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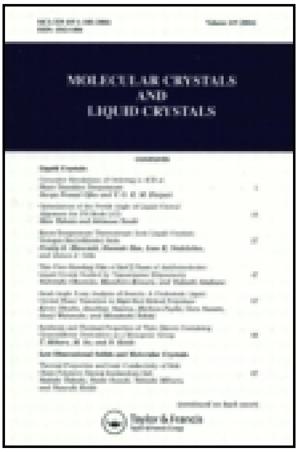

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Cure Properties of Naphthalene-Based Epoxy Resin Systems with Hardeners and Latent Catalysts for Semiconductor Packaging Materials

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Cure Properties of Naphthalene-Based Epoxy Resin Systems with Hardeners and Latent Catalysts for Semiconductor Packaging Materials

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The cure properties of naphthalene-based epoxy resin (EXA-4700) systems with different hardeners and latent catalysts were investigated. The latent catalysts used in this study were tetraphenyl phosphonium-thiocyanate (TPP-SCN) and 2-ethyl-4-methyl imidazolium tetraphenyl borate (EMZ-K). The cure kinetics of these systems were analyzed by dynamic and isothermal data from the Differential Scanning Calorimetry (DSC) experiments, and the kinetic parameters of all systems were reported in generalized kinetic equations with diffusion effects. Thermal expansion coefficients of these epoxy systems were obtained by mean of Thermo Mechanical Analyzer (TMA) measurement. The conversion reaction rate of EXA-4700 system with TPP-SCN is higher than that with EMZ-K, irrespective of the location of hydroxyl group in naphthol hardeners or the differences in cure mechanisms between these latent catalysts. The thermal expansion coefficient in low temperature region ($\alpha 1$) of EXA-4700 resin systems with 2,7-naphthol as a hardener is lower than that with 1,6-naphthol. The cure properties of these epoxy resin systems with different hardeners and catalysts were investigated with respect to the curing molecular structure.

Keywords Cure kinetics; epoxy resin; latent catalyst; semiconductor

Introduction

High thermal resistant epoxy resin systems with lower coefficients of thermal expansion should be required in electronic packaging applications [1–3]. The application of the current commercial epoxy resins to electronic components is expected to be seriously limited with the advance of information technology. When epoxy resin was used as electronic packaging materials, serious problems such as a crack in the package, delamination, and metal deformation often originated from a mismatch of thermal expansion coefficients among the component materials, including epoxy resin systems [4].

The naphthalene-based epoxy resin systems have shown specific thermal performance applicable for potential use in microelectronic devices [5, 6]; the multifunctional epoxy resins based on 2,7-dihydroxynaphthalene have especially performed high thermal resistance with good moldability [7]. It was also reported that the incorporation of naphthalene

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moiety into the epoxy network was effective in lowering the coefficient of thermal expansion of the resin system [8, 9]. However, these naphthalene-based epoxy resins with low molecular weight have low crosslinking density for fast reactions with crystallinity and low storage stability at room temperature. Therefore, the development of efficient latent catalysts is desirable for the enhancement of both the storage stability and handling of thermosetting resins.

This study investigated the curing properties of multifunctional EXA-4700 systems with a charge transfer complex type latent catalyst according to the change of a naphthol hardener with different locations of a hydroxyl group. The curing characteristics of these systems with triphenylphosphine-based charge transfer complex and imidazole-based charge transfer complex as a latent catalyst were examined with DSC and TMA. The curing kinetics in the overall conversion region has been interpreted by means of the kinetic and diffusion model [10, 11].

Experimental

The epoxy resin used in this experiment was commercially available multifunctional naphthalene-based epoxy resin EXA-4700 (DIC, Tokyo, Japan). The hardeners used were 1,6-naphthol and 2,7-naphthol (Aldrich Chemical Co., St. Louis, MO). TPP-SCN and EMZ-K (Hokko Chemical Co., Tokyo, Japan) as a latent catalyst were used as received. Detailed descriptions of the chemicals used in this study are summarized in Table 1.

