

Studies on New Type of Phenolic Resin—Curing Reaction of Bisphenol-A-Based Benzoxazine with Epoxy Resin Using Latent Curing Agent and the Properties of the Cured Resin

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ABSTRACT: Curing reaction of bisphenol-A-based benzoxazine (Ba) with epoxy resin (Ep) using latent curing agent, and the properties of the cured resin were investigated. Consequently, by using latent curing agent, the ring opening reaction of benzoxazine ring occurred more rapidly, and then also the phenolic hydroxyl group generated by the ring opening reaction of benzoxazine ring reacted with epoxy ring more rapidly. And it was found that the cure time of the molten resins from Ba and Ep with latent curing agent could be reduced and also the cure temperature could be lowered, compared with those from Ba and Ep without latent curing agent. The melt viscosity of the molten resins from Ba and Ep with latent curing

agent was kept about 50 [Pa s] at 100°C even after 30 min, the molten resins from Ba and Ep with latent curing agent showed good thermal stability below 100°C. However, above 170°C the curing reaction of Ba with Ep with latent curing agent proceeded rapidly. The cured resin from Ba and Ep with latent curing agent showed good heat resistance, flame resistance, mechanical properties, and electrical insulation, compared with the cured resin from Ba and Ep without latent curing agent. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1248–1256, 2008

Key words: phenolic resin; benzoxazine; latent curing agent; epoxy resin; curing reaction

INTRODUCTION

Phenolic resin is used widely as an industrial material because of its good heat resistance, electrical insulation, dimensional stability, flame resistance, and chemical resistance. However, there are a number of shortcomings associated with those traditional phenolic resins. For example, hexamethylenetetramine (hexamine) is used as a curing agent. In the curing process of novolac-hexamine, volatiles such as water or ammonia compounds etc. are released due to the condensation reaction. These volatiles sometimes reduce the properties of cured phenolic resin because of the formation of microvoid. And acid or base compounds as catalysts, which result in corrosion of the processing equipment, must be used to synthesize novolac or resole precursors of cured phenolic resin. Another problem is that the cured phenolic resin is brittle.

It is well known that the benzoxazine ring is stable at low temperature, but the ring opening reaction occurs at high temperature, and novolac type

oligomer having both the phenolic hydroxyl group and the tertiary amine group are produced¹ (Fig. 1). By using this benzoxazine compound as a phenolic resin, a new type of phenolic resin that releases no volatiles during curing reaction and needs no catalysts has been developed.

Ishida and coworkers^{2–24} synthesized a lot of types of oxazines and studied the cure kinetics, molecular structures, mechanical, and dynamic mechanical properties, and so on. Shin and coworkers²⁵ also studied the cure kinetics of a benzoxazine-based phenolic resin. Jang et al.²⁶ studied the performance improvement of rubber-modified polybenzoxazine. Recently, maleimide-modified^{22,23,27,28} or furan-modified²⁹ benzoxazines have been synthesized and the properties of the cured resins have been investigated. Nanocomposites using benzoxazines also recently have been reported.^{30–33} The reactivity of compounds that have benzoxazine ring with other compounds has been investigated. We have already investigated the curing behavior of the bisphenol-A, terphenyldiphenol or poly(*p*-vinylphenol)-based benzoxazines with epoxy resin or bisoxazoline and the properties of the cured resins.^{34–38} Consequently, the molding compound from bisphenol-A-based benzoxazine that contained no oligomers and bisoxazoline showed good flowability below 140°C, curing reac-

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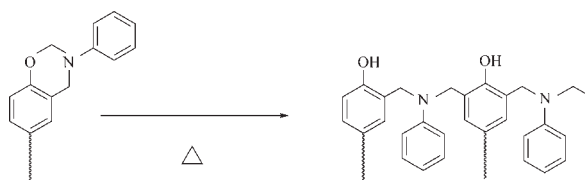


Figure 1 Ring opening reaction of a benzoxazine ring.

tion proceeded above 180°C rapidly. And the cured resins from benzoxazine compounds and epoxy resin or bisoxazoline had superior heat resistance, electrical insulation, and water resistance to the cured resins from conventional bisphenol-A type novolac and epoxy resin or bisoxazoline.

Despite their high performance (for example, good heat and water resistance) of the benzoxazine-based resin, it is believed that the benzoxazine-based resins show surprisingly low crosslink densities in comparison with the ordinary thermosetting resin.⁸ Then, most important problem is that the cure time of the benzoxazine compounds is long, and also the cure temperature is high.

In this report, we aimed to reduce the cure time of the benzoxazine compound, and to lower the cure temperature of the benzoxazine compound. Therefore, we prepared heat latent curing agents from acids and amines, and investigated the catalytic effect of the latent curing agents on the curing reaction of bisphenol-A-based benzoxazine (Ba) with epoxy resin (Ep) and the properties of the cured resin.

