New Type of Phenolic Resin—The Curing Reaction of Bisphenol A Based Benzoxazine with Bisoxazoline and the Properties of the Cured Resin. III. The Cure Reactivity of Benzoxazine with a Latent Curing Agent

Hajime Kimura, Akihiro Matsumoto, Keiko Ohtsuka

Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-Ku, Osaka, 536-8553 Japan

ABSTRACT: The curing reaction of a bisphenol A based benzoxazine [2,2-bis(3,4-dihydro-3-phenyl-1,3-benzoxazine) propane (Ba)] and bisoxazoline with a latent curing agent and the properties of the cured resins were investigated. With a latent curing agent, the ring-opening reaction of the benzoxazine ring occurred more rapidly, and then the phenolic hydroxyl group generated by the ring-opening reaction of the benzoxazine ring also reacted with the oxazoline ring more rapidly. The cure time of molten resins from Ba and bisoxazoline with a latent curing agent was reduced, and the cure temperature was lowered, in comparison with those of resins from Ba and bisoxazoline without a latent curing agent. The melt viscosity of molten resins from Ba and bisoxazoline with a latent curing agent was kept around 50 Pa s at 80°C even after 30 min, and molten resins from Ba and bisoxazoline with a latent curing agent showed good thermal stability below 80°C. However, above 170°C, the curing reaction of Ba with bisoxazoline with a latent curing agent proceeded rapidly. Cured resins from Ba and bisoxazoline with a latent curing agent showed good heat resistance, flame resistance, mechanical properties, and electrical insulation in comparison with cured resins from Ba and bisoxazoline without a latent curing agent. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 710–718, 2008

Key words: curing of polymers; resins; thermosets

INTRODUCTION

Phenolic resins are used widely as industrial materials because of their good heat resistance, electrical insulation, dimensional stability, flame resistance, and chemical resistance. However, there are a number of shortcomings associated with traditional phenolic resins. For example, hexamethylenetetramine (hexamine) is used as a curing agent. In the curing process of novolac hexamine, volatiles such as water and ammonia compounds are released because of a condensation reaction. These volatiles sometimes reduce the properties of cured phenolic resins because of the formation of microvoids. Acid or base compounds, which result in corrosion of the processing equipment, must be used as catalysts to synthesize novolac or resole precursors for cured phenolic resins. Another problem is the brittleness of cured phenolic resins.

It is well known that the benzoxazine ring is stable at low temperatures, but the ring-opening reaction occurs at high temperatures, and novolac-type oligomers having both phenolic hydroxyl and tertiary amine groups are produced[1] (Fig. 1). Through the use of this benzoxazine compound as a phenolic resin, a new type of phenolic resin that releases no volatiles during the curing reaction and needs no catalysts has been developed.

Ishida and coworkers[2–24] synthesized many 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[27–30] and furan-modified[31] benzoxazines have been synthesized, and the properties of the cured resins have been investigated. Nanocomposites using benzoxazines also recently have been reported.[32–35] The reactivity of compounds that have benzoxazine rings with other compounds has been investigated. We have already investigated the curing behavior of bisphenol A based, terpenediphenol-based, and poly(p-vinylphenol)-based benzoxazines with epoxy resins or bisoxazoline and the properties of the cured resins.[36–40] A molding compound from a bisphenol A based benzoxazine that contained no oligomers [2,2-bis(3,4-dihydro-3-phenyl-1,3-benzoxazine)propane (Ba)] and bisoxazoline showed good flowability below 140°C, and the curing

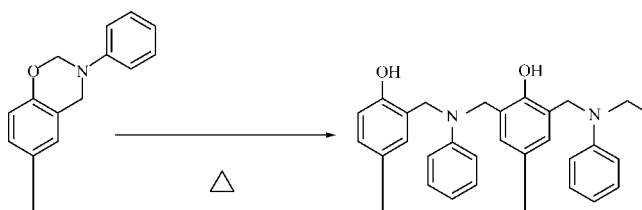*Correspondence to:* H. Kimura (kimura@omtri.city.osaka.jp).

Figure 1 Ring-opening reaction of a benzoxazine ring.

reaction proceeded rapidly above 180°C. The cured resins from the benzoxazine compounds and epoxy resins or bisoxazoline had superior heat resistance, electrical insulation, and water resistance versus the cured resins from conventional bisphenol A type novolac and epoxy resins or bisoxazoline.

