Epoxy Resin Cured by Bisphenol A Based Benzoxazine

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ABSTRACT: Bisphenol A based benzoxazine was prepared from bisphenol A, formaline, and aniline. This benzoxazine was used as a hardener of the epoxy resin. Curing behavior of the epoxy resin and the properties of the cured resin were investigated. Consequently, curing reaction proceeded without a curing accelerator. The molding compound showed good thermal stability under 150°C, which corresponded to the temperature in the cylinder of injection molding. Above 150°C, the curing reaction proceeded rapidly. The cured epoxy resin showed good heat resistance, water resistance, electrical insulation, and mechanical properties compared with the epoxy resin cured by the bisphenol A type novolac. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1903–1910, 1998

Key words: epoxy resin; bisphenol A; benzoxazine

INTRODUCTION

Epoxy resin is widely used as adhesives, coatings, and laminates in the chemical, electrical, and mechanical industries. Generally, epoxy resin shows good mechanical strength and chemical resistance, but the properties depend on the type or quantity of hardeners or curing conditions. There are many kinds of hardeners such as novolac, amine, acid anhydride, and so on. They are selected according to various uses. The molding compound has been molded mainly not by injection molding but by compression or transfer molding. Compression and transfer molding are the two main methods for molding parts from thermosetting plastics. For example, in compression molding the molding compound is put between stationary and movable members of a mold. The mold is closed, and heat and pressure are applied so that the material becomes plastic, flows to fill the mold, and after a minute or more, depending on the material and thickness of the part, becomes thermosetting resin. The necessary temperature and pressure depend on the thermal and rheologi-

cal properties of the material, they may be at 150–170°C and 1000–3000 psi. In injection molding, the molding compound is preheated in a cylindrical chamber to a temperature at which it will flow, and then is forced into closed mold by means of a reciprocating screw that serves the dual purposes of providing the molten polymer and forcing it into the mold. The screw rotates to pick up the molding compound, compact and melt it, and deliver it to the entrance to the mold. The screw then moves forward to force a fixed volume of the molten polymer into the closed mold. After the molten polymer has solidified in the mold, the screw rotates and moves backward to ready the charge of the molding compound for the next cycle.[1] The preheated temperature in the cylinder is about 120–150°C, depending on the material. Because the epoxy molding compound has poor heat resistance even in the cylinder of injection molding at 120–150°C and cures easily, it cannot be molded by injection molding.

Our object in this study is to develop a new type of epoxy resin, which has good thermal stability at 120–150°C and can be molded by injection molding. 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
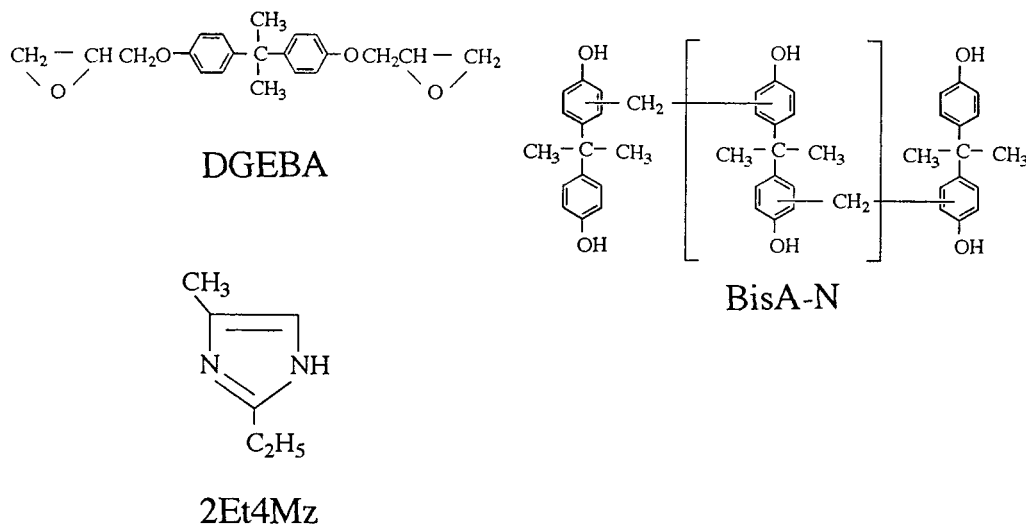
Figure 1 Chemical structure of DGEBA, BisA-N, and 2Et4Mz.

group are produced.[2] Recently, Ishida et al.[3-9] synthesized a lot of types of oxazines and studied the cure kinetics, mechanical, dynamic mechanical properties, and so on. Shin et al.[10] also studied the cure kinetics of a benzoxazine-based phenolic resin. However, the reactivity of compounds that have a benzoxazine ring with other compounds are scarcely investigated. Therefore, we investigated the curing behavior and the properties of the cured epoxy resin by bisphenol A based benzoxazine.