EXPERIMENTAL

Materials

2,2-bis(3,4-dihydro-3-phenyl-1,3-benzoxazine)propane (Ba) was supplied by Shikoku Chemicals. Bisphenol-A-based epoxy resin (EPIKOTE 828, epoxy equivalent 186) as epoxy resin (Ep) was supplied by Japan Epoxy Resins. Diethanolamine, isopropanolamine, diethylethanolamine, methylamine, and *p*-toluenesulfonic acid were purchased from Nacalai Tesque. All chemicals were used without further purification. The chemical structures of Ba and Ep are shown in Figure 2.

Preparation of the heat latent curing agent

The preparation of the heat latent curing agent was carried out using the reaction of acids and amine compounds. In a typical experiment, diethanolamine as an amine compound (5.26 g, 0.05 mol) was charged to a beaker, and *p*-toluenesulfonic acid (9.5 g, 0.05 mol) was added to the beaker. The product was the neutral salt obtained from acid and

amine, and used as the heat latent curing agent without purification.

Preparation of the cured resin, and curing condition

Samples containing 50 mol% Ba and 50 mol% Ep with 1, 3, 5, or 10 wt % latent curing agent were prepared and cured in a mold at a specified temperature in the oven. At first, the sample containing 50 mol% Ba and 50 mol% Ep was heated to about 130°C, and a clear molten mixture was obtained. After the temperature of the molten mixture was cooled down to 100°C, 1, 3, 5, or 10 wt % latent curing agent was added into the molten mixture and stirred. The clear molten mixture obtained was poured into the silicone rubber mold and cured at a specified temperature in the oven. The curing condition was determined as 150°C/2 h + 170°C/2 h or 150°C/2 h + 170°C/2 h + 200°C/2 h from the results of differential scanning calorimetry (DSC). DSC was measured with heating rate of 10°C/min under N₂ atmosphere on a Seiko Instruments. STI EXSTAR 6000. For comparison, the curing reaction of 50 mol% Ba with 50 mol% Ep was also carried out on the same condition.

Properties of the molten resins and the cured resin

To investigate the catalytic effect of the latent curing agent on the curing reaction, measurements for melt viscosity (η) and storage modulus (G') were conducted on a UBM. Dynamic Mechanical Spectrometer (Rheosol-G3000) by using a 25-mm parallel plate

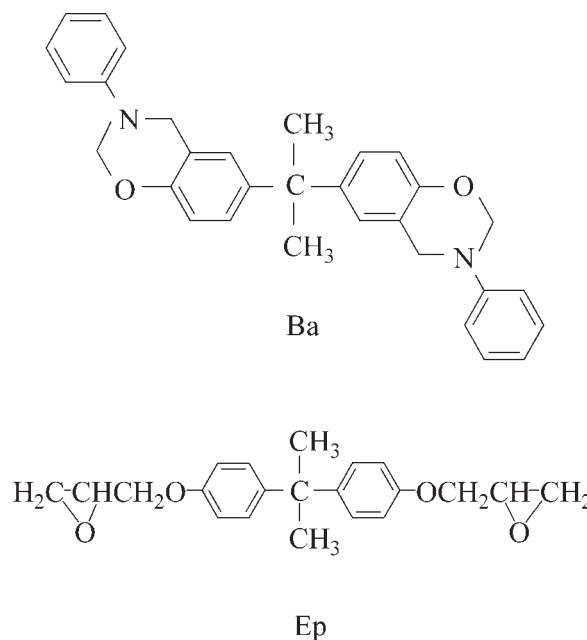


Figure 2 Chemical structures of Ba and Ep.

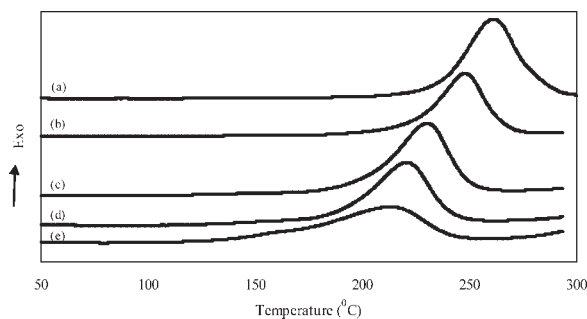


Figure 3 DSC curves of the molten resins from Ba and Ep with or without the latent curing agent. (a) Ba/Ep, (b) Ba/Ep/cat 1 (1 wt %), (c) Ba/Ep/cat 1 (3 wt %), (d) Ba/Ep/cat 1 (5 wt %), and (e) Ba/Ep/cat 1 (10 wt %).

fixture at various temperatures. The plates were preheated to 100°C before the test. Next, the plates were heated from 100°C to the measuring temperature (100, 150, 170, and 200°C) at a rate of 30°C/min. And the melt viscosity (η) and storage modulus (G') for isothermal test at the measuring temperature were measured as a function of time.

The structure of the cured resin was analyzed by Fourier Transform Infrared Spectrophotometer (FT-IR). FT-IR measurement was carried out on Nicolet Impact 420 instrument. The spectral range was 4000–600 cm^{-1} . One hundred twenty-eight scans were coadded at a resolution of 4 cm^{-1} .

