

# Epoxy Curing Process with Small Shrinkage Based on Binary Nucleophilic Reagent System Consisting of Amine and Carboxylic Acid

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**ABSTRACT:** A curing process of bisphenol-A diglycidyl ether using amine-carboxylic acid salts was studied with focusing on its small-volume shrinkage. The characteristic point of the curing process was the initial high-density created by strong interactions between the ionic species such as electro-statistic one and hydrogen-bonding, which

disappeared on the consumption of these species by their reactions with the epoxide to give the low-density neutral polymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 836–842, 2009

**Key words:** crosslinking; curing of polymers; density

## INTRODUCTION

Curing process of thermosetting epoxy resins generally accompanies a large volume shrinkage, which is one of the most serious concerns in the field of adhesive application.<sup>1–3</sup> Such shrinkage gives rise to internal stress in the cured resin<sup>4–6</sup> as well as voids and cracks<sup>7</sup> that permit foreign destructive substances to penetrate the resin. These phenomena cause fatal problems, particularly in use of various sophisticated materials such as highly reliable structural adhesives, electrochip-bonders, and chip underfills. The conventional method to reduce volume shrinkage is addition of inorganic fillers, which is always accompanied by disadvantages such as a serious increase in the viscosity and that in the modulus of the cured material. Another promising strategy is addition of so-called “expandable monomers,” which are designed so that they undergo the ring-opening polymerizations with exhibiting volume expansion.<sup>8</sup> As some of them underwent copolymerization with epoxide by ionic initiator, their expanding nature can compensate the intrinsic shrinkage nature of epoxide.<sup>9–12</sup> On the other hand, for curing reactions based on polyaddition-type reactions, such as epoxy-amine, epoxy-carboxylic acid, and epoxy-phenol reactions, there has been only one example of shrinkage suppression by adding an expandable monomer.<sup>13</sup>

Herein, we report a new concept for development of curing systems undergoing small shrinkage. The concept is based on combination of two different nucleophilic reagents, amine and carboxylic acid, each of which is generally used in an independent curing system. As is widely known, amine and carboxylic acid have totally different reactivity, but they recognize each other as a counterpart for the formation of the corresponding salt, where electrostatic interaction and hydrogen bonding are dominating to create a highly dense state. On heating the salt with epoxide, these relatively strong interactions in the system would disappear, because the reactions of the amine and acid components with epoxide would give less polar products. Between these products, the dominant interaction would be vander-Waals one, to allow minimum increase in density during the curing reaction.

## EXPERIMENTS

### Materials

Glycidyl phenyl ether (GPE), bisphenol-A diglycidyl ether (Bis A-DGE), and benzoic acid (BA) were purchased from Wako Chemical, Co., and were used as received. 2-Amino-1-methoxypropane (AMP) and poly(propylene glycol) bis(2-aminopropyl ether) (PPG-diamine) were purchased from Aldrich Japan, Co., and were used as received.

### Instruments and measurements

<sup>1</sup>H-NMR spectra were recorded on JEOL  $\lambda$ -300 with tetramethylsilane as an internal standard. Dynamic

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mechanical analysis (DMA) was performed on a DMA Q800 V3.13 (TA Instruments). The measurement conditions are as follows, heating rate: 3°C/min; probe: single cantilever; frequency: 1 Hz; and strain: 20  $\mu\text{m}$ . To evaluate adhesion performances, formulation was applied to aluminum bonding, and the corresponding tensile shear strengths were measured according to the standard method (ASTM D1002 apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (metal-to-metal)). For measurement of tensile strength, a tension loading apparatus model INSTRON 4204 was used. The specimens used were grid blasted mild aluminum lapshear specimens (25.4 mm  $\times$  101.6 mm  $\times$  1.6 mm). The test was carried out at 23°C and 50% relative humidity (RH). Differential scanning calorimetric (DSC) analysis was performed with SEIKO EXSTAR6000. Density measurement was performed with a gas pycnometer, AccuPyc 1330 (Micrometrics).