EXPERIMENTAL

Materials

Bisphenol A, dioxane (98%), aniline (99%), p-cresol (98%), phenylglycidyl ether (PGE, 98%), and formaldehyde (37% in water) were purchased from Nakarai Tesuku Co., Ltd. Diglycidyl ether of bisphenol A (DGEBA; epoxy equivalent, 186), bisphenol A type novolac (BisA-N, $M_n = 560$, $M_w = 1670$) were supplied from Yuka-Shell Epoxy Co., Ltd., and 2-ethyl-4-methylimidazole (2Et4Mz)

was supplied from Shikoku Chemical Co., Ltd. (Fig. 1). All chemicals were used without further purification.

Synthesis of Benzoxazines

Both bisphenol A based benzoxazine (B-a) and p-cresol based benzoxazine (C-a) were synthesized according to the method explained by Ishida et al.[3] (Figs. 2 and 3). A general procedure is as follows: 0.2 mol aniline in 20 mL dioxane was added slowly to 0.4 mol formaldehyde (37% in water) in 80 mL dioxane, keeping the temperature below 10°C in an ice bath. The mixture was stirred for 10 min, 0.1 mol bisphenol A 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 ether. The ether solution was washed with water and 3 N NaOH solution several times. Ethyl ether was evaporated to give the white fine powder.

Model Reaction

It is difficult to investigate the curing reaction of B-a with DGEBA in detail because both B-a and DGEBA have two functionality and gelation oc-
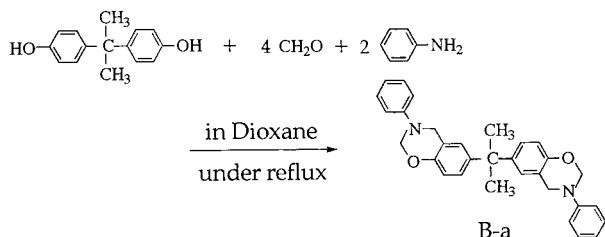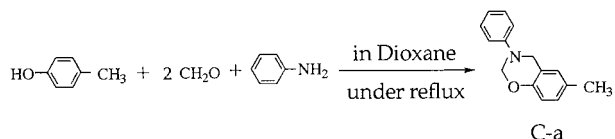

Figure 2 Synthesis of B-a.
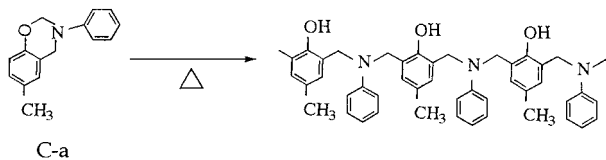

Figure 3 Synthesis of C-a.

Figure 4 Model reaction 1.

curs easily, and so the compound from the reaction is partially insoluble in the solution for measurement of nuclear magnetic resonance (NMR) such as CDCl$_3$, acetone-D, CD$_3$OD, and so on. In this way, C-a and PGE were used as each model compounds to investigate curing behavior of B-a with the epoxy resin, because both C-a and PGE have one functionality and gelation does not occur, and it is easy to investigate the curing reaction. Model reaction 1 (homopolymerization of C-a) and model reaction 2 (reaction of C-a with PGE) were investigated (Figs. 4 and 5). Compounds synthesized by model reactions were analyzed by ^{13}C-NMR and gel permeation chromatography (GPC).

Curing Condition

These samples containing 50 mol % B-a and 50 mol % DGEBA were prepared and cured in a mold at a specified temperature in the oven. The curing condition of DGEBA using B-a as a hardener was determined as 150°C/1 h + 170°/1 h + 190°C/2 h + 200°C/2 h + 220°C/2 h from the results of model reaction 2. For comparison, the curing reaction of 50 mol % DGEBA using 50 mol % BisA-N as a hardener was also carried out on the same condition (150°C/1 h + 170°C/1 h + 190°C/2 h + 200°C/2 h + 220°C/2 h).

