New Type of Phenolic Resin: Curing Reaction of Phenol-Novolac Based Benzoxazine with Bisoxazoline or Epoxy Resin Using Latent Curing Agent and the Properties of the Cured Resin

Hajime Kimura, Akihiro Matsumoto, Keiko Ohtsuka

Organic Materials Research Division, Osaka Municipal Technical Research Institute, Joto-ku, Osaka 536-8553, Japan

ABSTRACT: In this study, we aimed to reduce the cure time, and to lower the cure temperature of the benzoxazine compound. Therefore, curing reaction of benzoxazine with bisoxazoline or epoxy resin using the latent curing agent and the properties of the cured resins were investigated. The cure behavior of benzoxazine with bisoxazoline or epoxy resin using the latent curing agent was monitored by differential scanning calorimetry and measurements for storage modulus (G'). The properties of the cured resin were estimated by mechanical properties, electrical insulation, water resistance, heat resistance, and flame resistance. As a result, it was confirmed that by using the latent curing agent, cure time of benzoxazine and bisoxazoline or epoxy resin was reduced, and cure temperature was lowered. And it was found that the curing reaction using phenol-novolac based benzoxazine (Na) as the benzoxazine compound could proceed more rapidly than that using bisphenol-A based benzoxazine (Ba) as the benzoxazine compound. However, the cured resins from Ba and bisoxazoline or epoxy resin using the latent curing agent showed good heat resistance, flame resistance, and mechanical properties compared with those from Na and bisoxazoline or epoxy resin using the latent curing agent. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1762–1770, 2009

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

INTRODUCTION

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 (benzoxazine resin) having both the phenolic hydroxyl group and the tertiary amine groups are produced[1] (Fig. 1). This benzoxazine-based resin has attracted significant attention as a new type of phenolic resin that releases no volatiles during curing reaction and needs no catalysts.

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. Jang and Shin[25] also studied the cure kinetics of a benzoxazine-based phenolic resin. Jang and Seo[26] studied the performance improvement of rubber-modified polybenzoxazine. Recently, maleimde-modified[22,23,27,28] and furan-modified[29] 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 rings with other compounds has been investigated. We have already investigated the curing behavior of the bisphenol-A, terpenediphenol, or poly(p-vinylphenol)-based benzoxazines with epoxy resin or bisoxazoline and the properties of the cured resins.[34–38] A molding compound from a bispheno-A based benzoxazine and bisoxazoline showed good flowability below 140°C, the curing reaction 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 bispheno-A type novolac and epoxy resin or bisoxazoline.

Despite their high performance (e.g., good heat and water resistance) of benzoxazine-based resin, it is believed that 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 that the cure temperature is high.

We have been studying 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

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Correspondence to: H. Kimura (kimura@omtri.city.osaka.jp).
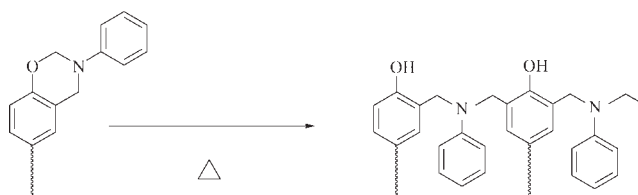
Figure 1 Ring-opening reaction of a benzoxazine ring.

acids and amines, and investigated the catalytic effects of the latent curing agents on the curing reaction of bispheno-A based benzoxazine (Ba) with bisoxazoline or epoxy resin and the properties of the cured resins.[39,40] As a result, the cure time of molten resins from Ba and bisoxazoline or epoxy resin with latent curing agent was reduced, and the cure temperature was lowered, in comparison with those of resins from Ba and bisoxazoline or epoxy resin without latent curing agent. Cured resins from Ba and bisoxazoline or epoxy resin with latent curing agent showed good heat resistance, flame resistance, mechanical properties, and electrical insulation, in comparison with cured resins from Ba and bisoxazoline or epoxy resin without latent curing agent.

In this study, to reduce the cure time and lower the cure temperature of the benzoxazine compound much more, phenol-novolac based benzoxazine (Na) was used as benzoxazine compound instead of Ba. The curing reaction of Na with bisoxazoline or epoxy resin using latent curing agent, and the properties of the cured resin were investigated.