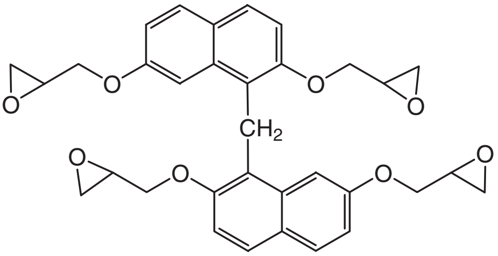
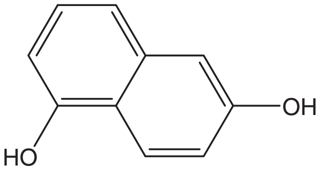
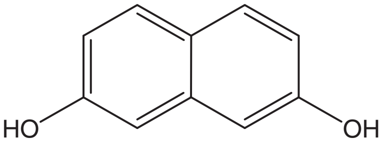
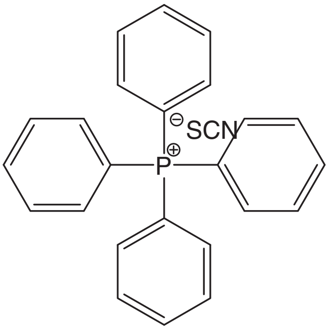
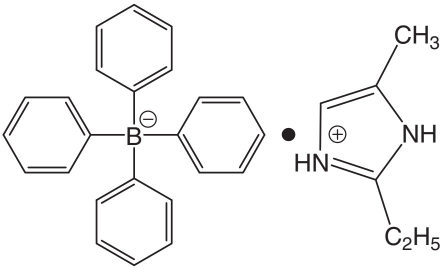
All the epoxy resin compositions in this study were composed of the same equivalent weight ratio (1:1) of epoxy and hydroxyl groups, and a latent catalyst was added to these composition with phr (per hundred resin) unit. All the components in each composition were mixed well in Methyl Ethyl Ketone (MEK) solvent at room temperature until a homogeneous solution was obtained. After vacuum evaporation of MEK was done and fully dried in order to remove the solvent, each sample was immediately quenched and stored in a refrigerator at 4°C to prevent the cure reaction.

Calorimetric measurements were performed using a TA-2020 differential scanning calorimeter (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 measure the thermal expansion coefficient and glass transition temperature of these systems, each sample specimen was prepared in a mold with a hot press. Thermal mechanical properties were obtained with the post cured specimen of 3 mm thickness using TA-TMA Q400 thermomechanical analyzer (TA Instruments, New Castle, DE) at a heating rate of 5°C/min under a nitrogen atmosphere. The thermal expansion coefficient in the glass state region ($\alpha 1$) was taken in the temperature range of 60 to 120°C.

Results and Discussion

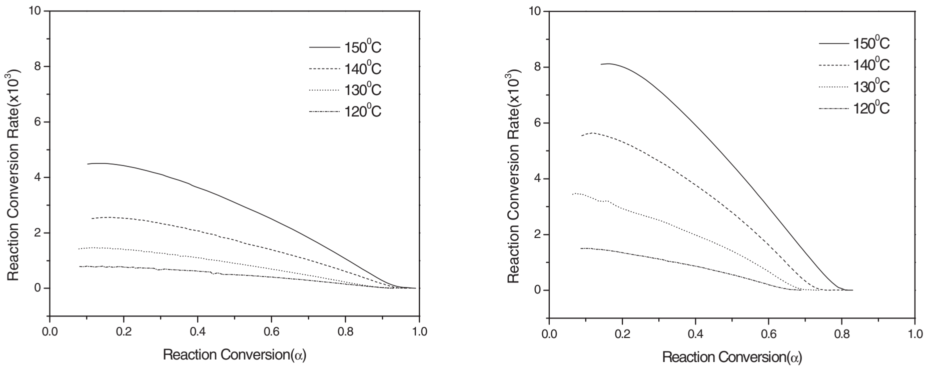
The series of isothermal reaction conversion rates of EXA-4700/1,6-naphthol resin systems with different kinds of latent catalysts are plotted as a function of reaction conversion (α) in Fig. 1. It can be seen that the curing reactions in all systems proceeded through an nth-order kinetic mechanism, irrespective of catalysts employed. The reaction conversion rates of

