### New Thermosetting Resin From Bisphenol A-Based Benzoxazine and Bisoxazoline

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Received 10 April 1998; accepted 12 November 1998

**ABSTRACT:** Bisphenol A-based benzoxazine was prepared from bisphenol A, formaline, and aniline. Curing reaction of bisphenol A-based benzoxazine with bisoxazoline and the properties of the cured resin were investigated. Consequently, using triphenylphosphite as a catalyst, for the first time the ring-opening reaction of benzoxazine ring occurred at 170°C, and then the phenolic hydroxyl group generated by the ring-opening reaction of the benzoxazine ring reacted with the oxazoline ring at 200°C. The melt viscosity of the molding compound was kept 0.1–1 Pa · s at 140°C even after 1.5 h, and increased rapidly at 180°C. It was realized that the molding compound showed good flowability below 140°C, curing reaction proceeded above 180°C rapidly. The cured resin from bisphenol A-based benzoxazine and bisoxazoline showed good heat resistance, water resistance, electrical insulation, and mechanical properties, compared with the cured resin from bisphenol A-type novolac and bisoxazoline. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1551–1558, 1999

**Key words:** phenolic resin; benzoxazine; bisoxazoline; ring opening reaction; thermal stability

### INTRODUCTION

Phenolic resin is widely used as an industrial material because of its good heat resistance, electrical insulation, dimensional stability, and chemical resistance. Recently, the improvement in properties, especially toughness and heat resistance, have been required, particularly for the industrial field. However, the improvement of mechanical properties, especially toughness, is usually incompatible with the improvement of heat resistance.

Many approaches have been tried in an attempt to improve the heat resistance of phenolic resin. Fukuda et al.<sup>1</sup> have improved the heat resistance of the phenolic resins by means of the after-cure or the increase in hardening agent con-

tent. It was reported<sup>2</sup> that high heat-resistant phenolic resins were produced by the addition of a modifier with good heat resistance. But in these approaches, mechanical properties of phenolic resin, for example, flexural strength or impact resistance, were reduced. There were a few articles<sup>3–5</sup> related to the modified phenolic resins of which both heat resistance and mechanical properties were superior to unmodified phenolic resin. But in these studies, hexamethylenetetramine (hexamine) was used as a curing agent. In the curing process of novolac-hexamine, volatiles such as water, ammonia compounds, etc., are released. These volatiles sometimes reduced the properties of cured phenolic resin due to the formation of microvoid.

Culbertson et al.<sup>6</sup> have developed phenolic resin cured by phenylene-bisoxazoline. Phenolic resin cured by phenylene-bisoxazoline had low cure shrinkage and good toughness while retaining high heat resistance, low flammability, and

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Journal of Applied Polymer Science, Vol. 72, 1551–1558 (1999)

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**Figure 1** Ring-opening reaction of an oxazoline ring with a phenolic hydroxyl group.

low smoke emission. The chain-extending and crosslinking reaction of phenolic resin with bisoxazolines take advantage of the heat-activated ring-opening reaction of an oxazoline ring compound with an acidic phenolic hydroxyl group, as shown in Figure 1.

However, the pure bisoxazoline monomer has a relatively high melting point and a crystalline structure. Melting point of 2,2'-(1,3-phenylene)bis(4,5-dihydro-oxazoles) (i.e., 1,3-PBO) is 149-151°C. Thus, the processability of the molding compound prepared from phenolic resin and 1,3-PBO is very poor. Even if the phenolic resin is kneaded with 1,3-PBO, it is necessary to increase the kneading temperature above 170°C to decrease the melt viscosity of the molding compound. But when the catalyst for the curing reaction is added at this temperature, it is difficult to process the molding compound, because gelation occurs very fast. It is highly desirable that the molding compounds prepared from phenolic resin and 1,3-PBO have low viscosities at 100-140°C. Namely, the resin system must maintain the high flowability at 100-140°C during the required time to achieve melt impregnation of unidirectional fiber, fiber mats, etc., or the required time to fill a mold cavity in a resin transfer molding (RTM) process.<sup>6</sup>

Our objective in this study is to develop a new type of bisoxazoline-phenolic resin, which has a good thermal stability and good flowability at 100-140°C and can be molded by melt impregnation or RTM.