EXPERIMENTAL

Materials

Dioxane, aniline, formaldehyde (37% in water), diethanolamine, and *p*-toluenesulfonic acid were purchased from Nacalai Tesque Co., Ltd. (Kyoto, Japan). 2,2-Bis(3,4-dihydro-3-phenyl-1,3-benzoxazine)propane (bisphenol-A based benzoxazine, Ba) was supplied by Shikoku Chemicals Co., Ltd. (Kagawa, Japan). Phenol-novolac resin (phenolite TD-2131) was supplied from Dainippon Ink and Chemicals Co., Ltd. (Tokyo, Japan). 2,2′-(1,3-Phenylene)-bis(4,5-dihydrooxazoles) as a bisoxazoline (1,3-PBO) was supplied by Mikuni Pharmaceutical Industrial Co., Ltd. (Osaka, Japan). Bisphenol-A based epoxy resin (EPIKOTE 828, epoxy equivalent 186) as an epoxy resin (Ep) was supplied by Japan Epoxy Resins Co., Ltd. (Tokyo, Japan). All chemicals were used without further purification. The chemical structures of 1,3-PBO and Ep are shown in Figure 2.

Synthesis and characterization of phenol-novolac based benzoxazine (Na)

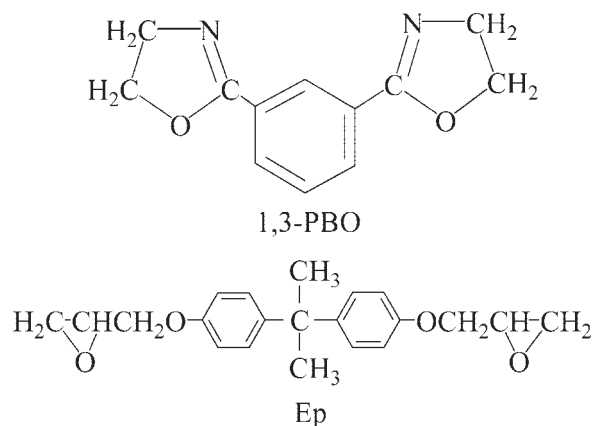Phenol-novolac based benzoxazine (Na) was synthesized according to the method explained by Ishida

Figure 2 Chemical structures of 1,3-PBO and Ep.

et al.[2] (Fig. 3). A general procedure is as follows: 0.1 mol aniline in 20 mL dioxane was added slowly to 0.2 mol formaldehyde (37% in water) in 80 mL dioxane, keeping the temperature below 10°C in ice bath. The mixture was stirred for 10 min, 0.1 mol phenol-novolac in 100 mL dioxane was added to the mixture, and then the temperature was raised and the mixture solution was refluxed for 6 h. The solvent was then evaporated and the viscous fluid was dissolved in ethyl acetate. The ethyl acetate solution was washed with water several times. Ethyl acetate was evaporated to give the fine powder. The structure of Na was analyzed by ^{1}H-NMR measurement and gel permeation chromatography (GPC). ^{1}H-NMR measurement was carried out on Japan Electron Company (Tokyo, Japan). JMN-GSX-270 instrument operating at 270 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane was used as an internal standard. GPC measurement was carried out on Waters Alliance 2695 Separation Module with a refractive index (RI) detector. Tetrahydrofuran was used as an eluent, and polystyrene was used as a standard.

Preparation of the heat latent curing agent

The preparation of the heat latent curing agent was carried out using the reaction of the acids and amine compounds. In a typical experiment, diethanolamine
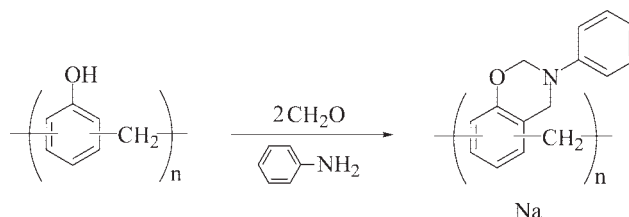

Figure 3 Synthesis of phenol-novolac based benzoxazine (Na).

as an amine compound (5.26 g, 0.05 mol) was changed 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 the acid and amine, and it was used as the heat latent curing agent without purification.

Preparation of the cured resin and curing condition

Samples containing 50 mol % Na and 50 mol % 1,3-PBO or Ep with 10 wt % latent curing agent were prepared and cured in a mold at a specified temperature in the oven. At first, each sample, containing 50 mol % Na and 50 mol % 1,3-PBO or Ep, was heated to about 150°C, and a clear molten mixture was obtained. After the temperature of the molten mixture was cooled down to 100°C, 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 for 2 h and 170°C for 2 h from the results of differential scanning calorimetry (DSC). DSC was measured with heating rate of 10°C/min under N_2 atmosphere on a Seiko Instruments Co., Ltd., (Tiba, Japan). STI EXSTAR 6000.