Table 1. Description of chemicals used in this study

Grade Name	Structure	Remarks
EXA-4700		^{1}EEW = 162
1,6-Naphthol (1,6-dihydroxy naphthalene)		^{2}HEW = 175
2,7-Naphthol (2,7-dihydroxy naphthalene)		^{2}HEW = 175
TPP-SCN (Tetraphenyl phophonium thiocyante)		
EMZ-K (2-ethyl-4-methyl imidazolium tetraphenyl borate)		

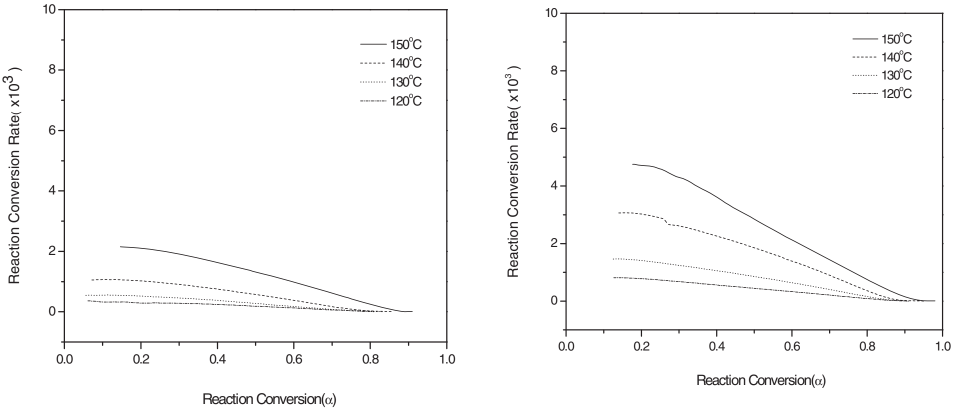
[1] EEW: Epoxy Equivalent Weight (g/equiv.).

[2] HEW: Hydroxy Equivalent Weight (g/equiv).



(a) TPP-SCN (1phr)

(b) TPP-SCN (3phr)



(c) EMZ-K (1phr)

(d) EMZ-K (3phr)

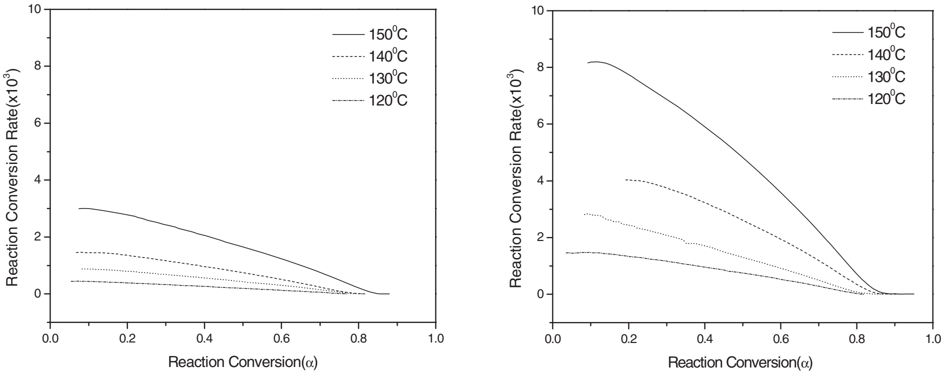
Figure 1. Isothermal conversion rate as a function of the conversion of the EXA-4700/1,6-naphthol resin systems with different catalysts.

epoxy resin systems with EMZ-K latent catalyst were lower than those with TPP-SCN. Figure 2 shows a series of isothermal reaction rate curves as a function of the reaction conversion for EXA-4700/2,7-naphthol resin compositions with different latent catalysts. It can be shown that the curing reactions in these systems also proceeded by an *n*th-order kinetic mechanism and that the reaction conversion rates of these compositions with EMZ-K as a latent catalyst were lower than those with TPP-SCN.