It is well known that the benzoxazine ring is stable at low temperature, but the ring-opening reaction occurs at high temperature, and both the phenolic hydroxyl group and the tertiary amine group are produced<sup>7</sup> (Fig. 2). Using this benzoxazine compound as phenolic resin, it is expected to develop a new type of bisoxazoline-phenolic resin that has good thermal stability at low temperature.

Recently, Ishida et al.<sup>8-15</sup> synthesized many types of oxazines and studied the cure kinetics, mechanical and dynamic mechanical properties, and so on. Shin et al.<sup>16</sup> also studied the cure kinetics of a benzoxazine-based phenolic resin.



Figure 2 Ring-opening reaction of a benzoxazine ring.

Jang et al.<sup>17</sup> studied the performance improvement of rubber-modified polybenzoxazine. However, the reactivity of compounds that have a benzoxazine ring with other compounds are scarcely investigated. We also investigated the curing behavior of the bisphenol A-based benzoxazine with epoxy resin and the properties of the cured epoxy resin.<sup>18</sup>

In this report, we investigated the curing behavior of bisphenol A-based benzoxazine with bisoxazoline and the properties of the cured resin.

#### **EXPERIMENTAL**

#### Materials

Bisphenol A, dioxane (98%), aniline (99%), and formaldehyde (37% in water) were purchased from Nakarai Tesuku Co., Ltd. Triphenylphosphite, used as a catalyst, was purchased from Yoneyama Chemical Co., Ltd. 2,2'-(1,3-Phenylene)-bis(4,5-dihydro-oxazoles) (i.e., 1,3-PBO) was supplied by Takeda Chemical Industries Ltd. Bisphenol A-type novolac (BisA-N,  $M_n = 560$ ,  $M_w = 1670$ ) was supplied by Yuka-Shell Epoxy Co., Ltd. (Fig. 3). All chemicals were used without further purification.



1,5-1 00

Figure 3 Chemical structure of BisA-N and 1,3-PBO.



Figure 4 Synthesis of B-a.

#### Synthesis of Benzoxazine

Bisphenol A-based benzoxazine (B-a) was synthesized according to the method explained by Ishida et al.<sup>8</sup> (Fig. 4). The general procedure is as follows: 0.2 mol aniline in 20 mL dioxane is added slowly to 0.4 mol formaldehyde (37% in water) in 80 mL dioxane, keeping the temperature below 10°C in ice bath. The mixture is stirred for 10 min, 0.1 mol bisphenol A in 100 mL dioxane is added to the mixture, and then the temperature is raised and the mixture solution is refluxed for 6 h. The solvent is then evaporated and the viscous fluid is dissolved in ethyl ether. The ether solution is washed with water and 3 N NaOH solution several times. Ethyl ether is evaporated to give a white fine powder.

#### **Curing Condition**

Samples containing 50 mol % B-a and 50 mol % 1,3-PBO were prepared and cured in a mold at a specified temperature in the oven. The curing condition was determined as  $170^{\circ}C/2$  h +  $200^{\circ}C/2$  h +  $230^{\circ}C/2$  h +  $250^{\circ}C/2$  h from the results of differential scanning calorimetry (DSC) measurement. For comparison, the curing reaction of 50 mol % BisA-N with 50 mol % 1,3-PBO was also carried out on the same condition ( $170^{\circ}C/2$  h +  $200^{\circ}C/2$  h +  $230^{\circ}C/2$  h +  $250^{\circ}C/2$  h.

## Properties of the Cured Bisoxazoline-Phenolic Resin

The structure of the cured bisoxazoline-phenolic resin was analyzed by Fourier Transform Infrared Spectrophotometer.