#### Reaction of GPE with AMP-BA salt: Investigation on chemical structures of the products

GPE (5.68 g, 38.0 mmol) and AMP-BA salt (2.00 g, 9.5 mmol) were mixed and heated at 120°C for 1 h. After cooling, a part of the resulting mixture was fractionated by preparative TLC (silica gel, eluent = hexane + ethyl acetate (4/1 = vol/vol)) into three fractions: The fraction-1 ( $R_f = 0.12$ ) was GPE-BA adduct **1a** (32% from GPE). The fraction-2 ( $R_f = 0.08$ ) was another GPE-BA adduct **1b** (5% from GPE). The fraction-3 ( $R_f \sim 0$ ) was a mixture of GPE-AMP adducts **2** (35% from GPE).

#### Reactivity of AMP-BA salt with GPE at 4 and 120°C

GPE (1.35 g, 9.0 mmol) and AMP-BA salt (0.63 g, 3.0 mmol) were mixed, and the resulting mixture was divided into two portions. One portion was kept at 4°C, and the other portion was heated at 120°C. From each of the portions, a small amount ( $\sim 10$  mg) was taken and was analyzed with  $^1\text{H-NMR}$  to determine conversion of GPE. For referential experiments, GPE (1.35 g, 9.0 mmol) and AMP (0.40 g, 4.5 mmol) were mixed and similarly treated as the GPE + AMP-BA salt mixture.

#### Reactivity of a formulation consisting of Bis A-DGE and PPG-diamine-BA salt

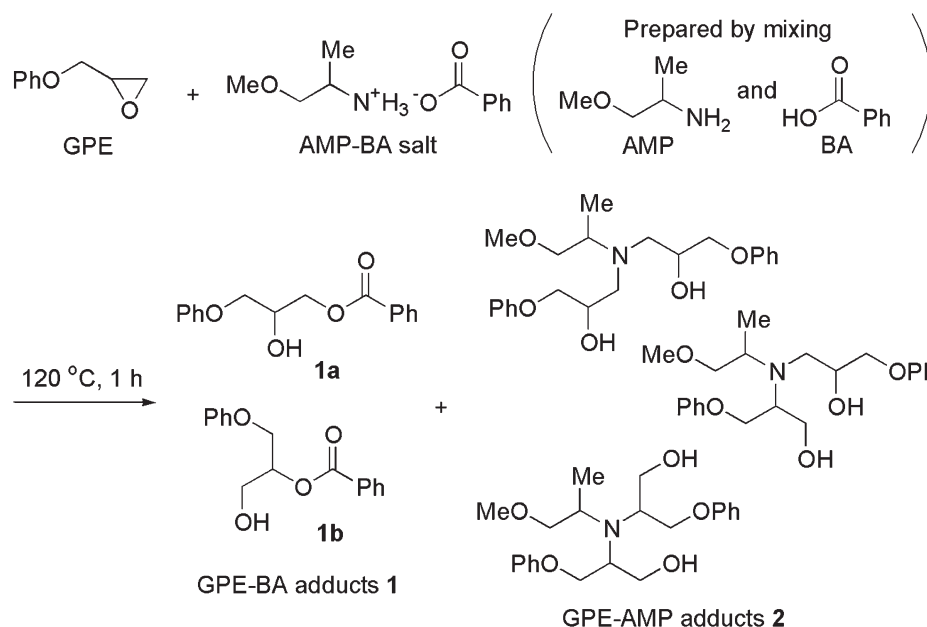
PPG-diamine (0.80 g, 2.0 mmol) and BA (0.49 g, 4.0 mmol) were mixed to prepare the corresponding salt. Bis A-DGE (2.04 g, 6.0 mmol) and the prepared PPG-diamine-BA salt were mixed, and a small amount ( $\sim 20$  mg) of the resulting formulation (f-1)

was divided into four portions in a DSC aluminum cup. One portion was kept at 4°C, and the other portion was then subjected to DSC measurement at the prescribed temperature (1st step: from 40 to 200°C, heating rate = 10°C/min; 2nd step: at the prescribed temperature until completion of heat evolution) to calculate heat evolution. DSC measurement for the sample stored at 4°C for 5 days was performed under the same driving conditions as the sample measured at the prescribed temperature of 120°C. For referential experiments, Bis A-DGE (3.40 g, 10.0 mmol) and PPG-diamine (2.00 g, 5.0 mmol) were mixed, and the resulting formulation (f-2) was similarly treated as the formulation f-1.