The properties of the cured resin were characterized by heat resistance, flexural properties, fracture toughness, electrical insulation, water absorption and flame resistance. Heat resistance was estimated by glass transition temperature (T_g) on dynamic mechanical analysis (DMA). DMA was measured by a three points bending method at 1 Hz, with a heating rate of 2°C/min on a Seiko Instruments. DMS-110 DMA spectrometer. The peak temperature of $\tan \delta$ by DMA was considered as T_g .³⁹

Flexural properties were measured on the rectangular samples according to JIS K6911. The test piece

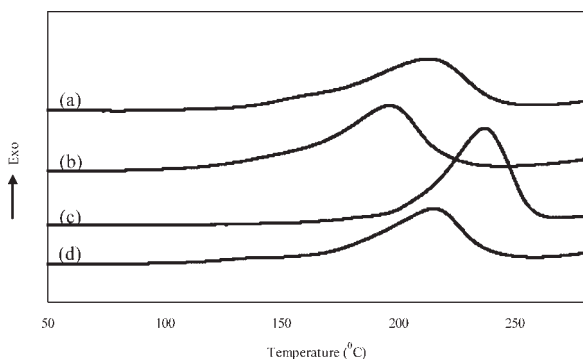


Figure 4 DSC curves of the molten resins from Ba and Ep with the latent curing agent (10 wt %). (a) Ba/Ep/cat 1, (b) Ba/Ep/cat 2, (c) Ba/Ep/cat 3, and (d) Ba/Ep/cat 4.

was supported with 100-mm span. A load was applied at its center by the loading nose and the load at the break of the test piece was measured at the nearest 0.1 kgf. The flexural strength and modulus were calculated by the following equation.

$$\sigma = \frac{3PL}{2Wh^2}$$

where σ , flexural strength; P , load at break of test piece; L , support span; W , width of test piece; and h , depth of test piece.

$$E = (L^3/4Wh^3) \times (F/Y)$$

where E , flexural modulus; L , support span; W , width of test piece; h , depth of test piece; and F/Y , gradient of load-deflection curve in linear portion.

Fracture toughness was estimated by critical stress intensity factor (K_{IC}) according to Astm D5045.

Electrical insulation was estimated by volume resistivity. Volume resistivity was measured by Yokogawa-Hewlett-Packard. HP4339A according to JIS K6911. Namely, the disk test pieces (~ 50 mm diameter and 3 mm thickness) were charged with electricity (500 V), and after 1-min volume resistance was measured. Volume resistivity was calculated by the following equation.

$$\rho_V = \pi d^2/4t \times R_V$$

where ρ_V is the volume resistivity, d is the outside diameter of inner circle of face electrode, t is the thickness of test piece, and R_V is the volume resistance.

Water absorption was estimated according to JIS K7209. Namely, the disk test pieces (~ 50 mm diam-

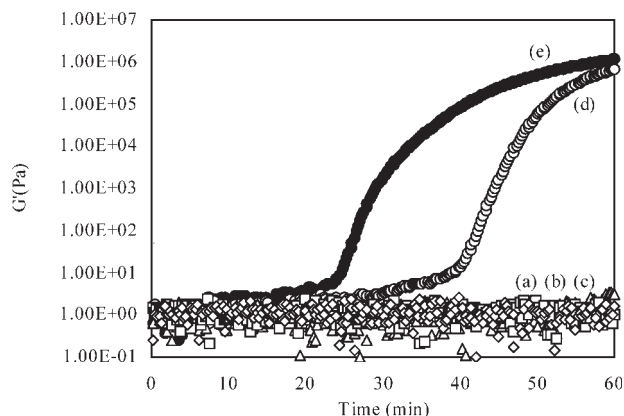


Figure 5 Dynamic mechanical analysis of the molten resins from Ba and Ep with or without the latent curing agent at 170°C. (a) Ba/Ep, (b) Ba/Ep/cat 1 (1 wt %), (c) Ba/Ep/cat 1 (3 wt %), (d) Ba/Ep/cat 1 (5 wt %), and (e) Ba/Ep/cat 1 (10 wt %).

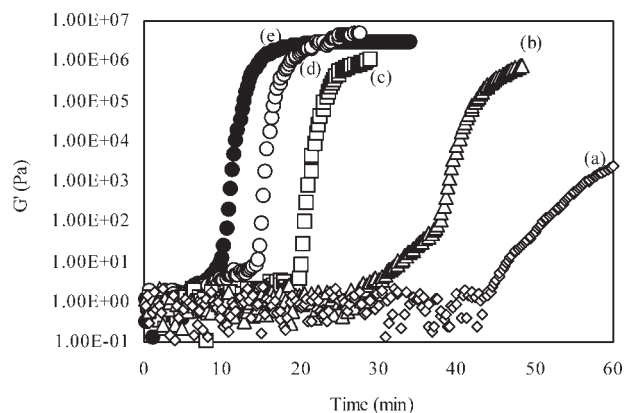


Figure 6 Dynamic mechanical analysis of the molten resins from Ba and Ep with or without the latent curing agent at 200°C. (a) Ba/Ep, (b) Ba/Ep/cat 1 (1 wt %), (c) Ba/Ep/cat 1 (3 wt %), (d) Ba/Ep/cat 1 (5 wt %), and (e) Ba/Ep/cat 1 (10 wt %).