To investigate the thermal stability of the molding compound, gelation time was estimated according to JIS K6910. Namely, a spatula was placed on the steel plate and the steel plate and spatula were heated to a constant temperature. Approximately 0.5 g of the sample was put on the steel plate and spread to a disc approximately 3 cm in diameter with the spatula. Then the sample was kneaded by pressing it uniformly approximately once per second, but with care to avoid



**Figure 5** DSC curves of the molding compound prepared from 50 mol % B-a and 50 mol % 1,3-PBO (a) with triphenylphosphite, (b) without triphenylphosphite as a catalyst.

Temp. (°C)	Gelation Time (min)			
	B-a + 1,3-PBO <sup>a</sup>	B-a + 1,3-PBO		
170	43	72		
180	22	51		
190	14	32		
200	7	16		
210	5	9		
220	4	6		

Table I Gelation Time of B-a + 1,3-PBO + cat. and B-a + 1,3-PBO

<sup>a</sup> Cat. Triphenylphosphite, 1 wt %.

spreading. The time until when the sample does not string to the spatula any more was measured. It was taken as the gelation time of the sample.

The properties of the cured bisoxazoline-phenolic resin were characterized by heat resistance, fracture toughness, electrical insulation, and water absorption. Heat resistance was estimated by glass transition temperature  $(T_g)$  on dynamic mechanical analysis. The peak temperature of tan  $\delta$ by dynamic mechanical analysis was considered as  $T_{\sigma}$ .<sup>19</sup> 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 Co., Ltd. HP4339A according to JIS K6911. Namely, the disk test pieces (approximately 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.

$$ho_v = \pi d^2/4t imes R_v$$

where  $\rho_v$  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 (approximately 50-mm diameter 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.

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

Melt viscosity was measured on dynamic mechanical analysis using a 40-mm parallel plate fixture. The plates were preheated to 100°C before the test. The melt viscosity for nonisothermal test from 100°C to the measuring temperature at 30°C/min, and the melt viscosity for isothermal test at the measuring temperature were measured as a function of time.

#### Characterization

FTIR measurement was carried out on Nicolet Impact 420 instrument. The spectral range was 4000–400 cm<sup>-1</sup>. One hundred twenty-eight scans were cumulated at a resolution of 4 cm<sup>-1</sup>. Samples were prepared as KBr pellets. Differential scanning calorimetry was measured with a heating rate of 10°C/min under N2 atmosphere on a Seiko Instruments Co., Ltd. STI EXATAR6000. Dynamic mechanical analysis was measured by a three-point bending method at 1 Hz with a heating rate of 2°C/min on a Seiko Instruments Co., Ltd. DMS-110 Dynamic Mechanical Analysis Spectrometer. Measurements for melt viscosity were conducted on a Rheometric Scientific F. E. Ltd. Dynamic Mechanical Spectrometer (ARES-2KFRTN1) by using a 40-mm parallel plate fixture at various temperatures.

#### **RESULTS AND DISCUSSION**

# Effect of Catalyst on Curing Reaction of B-a with 1,3-PBO

DSC curves of the molding compound prepared from 50 mol % B-a and 50 mol % 1,3-PBO are



**Figure 6** Reciprocal plot of gelation time vs. temperature.



shown in Figure 5. An exothermic peak derived from the curing reaction was observed in both cases of (a) with 1% triphenylphosphite as a catalyst, and (b) without a catalyst. However, the curve of the molding compound with a catalyst had the sharper slope and shifted to the lower temperature than that of the molding compound without a catalyst. It was realized that curing reaction of the molding compound with a catalyst



**Figure 8** Reaction of the oxazine ring with the oxazoline ring.

proceeded more rapidly than that of the molding compound without a catalyst.

