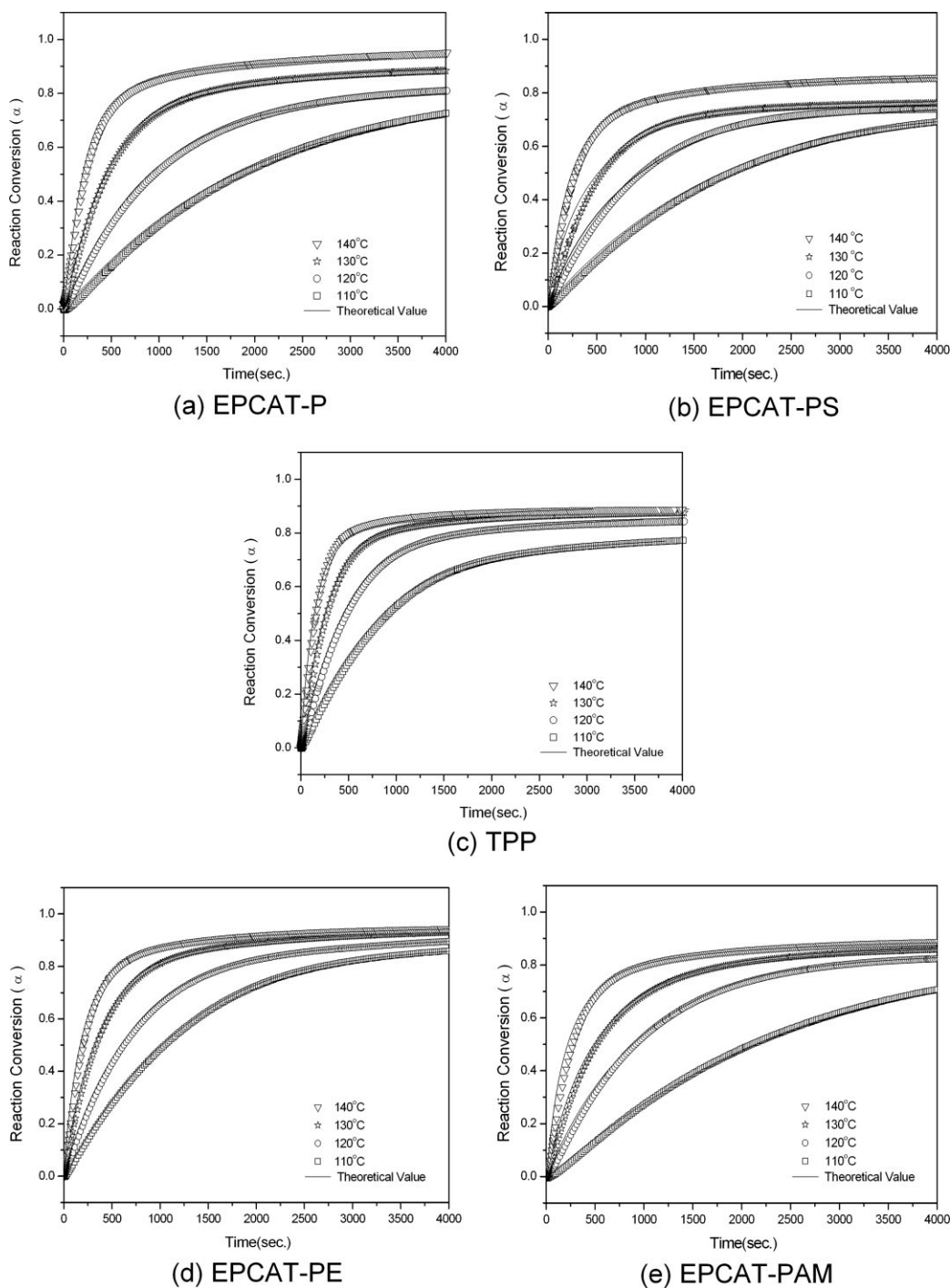
Figure 5 Comparisons between the experimental values of α and theoretical values obtained from the generalized nth-order kinetic model for the NC-3000H/MEH-7800SS resin systems with different catalysts: (a) EPCAT-P, (b) EPCAT-PS, (c) TPP, (d) EPCAT-PE, and (e) EPCAT-PAM.