Despite the high performance (e.g., good heat and water resistance) of benzoxazine-based resins, it is believed that benzoxazine-based resins have surprisingly low crosslink densities in comparison with ordinary thermosetting resins.[8] Then, the most important problems are that the cure time of benzoxazine compounds is long and that the cure temperature is high.

In this study, we aimed to reduce the cure time of a benzoxazine compound and to lower its cure temperature. Therefore, we prepared heat latent curing agents from acids and amines and investigated the catalytic effects of the latent curing agents on the curing reaction of Ba with bisoxazoline and the properties of the cured resins.

EXPERIMENTAL

Materials

Ba was supplied by Shikoku Chemicals Co., Ltd. (Kagawa Prefecture, Japan). Diethanolamine, isopropanolamine, diethylethanolamine, methylamine, and *p*-toluenesulfonic acid were purchased from Nacalai Tesque Co., Ltd. (Kyoto Prefecture, Japan). 2,2′-(1,3-Phenylene)-bis(4,5-dihydro-oxazole) (1,3-PBO) as a bisoxazoline was supplied by Mikuni Pharmaceutical Industrial Co., Ltd. (Osaka Prefecture, Japan). All chemicals were used without further purification. The chemical structures of Ba and 1,3-PBO are shown in Figure 2.

Preparation of the heat latent curing agent

The preparation of the heat latent curing agent was carried out through the reaction of the acids and amine compounds. In a typical experiment, diethanolamine as an amine compound (5.26 g, 0.05 mol) was charged into 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 resins and curing conditions

Samples containing 50 mol % Ba and 50 mol % 1,3-PBO with a 1, 3, 5, or 10 wt % concentration of a latent curing agent were prepared and cured in a mold at a specified temperature in an oven. At first, each sample, containing 50 mol % Ba and 50 mol % 1,3-PBO, was heated to about 150°C, and a clear molten mixture was obtained. After the molten mixture cooled to 100°C, a latent curing agent (1, 3, 5, or 10 wt %) was added to the molten mixture, which was stirred. The clear molten mixture that was obtained was poured into a silicone rubber mold and cured at a specified temperature in the oven. The curing conditions were determined to be 150°C for 2 h and 170°C for 2 h or 150°C for 2 h, 170°C for 2 h, and 200°C for 2 h from the results of differential scanning calorimetry (DSC). DSC was performed at a heating rate of 10°C/min under an N_2 atmosphere on a Seiko Instruments Co., Ltd. (Chiba Prefecture, Japan), STI EXSTAR 6000. For comparison, the curing reaction of 50 mol % Ba and 50 mol % 1,3-PBO was also carried out under the same conditions.

Properties of the molten and cured resins

To investigate the catalytic effect of the latent curing agent on the curing reaction, the gelation time was estimated according to JIS K6910. That is, a spatula was placed on a steel plate, and the steel plate and spatula were heated to a constant temperature. Approximately 0.5 g of a sample was put on the steel plate and spread
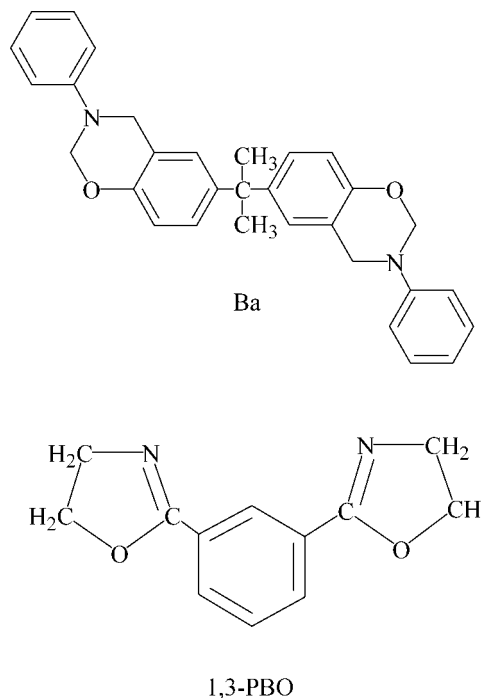

Figure 2 Chemical structures of Ba and 1,3-PBO.

into a disc approximately 3 cm in diameter with the spatula. Then, the sample was kneaded by uniform pressing approximately once a second, but with care to avoid spreading. The time at which the sample did not string to the spatula anymore was measured. It was taken as the gelation time of the sample.