Properties of the molten resins and cured resin

To investigate the catalytic effect of the latent curing agent on the curing reaction, measurements for storage modulus (G') were conducted on a UBM Co., Ltd. (Kyoto, Japan). Dynamic mechanical spectrometer (Rheosol-G3000) by using a 25 mm parallel plate 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 (170°C) at a rate of 30°C/min. And storage modulus (G') for isothermal test at 170°C were measured as a function of time.

The properties of the cured resins were characterized by their heat resistance, flexural properties, fracture toughness, electrical insulation, water absorption, and flame resistance. The heat resistance was estimated via the glass-transition temperature (T_g) by dynamic mechanical analysis (DMA). DMA was measured by a three-point-bending method at 1 Hz, with heating rate of 2°C/min on a Seiko Instruments DMS-110 DMA spectrometer. The peak temperature of tan δ by DMA was considered to be T_g.[41]

The flexural properties were measured on rectangular samples according to JIS K6911. The test piece was supported with a 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 (σ) and flexural modulus (E) were calculated with the following equations:

$$\sigma = 3PL/2Wh^2$$

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

where P is the load at break of test piece, L is the support span, W is the width of the test piece, h is the depth of test piece, and F/Y is the gradient of load-deflection curve in the linear portion.

The fracture toughness was estimated with critical stress intensity factor (K_{IC}) according to ASTM D5045.

Electrical insulation was estimated with volume resistivity (ρ_v). The ρ_v was measured by Yokogawa-Hewlett-Packard Co., Ltd. HP4339A according to JIS K6911. Namely, the disk test pieces (ca. 50 mm in diameter and 3 mm thick) were charged with electricity (500 V), and after 1 min the volume resistance (R_v) was measured. The ρ_V was calculated by the following equation:

$$\rho_v = \pi d^2/4t \times R_v$$

where d is the outside diameter of inner circle of face electrode, and t is the thickness of test piece.

The water absorption was estimated according to JIS K7209. That is, the disk test pieces (ca. 50 mm in diameter and 3 mm thick) 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. The water absorption was calculated by the following equation:

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

Flame resistance was estimated by UL-94 and the limited oxygen index (LOI). UL-94 was conducted according to UL-94 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-
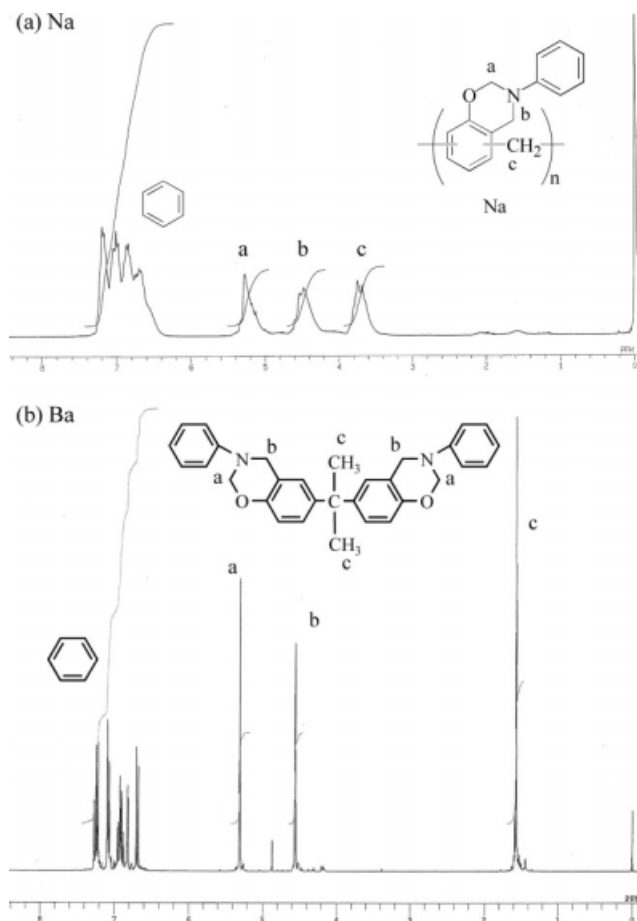
Figure 4 ¹H-NMR spectra of (a) Na and (b) Ba.

extinguishing time/dripping characteristics were recorded. If the sample self-extinguished in <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.