For thermosets that follow an *n*th-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:

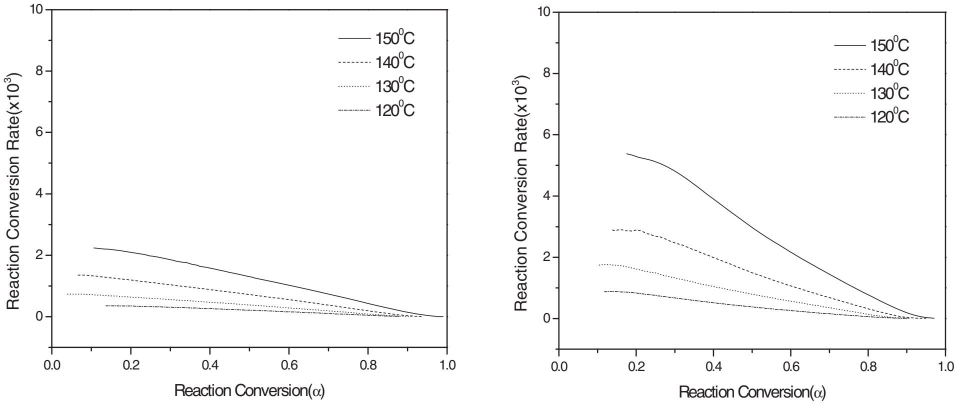
$$\frac{d\alpha}{dt} = k\,(1-\alpha)^n \tag{1}$$

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 cure 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



(a) TPP-SCN (1phr)

(b) TPP-SCN (3phr)



(c) EMZ-K (1phr)

(d) EMZ-K (3phr)

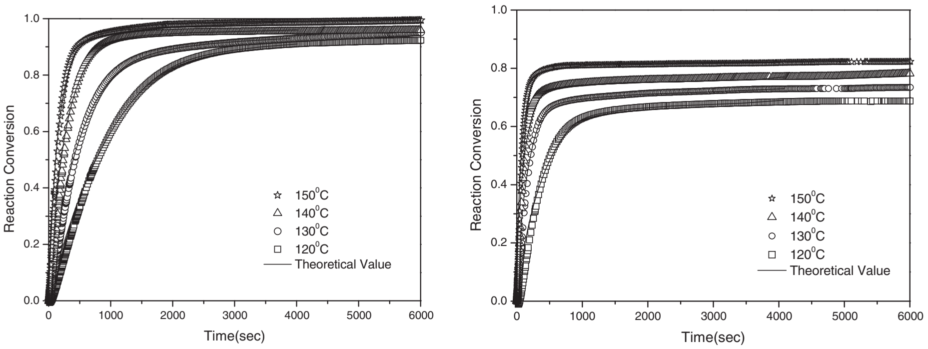
Figure 2. Isothermal conversion rate as a function of the conversion of the EXA-4700/2,7-naphthol resin systems with different catalysts.

eq. (2) [3, 10]. When the diffusion effect is considered, eq. (1) can be rewritten as eq. (2):

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

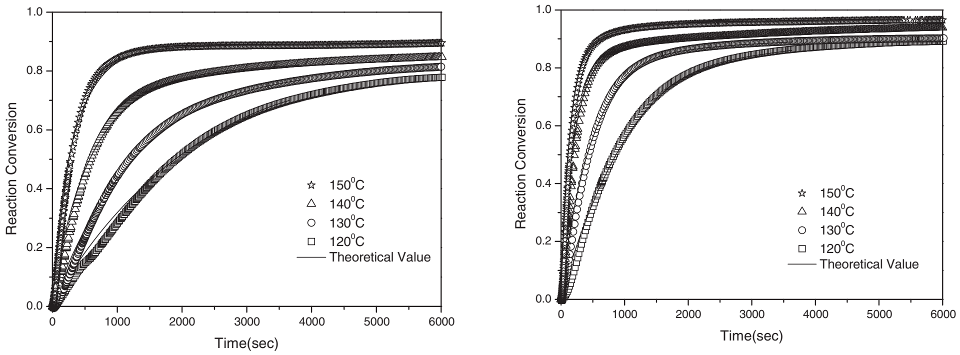
where C is a constant and α_c is the critical conversion.