eter and 3 mm thickness) were weighed to the nearest 0.1 mg, and the mass was taken as M_1 . Then the test pieces were put in a container containing boiling water. After 2 h, the test pieces were taken out of the boiling water and cooled down by putting them in water kept at the temperature of the testing room for 15 min. After taking the test pieces out of the water, they were weighed to the nearest 0.1 mg, and the mass was taken as M_2 . Water absorption was calculated by the following equation.

$$\text{Water absorption (\%)} = (M_2 - M_1)/M_1 \times 100$$

Flame resistance was estimated by UL94 and the limited oxygen index (LOI). UL94 was conducted according to UL94 standard. Five specimens with dimensions of 125-mm long and 13-mm wide were tested. Town gas supplied to the burner shell, and the burner was adjusted to produce a blue flame of 20 mm high. By applying the flame centrally to the middle point of the bottom edge of the specimen, and the distance was maintained for 10 s. After the first ignition, the flame was then removed and we recorded the time for self-extinguishing and the dripping characterization. The second ignition was then performed on the same sample and the self-extinguishing time/dripping characteristics were recorded. If the sample self-extinguished in less than 10 s with no dripping, we considered it to be a V-0 material, which is an industry standard for flame retardancy. LOI was tested according to ASTM D2863. The percentage in the oxygen/nitrogen mixture deemed sufficiently to sustain the flame was taken as the LOI.

Thermal gravimetric analysis (TGA) was applied to evaluate the thermal stability. TGA was measured with heating rate of 10°C/min under N₂ atm on a

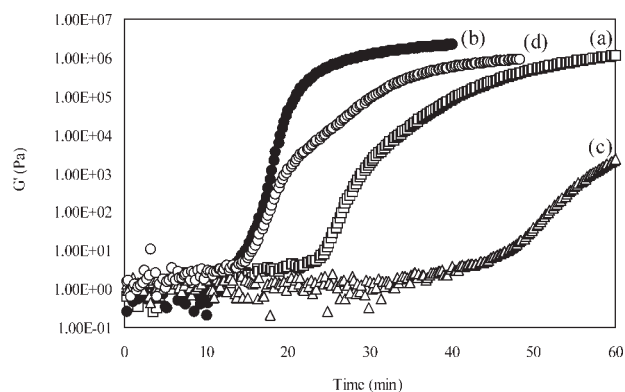


Figure 7 Dynamic mechanical analysis of the molten resins from Ba and Ep with the latent curing agent (10 wt %) at 170°C. (a) Ba/Ep/cat 1, (b) Ba/Ep/cat 2, (c) Ba/Ep/cat 3, and (d) Ba/Ep/cat 4.

Seiko Instruments. TGA 5200 thermal gravimetric analyzer.

RESULTS AND DISCUSSION

Curing behavior of the molten resins from Ba and Ep with the latent curing agent

Curing behaviors were estimated from DSC, and measurements for storage modulus (G'). DSC and measurements for G' are very effective methods for evaluating properties of the cure of the thermosetting resins.

Figures 3 and 4 show DSC results of the molten resins from 50 mol% Ba and 50 mol% Ep with or without the latent curing agent. Four kinds of the latent curing agents were used, which were the salts of *p*-toluensulfonic acid and diethanolamine (cat 1), isopropanolamine (cat 2), diethylethanolamine (cat 3), or methylamine (cat 4). *P*-toluensulfonic acid was used

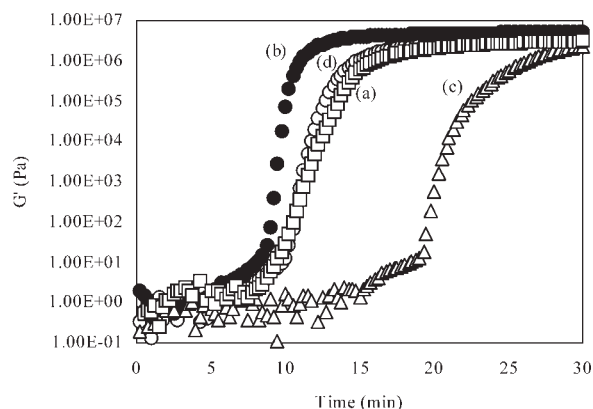


Figure 8 Dynamic mechanical analysis of the molten resins from Ba and Ep with the latent curing agent (10 wt %) at 200°C. (a) Ba/Ep/cat 1, (b) Ba/Ep/cat 2, (c) Ba/Ep/cat 3, (d) Ba/Ep/cat 4.