RESULTS AND DISCUSSION

Synthesis and characterization of phenol-novolac based benzoxazine (Na)

The synthesis of Na was carried out using 1,4-dioxane as a solvent. The yield was 80–90%. ¹H-NMR spectra of Na and Ba are shown in Figure 4. The peaks (a and b) assigned to the proton of benzoxazine ring were detected, and the structures of Na and Ba were confirmed. Then, by examining the ratio between the integrated intensities of the resonance peaks in ¹H-NMR, the benzoxazine ring contents in Na and Ba were calculated. The ratio between the integrated intensity of the methylene units in the benzoxazine ring [Fig. 4(a), peaks a and b], and the integrated intensity of methylene units [Fig. 4(a), peak c] in the Na oligomer chain was

9 : 1. Consequently, the benzoxazine ring content in Na was calculated as 90%. The presence of the phenolic hydroxyl groups (about 10% in Na) with free ortho-positions in the oligomers may have an accelerative effect on the curing reaction, that is, it may reduce the cure time, and lower the cure temperature. On the other hand, the ratio between the integrated intensity of the methylene units in the benzoxazine ring [Fig. 4(b), peaks a and b], and the integrated intensity of methyl units [Fig. 4(b), peak c] in the Ba chain was 4 : 6. The ratio between the number of the methylene units in the benzoxazine ring and the number of methyl units in the Ba chain is 4 : 6 theoretically. Consequently, the benzoxazine ring content in Ba was calculated as about 100%.

GPC chromatographs of Na and Ba are shown in Figure 5. In Figure 5(b), the strongest peak at 31.6 min retention time is assigned to the difunctional benzoxazine Ba monomer. The peaks with shorter retention time represent dimmers and higher oligomers. The area ratio between the dimmers and higher oligomers peak and difunctional benzoxazine Ba was 1 : 9. Consequently, the dimmers or higher oligomers content in Ba was about 10%. On the other hand, it was found that Na contained a lot of higher oligomers as shown in Figure 5(a).

Curing behavior of the molten resins from Na and 1,3-PBO or Ep with the latent curing agent

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

Figure 6 shows DSC results of the molten resins from 50 mol % Na or Ba and 50 mol % 1,3-PBO with
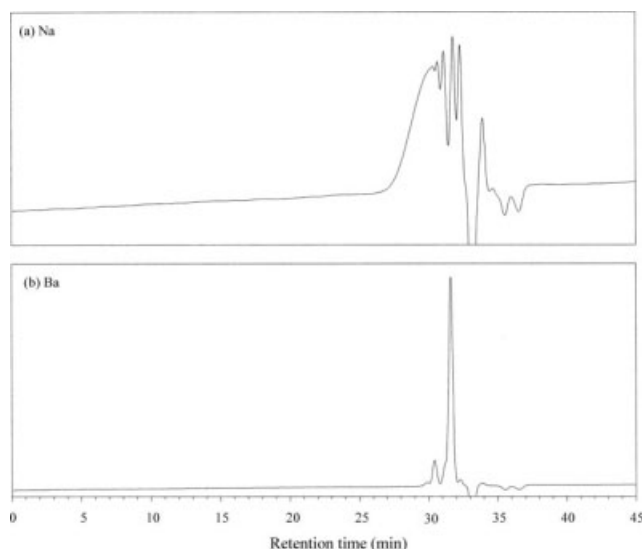

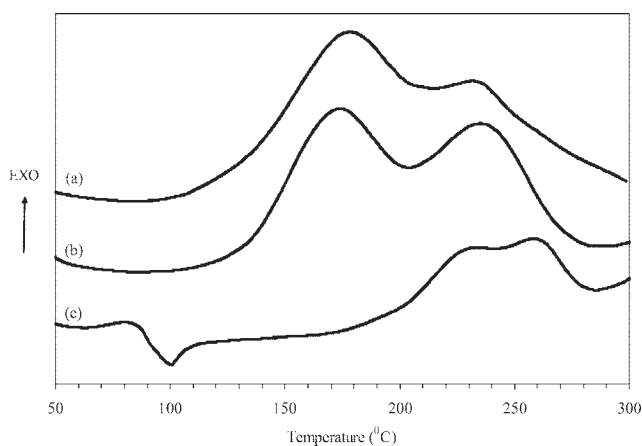**Figure 5** GPC chromatographs of (a) Na and (b) Ba.

Figure 6 DSC curves of the molten resins from Na or Ba and 1,3-PBO with or without the latent curing agent: (a) Na/1,3-PBO with curing agent, (b) Ba/1,3-PBO with curing agent, and (c) Na/1,3-PBO.