All kinetic constants in this equation for each resin system were obtained with a previous method [2, 12]. Since conversion rates are that enthalpy change rate with time is divided into total reaction enthalpy, the enthalpy change rates with time were obtained by measuring isothermal experiments and the total reaction enthalpy was measured by dynamic-heating experiments using DSC [13]. To compute the kinetic parameters in eq. (2) without any constraints on the parameters, n, k, C, and α_c, they were calculated by fitting the experimental data to eq. (2). Figure 3 shows the comparisons between the experimental values of reaction conversion and the values calculated using a generalized *n*th-order model for EXA-4700/1,6-naphthol resin system with different latent catalyst. Favorable results were found over the whole curing temperature range for all resin systems. The kinetic



(a) TPP-SCN (1phr)

(b) TPP-SCN (3phr)



(c) EMZ-K (1phr)

(d) EMZ-K (3phr)

Figure 3. Comparisons between the experimental values of α and theoretical values obtained from the generalized *n*th-order kinetic model for the EXA-4700/1,6-naphthol resin systems with different catalysts.

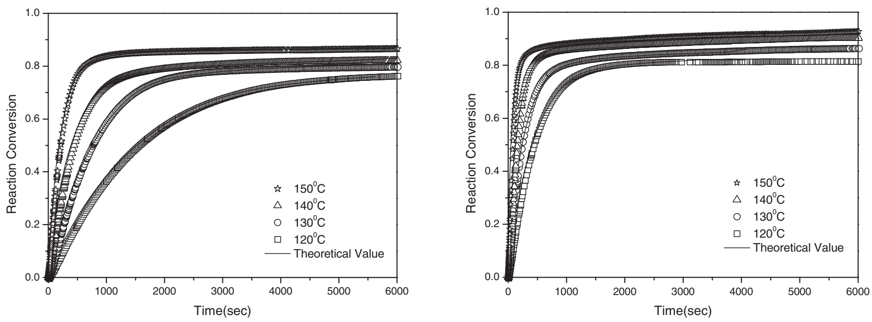
parameters are reported in Table 2 for systems with different kinds of latent catalysts that follow the *n*th-order curing reaction.

Figure 4 shows the comparisons between the experimental values of reaction conversion and the values calculated with a generalized *n*th-order kinetic model for EXA-4700/2,7-naphthol resin system with various 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 3.

As shown in Figs. 1 and 2, the reaction rate of EXA-4700 resin systems with TPP-SCN as a latent catalyst was faster than those with EMZ-K, irrespective of the hardeners employed. It was postulated that the faster reaction rate of EXA-4700/1,6-naphthol resin system with TPP-SCN was attributable to its lower activation energy as shown in Table 2, and the increase in the reaction conversion rate of EXA-4700/2,7-naphthol resin system with TPP-SCN was the result of its higher pre-exponential factor of rate constant, as shown in Table 3. The differences of activation energy of these systems with the latent catalyst were reduced with content of latent catalyst. As a hardener was changed from 1,6-naphthol to 2,7-naphthol, the activation energy of EXA-4700 resin compositions with EMZ-K was lower as opposed to that of TPP-SCN. Therefore, the reaction conversion rate increase of EXA-4700/2,7-naphthol resin system with TPP-SCN is attributed to the

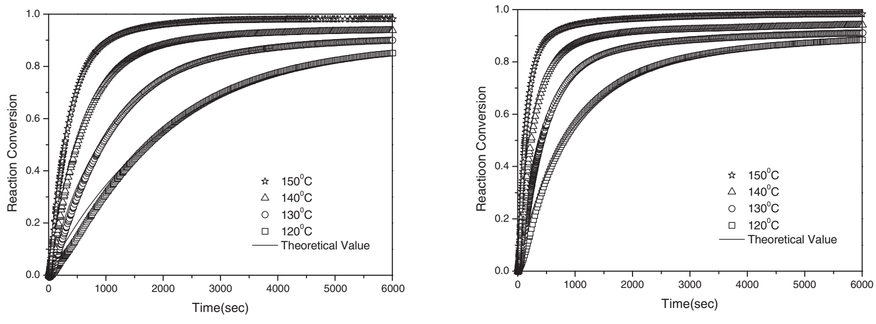
Table 2. Kinetic parameters of the EXA-4700/1,6-naphthol resin systems