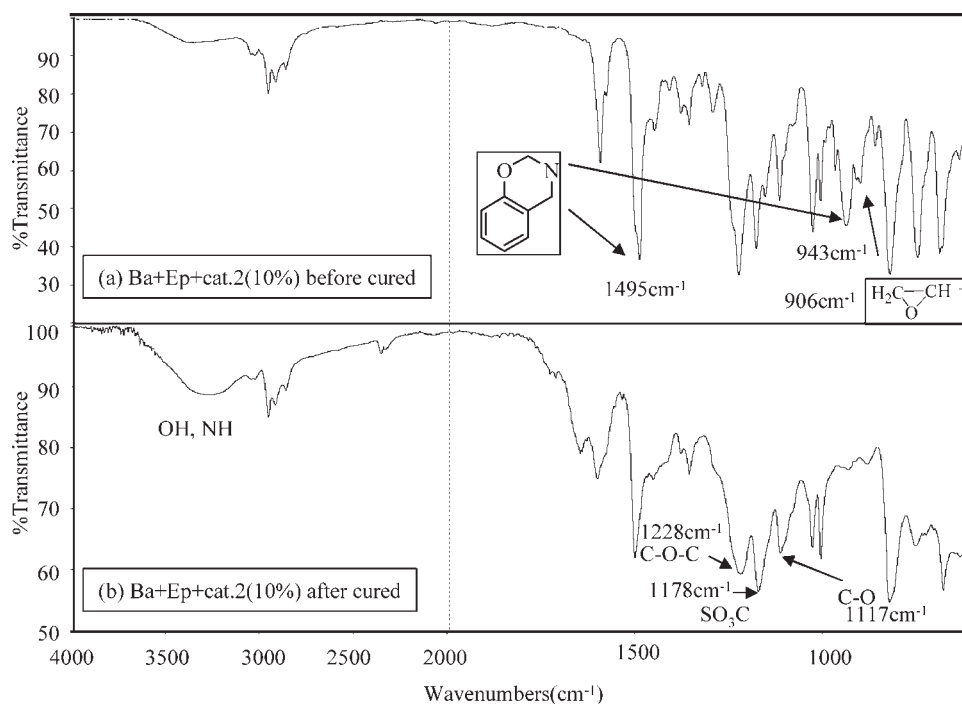


Figure 9 FTIR spectra of Ba/Ep/cat 2 (10 wt %) before and after curing reaction.

as acids because it was more reactive than other acids such as carboxylic acid, phenol, and so on.⁴⁰ From the results of DSC (Fig. 3), both the peak start temperature and peak temperature decreased when the amount of the latent curing agent (cat 1: the salt of diethanolamine and *p*-toluensulfonic acid) was increased from 0 to 10 wt %. And from Figure 4, when cat 2 was used as the latent curing agent, the peak temperature from DSC decreased to the lowest temperature of all.

Figures 5–8 show the G' value of the molten resins from 50 mol% Ba and 50 mol% Ep with or without the latent curing agents. From the G' value at 170°C

or 200°C, which is typical curing temperature for thermosetting resin, the G' value of the molten resins from Ba and Ep without the latent curing agents did not increase above 60 min at 170°C (Fig. 5), and did not increase much for a relatively long time (about 43 min) even at 200°C (Fig. 6). Namely, it was found that the reaction induction time for curing reaction of Ba and Ep molten resins was long, and also cure speed was slow. On the other hand, the storage modulus (G') value of the molten resins from Ba and Ep with the latent curing agents increased more rapidly than that of the molten resins from Ba and Ep

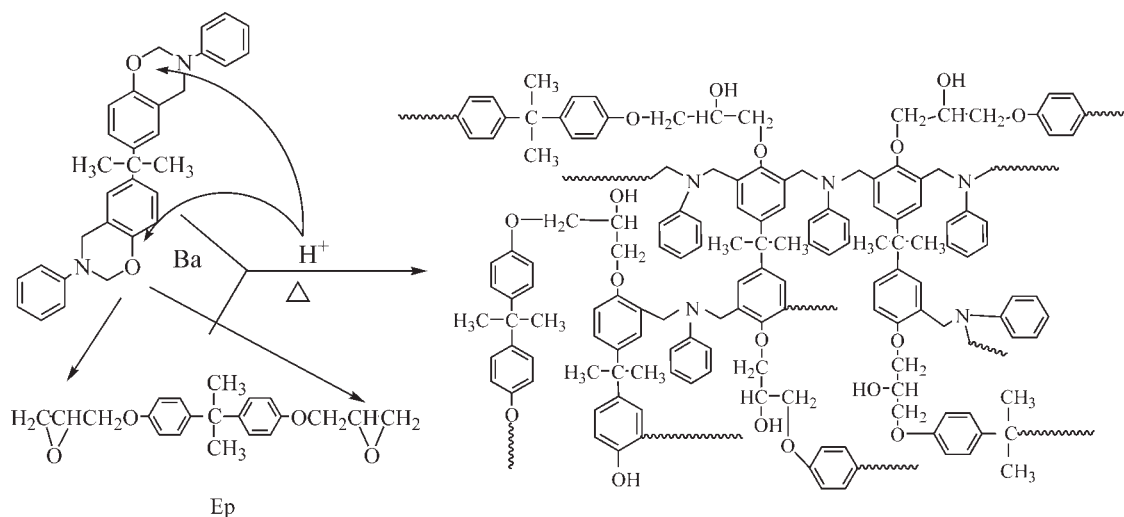


Figure 10 The curing reaction (copolymerization) of benzoxazine (Ba) with epoxy resin (Ep).