Figure 8 Dynamic mechanical analysis of the molten resins from Na or Ba and 1,3-PBO with or without the latent curing agent at 170°C: (a) Na/1,3-PBO with curing agent, (b) Ba/1,3-PBO with curing agent, and (c) Na/1,3-PBO.

the latent curing agent, and 50 mol % Na and 50 mol % 1,3-PBO without the latent curing agent. And Figure 7 shows DSC results of the molten resins from 50 mol % Na or Ba and 50 mol % Ep with the latent curing agent, and 50 mol % Na and 50 mol % Ep without the latent curing agent. From the results of DSC, both the peak start temperature and peak temperature decreased when latent curing agent was added. And also, compared Na with Ba, the curing reaction of the molten resins from Na and 1,3-PBO or Ep with the latent curing agent could proceed a little more rapidly than that of the molten resins from Ba and 1,3-PBO or Ep with the latent curing agent.

Figure 8 shows the G' value of the molten resins from 50 mol % Na or Ba and 50 mol % 1,3-PBO with the latent curing agent, and 50 mol % Na and 50 mol % 1,3-PBO without the latent curing agent. And Figure 9 shows the G' value of the molten resins from 50 mol % Na or Ba and 50 mol % Ep with the

latent curing agent, and 50 mol % Na and 50 mol % Ep without the latent curing agent. From the G' value at 170°C, which is typical curing temperature of thermosetting resin, the G' value of the molten resins from Na and 1,3-PBO or Ep without the latent curing agents did not increase for about 40–50 min. Namely, it was found that the reaction induction time for curing reaction of Na and 1,3-PBO or Ep molten resins was long, and cure speed was slow. On the other hand, the storage modulus (G') value of the molten resins from Na and 1,3-PBO or Ep with the latent curing agents increased more rapidly than that of the molten resins from Na and 1,3-PBO or Ep without the latent curing agents. And also, compared Na with Ba, the G' value of the molten resins from Na and 1,3-PBO or Ep with the latent curing agents increased more rapidly than that of the molten resins from Ba and 1,3-PBO or Ep with the latent curing agents.
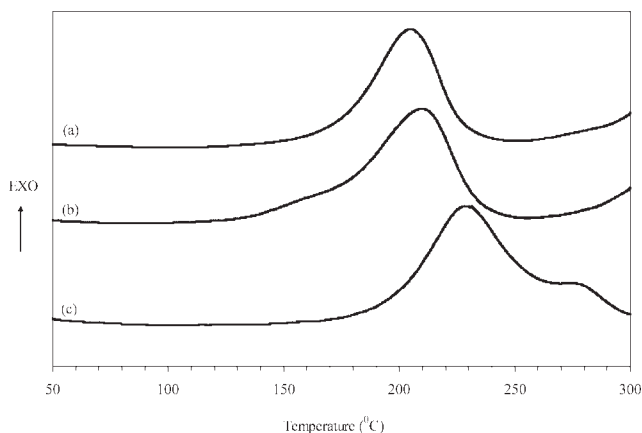

Figure 7 DSC curves of the molten resins from Na or Ba and Ep with or without the latent curing agent: (a) Na/Ep with curing agent, (b) Ba/Ep with curing agent, and (c) Na/Ep.
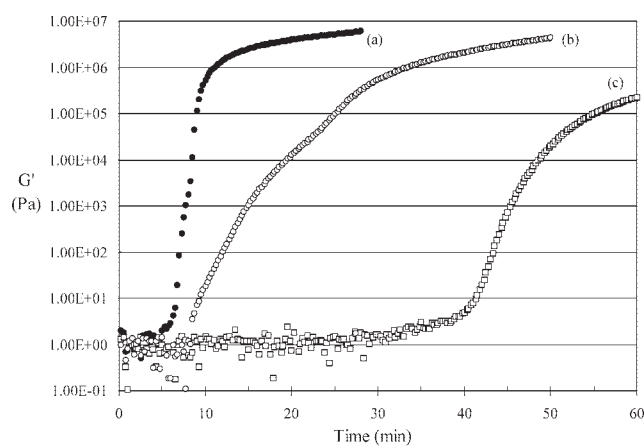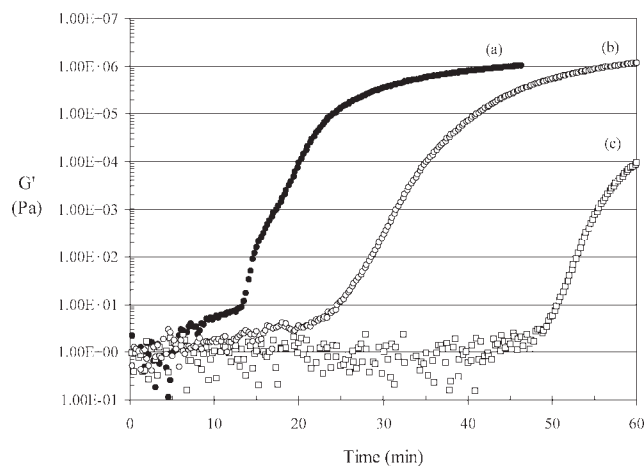