Catalyst	T (°C)	k_1 (s^{-1})	n	C	α_c	Temperature dependency of the rate constant	n (Avg.)
TPP-SCN (1 phr)	120	8.90×10^{-4}	1.0	31.03	0.86	$k_1 = 1.01 \times 10^9$	1.2
	130	1.92×10^{-3}	1.3	29.83	0.88	exp $(-9.05 \times 10^4/\mathrm{RT})$	
	140	3.79×10^{-3}	1.3	73.63	0.92		
	150	6.28×10^{-3}	1.3	44.76	0.94		
TPP-SCN (3 phr)	120	1.93×10^{-3}	2.1	54.29	0.62	$k_1 = 3.97 \times 10^9$	2.4
	130	5.23×10^{-3}	2.3	56.49	0.65	exp $(-9.20 \times 10^4/\mathrm{RT})$	
	140	1.16×10^{-2}	2.8	98.24	0.72		
	150	1.35×10^{-2}	2.3	95.36	0.78		
EMZ-K (1 phr)	120	3.92×10^{-4}	1.2	26.58	0.74	$k_1 = 2.70 \times 10^{10}$	1.5
	130	6.13×10^{-4}	1.3	20.13	0.73	exp $(-7.87 \times 10^6/\mathrm{RT})$	
	140	1.59×10^{-3}	1.8	32.92	0.77		
	150	3.58×10^{-3}	1.7	72.59	0.86		
EMZ-K (3 phr)	120	7.90×10^{-4}	1.0	22.15	0.80	$k_1 = 4.90 \times 10^{10}$	1.3
	130	1.92×10^{-3}	1.4	40.14	0.84	exp $(-1.03 \times 10^5/\mathrm{RT})$	
	140	5.10×10^{-3}	1.6	44.51	0.86		
	150	6.86×10^{-3}	1.3	24.95	0.88		



(a) TPP-SCN (1phr)

(b) TPP-SCN (3phr)



(c) EMZ-K (1phr)

(d) EMZ-K (3phr)

Figure 4. Comparisons between the experimental values of α and theoretical values obtained from the generalized nth-order kinetic model for the the EXA-4700/2,7-naphthol resin systems with different catalysts.

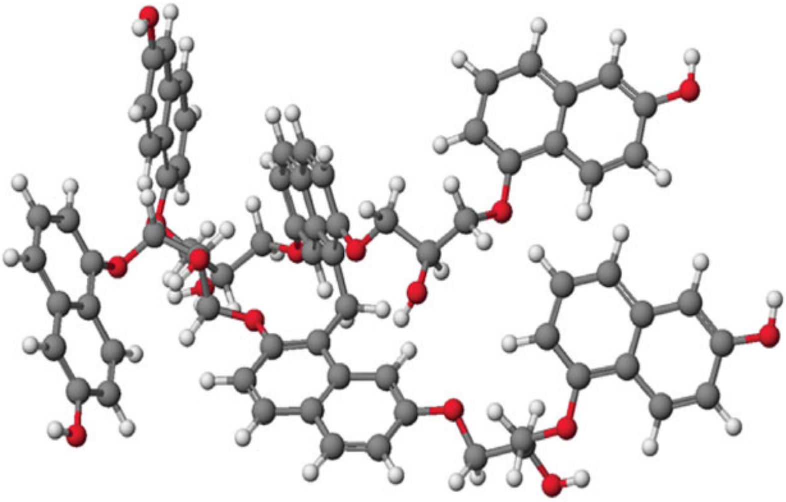
Table 3. Kinetic parameters of the EXA-4700/2,7-naphthol resin systems