From a series of the heat evolution values, degrees of reaction were calculated according to the following equation: Degree of reaction (%) =  $([\text{total heat evolution at } 120^\circ\text{C}]_{t=0} - [\text{heat evolution}]_t) / [\text{total heat evolution at } 120^\circ\text{C}]_{t=0}$ , where  $t$  represents reaction time.

## RESULTS AND DISCUSSIONS

Prior to investigating shrinkage nature of the newly designed curing system, a model system that consisted of monofunctional reactants was studied to clarify their reaction behaviors and chemical structures of the corresponding reaction products (Scheme 1). As a monofunctional epoxide, glycidyl phenyl ether (GPE) was chosen. A model amine (2-amino-1-methoxypropane; AMP) and benzoic acid (BA) were mixed in an 1 : 1M ratio to prepare the corresponding salt. 0.25 Equivalent amount of the salt was added to GPE and mixed to obtain a homogeneous mixture. Theoretically, this salt can react with its 3 equivalent amount of GPE, because primary amine can react with its 2 equivalent amount of epoxide and carboxylic acid can react with its 1 equivalent amount of epoxide. Therefore, for the formulation containing GPE and 0.25 equivalent of the salt, the maximum conversion of GPE will be 75%. The mixture was heated at 120°C for 1 h, and the resulting mixture was analyzed by  $^1\text{H-NMR}$  spectroscopy to find that both of AMP and BA were completely consumed. The final conversion of GPE was 72%, which was in good agreement with the theoretical value, suggesting that the system would involve only a negligible extent of cationic ring-opening polymerization of GPE that can be initiated by acidic proton.  $^1\text{H-NMR}$  analyses of the products, which were separated from each other by chromatography, revealed that (1) AMP reacted with 2 equivalent of GPE, (2) BA reacted with 1 equivalent of GPE, (3) the resulting GPE-BA adduct having ester structure was not attacked by AMP to form the corresponding amide-type by-product, and (4) the

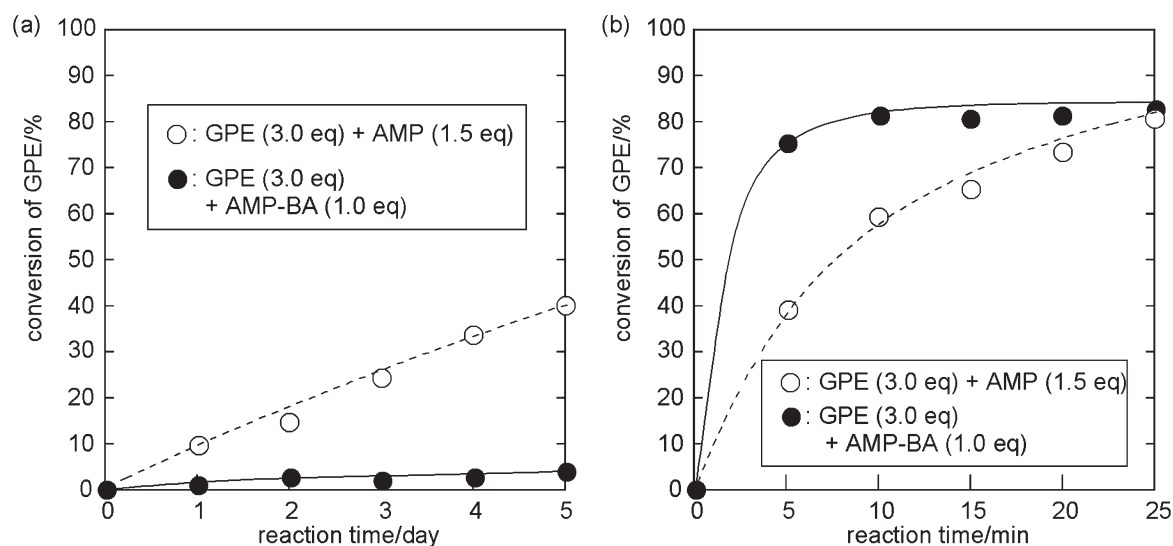


Scheme 1 Reaction of GPE and AMP-BA salt.