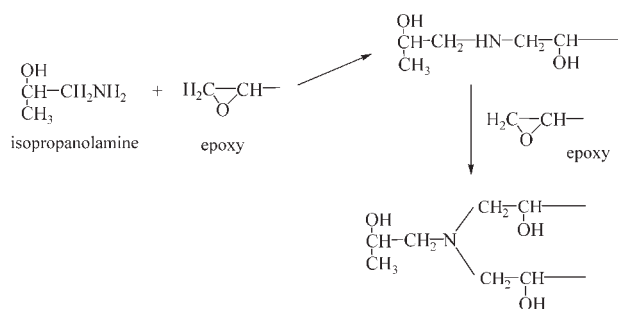


Figure 11 The curing reaction of amines liberated with epoxy ring.

without the latent curing agents, especially at 200°C. And from Figures 5 and 6, the G' value increased more rapidly as the amount of the latent curing agent (cat 1) was increased from 0 to 10 wt % at each temperature. And also from Figures 7 and 8, when cat 2 or cat 4 was used as the latent curing agent, the G' value increased most rapidly of all latent curing agents.

From these results of DSC and measurements for storage modulus, it was found that the most effective amount of the latent curing agent on the rapid curing reaction was 10 wt %, and also that the most effective latent curing agent on the rapid curing reaction was the salt of *p*-toluenesulfonic acid and isopropanolamine (cat 2) or methylamine (cat 4). This might be because bivalent amine of isopropanolamine or methylamine was more effective than univalent amine of diethanolamine or diethylethanolamine.

Curing reaction of Ba with Ep using the latent curing agent

To investigate the curing reaction of Ba with Ep using the latent curing agent, FT-IR measurement was carried out. FT-IR spectra of the compound before and after the curing reaction of Ba with Ep using the latent curing agent (cat 2: the salt of *p*-toluenesulfonic acid and isopropanolamine) are shown in Figure 9. As a result, both the absorptions at 1495 and 943 cm^{-1} assigned to the trisubstituted benzene ring in the benzoxazine ring structure and the absorption at 906 cm^{-1} assigned to the epoxy group disappeared. From Figure 9(b) after the curing reaction, the broad absorption at ca. 3360 cm^{-1} assigned to the secondary hydroxyl group by ring opening reaction of epoxy group, amine group from the latent curing agent and very small amount of phenolic hydroxyl group that could not react with epoxy ring appeared. And the absorption at 1228 cm^{-1} assigned to the asymmetric stretching of C—O—C ether group, the absorption at 1178 cm^{-1} assigned to the symmetric stretching of $\text{SO}_3\text{—C}$ group, and the

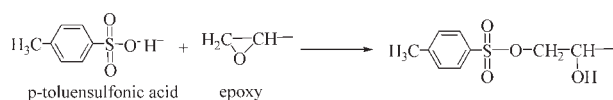


Figure 12 The curing reaction of acids liberated (*p*-toluenesulfonic acid) with epoxy ring.

absorption at 1117 cm^{-1} assigned to the stretching of secondary alcohol (C—O) group also appeared.

The latent curing agent shows no activity under normal condition but does under external stimulation such as heating. The latent curing agent in this study consisted of the salt of the acid and amine compounds that would liberate the free acids and amines by high-temperature decomposition. Therefore acids and amines that were liberated at the high temperature could act as the curing agent in the curing reaction of benzoxazines (Ba) and epoxy resin (Ep).

From the results of FT-IR measurements, we might suggest the curing reaction mechanism of Ba and Ep with the latent curing agents as follows. In the presence of acids liberated, a rapid proton transfers and generates a phenolate ion. This phenolate ion can then react with another benzoxazines (Ba) or epoxy groups (Ep), and the curing reaction (copolymerization) of Ba with Ep proceeded as shown in Figure 10.³⁴ And also amines liberated at the high temperature can react with epoxy ring as shown in Figure 11. Acids liberated (*p*-toluenesulfonic acid) can react with epoxy ring as shown in Figure 12. In this way, curing reaction of benzoxazines (Ba) and epoxy resin (Ep) with the latent curing agent could proceed more rapidly than that without the latent curing agent, that is, it could reduce the cure time, and lower the cure temperature. And it was considered that acids and amines, which the latent curing agent liberated by the high-temperature decomposition, might be incorporated in the curing system of benzoxazine and epoxy resin.

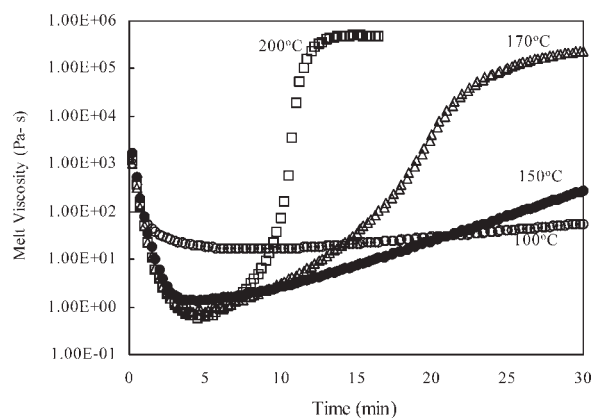


Figure 13 Melt viscosity of the molten resins from Ba and Ep with cat 2 (10 wt %).