Figure 9 Dynamic mechanical analysis of the molten resins from Na or Ba and Ep with or without the latent curing agent at 170°C: (a) Na/Ep with curing agent, (b) Ba/Ep with curing agent, and (c) Na/Ep.
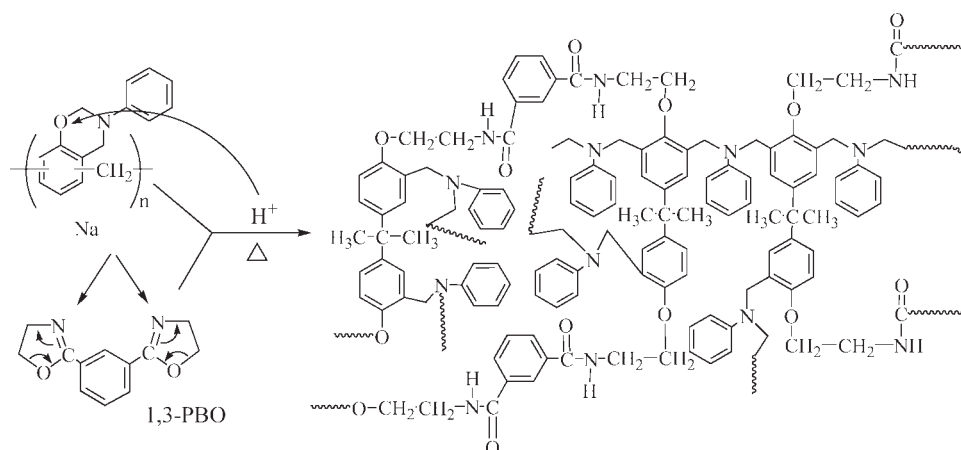
Figure 10 Curing reaction (copolymerization) of Na with 1,3-PBO.

From these results of DSC and measurements for storage modulus (G'), it was found that the latent curing agent was effective on the rapid curing reaction, and also that compared Na with Ba, the curing reaction using Na as benzoxazine compound could proceed more rapidly than that using Ba as benzoxazine compound. The reason was considered that Na contained oligomers that had phenolic hydroxyl groups and the presence of the phenolic hydroxyl groups might have an accelerative effect on the curing reaction. As a result, the molten resin using Na as benzoxazine compound could reduce the cure time, and lower the cure temperature much more than that using Ba as benzoxazine compound.

Curing reaction of Na with 1,3-PBO or Ep using the latent curing agents

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 curing agents in the curing reaction of benzoxazines (Na) and bisoxazoline (1,3-PBO) or epoxy resin (Ep).

As previously reported,[39–40] we might suggest the curing reaction mechanism of Na and 1,3-PBO or 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 or bisoxazoline groups or epoxy groups, and the curing reaction (copolymerization) of Na with 1,3-PBO or Ep proceeded as shown in Figures 10 or 11. And also, amines liberated at the high temperature can react with oxazoline or epoxy ring as shown in Figure 12. Acids liberated (*p*-toluenesulfonic acid) can react with oxazoline or epoxy ring as shown in Figure 13. In this way, the curing reaction of benzoxazines (Na) and bisoxazoline (1,3-PBO) or epoxy resin (Ep) with the latent curing agent could proceed. It was considered that acids and amines, which the latent curing agents liberated by high-temperature decomposition, might be incorporated in the curing system of benzoxazine and bisoxazoline or epoxy resin.
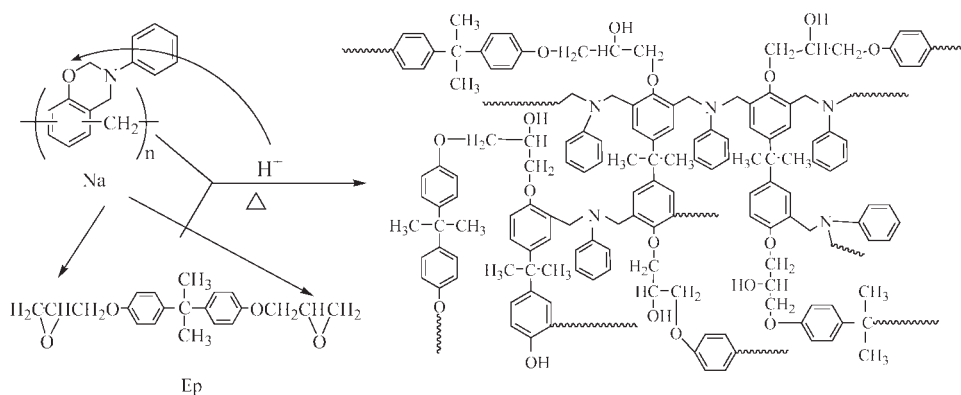