Table I shows the gelation time of the molding compound prepared from 50 mol % B-a and 50 mol % 1,3-PBO with a catalyst or without a catalyst. Furthermore, the reciprocal plot of gelation time as a function of temperature is shown in Figure 6. The molding compound was thermally stable for a long time, and curing reaction could not occur under 150°C, which corresponded to the molding temperature in the hot-melt production of prepregs, RTM, etc. It was because the ring opening reaction of benzoxazine ring occurred with difficulty under 150°C, and the phenolic hydroxyl groups that contributed to the curing reaction were not produced. However, the gelation time was shortened with the rise of the molding temperature, because the benzoxazine ring opened and the phenolic hydroxyl groups were easily produced. The reaction rate of the molding compound with a catalyst was faster than that of the molding compound without a catalyst, especially above 180°C, as shown in Figure 6. It was assumed that triphenylphosphite as a catalyst accelerated the reaction of the phenolic hydroxyl



**Figure 9** FTIR spectra of the compound prepared from 50 mol % BisA-N and 50 mol % 1,3-PBO (a) before reaction, (b)  $170^{\circ}C/1$  h, (c)  $170^{\circ}C/2$  h, (d)  $170^{\circ}C/2$  h +  $200^{\circ}C/1$  h, (e)  $170^{\circ}C/2$  h +  $200^{\circ}C/2$  h, (f)  $170^{\circ}C/2$  h +  $230^{\circ}C/1$  h, (g)  $170^{\circ}C/2$  h +  $230^{\circ}C/2$  h +  $230^{\circ}C/2$  h +  $230^{\circ}C/2$  h.

group with the oxazoline ring, and also the reaction of the amide group with the oxazoline ring.

#### Curing Reaction of B-a or BisA-N with 1,3-PBO Using a Catalyst

To investigate the curing reaction of B-a or BisA-N with 1,3-PBO using a catalyst in detail, FTIR



**Figure 10** The plot of melt viscosity of the molding compound prepared from 50 mol % B-a and 50 mol % 1,3-PBO vs. time.

measurement was carried out. FTIR spectra of the compound prepared from the curing reaction of B-a with 1,3-PBO are shown in Figure 7. The absorption at 1497 cm<sup>-1</sup> assigned to the trisubstituted benzene ring in the benzoxazine ring structure started to disappear within 1 h at 170°C [Fig. 7(b)]. When the curing condition is  $170^{\circ}$ C/2 h + 200°C/1 h, both the absorption at 3365  $\text{cm}^{-1}$ assigned to the phenolic hydroxyl group and the absorption at 1520 and 1620  $\text{cm}^{-1}$  assigned to the amide group appeared [Fig. 7(d)]. Using triphenylphosphite as a catalyst, the ring-opening reaction of the benzoxazine ring occurs at 170°C, and then the phenolic hydroxyl groups generated by the ring-opening reaction of benzoxazine ring react with the oxazoline ring at 200°C, as shown in Figure 8.

FTIR spectra of the compound prepared from the curing reaction of BisA-N with 1,3-PBO are shown in Figure 9. In contrast with the results in Figure 7 (the curing reaction of B-a with 1,3-PBO), the absorption at 1520 cm<sup>-1</sup> assigned to the amide group has already appeared within 1 h at 170°C [Fig. 9(b)]. It shows that the curing reaction of BisA-N with 1,3-PBO proceeds at a lower temperature than the curing reaction of B-a with 1,3-PBO, because BisA-N had the phenolic hy-

Sample	<i>T</i> <sup>a</sup> <sub>g</sub> (°C)	$\frac{K_{IC}}{(\mathrm{MPam}^{1/2})}$	Volume Resistivity ( $\Omega$ cm)		
			Before Boiling	After 2 h Boiling	Water Absorption <sup>b</sup> (%)
B-a/PBO BisA-N/PBO	195 189	$\begin{array}{c} 0.93 \\ 0.84 \end{array}$	$3.5 imes10^{16}\ 3.3 imes10^{16}$	$7.2  imes 10^{15} \ 6.7  imes 10^{15}$	0.28 0.60

#### Table II Properties of the Cured Resin

<sup>a</sup> Peak temp. of tan  $\delta$  by DMA.