Properties of the Cured Epoxy Resin

The structure of the cured epoxy resin was analyzed by Fourier Transform Infrared Spectrophotometer.

To investigate the thermal stability of the molding compound, gelation time was estimated according to a JIS K6910. Namely, a spatula was placed on the steel plate and the steel plate and spatula was heated to the 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 a second but with care to avoid 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 epoxy 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 δ by dynamic mechanical analysis was considered as T_g.[11]. Fracture toughness was estimated by critical stress intensity factor (K_{IC}) according to ASTM D5045. Electrical insulation was estimated by volume resistivity. Volume resisitivity was measured by Yokogawa-Hewlett-Packard Co., Ltd. HP4339A according to a 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 resisitivity was calculated by the following equation.

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

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

Water absorption was estimated according to a 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(%) = $(M_2 - M_1)/M_1 \times 100$

Characterization

^{13}C-NMR measurement was carried out on a Japan Electron Company JMN-GSX-270 instru-
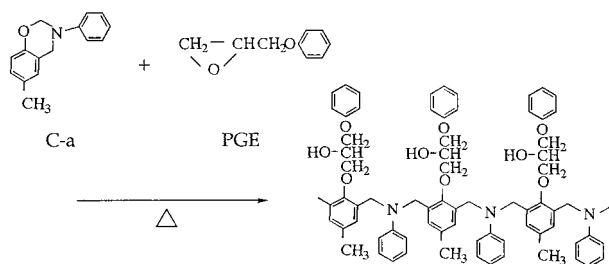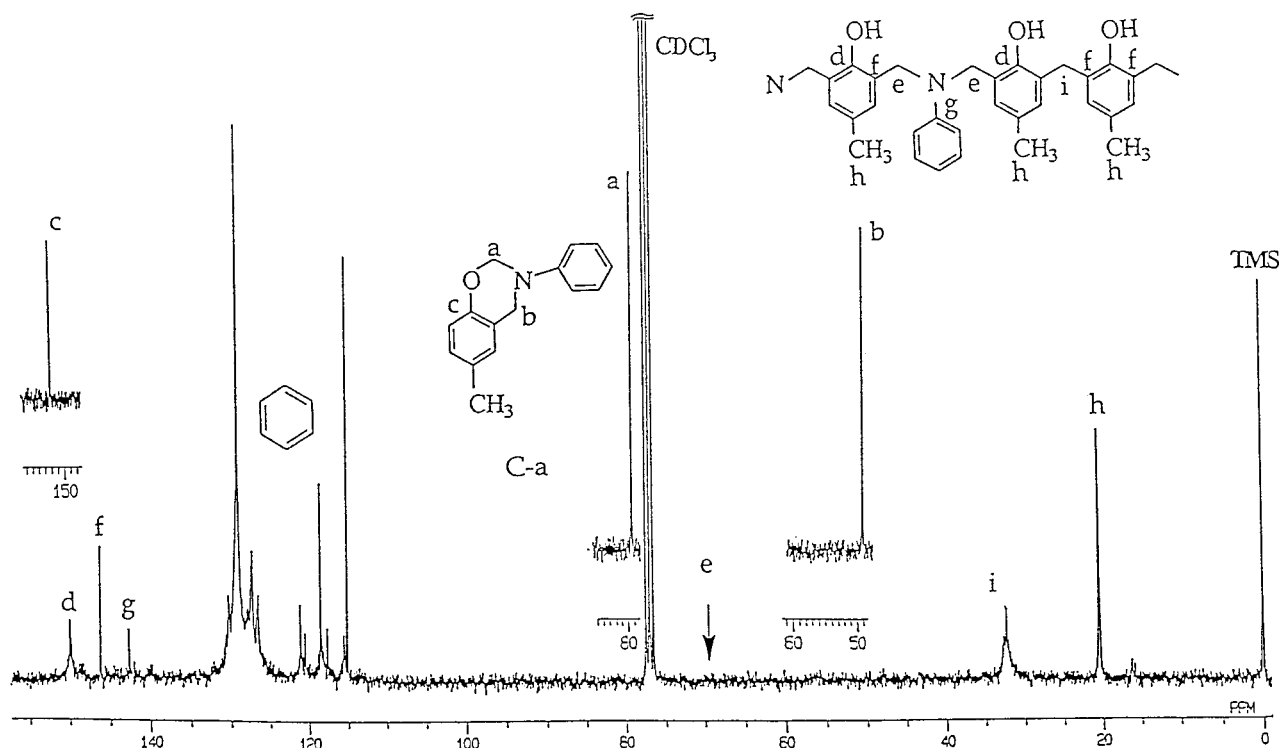

Figure 5 Model reaction 2.