The structure of the cured resins was analyzed with a Fourier transform infrared (FTIR) spectrophotometer. FTIR measurements were carried out on a Nicolet (Kanagawa Prefecture, Japan) Impact 420 instrument. The spectral range was 4000–400 cm^{-1}. One hundred twenty-eight scans were coadded at a resolution of 4 cm^{-1}. The samples were prepared as KBr pellets.

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 performed with a three-point-bending method at 1 Hz, at a 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 to 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 the test piece, L is the support span, W is the width of the test piece, h is the depth of the test piece, and F/Y is the gradient of the load–deflection curve in the linear portion.

The fracture toughness was estimated with the critical stress intensity factor (K_{IC}) according to ASTM D 5045.

The electrical insulation was estimated with the volume resistivity (ρ_V). ρ_V was measured with a Yokogawa–Hewlett–Packard Co., Ltd. (Tokyo, Prefecture, Japan), HP4339A according to JIS K6911. That is, 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. ρ_V was calculated with the following equation:

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

where d is the outside diameter of the inner circle of the face electrode and t is the thickness of the 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 by being placed in water kept at the temperature of the testing room for 15 min. After being taken 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 with the following equation:

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

The flame resistance was estimated by UL-94 and the limited oxygen index (LOI). UL-94 was conducted according to the UL-94 standard. Five specimens with dimensions of 125 mm × 13 mm were tested. Town gas was supplied to the burner shell, and the burner was adjusted to produce a blue flame 20 mm high. By applying the flame centrally to the middle point of the bottom edge of the specimen, we maintained the distance 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 D 2863. The percentage in the oxygen/nitrogen mixture deemed sufficient to sustain the flame was taken as the LOI.

The measurements for the melt viscosity were conducted on a UBM Co., Ltd. (Kyoto Prefecture, Japan), Rheosol-G3000 dynamic mechanical spectrometer with a 25-mm parallel-plate fixture at various temperatures. The plates were preheated to 50°C before the test. Next, the plates were heated from 50°C to the measuring temperature (80, 150, 170, or 200°C) at a rate of 30°C/min. The melt viscosity for the isothermal test at the measuring temperature was measured as a function of time.

Thermogravimetric analysis (TGA) was applied to evaluate the thermal stability. TGA was performed at heating rate of 10°C/min under an N$_2$ atmosphere on a Seiko Instruments TGA 5200 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Curing behavior of the molten resins from Ba and 1,3-PBO with the latent curing agents

The curing behaviors were estimated with DSC and the gelation time. DSC and the gelation time are

TABLE I
DSC Results for the Molten Resins of Ba and 1,3-PBO with or Without the Latent Curing Agent

Sample	Peak starting temperature (°C)	Peaking temperature (°C)
Ba/1,3-PBO/cat.1 (1 wt %)	120	235
Ba/1,3-PBO/cat.1 (3 wt %)	113	234
Ba/1,3-PBO/cat.1 (5 wt %)	105	233
Ba/1,3-PBO/cat.1 (10 wt %)	98	171
Ba/1,3-PBO	180	234

TABLE III
DSC Results for the Molten Resins of Ba and 1,3-PBO with or Without the Latent Curing Agent

Sample	Peak starting temperature (°C)	Peak temperature (°C)
Ba/1,3-PBO/cat.1 (10 wt %)	98	171
Ba/1,3-PBO/cat.2 (10 wt %)	74	164
Ba/1,3-PBO/cat.3 (10 wt %)	107	191
Ba/1,3-PBO/cat.4 (10 wt %)	77	162
Ba/1,3-PBO	180	234

very effective methods for evaluating the curing properties of thermosetting resins.