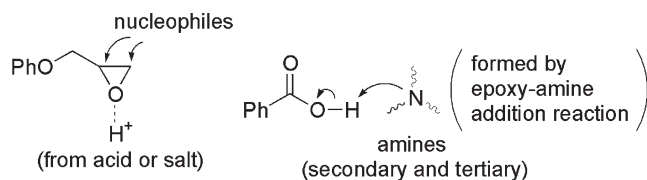
total yield of these products was 72%, which was in good agreement with the conversion of GPE.

Temperature-dependence of the reaction was also investigated. A mixture of GPE and AMP-BA salt (3 : 1 in a molar ratio) was prepared. The resulting homogeneous mixture was divided into two portions. These portions were stirred at 4 and 120°C, respectively. Conversion of GPE was measured by <sup>1</sup>H-NMR. The resulting time-conversion relationships are shown in Figure 1. To perform a referential experiment, a mixture of GPE and AMP (3.0 : 1.5 in a molar ratio) was also prepared, and its reactivity

was evaluated. The resulting time-conversion relationships showed that (1) at 4°C, the reaction of GPE and the salt was negligible while that of GPE and AMP proceeded slowly and (2) at 120°C, the former was faster than the latter. The low reactivity of the salt at low temperature was predictable because the reactivity of the amino group would be suppressed by salt-formation, and the carboxylate anion would be tightly bonded with the ammonium counterpart. On the other hand, the higher reactivity of the mixture at the elevated temperature would be arisen by cooperation of the following two factors (Scheme 2):

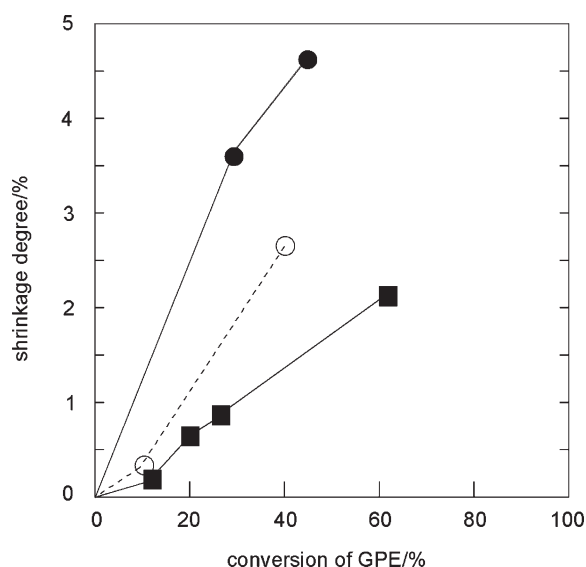


**Figure 1** Time-dependences of conversion of GPE: (a) In the reactions with AMP (○) and with the salt (●) at 4°C and (b) in the reactions with AMP (○) and with the salt (●) at 120°C.

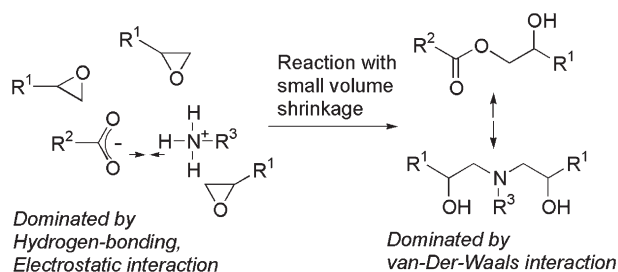


**Scheme 2** Mechanism for the accelerated reaction at elevated temperature.

The first factor would be donation of proton from acid and/or salt to epoxide, which would activate the epoxide and promote its reaction with amine.<sup>14</sup> The second factor would be increase in the basicity of the system during the reactions. The reaction of primary amine with epoxide gives more basic secondary and tertiary amine, which would promote deprotonation from free carboxylic acid to give more reactive carboxylate anion. The temperature-dependence of the present binary nucleophile system is quite favorable for its potential practical applications. The low reactivity of curing reagent with epoxide at room temperature allows production of curable material containing both of epoxy resin and curing reagent, which can be stored and used as a one-component adhesive and other materials. This advantage is generally in a relationship of trade-off with high curability of the curable material. Contrary to this general tendency, the present reaction system consisting of epoxide, amine, and carboxylic acid exhibits high reactivity at elevated temperature, to make the two contradictory factors compatible.