TABLE I
Properties of the Cured Resin from Ba and Ep with or without the Latent Curing Agent^a

| Sample | Flexural strength (MPa) | Flexural modulus (GPa) | K_{IC} (MPa m ^{1/2}) | Volume resistivity (Ω cm) | | Water ^b absorption (wt%) |
|--------------------|-------------------------|------------------------|----------------------------------|-----------------------------------|----------------------|-------------------------------------|
| | | | | Before boiling | After 2-h boiling | |
| Ba/Ep/cat 1 | 105 | 3.5 | 1.11 | 4.3×10^{16} | 6.8×10^{15} | 0.60 |
| Ba/Ep/cat 2 | 104 | 3.7 | 0.82 | 5.9×10^{16} | 5.4×10^{15} | 0.85 |
| Ba/Ep ^c | – | – | – | – | – | – |

^a Amount of the latent curing agent is 10 wt %. Curing condition is 150°C/2 h + 170°C/2 h.

^b After 2-h boiling.

^c Not cured.

Melt viscosity of the molten resins from Ba and Ep with the latent curing agent

Results of measurements for melt viscosity (η) at 100, 150, 170, and 200°C are shown in Figure 13. The melt viscosity of the molten resins from Ba and Ep with cat 2 was kept a low value about 50 [Pa s] at 100°C even after 30 min. The molten resins showed good thermal stability under 100°C, because the ring opening reaction of benzoxazine ring was difficult to occur at low temperature, at which the latent curing agent could not liberate acids and amines, and the phenolic hydroxyl groups that contributed to the curing reaction were not produced. However, since the benzoxazine ring opened and the phenolic hydroxyl groups were produced easily above 170°C, at which the latent curing agent could liberate acids and amines, and then the curing reactions as shown in Figures 10–12 occurred, the melt viscosity increased rapidly as shown in Figure 13.

Properties of the cured resin

The properties of the cured resin from Ba and Ep are shown in Tables I–IV. The curing condition is 150°C/2 h + 170°C/2 h in Tables I and III. The curing condition is 150°C/2 h + 170°C/2 h + 200°C/2 h in Tables II and IV. The molten resins from Ba and Ep without the latent curing agent could not cure under the condition such as 150°C/2 h + 170°C/2 h. As a result, from Tables I and II, mechanical properties (flexural strength and K_{IC}) of the cured resin from Ba and Ep with the latent curing agent were

higher than those of the cured resin from B-a and Ep without the latent curing agent. And both cured resins from Ba and Ep with or without the latent curing agent had extremely high volume resistivity of commercial resins. However, water absorption after 2-h boiling of the cured resin from Ba and Ep with the latent curing agent was inferior to that of the cured resin from Ba and Ep. This higher water absorption was because hydrophilic components of the latent curing agent were incorporated in the curing system.

And from Tables III and IV, glass transition temperature (T_g) of the cured resin from Ba and Ep with the latent curing agent was much higher than that of the cured resin from Ba and Ep without the latent curing agent. As the results of flammability tests, LOI of the cured resin from Ba and Ep with the latent curing agent (especially when cat 1 was used) was higher than that of the cured resin from Ba and Ep without the latent curing agent. From the results of UL94 tests, all samples with the latent curing agent exhibited V-0 grade, but sample without the latent curing agent was burned out. The reason of these results (higher mechanical properties, heat resistance, and flame resistance) was considered that crosslink density might be augmented.

This idea was supported by DMA. Crosslink density $\rho(E')$ can be calculated using the equation of state for rubbery elasticity.⁴¹

$$\rho(E') = \frac{E'}{3\Phi RT}$$

TABLE II
Properties of the Cured Resin from Ba and Ep with or without the Latent Curing Agent^a

| Sample | Flexural strength (MPa) | Flexural modulus (GPa) | K_{IC} (MPa m ^{1/2}) | Volume resistivity (Ω cm) | | Water ^b absorption (wt%) |
|-------------|-------------------------|------------------------|----------------------------------|-----------------------------------|----------------------|-------------------------------------|
| | | | | Before boiling | After 2-h boiling | |
| Ba/Ep/cat 1 | 105 | 3.5 | 0.96 | 4.1×10^{16} | 8.2×10^{15} | 0.47 |
| Ba/Ep/cat 2 | 109 | 3.6 | 0.75 | 5.5×10^{16} | 4.6×10^{15} | 0.57 |
| Ba/Ep | 93 | 3.4 | 0.43 | 8.9×10^{16} | 3.0×10^{15} | 0.38 |

^a Amount of the latent curing agent is 10 wt%. Curing condition is 150°C/2 h + 170°C/2 h + 200°C/2 h.

^b After 2-h boiling.

TABLE III
Properties of the Cured Resin from Ba and Ep with or without the Latent Curing Agent^a

| Sample | T_g^b (°C) | LOI | UL-94 | | | | $\rho(E')$ (mol/m ³) |
|--------------------|--------------|-----|------------------|------------------|----------|------------|----------------------------------|
| | | | 1st ignition (s) | 2nd ignition (s) | Dripping | Evaluation | |
| Ba/Ep/cat 1 | 151 | 27 | 2.2 | 5.0 | No | V-0 | 1.5×10^3 |
| Ba/Ep/cat 2 | 152 | 25 | 4.4 | 3.8 | No | V-0 | 1.1×10^3 |
| Ba/Ep ^c | – | – | – | – | – | – | – |

^a Amount of the latent curing agent is 10 wt %. Curing condition is 150°C/2 h + 170°C/2 h.