Tables I–IV show the DSC results and gelation times of the molten resins from 50 mol % Ba and 50 mol % 1,3-PBO with or without a latent curing agent. Four kinds of latent curing agents were used; they were the salts of p-toluenesulfonic acid and diethanolamine (cat.1), p-toluenesulfonic acid and isopropanolamine (cat.2), p-toluenesulfonic acid and diethylethanolamine (cat.3), and p-toluenesulfonic acid and methylamine (cat.4). p-Toluenesulfonic acid was used as an acid because it was more reactive than other acids such as carboxylic acid and phenol.[42] From the results of DSC (Table I), both the peak starting temperature and peak temperature decreased when the concentration of the latent curing agent (cat.1) was increased from 1 to 10 wt %. As also shown in Table II, the gelation time decreased when the concentration of the latent curing agent (cat.1) was increased from 1 to 10 wt % at each temperature. The most effective concentration of the latent curing agent for the rapid curing reaction was 10 wt %.

Tables III and IV show the DSC results and gelation times of the molten resins from 50 mol % Ba and 50 mol % 1,3-PBO with a latent curing agent (10 wt %). When cat.2 or cat.4 was used as the latent curing agent, the peak starting temperature or peak temperature from DSC decreased to about 70 or 160°C, and the gelation time decreased to 3 min at 150°C. The most effective latent curing agent for the rapid curing reaction was cat.2 or cat.4. This might be because the bivalent amine of isopropanolamine or methylamine was more effective than the univa-lent amine of diethanolamine or diethylethanol-amine.

As shown in Table IV, the molten resins from Ba and 1,3-PBO without a latent curing agent were thermally stable, and the gelation reaction could not occur, for example, at 150°C for more than 60 min. This was because the ring-opening reaction of the benzoxazine ring was difficult to produce under 150°C, and the phenolic hydroxyl groups that contributed to the curing reaction were not produced. That is, the cure time of the benzoxazine compounds was long, and the cure temperature was high.

However, the gelation time was shortened with the amount of the latent curing agent. This was because, with the addition of a latent curing agent, the benzoxazine ring opened, and the phenolic hydroxyl groups that contributed to the curing reaction were produced more easily; then, the curing reaction of Ba and 1,3-PBO proceeded.

A latent curing agent shows no activity under normal conditions but does show activity under external stimulation such as heating or photoirradiation. The latent curing agents in this study consisted of the salts of 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 the benzoxazine (Ba) and bisoxazoline (1,3-PBO). In the presence of liberated acids, a proton rapidly transferred and generated a phenolate ion. This phenolate ion could then react with another benzoxazine (Ba) or bisoxazoline (1,3-PBO), and the curing reaction (copolymerization)

TABLE II
Gelation Time for the Molten Resins of Ba and 1,3-PBO with or Without the Latent Curing Agent

Sample	120°C	150°C	170°C	200°C
Ba/1,3-PBO/cat.1 (1 wt %)	>60	32	14	5
Ba/1,3-PBO/cat.1 (3 wt %)	55	17	6	2
Ba/1,3-PBO/cat.1 (5 wt %)	47	12	5	2
Ba/1,3-PBO/cat.1 (10 wt %)	25	6	2	1
Ba/1,3-PBO	>60	>60	43	7

TABLE IV
Gelation Time for the Molten Resins of Ba and 1,3-PBO with or Without the Latent Curing Agent

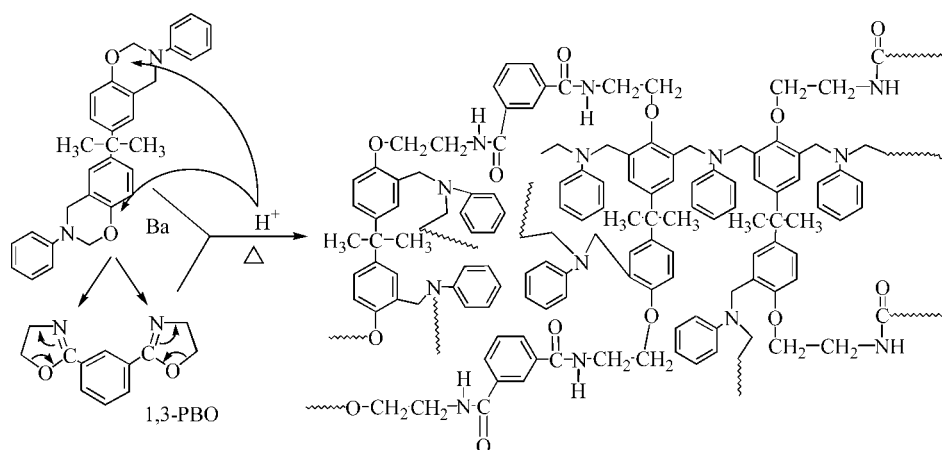| Sample	120°C	150°C	170°C
Ba/1,3-PBO/cat.1 (10 wt %)	25	6	2
Ba/1,3-PBO/cat.2 (10 wt %)	11	3	1
Ba/1,3-PBO/cat.3 (10 wt %)	25	6	2
Ba/1,3-PBO/cat.4 (10 wt %)	12	3	1
Ba/1,3-PBO	>60	>60	43