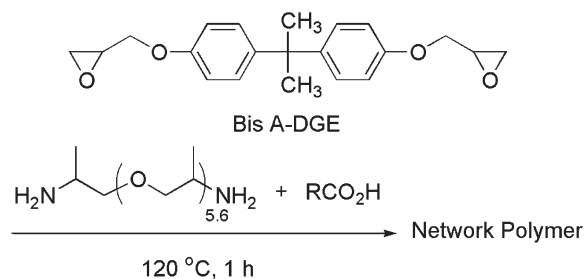


**Figure 2** Shrinkage versus conversion of GPE for the reactions of GPE with nucleophiles at 120°C: (a) The reaction with 0.5 equivalent of AMP (●), (b) the reaction with 0.25 equivalent of BA (○), and (c) the reaction with 0.25 equivalent of AMP-BA salt (■). The lines were added for the ease of comparison between the three relationships.

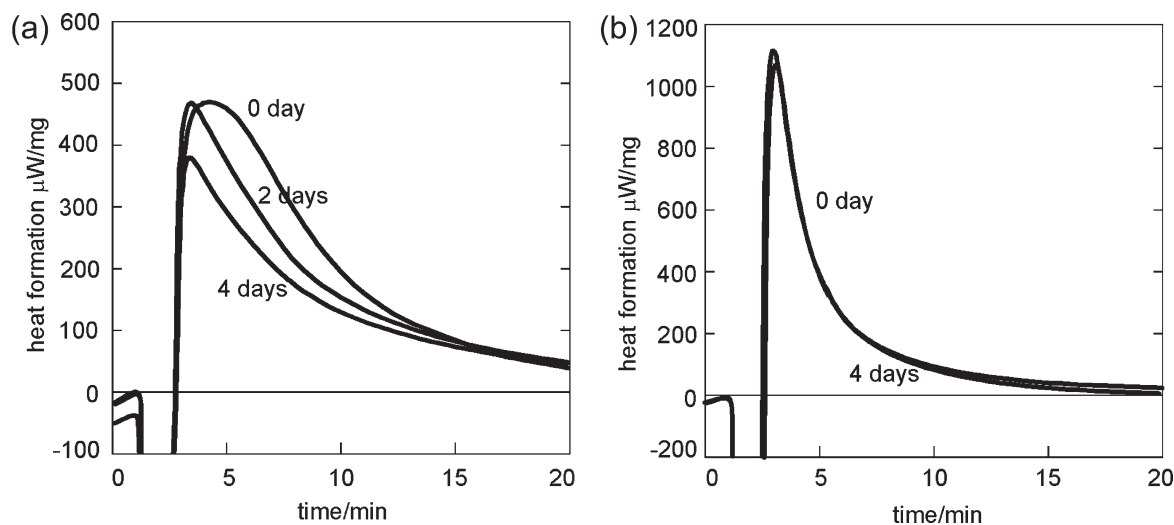


**Scheme 3** Mechanism for the shrinkage suppression.

In addition to the above-mentioned advantage in the reactivity aspect, the present binary nucleophile system exhibited small shrinkage nature to confirm the feasibility of our basic concept in designing the system: Figure 2 shows the relationships between conversion of GPE and volume shrinkage for the reactions of GPE with AMP, BA, and AMP-BA salt. The reaction with AMP accompanies a significant volume shrinkage, which reached nearly 5% when the conversion exceeded 40%. The reaction with BA also led to significant volume shrinkage although it was less serious than that with AMP. In this case, GPE was consumed not only by its 1 : 1 addition reaction with GPE but also its cationic oligomerization, and thus the conversion of GPE was much larger than 25%, which was the maximum amount expected from the amount of BA added to the system. Contrary to these cases, utilization of the amine-acid salt resulted in an unexpectedly low volume shrinkage. Even at 60% conversion, the volume shrinkage was only 2%. This small shrinkage would be due to the drastic change in dominant intermolecular interaction caused by the reactions (Scheme 3): Before the reactions, the dominant interactions are electrostatic one and hydrogen bonding in the pair of ammonium and carboxylate parts and between the salt units. These interactions are much stronger than vander-Waals one and thus, the epoxy formulation containing the salt has intrinsically high density accordingly. On the other hand, after the reactions, these interactions disappear to give electronically neutral molecules such as tertiary amine and ester.