^b Peak temperature of tan δ by DMA.

^c Not cured.

where Φ is the front factor, T is the absolute temperature, R is the gas constant, and E' is the storage modulus of the sample at temperature T .

This equation is applicable to polymer networks that have a rubbery plateau region.⁴¹ Though the adoption of this equation to the highly crosslinked systems is over the applicability of the rubber elasticity theory, there is no theoretical equation to calculate crosslink density for highly crosslinked polymers. Therefore, in our study, the value of $\rho(E')$ of the samples was calculated at $T_g + 40^\circ\text{C}$ according to this equation to compare crosslink density of each sample.^{10,42,43} The results are shown in Tables III and IV, assuming that Φ is equal to 1.⁴⁴ The value of $\rho(E')$ of the cured resin from Ba and Ep with the latent curing agent was higher than that of the cured resin from Ba and Ep without the latent curing agent. This high crosslink density might be due to several reactions including the reactions such as Figures 10–12. We might associate this good performance in the cured resin with the high crosslink density.

TGA results

Figure 14 shows the TGA curves of the molten resins from Ba and Ep with or without the latent curing agent. For the molten resins from Ba and Ep with the latent curing agent, the initial decomposition that was defined as 5 wt % of mass loss occurred about 302°C and the char yield at 600°C was 28 wt %. For the molten resins from Ba and Ep without the latent

curing agent, the initial decomposition that was defined as 5 wt % of mass loss occurred about 309°C and the char yield at 600°C was 27 wt %. In terms of the thermal gravimetric results, the thermal stability of the molten resins from Ba and Ep with the latent curing agent was almost same as the molten resins from Ba and Ep without the latent curing agent, as shown in Figure 14.

CONCLUSIONS

The purpose of this study is to achieve a higher crosslink density of the cured resin from benzoxazine-based resin, especially to reduce the cure time of the benzoxazine compound, and to lower the cure temperature of the benzoxazine compound. We investigated the curing reaction of bisphenol-A-based benzoxazine and epoxy resin using the latent curing agent and the properties of the cured resin. As a result, the molten resins from benzoxazine and epoxy resin with the latent curing agent showed good thermal stability below 100°C. However, above 170°C the curing reaction of benzoxazine with epoxy resin with the latent curing agent proceeded more rapidly than that of benzoxazine and epoxy resin without the latent curing agent. It was found that the cure time of the molten resins from benzoxazine and epoxy resin with the latent curing agent could be reduced and also the cure temperature could be lowered, compared with those from benzoxazine and epoxy resin without the latent curing agent. The cured resin from benzoxazine and epoxy resin with

TABLE IV
Properties of the Cured Resin from Ba and Ep with or without the Latent Curing Agent^a

| Sample | T_g^b (°C) | LOI | UL-94 | | | | $\rho(E')$ (mol/m ³) |
|--------------------|--------------|-----|------------------|------------------|----------|------------|----------------------------------|
| | | | 1st ignition (s) | 2nd ignition (s) | Dripping | Evaluation | |
| Ba/Ep/cat 1 | 164 | 30 | 0.6 | 1.3 | No | V-0 | 1.8×10^3 |
| Ba/Ep/cat 2 | 160 | 25 | 2.5 | 3.8 | No | V-0 | 1.4×10^3 |
| Ba/Ep ^c | 122 | 24 | – | – | – | – | 1.2×10^3 |

^a Amount of the latent curing agent is 10 wt %. Curing condition is 150°C/2 h + 170°C/2 h + 200°C/2 h.

^b Peak temperature of tan δ by DMA.

^c Burned out after the first ignition on UL94 test.

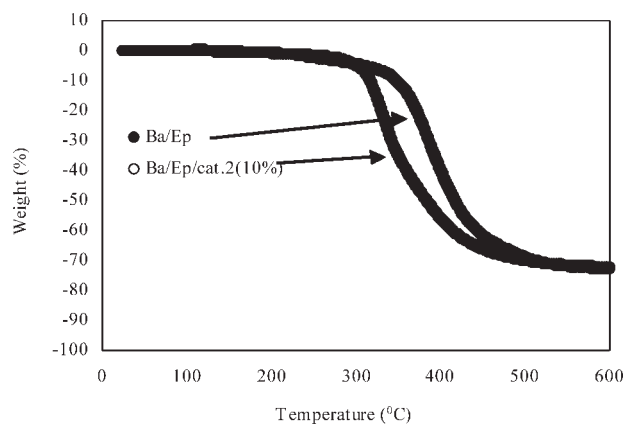


Figure 14 TGA curves of the molten resins from Ba and Ep with or without the latent curing agent.

the latent curing agent had superior heat resistance, flame resistance, mechanical properties, and electrical insulation to those from benzoxazine and epoxy resin without the latent curing agent because of higher crosslink density.

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