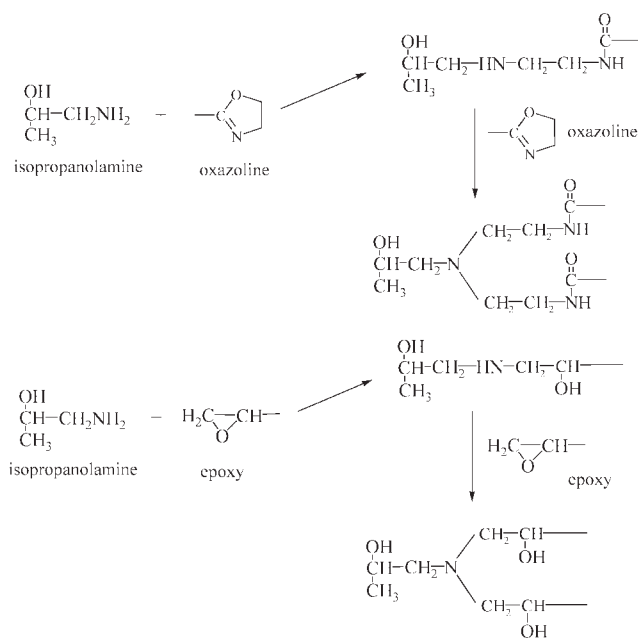**Figure 11** Curing reaction (copolymerization) of Na with Ep.

Figure 12 Curing reaction of amines liberated with oxazoline or epoxy ring.

Properties of the cured resin

The properties of the cured resins from Na and 1,3-PBO (or Ep) with or without the latent curing agent are shown in Tables I and II. And also, the properties of the cured resins from Ba and 1,3-PBO or Ep with the latent curing agent are shown in Tables I and II. As a result, the mechanical properties (σ and K_{IC}) of the cured resins from Na and 1,3-PBO or Ep with the latent curing agents were higher than those of the cured resins from Na and 1,3-PBO or Ep without the latent curing agents. And both cured resins from Na and 1,3-PBO (Ep) with or without the latent curing agent had extremely high volume resistivity for commercial resins. However, water absorption after 2 h boiling of the cured resins from Na and 1,3-PBO or Ep with the latent curing agent was inferior to that of the cured resin from Na and 1,3-PBO or Ep without the latent curing agents. This higher water absorption was because hydrophilic compo-
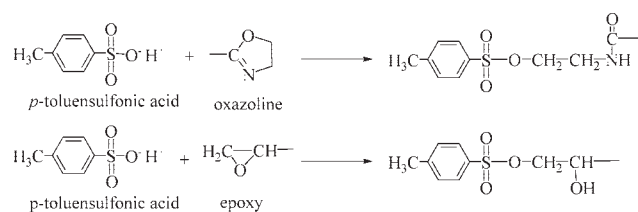

Figure 13 Curing reaction of acids liberated (*p*-toluenesulfonic acid) with oxazoline or epoxy ring.

nents of the latent curing agent were incorporated into the curing system.

Glass transition temperature (T_g) of the cured resins from Na and 1,3-PBO or Ep with the latent curing agent was much higher than that of the cured resins from Na and 1,3-PBO or Ep without the latent curing agent. As the results of the flammability tests, LOI of the cured resins from Na and 1,3-PBO or Ep with the latent curing agent was higher than that of the cured resins from Na and 1,3-PBO or Ep without the latent curing agent. From the results of UL-94 tests, the cured resin from Na and 1,3-PBO with the latent curing agent exhibited V-0 grade. 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. The crosslink density $\rho(E')$ can be calculated using the equation of state for rubbery elasticity.[42]

$$\rho(E') = E'/3\Phi RT$$

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.[42] Although the adoption of this equation to the highly crosslinked system is beyond 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 $T_g + 40°C$ accord-