Catalyst	T (°C)	k_1 (s^{-1})	n	C	α_c	Temperature dependency of the rate constant	n (Avg.)
TPP-SCN (1 phr)	120	5.37×10^{-4}	1.5	27.45	0.71	$k_1 = 1.38 \times 10^{10}$	1.6
	130	1.06×10^{-3}	1.4	40.16	0.74	$\exp(-1.01 \times 10^5/RT)$	
	140	2.36×10^{-3}	1.8	42.13	0.75		
	150	4.70×10^{-3}	1.6	54.19	0.81		
TPP-SCN (3 phr)	120	2.11×10^{-3}	1.6	46.72	0.77	$k_1 = 2.72 \times 10^{11}$	1.9
	130	3.87×10^{-3}	1.8	48.07	0.79	$\exp(-1.07 \times 10^5/RT)$	
	140	7.24×10^{-3}	1.8	68.30	0.83		
	150	2.26×10^{-2}	2.3	56.75	0.84		
EMZ-K (1 phr)	120	4.33×10^{-4}	1.2	31.13	0.84	$k_1 = 1.32 \times 10^8$	1.2
	130	8.79×10^{-4}	1.3	34.30	0.86	$\exp(-6.44 \times 10^5/RT)$	
	140	1.65×10^{-3}	1.3	35.91	0.89		
	150	2.81×10^{-3}	1.1	20.63	0.92		
EMZ-K (3 phr)	120	1.07×10^{-3}	1.7	32.26	0.86	$k_1 = 5.59 \times 10^9$	1.7
	130	2.31×10^{-3}	1.7	41.76	0.86	$\exp(-9.56 \times 10^4/RT)$	
	140	4.75×10^{-3}	1.8	52.69	0.90		
	150	8.42×10^{-3}	1.5	29.57	0.92		

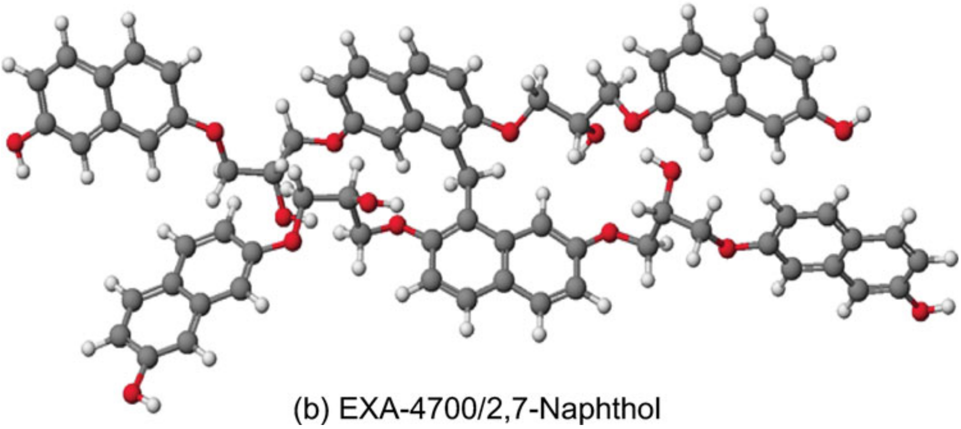
increase of collision frequency and the improvement of orientation effect according to the position change of the hydroxyl group in the naphthol hardener. The cure reaction model compounds between EXA-4700 and naphthol hardener are represented in Fig. 5 using CAChe 5.0 molecular modeling program (Fujitsu Ltd.). As shown in Fig. 5, it can be postulated that the EXA-4700/2,7-naphthol resin system represented a higher collision frequency and better orientation for cure reaction conversion because the EXA-4700/2,7-naphthol system has a flatter structure than EXA-4700/1,6-naphthol. As shown in Fig. 3, it can be thought that the decreases in EXA-4700/1,6-naphthol conversion by increasing the content of TPP-SCN are due to the bulky structures and difficult orientation of these system to cure reaction conversion, comparing with EXA-4700/2,7-naphthol system in Fig. 4.