Figure 6 ^{13}C-NMR spectrum of the compund synthesized by model reaction 1 at 200°C for 2 h.

ment operating at 67.8 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane was used as an internal standard. GPC measurement was carried out on Waters 150C ALC/GPC instrument with a refractive index (RI) detecter. Tetrahydrofuran was used as the eluent. Column temperature was 40°C and the flow rate was 1.0 mL/min. Polystyrene (M_n = 1800 × 10³, 670 × 10³, 200 × 10³, 110 × 10³, 37 × 10³, 20.4 × 10³, 10 × 10³, 4 × 10³, 2 × 10³, 0.8 × 10³) was used as a standard. FTIR measurement was carried out on Nicolet 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}. Samples were prepared as KBr pellets. Dynamic mechanical analysis was measured by

Table I   Results of Model Reaction 1

Temp. (°C)	Ring-Opening of Oxazine[a]	Elimination of N-Ph[a]	M_n[b]	M_w[b]	M_w/M_n[b]
140	A[c]	C[e]	—	—	—
150	A	C	240	350	1.5
160	B[d]	D[f]	570	1700	3.0
170	B	D	600	1900	3.2
180	B	D	600	1900	3.2
190	B	D	600	2100	3.5
200	B	D	600	2100	3.4
210	B	D	600	2000	3.3
220	B	D	600	1900	3.3

[a] By NMR; [b] by GPC.
[c] A; Ring-opening reaction of oxazine did not occur.
[d] B; Ring-opening reaction of oxazine occurred.
[e] C; N-Ph group was not eliminated.
[f] D; N-Ph group was eliminated.

the 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.

RESULTS AND DISCUSSION

Model Reaction

^{13}C-NMR spectrum of the compound synthesized by model reaction 1 at 200°C for 2 h is shown in Figure 6. As a result, three peaks (a,b,c) assigned to the carbon of benzoxazine ring were not detected. It was found that the ring-opening reaction of the benzoxazine ring occurred. However the peak (e) assigned to methylene carbon of Ph(OH)— CH_2—N(Ph)—CH_2—Ph(OH), which was produced by the ring-opening reaction of benzoxazine ring, was not detected. Instead, the peak (i) assigned to methylene carbon of Ph(OH)—CH_2—Ph(OH) was detected. It was considered that —N(Ph)—CH_2— bond between phenolic nuclei was eliminated at high temperature to produce Ph(OH)—CH_2—Ph(OH). The results of model reaction 1 at various temperatures are shown in Table I. At 150°C, the N(Ph) group was detected in the product, but above 160°C the N(Ph) group was not detected. The reason for this was considered because of the formation of the quinone methide intermediate[12] at a high temperature, as shown in Figure 7.

^{13}C-NMR spectrum of the compound synthesized by model reaction 2 at 220°C for 2 h is shown in Figure 8. As a result, both peaks (a,b) assigned to the carbon of benzoxazine ring and two peaks (c,d) assigned to the carbon of epoxy ring were not detected. And both peak (f) assigned to C1 carbon of the benzene ring adjacent to ether bond and peak (g) assigned to methylene carbon of Ph(OH)—CH_2—N(Ph)—CH_2—Ph(OH) were detected. As model reaction 1, the peak of methyl-ene carbon of Ph(OH)—CH_2—Ph(OH) was not detected. It was suggested that the phenolic hydroxyl group produced by the ring opening reaction of C-a reacted with the epoxy group of PGE rapidly, and the —N(Ph)—CH_2— bond between phenolic nuclei was not eliminated.

The results of model reaction 2 at various temperatures are shown in Table II. C-a could react with PGE above 170°C, especially above 190°C, rapidly. It was suggested that the epoxy group reacted with the phenolic hydroxyl group without a catalyst such as amine, because tertiary amine group produced by the ring opening reaction of benzoxazine ring accelerated the reaction. In model reaction 2, the N(Ph)—CH_2 bond was not eliminated. The reason for this is as follows: the protection of the phenolic hydroxyl group by the epoxy group prevents the formation of quinone methido intermediate, as shown in Figure 7.