TABLE I
Properties of the Cured Resin from Na and 1,3-PBO (Ep) with or without the Latent Curing Agent

Sample	σ (MPa)	E (GPa)	K_{IC} (MPa m$^{1/2}$)	$\rho(\Omega$ cm) Before boiling	$\rho(\Omega$ cm) After 2 h boiling	Water absorption[a] (wt %)
Na/1,3-PBO/cat	76	4.5	0.66	6.9×10^{15}	4.8×10^{14}	0.67
Na/1,3-PBO	62	5.4	0.45	2.2×10^{16}	8.9×10^{15}	0.34
Ba/1,3-PBO/cat	114	4.6	1.05	2.6×10^{16}	1.3×10^{14}	1.34
Na/Ep/cat	69	3.7	0.78	1.4×10^{16}	7.5×10^{15}	0.43
Na/Ep	49	4.3	0.10	3.9×10^{16}	3.4×10^{16}	0.31
Ba/Ep/cat	105	3.5	1.11	4.3×10^{16}	6.8×10^{15}	0.60

cat, latent curing agent.
[a] After 2 h boiling.

| Sample | $T_g{}^a$ (°C) | LOI | UL-94 | | | | $\rho(E')$ (mol/m^3) |
			1st ignition (s)	2nd ignition (s)	Dripping	Evaluation	
Na/1,3-PBO/cat	175	30	0.5	7.0	No	V-0	3.9×10^3
Na/1,3-PBO	126	20	0.5	20.8	No	V-0	3.3×10^2
Ba/1,3-PBO/cat	177	33	0.9	2.5	No	V-0	2.6×10^3
Na/Ep/cat	147	24	0.0	118.0	No	–	1.9×10^3
Na/Ep^b	92	20	–	–	–	–	7.4×10^2
Ba/Ep/cat	151	27	2.2	5.0	No	V-0	1.5×10^3

cat, latent curing agent.
^{a} The peak temperature of tan δ by DMA.
^{b} Burned out after the first ignition by UL-94 test.

ing to this equation to compare the crosslink density of each sample.[10,43,44] The results are shown in Table I, under the assumption that Φ is equal to 1.[45] The value of $\rho(E')$ of the cured resins from Na and 1,3-PBO or Ep with the latent curing agent were higher than those of the cured resins from Na and 1,3-PBO or Ep without the latent curing agent. This high crosslink density might be due to several reactions including the reactions in Figures 10–13. We might associate this good performance in the cured resin with high crosslink density.

Next, the properties of the cured resin using Na as benzoxazine compound were compared with those of the cured resin using Ba as benzoxazine compound. In terms of mechanical properties (σ and K_{IC}), heat resistance (T_g), and flammability (LOI and UL94), the properties of the cured resin using Na was inferior to those of the cured resin using Ba. However, water absorption after 2 h boiling and $\rho(E')$ of the cured resin using Na as benzoxazine compound was superior to those of the cured resin using Ba. These were considered as follows; the curing reaction of Na with 1,3-PBO or Ep using latent curing agent could not proceed more uniformly than that of Ba with 1,3-PBO or Ep using latent curing agent because the melt viscosity of the molten resin from Na and 1,3-PBO or Ep with the latent curing agent could rise more rapidly than that of the molten resin from Ba and 1,3-PBO or Ep with the latent curing agent. Therefore, the cured resin from Na and 1,3-PBO or Ep with the latent curing agent might have densely or sparsely packed crosslink structures.

CONCLUSION

The purpose of this study was to achieve a higher crosslink density of the cured resin from a benzoxazine-based resin, especially to reduce the cure time, and to lower the cure temperature of the benzoxazine compound. We investigated the curing reaction of phenol-novolac based benzoxazine and bisoxazoline or epoxy resin using the latent curing agent and the properties of the cured resins. As a result, cure time of the molten resins from phenol-novolac based benzoxazine and bisoxazoline or epoxy resin with the latent curing agent could be more reduced, and also cure temperature could be more lowered, compared with those from bisphenol-A based benzoxazine and bisoxazoline or epoxy resin with the latent curing agent. The reason was considered that phenol-novolac based benzoxazine had a lot of oligomers and phenolic hydroxyl groups. The cured resins from phenol-novolac based benzoxazine and bisoxazoline or epoxy resin with the latent curing agent had inferior heat resistance, flame resistance, and mechanical properties to those from bisphenol-A based benzoxazine and bisoxazoline or epoxy resin with the latent curing agent because of the ununiform curing reaction.

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