of YX-4000H/MEH-7800SS resin compositions are represented in Figure 6, whereas those of NC-3000H/MEH-7800SS resin compositions are exhibited in Figure 7. It can be shown that the storage stabilities for the YX-4000H/MEH-7800SS resin composition with EPCAT-PS, EPCAT-PAM, and EPCAT-P were better than those using EPCAT-PE and TPP,

and that the better results of the storage stabilities for the NC-3000H/MEH-7800SS resin system were obtained while using EPCAT-PAM, EPCAT-PS, and EPCAT-P. At 50°C, the YX-4000H/MEH-7800SS resin system with EPCAT-PS and the NC-3000H/MEH-7800SS resin system with EPCAT-PAM showed especially good stability when compared

Catalyst	T (°C)	k_1 (s^{-1})	n	C	α_c	Temperature dependency of the rate constant	n (Avg.)
TPP	110	0.88×10^{-3}	1.3	20.60	0.68	$k_1 = 1.74 \times 10^8 \exp\left(-8.28 \times 10^4/RT\right)$	1.4
	120	1.66×10^{-3}	1.3	20.52	0.74		
	130	3.00×10^{-3}	1.3	22.09	0.76		
	140	5.91×10^{-3}	1.6	23.11	0.77		
EPCAT-P	110	0.38×10^{-3}	1.2	18.26	0.76	$k_1 = 6.33 \times 10^{11} \exp\left(-11.15 \times 10^4/RT\right)$	1.6
	120	0.94×10^{-3}	1.6	26.88	0.77		
	130	2.38×10^{-3}	1.7	24.48	0.82		
	140	4.73×10^{-3}	1.7	18.42	0.87		
EPCAT-PS	110	0.44×10^{-3}	1.4	24.53	0.67	$k_1 = 9.57 \times 10^9 \exp\left(-9.77 \times 10^4/RT\right)$	1.9
	120	1.00×10^{-3}	1.9	30.38	0.69		
	130	2.21×10^{-3}	2.3	33.14	0.70		
	140	3.96×10^{-3}	1.9	21.83	0.76		
EPCAT-PE	110	0.70×10^{-3}	1.1	20.81	0.81	$k_1 = 3.43 \times 10^8 \exp\left(-8.58 \times 10^4/RT\right)$	1.4
	120	1.27×10^{-3}	1.3	18.77	0.83		
	130	2.49×10^{-3}	1.4	21.89	0.85		
	140	4.95×10^{-3}	1.6	23.40	0.86		
EPCAT-PAM	110	0.33×10^{-3}	1.0	11.82	0.74	$k_1 = 1.34 \times 10^{12} \exp\left(-11.43 \times 10^4/RT\right)$	1.5
	120	0.92×10^{-3}	1.4	31.57	0.79		
	130	1.94×10^{-3}	1.7	22.51	0.80		
	140	4.65×10^{-3}	2.0	23.52	0.81		

with others. For both the epoxy resin systems, those using EPCAT-PAM, a core–shell-type latent catalyst, demonstrated good stability.

CONCLUSIONS

The curing reactions of self-extinguishing epoxy resin systems with several microencapsulated latent catalysts were investigated by the thermal analysis method. The curing reactions in all systems pro-

TABLE V
Summary of Critical Cure Reaction Conversion According to the Changes of Latent Catalysts in Each Resin Composition Used in This Experiment

Catalyst	T (°C)	α_c (YX-4000H)	α_c (NC-3000H)
TPP	110	0.84	0.68
	120	0.85	0.74
	130	0.88	0.76
	140	0.93	0.77
EPCAT-P	110	0.87	0.76
	120	0.89	0.77
	130	0.93	0.82
	140	0.97	0.87
EPCAT-PS	110	0.88	0.67
	120	0.89	0.69
	130	0.92	0.70
	140	0.95	0.76
EPCAT-PE	110	0.86	0.81
	120	0.89	0.83
	130	0.88	0.85
	140	0.90	0.86
EPCAT-PAM	110	0.94	0.74
	120	0.95	0.79
	130	0.96	0.80
	140	0.98	0.81