Figure 3 Curing reaction (copolymerization) of Ba with 1,3-PBO.

of Ba with 1,3-PBO proceeded, as shown in Figure 3.[43] Also, amines liberated at a high temperature could react with the oxazoline ring, as shown in Figure 4. Liberated acids (p-toluenesulfonic acid) could react with the oxazoline ring, as shown in Figure 5. In this way, the curing reaction of benzoxazine (Ba) and bisoxazoline (1,3-PBO) with a latent curing agent could proceed more rapidly than that without a latent curing agent; that is, it could reduce the cure time and lower the cure temperature. It was though that acids and amines, which the latent curing agents liberated by high-temperature decomposition, might be incorporated into the curing system of benzoxazine and bisoxazoline.

Melt viscosity of the molten resins from Ba and 1,3-PBO with the latent curing agents

The results of DMA at 80, 150, 170, and 200°C are shown in Figure 6. The melt viscosity of the molten resins was kept at a low value of about 50 Pa s at 80°C even after 30 min. The molten resins showed good thermal stability under 80°C because the ring-opening reaction of the benzoxazine ring was diffi-
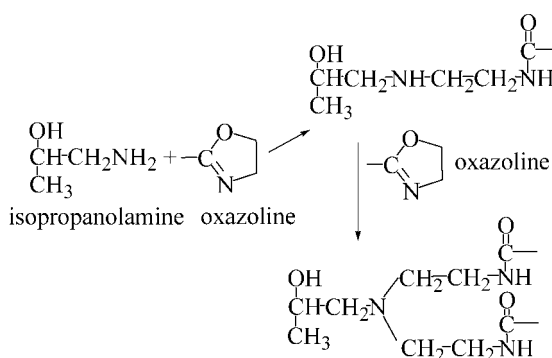
cult to perform at the low temperature at which the latent curing agent could not liberate acids and amines, and the phenolic hydroxyl groups that contributed to the curing reaction were not produced. However, because the benzoxazine ring opened and the phenolic hydroxyl groups were produced easily above 150°C, at which the latent curing agent could liberate acids and amines, and then the curing reactions, as shown in Figures 3–5, occurred, the melt viscosity increased rapidly, as shown in Figure 6.

Curing reaction of Ba and 1,3-PBO with the latent curing agents

To investigate the curing reaction of Ba with 1,3-PBO with the latent curing agents, FTIR measurements were carried out. FTIR spectra of the compound before and after the curing reaction of Ba and 1,3-PBO with a latent curing agent (cat.2) are shown in Figure 7. The absorptions at 1492 and 939 cm^{-1}, assigned to the trisubstituted benzene ring in the benzoxazine ring structure, disappeared [Fig. 7(a)]. As shown in Figure 7(b), after the curing reaction, a broad absorption at about 3360 cm^{-1}, assigned to the secondary amine group and a very small amount of the phenolic hydroxyl group that could not react with the oxazoline ring, appeared. An absorption at 1504 and 1600 cm^{-1}, assigned to the amide group, an absorption at 1222 cm^{-1}, assigned to the asymmetric stretching of the C—O—C ether group, an absorption at 1166 cm^{-1}, assigned to the symmetric stretching of

Figure 4 Curing reaction of amines liberated with an oxazoline ring.
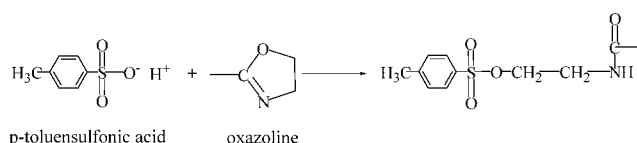