**Scheme 4** Curing reaction of Bis A-DEG with amine-acid salt.



**Figure 3** DSC-profiles (scanned with heating at a rate of  $10^\circ\text{C}/\text{min}$ ) for the formulations kept at  $4^\circ\text{C}$ : (a) The formulation f-1 [Bis A-DGE (3.0 eq) + PPG-DA (1.5 eq)]; (b) the formulation f-2 [Bis A-DGE (3.0 eq) + PPG-DA (1.0 eq) + BA (2.0 eq)].

The interaction between these molecules is vander-Waals one, which does not contribute to increase density of the reaction mixture. Chemical transformation from reactants with high density into products with low density created a factor to suppress volume shrinkage during the reactions.

On the basis of the successful findings on the advantageous features of the amine-acid binary system in the model studies, we next performed curing reactions using a bifunctional epoxide, a diamine, and monofunctional acids (Scheme 4). As a bifunctional epoxide and a diamine, bisphenol A diglycidyl ether (Bis A-DGE) and amine-terminated poly(propylene glycol) (PPG-diamine,  $M_n = 400$ ) were employed, respectively. Bis A-DGE is one of the most commonly used epoxy resins in various applications and thus is appropriate as a representative one. PPG-diamine is also frequently used as an amine-type hardener, of which reaction with epoxy resin gives the corresponding cured materials with good toughness.

By mixing PPG-diamine with two equivalent of BA, the corresponding salt was prepared. The salt was viscous liquid, which was mixed with Bis A-DGE easily. First, we prepared a formulation (f-1), of which composition  $[\text{Bis A-DGE}]_0 : [\text{PPG-diamine}]_0 : [\text{BA}]_0$  was 30 : 10 : 20. This ratio agrees with an equation,  $[\text{epoxy group}]_0 = [\text{active hydrogen}]_0 = 2[\text{amino group}]_0 + [\text{BA}]_0$  [eq. (1)]. The formulation was stored at  $4^\circ\text{C}$ , with sampling small portions of it to estimate progress of the curing reaction by DSC (Fig. 3). The detailed procedure is described in the experimental section, and the results are shown in Table I. Until 5 days, no significant change was observed in DSC analysis, supporting the high sta-

bility of the formulation f-1 at this temperature. In contrast, a referential formulation composed of Bis A-DGE and PPG-diamine (f-2) (100 : 50 in a molar ratio) underwent its curing reaction even at  $4^\circ\text{C}$ , and the degree of reaction reached 35% after 5 days. Then, reactivity of f-1 and that of f-2 at various temperatures were studied similarly with using DSC. At  $50^\circ\text{C}$ , f-1 underwent its curing reaction, but it was still slower than that of f-2. On the other hand, above  $80^\circ\text{C}$ , the curing reaction of f-1 became faster than that of f-2. This significant difference in reactivity in these two formulations is in good agreement with that found in the model reactions: At low temperature, the reactivity of amine is suppressed by formation of the corresponding salt with carboxylic acid, while heating the system lead to its enhanced reactivity by the cooperation of (1) activation of epoxide by acid and (2) activation of acid by tertiary amine formed by the curing reaction.

The highlight of this article is the small shrinkage nature of the curing system. As shown in Table II,

**TABLE I**  
Reactivity of the Curable Formulations at Various Temperatures

Curing conditions	Degree of reaction	
	f-1 <sup>a</sup>	f-2 <sup>b</sup>
At $4^\circ\text{C}$ for 5 days	<5	35
At $50^\circ\text{C}$ for 7 h	30	45
At $80^\circ\text{C}$ for 3 h	75	65
At $120^\circ\text{C}$ for 30 min	100	95

<sup>a</sup>  $[\text{Bis A-DGE}]_0 : [\text{PPG-diamine}]_0 : [\text{BA}]_0 = 30 : 10 : 20$ .

<sup>b</sup>  $[\text{Bis A-DGE}]_0 : [\text{PPG-diamine}]_0 = 100 : 50$ .