(a) 30 °C

(b) 50 °C

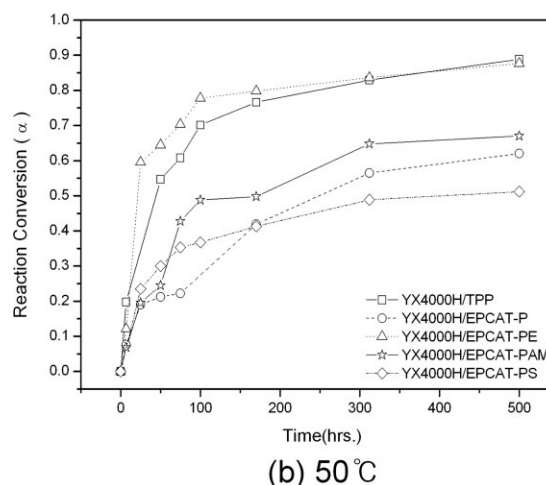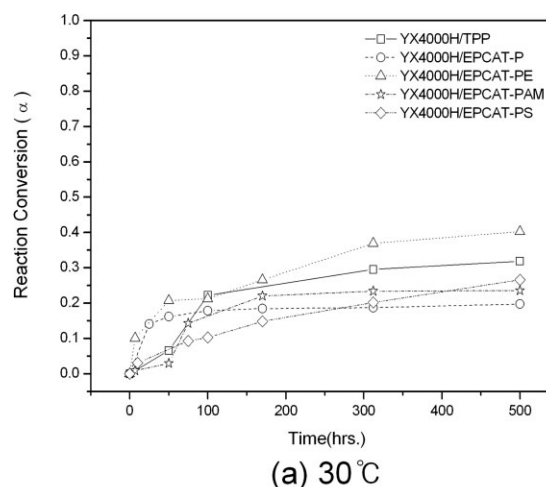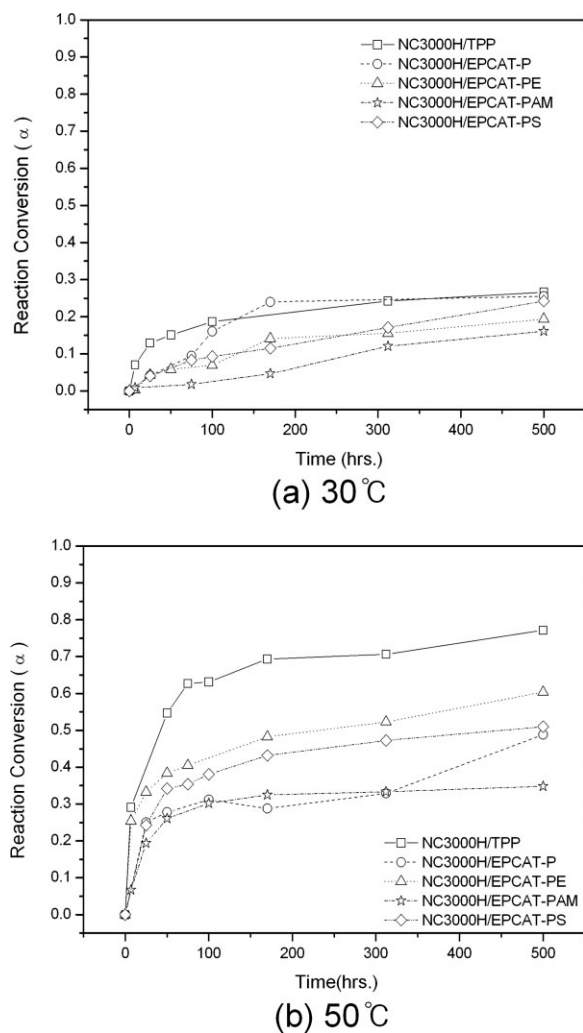**Figure 6** The shelf-life test for the YX-4000H/MEH-7800SS resin systems with different store temperatures: (a) 30 and (b) 50°C.

(a) 30 °C

(b) 50 °C

Figure 7 The shelf-life test for the NC-3000H/MEH-7800SS resin systems with different store temperatures: (a) 30 and (b) 50°C.

ceeded through an nth-order kinetic mechanism, irrespective of microencapsulated latent catalysts. The experimental values of the reaction conversion were compared with the values calculated using a generalized nth-order model including a diffusion term, and good agreements were found over the whole curing temperature range for all resin systems. The reaction conversion rates of epoxy resin systems with TPP as a catalyst including biphenyl groups increased with lower crystallinity of biphenyl-type epoxy resin. However, those with microencapsulated latent catalysts increased with lower activation energy of these systems. The use of microencapsulated TPP as a latent catalyst decreased the cure reaction conversion rate over the resin composition with TPP and increased the cure conversion over it. To test the shelf-life of these systems with microencapsulated latent catalysts, the changes of the reaction conversion of the systems according to the storage time and temperature were measured. The epoxy resin composition systems with EPCAT-PAM, a core–shell-type latent catalyst, showed good stability for both epoxy resin systems.

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