From the results of model reaction 2, the curing condition was determined as follows: after the molding compound softened at 150°C/1 h + 170°C/1 h to sufficiently remove any bubbles contained in it, the curing reaction was carried out stepwise at 190°C/2 h + 200°C/2 h. Finally, at 220°C/2 h the cured epoxy resin was postcured so that the curing reaction could proceed completely. In this way, the curing conditions of epoxy resin using B-a as a hardener were 150°C/1 h + 170°C/1 h + 190°C/2 h + 200°C/2 h + 220°C/2 h.

Thermal Stability of Epoxy Resin

Table III shows the gelation time of the molding compound prepared from DGEBA and B-a or BisA-N as a hardener. The molding compound prepared from DGEBA and B-a was thermally stable under 150°C for more than 60 min, and curing reaction could not occur, which corresponded to the temperature in the cylinder of injection molding, while the molding compound prepared from DGEBA and BisA-N cured rapidly even at 120°C. It was considered that the ring-opening reaction of benzoxazine ring was difficult to occur under 150°C, and the phenolic hydroxyl group and the tertiary amine group, which contributed to the curing reaction, were not produced. However, at a higher temperature the gelation time was shorter, because the phenolic hydroxyl group and tertiary amine group were produced easily.

Curing Reaction and Properties of Cured Epoxy Resin

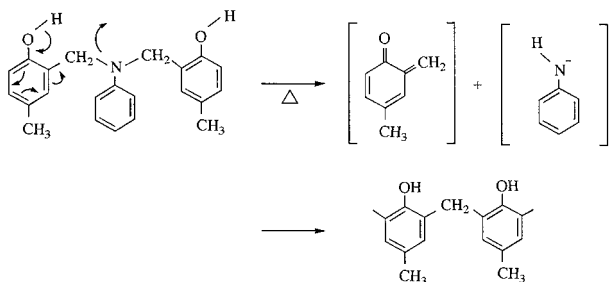The FTIR spectra of B-a, DGEBA, and the cured epoxy resin are shown in Figure 9. In Figure 9(c),

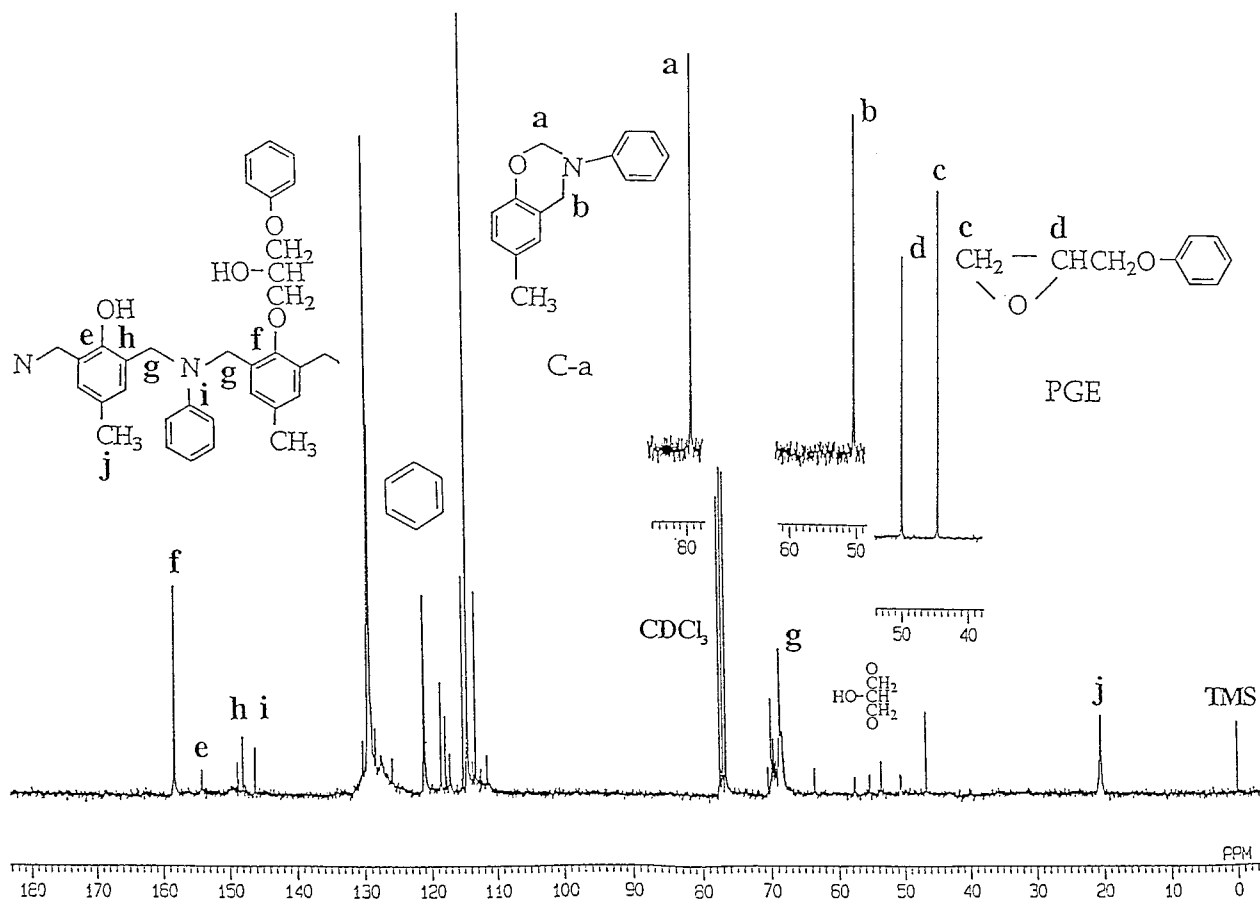**Figure 7** Speculation of elimination reaction of N-Ph group.