<sup>b</sup> After 2 h boiling.

droxyl group from the beginning, which contributes to the curing reaction. Therefore, the molding compound prepared from the ordinary novolac (BisA-N) and oxazoline (1,3-PBO) is difficult to process because of the rapid premature gelation, while the molding compound prepared from benzoxazine (B-a) and oxazoline (1,3-PBO) is easy to process because of the good thermal stability under 150°C.

### Melt Viscosity of the Molding Compound Prepared from B-a and 1,3-PBO

Figure 10 shows the plot of the melt viscosity of the molding compound prepared from B-a and 1,3-PBO vs. time at various temperatures. The melt viscosity of the molding compound was kept 0.1-1 Pa  $\cdot$  s at 140°C, even after 1.5 h, and increased rapidly at 180°C. The molding compound showed good flowability under 140°C, because the ring-opening reaction of the benzoxazine ring occurred with difficulty at a low temperature and the phenolic hydroxyl groups, which contributed to the curing reaction of B-a with 1,3-PBO, were not produced. However, because the benzoxazine ring opened and the phenolic hydroxyl groups were easily produced above 180°C, melt viscosity increased rapidly because of the curing reaction of B-a with 1,3-PBO, as shown in Figure 7.

#### **Properties of the Cured Resin**

Table II shows the properties of the cured resin from B-a or BisA-N and 1,3-PBO. The curing reaction of BisA-N with 1,3-PBO was also carried out on the same condition as the curing reaction of B-a with 1,3-PBO (170°C/2 h + 200°C/2 h + 230°C/2 h + 250°C/2 h). As a result, glass transition temperature  $(T_g)$  of the cured resin from B-a and 1,3-PBO was higher than that of the cured resin from BisA-N and 1,3-PBO. This was because the movement of the molecular chain was hindered by the bulky N-Ph group between bridging points of the cured resin. The volume resistivity of the cured resin from B-a and 1,3-PBO was almost the same as that of the cured resin from BisA-N and 1,3-PBO, but the cured resin from B-a and 1,3-PBO had a relatively high volume resistivity of the commercial resins.  $K_{IC}$  of the cured resin from B-a and 1,3-PBO was also slightly higher than that of the cured resin from BisA-N and 1,3-PBO. And water absorption after 2 h boiling of the cured resin from B-a and 1,3-PBO was superior to that of the cured resin from BisA-N



Figure 11 Curing reaction of B-a with 1,3-PBO.

and 1,3-PBO. The reason for this was as follows: the cured resin from B-a and 1,3-PBO had a hydrophobic phenyl group between bridging points, and density of crosslinking was augmented by hydrogen bonding<sup>14</sup> derived from the nitrogen atom between the phenolic nuclei, and so free volume of the cured resin from B-a and 1,3-PBO was smaller than that of the cured resin from BisA-N and 1,3-PBO, as reflected by the shift in  $T_g$ .

#### CONCLUSION

The purpose of this study was the development of a new bisoxazoline-phenolic resin that had good thermal stability and good flowability at 100-140°C, and can be molded by melt impregnation, resin-transfer molding (RTM), etc. We investigated the curing reaction of bisphenol A-based benzoxazine (B-a) with 1,3-phenylenebisoxazoline (1.3-PBO), as shown in Figure 11, and the properties of the cured epoxy resin. As a result, using triphenylphosphite as a catalyst, the molding compound showed good thermal stability, and good flowability below 140°C. Above 180°C, the curing reaction proceeded rapidly. The cured resin from bisphenol A-based benzoxazine and 1,3-phenylenebisoxazoline had superior heat resistance, water resistance, and electrical insulation to those of the cured resin from bisphenol A-type novolac and 1,3-phenylenebisoxazoline.

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