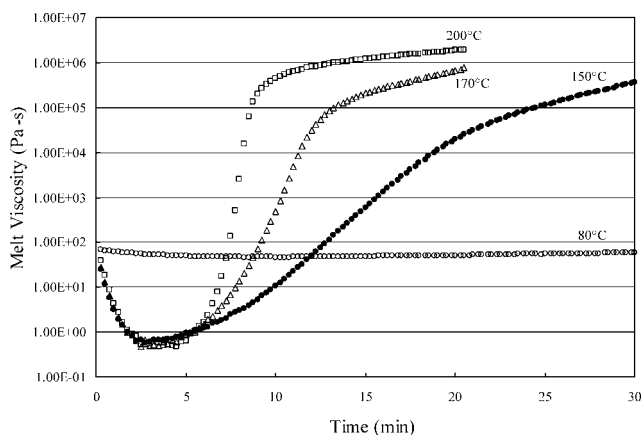**Figure 5** Curing reaction of acids liberated (p-toluenesulfonic acid) with an oxazoline ring.

Figure 6 Melt viscosity of the molten resins from Ba and 1,3-PBO with cat.2 (10 wt %).

the SO$_3$—C group, and an absorption at 1116 cm^{-1}, assigned to the stretching of the secondary alcohol (C—O) group, also appeared. It was suggested that the ring-opening reaction of the benzoxazine ring occurred, and then the phenolic hydroxyl groups generated by the ring-opening reaction of the benzoxazine ring reacted with the oxazoline ring, as shown in Figure 3. Then, it was suggested that the curing reaction, as shown in Figures 4 and 5, also occurred. It was thought that the amide groups generated by the ring-opening reaction of the oxazoline ring could not be associated with the curing reaction because the resonance effect of the amide group could lessen the nucleophilicity of nitrogen and the reactivity of the secondary amine group (amide group) to the oxazoline ring was lower than that of the phenolic

hydroxyl group or amine group liberated from the latent curing agent to the oxazoline ring.

Properties of the cured resins

The properties of the cured resins from Ba and 1,3-PBO are shown in Tables V–VIII. The curing conditions were 150°C for 2 h and 170°C for 2 h in Tables V and VII. The curing conditions were 150°C for 2 h, 170°C for 2 h, and 200°C for 2 h in Tables VI and VIII. As a result, the mechanical properties (σ and K_{IC}) of the cured resins from Ba and 1,3-PBO with the latent curing agents were higher than those of the cured resins from Ba and 1,3-PBO. The cured resins from Ba and 1,3-PBO with or without a latent curing agent had extremely high ρ_V values for commercial resins. However, the water absorption after 2 h of boiling of the cured resins from Ba and 1,3-PBO with a latent curing agent was inferior to that of the cured resins from Ba and 1,3-PBO. This higher water absorption occurred because the hydrophilic components of the latent curing agents were incorporated into the curing system.

T_g of the cured resins from Ba and 1,3-PBO with a latent curing agent was much higher than that of the cured resins from Ba and 1,3-PBO, especially when the curing conditions were 150°C for 2 h and 170°C for 2 h. From the results of the flammability tests, LOI of the cured resins from Ba and 1,3-PBO with a latent curing agent (especially cat.1) was higher than that of the cured resins from Ba and 1,3-PBO. From the results of the UL-94 tests, all samples were V-0 grade. A possible reason for these results (higher mechanical properties,
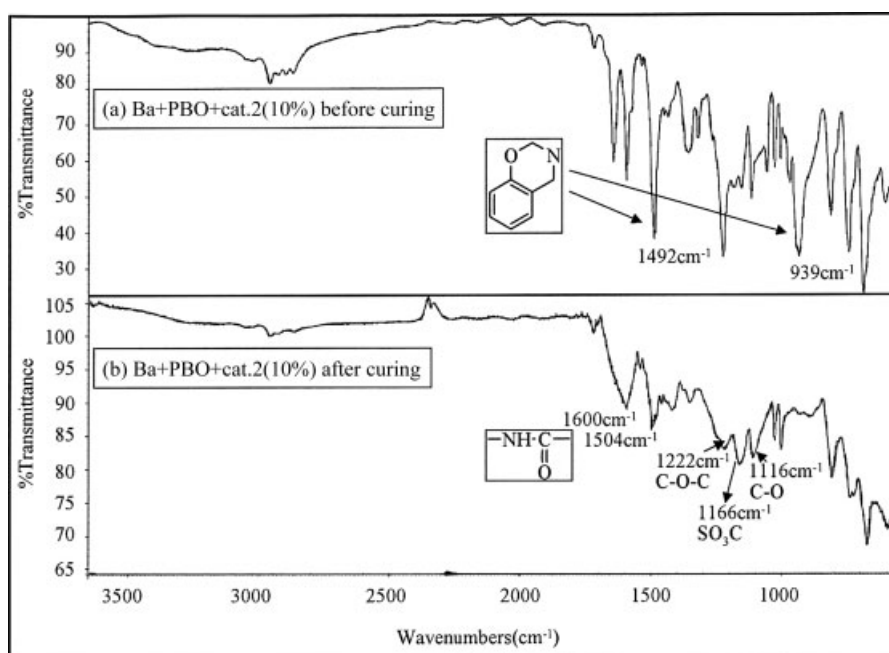