Figure 8 ^{13}C-NMR spectrum of the compound synthesized by model reaction 2 at 220°C for 2 h.

both the absorption at 1496 cm^{-1} assigned to the tri-substituted benzene ring in the benzoxazine ring structure, and the absorption at 916 cm^{-1} assigned to the epoxy ring disappeared. The absorption near 3400 cm^{-1} assigned to the hydroxyl group appeared. It was realized that the benzoxazine and epoxy ring opened, and the curing re-

action proceeded quantitatively without curing accelerators.

Table IV shows the properties of the cured epoxy resin using B-a or BisA-N as a hardener. The curing reaction of DGEBA using BisA-N as a hardener was also carried out on the same condition as the curing reaction of DGEBA using B-a

Table II   Results of Model Reaction 2

Temp. (°C)	Reaction of C-a with PGE[a]	Elimination of N-Ph[a]	M_n[b]	M_w[b]	M_w/M_n[b]
170	A[c]	C[e]	—	—	—
180	A	C	500	700	1.3
190	B[d]	C	700	1300	2.0
200	B	C	700	1600	2.2
210	B	C	700	1500	2.2
220	B	C	700	1500	2.2

[a] By NMR; [b] by GPC.
[c] A; Reaction of C-a with PGE occurred about 50%.
[d] B; Reaction of C-a with PGE occurred.
[e] C; N-Ph group was not eliminated.

Table III   Gel Time of B-a + DGEBA and BisA-N + DGEBA

Temp. (°C)	Gel Time (min)	
	B-a + DGEBA	BisA-N + DGEBA[a]
120	>60	2.5
150	>60	0.8
180	51	0.3
190	24	—
200	17	—
220	6	—

[a] Cat. 2Et4MZ, 5 phr.

as a hardener (150°C/1 h + 170°C/1 h + 190°C/2 h + 200°C/2 h + 220°C/2 h). As a result, the glass transition temperature (T_g) of the epoxy resin cured by B-a was higher than that of the epoxy resin cured by BisA-N. This was because movement of the molecular chain was hindered by the bulky N-Ph group between bridging points of the cured resin. K_{IC} of the epoxy resin cured by B-a was almost the same as that of the epoxy resin cured by BisA-N. But the volume resistivity after 2 h of boiling and water absorption of the epoxy resin cured by B-a was superior to those of the epoxy resin cured by BisA-N. The reason was considered as follows: the epoxy resin cured by B-a had a hydrophobic phenyl group between bridging points, and the free volume of that was smaller than that of the epoxy resin cured by BisA-N.