TABLE II  
Curing Reactions of Bis A-DGE by PPG-diamine + Carboxylic Acid<sup>a</sup>

Entry	Carboxylic acid	Amount of acid (mmol)	Amount of PPG-diamine (mmol)	$d_{\text{before curing}}$ (g/mL) <sup>b</sup>	$d_{\text{after curing}}$ (g/mL) <sup>c</sup>	Shrinkage (%) <sup>d</sup>	$T_g$ (°C) <sup>e</sup>
1 <sup>f</sup>	–	0	15	1.081	1.141	5.3	46
2	Benzoic acid	12	12	1.121	1.173	3.5	ND <sup>g</sup>
3 <sup>h</sup>		20	10	1.135	1.173	3.2	41
4	1-Naphthoic acid	12	12	1.128	1.169	3.5	ND <sup>g</sup>
5		20	10	1.147	1.181	2.9	44
6	2-Naphthoic acid	12	12	1.125	1.165	3.4	ND <sup>g</sup>
7		20	10	1.145	1.181	3.1	ND <sup>g</sup>
8	1-Phenoxy-acetic acid	12	12	1.120	1.166	4.0	ND <sup>g</sup>
9		20	10	1.140	1.180	3.4	ND <sup>g</sup>

<sup>a</sup> Conditions: [epoxy group]<sub>0</sub> = 2[amino group]<sub>0</sub> + [acid]<sub>0</sub> = 60 mmol, at 120°C for 1 h.

<sup>b</sup> Density before curing measured by a gas-pycnometer.

<sup>c</sup> Density after curing measured by a gas-pycnometer.

<sup>d</sup> Volume shrinkage (%) =  $[1 - (d_{\text{before curing}}/d_{\text{after curing}})] \times 100$ .

<sup>e</sup> Measured by DMA (peak top of tan  $\delta$ ).

<sup>f</sup> The formulation used herein is identical with f-2 in Table 1.

<sup>g</sup> Not determined.

<sup>h</sup> The formulation used herein is identical with f-1 in Table 1.

the shrinkage degree for the curing reaction Bis A-DGE + PPG-diamine was 5.3% (entry 1). With maintaining total amount of active hydrogen (N–H and COO–H) according to the eq. (1), we investigated addition effect of BA on the shrinkage nature. In entry 2, the amount of BA was controlled so that half of the amino group could form the corresponding salt. As a result, the corresponding shrinkage degree was 3.5%. Shrinkage degree was further reduced by increasing the amount of BA (entry 3). Similar shrinkage-reducing effects were also successfully attained by using other carboxylic acids such as naphthoic acids (entries 4–7) and 1-phenoxyacetic acid (entries 8 and 9), suggesting that the present concept of shrinkage reduction based on utilization of the amine-acid salt as a curing reagent is versatile. In terms of shrinkage suppression effect, 1-naphthoic acid and 2-naphthoic acid were slightly superior to benzoic acid, presumably due to stronger  $\pi$ – $\pi$  interaction between naphthalene moieties to increase the density of the formulation before its curing reaction. The reason for the slightly inferior effect of 1-phenoxyacetic acid in shrinkage suppression is not clear at present, but it may be corresponded to its more flexible structure.

Thermal properties of the cured materials were studied with dynamic mechanical analysis (DMA). The glass transition temperature ( $T_g$ ) was estimated from the peak top in the temperature-tan  $\delta$  relationship.  $T_g$  of the material obtained by the curing reaction of f-2 (without acid component) was 46°C. Only slight decrease in  $T_g$  was observed for the material obtained by the curing reaction of f-1 ( $T_g = 41^\circ\text{C}$ ) (in

Table I, entry 3). Using 1-naphthoic acid as an acid component lead to a slight increase in  $T_g$  to 44°C (entry 5), suggesting that thermal properties would be tailored by the structure of the acid component. Generally,  $T_g$  of cured material is relevant to its adhesion strength in tensile mode, to allow us to expect that f-1 and f-2 would exhibit similar performance in their applications as adhesives. In fact, our preliminary tests on adhesion strength using aluminum plates revealed that the tensile strength attained by f-1 and f-2 were 18.7 and 18.3 N/mm<sup>2</sup>, respectively, demonstrating that the ternary curable system comprised of epoxide, amine, and acid was applicable as a useful adhesive.

## CONCLUSIONS

Combination of two nucleophilic reagents, amine and carboxylic acid, exhibited two synergetic effects in application to curing reaction of epoxide: One is thermal latency, that is, compatibility of stability at low temperature and high reactivity at high temperature. The other remarkable effect is the low shrinkage nature, which has been quite difficult to attain so far in the epoxy curing systems based on addition reactions of epoxide.

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