Figure 7 FTIR spectra of Ba/1,3-PBO/cat.2 (10 wt %) before and after the curing reaction.

TABLE V
Properties of the Cured Resins from Ba and 1,3-PBO with or Without the Latent Curing Agent[a]

Sample	σ (MPa)	E (GPa)	K_{IC} (MPa m$^{1/2}$)	ρ_V (Ω cm)		Water absorption (wt %)[b]
				Before boiling	After 2 h of boiling	
Ba/1,3-PBO/cat.1	114	4.6	1.05	2.6×10^{16}	1.3×10^{14}	1.34
Ba/1,3-PBO/cat.2	113	4.5	1.06	8.2×10^{16}	4.8×10^{16}	0.50
Ba/1,3-PBO	66	5.2	0.76	3.0×10^{16}	5.8×10^{15}	0.30

[a] The concentration of the latent curing agent was 10 wt %. The curing conditions were 150°C for 2 h and 170°C for 2 h.
[b] After 2 h of boiling.

TABLE VI
Properties of the Cured Resins from Ba and 1,3-PBO with or Without the Latent Curing Agent[a]

Sample	σ (MPa)	E (GPa)	K_{IC} (MPa m$^{1/2}$)	ρ_V (Ω cm)		Water absorption (wt %)[b]
				Before boiling	After 2 h of boiling	
Ba/1,3-PBO/cat.1	126	5.2	1.08	3.8×10^{16}	2.5×10^{14}	1.32
Ba/1,3-PBO/cat.2	130	4.9	1.16	4.3×10^{16}	1.4×10^{16}	0.45
Ba/1,3-PBO	101	5.2	0.68	4.9×10^{16}	1.9×10^{15}	0.22

[a] The concentration of the latent curing agent was 10 wt %. The curing conditions were 150°C for 2 h, 170°C for 2 h, and 200°C for 2 h.
[b] After 2 h of boiling.

TABLE VII
Properties of the Cured Resins from Ba and 1,3-PBO with or Without the Latent Curing Agent[a]

Sample	T_g (°C)[b]	LOI	UL-94				$\rho(E')$ (mol/m^3)
			First ignition (s)	Second ignition (s)	Dripping	Evaluation	
Ba/1,3-PBO/cat.1	177	33	0.9	2.5	No	V-0	2.6×10^3
Ba/1,3-PBO/cat.2	181	29	0.7	0.4	No	V-0	2.9×10^3
Ba/1,3-PBO	149	24	1.2	22.3	No	V-0	8.7×10^2

[a] The concentration of the latent curing agent was 10 wt %. The curing conditions were 150°C for 2 h and 170°C for 2 h.
[b] The peak temperature of tan δ by DMA.

heat resistance, and flame resistance) was that the crosslink density might have been augmented.

This idea was supported by DMA. The crosslink density [$\rho(E')$] as a function of the storage modulus can be calculated with the equation of state for rubbery elasticity:[44]

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

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 T.