Generally, a two-step initiation mechanism in the curing reaction using imidazole as a catalyst has been reported [14]. The pyrrole-type nitrogen of imidazole attacks the terminal carbon of the epoxy functional group to generate the imidazole-epoxy (1:1) adduct, and then 1:1 adduct reacts with a second epoxy group to form the imidazole-epoxy (1:2) adduct through the pyridine-type nitrogen of imidazole. However, a one-step initiation mechanism in the curing reaction using TPP as a catalyst was proposed [15], in which the phosphorus of TPP attacks the terminal carbon of the epoxy functional group to generate the TPP-epoxy (1:1) adduct. The higher activation energy of the EXA-4700/1,6-naphthol resin composition with EMZ-K is caused by the difficulty of imidazole-epoxy (1:2) adduct formation due to steric hindrance. However, it can also be seen that the EXA-4700/2,7-naphthol resin system with EMZ-K showed a lower activation energy of cure reaction conversion due to the flat structure to form easily imidazole-epoxy (1:2) adduct when compared with the EXA-4700/1,6-naphthol resin system with EMZ-K.

Therefore, it can be assumed that the reaction conversion rates of EXA-4700/2,7-naphthol with TPP-SCN as a latent catalyst showed the orientation-dominant effect, and those with 1,6-naphthol hardener manifested the activation energy-dominant effect of these



(a) EXA-4700/1,6-Naphthol



(b) EXA-4700/2,7-Naphthol

Figure 5. The cured molecular structure of EXA-4700 resin systems with different hardeners using CAChe 5.02 molecular design modeling tool.

systems, kinetically. In case of EMZ-K latent catalyst, the reverse phenomena observed, which were caused by the increase of steric hindrance according to the imidazole-epoxy (1:2) adduct formation.

The changes of coefficients of thermal expansion (CTE) and glass transition temperature (Tg) of these systems were summarized in Table 4. These systems with TPP-SCN and EMZ-K as a latent catalyst have trends of higher TEC in glass state region (α_1) and lower Tg with the catalyst content, which are caused by the increase of free volume and the decrease of curing density according to the increase of cure reaction conversion rate as shown in Figs. 1 and 2. The decrease of α_1 can also be observed in the EXA-4700 resin systems with 2,7-naphthol hardener, irrespective of the latent catalysts employed. It was postulated that these phenomena were due to the improvement of packing efficiency

Table 4. Coefficients of thermal expansion in the glass state region (α_1), in the rubbery state region (α_2) and temperature of glass transition (Tg) according to the change of latent catalyst in each resin composition used in this experiment

Latent catalyst	Hardener	α_1 (ppm/°C)	α_2 (ppm/°C)	Tg (°C)
TPP-SCN (1 phr)	1,6-naphthol	68.36	168.5	180
	2,7-naphthol	61.86	178.6	185
TPP-SCN (3 phr)	1,6-naphthol	73.01	169.9	175
	2,7-naphthol	64.64	186.6	170
EMZ-K (1 phr)	1,6-naphthol	65.36	180.4	160
	2,7-naphthol	57.89	178.1	160
EMZ-K (3 phr)	1,6-naphthol	76.65	180.2	155
	2,7-naphthol	65.35	178.2	150

by the flatness of core structure in the EXA-4700/2,7-naphthol resin system as shown in Fig. 5 [8, 9].

Conclusions

The curing reactions of naphthalene-based epoxy and hardener systems with latent catalysts were investigated by the thermal analysis method. The curing reactions in all systems proceeded through an *n*th-order kinetic mechanism, irrespective of latent catalysts employed. The experimental values of the reaction conversion were compared with the values calculated using a generalized *n*th-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-SCN as a latent catalyst increased when compared with EMZ-K latent catalyst systems. Although these increases in EXA-4700/1,6-naphthol resin systems with TPP-SCN are due to the lower activation energy of these systems, it can be shown that the increases in EXA-4700/2,7-naphthol resin systems with TPP-SCN are attributable to the higher collision frequency, which results from the orientation effect with respect to the cure reaction conversion kinetic data. The increase of flatness of the core structure in EXA/2,7-naphthol resin system can be observed with the molecular modeling structure. Therefore, it can be seen that the lower thermal expansion coefficients of the epoxy resin composition systems with 2,7-naphthol hardener are due to the improvement of packing efficiency.

Acknowledgments

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