CONCLUSION

The purpose of this study was development of a new epoxy resin, which had good thermal stability of injection molding. We investigated the curing reaction of epoxy resin using bisphenol A based benzoxazine as a hardener and the properties of the cured epoxy resin. As a result, the molding compound showed good thermal stability under 150°C, which corresponded to the temperature in the cylinder of injection molding. Above 150°C, the curing reaction proceeded without curing accelerators. The epoxy resin cured by bisphenol A based benzoxazine had superior heat resistance, water resistance, and electrical insulation to those of the epoxy resin cured by bisphenol A type novolac. Consequently, bisphenol A based benzox-
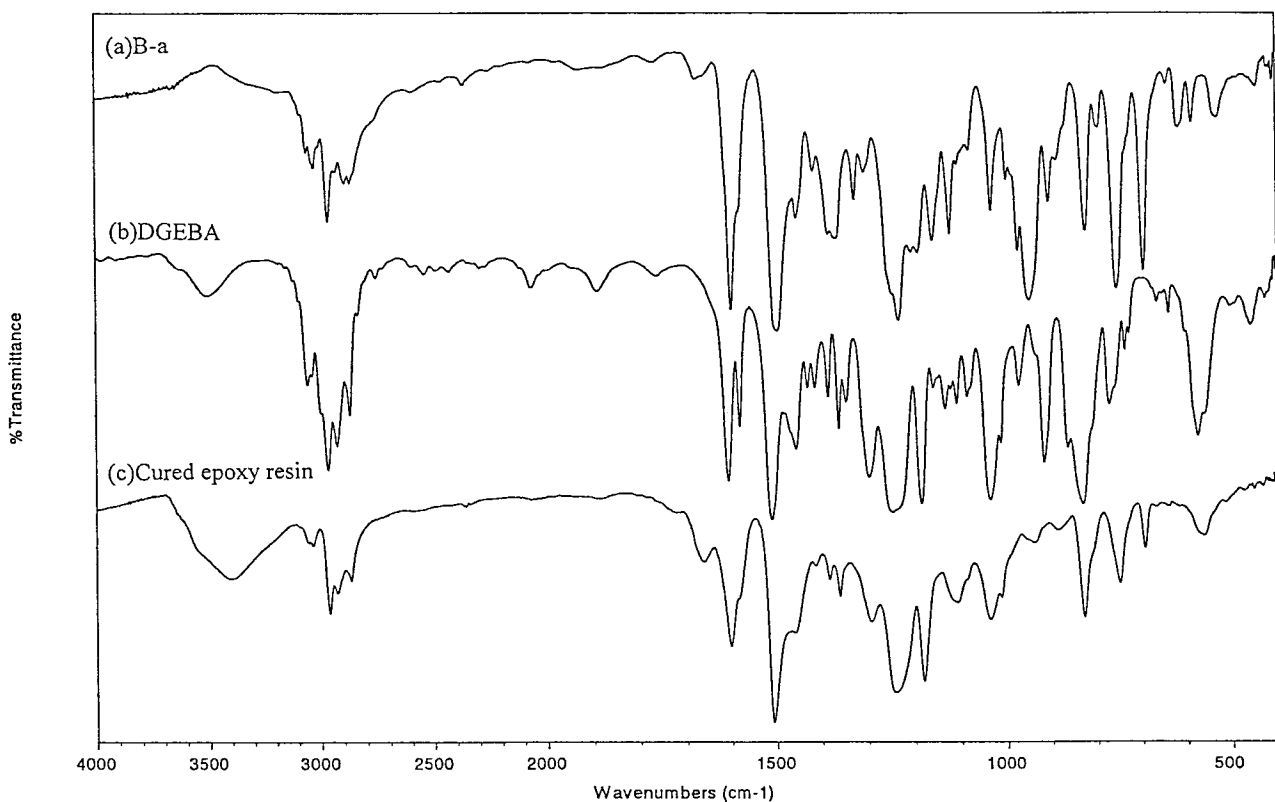

Figure 9   FTIR spectra of (a) B-a, (b) DGEBA, and (c) the cured epoxy resin.

Table IV   Properties of Cured Epoxy Resin

Hardener	$T_g{}^a$ (°C)	K_{IC} (MPam$^{1/2}$)	Volume Resistivity (Ω cm)		Water Absorption^b (%)
			Before Boiling	After 2 h Boiling	
B-a	175	0.54	4.0×10^{16}	1.2×10^{16}	0.46
BisA-N^c	149	0.51	3.0×10^{16}	3.1×10^{15}	0.53

^{a} Peak temp. of tan δ by DMA.
^{b} After 2 h boiling.
^{c} Cat. 2Et4MZ, 5 phr.

azine will be useful as a latent hardener of epoxy resin for injection molding.

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