This equation is applicable to polymer networks that have a rubbery plateau region.[44] Although the adoption of this equation to a highly crosslinked systems is beyond the applicability of the rubber elasticity theory, there is no theoretical equation to calculate the 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 according to this equation to compare the crosslink densities of the samples.[10,45,46] The results are shown in Tables VII and VIII, under the assumption that Φ is

TABLE VIII
Properties of the Cured Resins from Ba and 1,3-PBO with or Without the Latent Curing Agent[a]

Sample	T_g (°C)[b]	LOI	UL-94				$\rho(E')$ (mol/m^3)
			First ignition (s)	Second ignition (s)	Dripping	Evaluation	
Ba/1,3-PBO/cat.1	186	34	0.1	0.2	No	V-0	3.5×10^3
Ba/1,3-PBO/cat.2	185	29	0.0	0.1	No	V-0	3.6×10^3
Ba/1,3-PBO	186	33	2.1	2.4	No	V-0	2.5×10^3

[a] The concentration of the latent curing agent was 10 wt %. The curing conditions were 150°C for 2 h, 170°C for 2 h, and 200°C for 2 h.
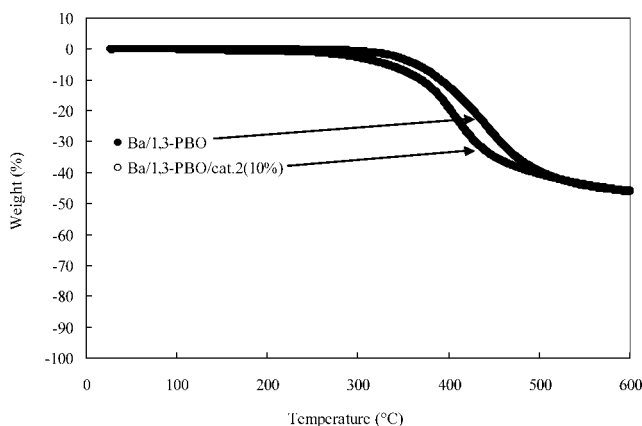[b] The peak temperature of tan δ by DMA.

Figure 8 TGA curves of the molten resins from Ba and 1,3-PBO with or without the latent curing agent.

equal to 1.[47] The values of $\rho(E')$ of the cured resins from Ba and 1,3-PBO with a latent curing agent were higher than those of the cured resins from Ba and 1,3-PBO without a latent curing agent. This suggests that the crosslink density of the cured resins from Ba and 1,3-PBO with a latent curing agent was higher than that of the cured resins from Ba and 1,3-PBO without a latent curing agent.

TGA results

Figure 8 shows the TGA curves of the molten resins from Ba and 1,3-PBO with or without a latent curing agent. For the molten resins from Ba and 1,3-PBO with a latent curing agent, the initial decomposition, which was defined as a 5 wt % mass loss, occurred around 332°C, and the char yield at 600°C was 54 wt %. For the molten resins from Ba and 1,3-PBO without a latent curing agent, the initial decomposition, which was defined as a 5 wt % mass loss, occurred around 364°C, and the char yield at 600°C was 54 wt %. In terms of the thermogravimetric results, the thermal stability of the molten resins from Ba and 1,3-PBO with a latent curing agent was almost same as that of the molten resins from Ba and 1,3-PBO without a latent curing agent, as shown in Figure 8.

CONCLUSIONS

The purpose of this study was to achieve a higher crosslink density for a cured resin from a benzoxazine-based resin and especially to reduce the cure time and lower the cure temperature of the benzoxazine compound. We investigated the curing reaction of Ba and bisoxazoline with latent curing agents and the properties of the cured resins. The molten resins from benzoxazine and bisoxazoline with a latent curing agent showed good thermal stability below 80°C. However, above 150°C, the curing reaction of ben-

zoxazine and bisoxazoline with a latent curing agent proceeded more rapidly than that of benzoxazine and bisoxazoline without a latent curing agent. The cure time of the molten resins from benzoxazine and bisoxazoline with a latent curing agent could be reduced, and the cure temperature could also be lowered, in comparison with those of the molten resins from Ba and bisoxazoline without a latent curing agent. The cured resins from benzoxazine and bisoxazoline with a latent curing agent had superior heat resistance, flame resistance, mechanical properties, and electrical insulation in comparison with those from Ba and bisoxazoline without a latent curing agent because of the higher crosslink density.

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