New Thermosetting Resin from Terpenediphenol-Based Benzoxazine and Epoxy Resin

HAJIME KIMURA,[1] YOUHEI MURATA,[2] AKIHIRO MATSUMOTO,[1] KIICHI HASEGAWA,[1] KEIKO OHTSUKA,[1] AKINORI FUKUDA[1]

[1] Osaka Municipal Technical Research Institute, 6-50, 1-chome, Morinomiya, Joto-ku, Osaka, 536-8553 Japan

[2] Kinki University, 3327-204 Nakamachi, Nara, 631-8505 Japan

ABSTRACT: Terpenediphenol-based benzoxazine was prepared from terpenediphenol, formaline, and aniline. Curing behavior of the benzoxazine with epoxy resin and the properties of the cured resin were investigated. Consequently, the curing reaction did not proceed at low temperatures, but it proceeded rapidly at higher temperatures without a curing accelerator. The properties of the cured resin both from neat resins and from reinforced resins with fused silica were evaluated, respectively. The cured resins showed good heat resistance, mechanical properties, electrical insulation, and especially water resistance, compared with the cured resin from bisphenol A type novolac and epoxy resin. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2266–2273, 1999

Key words: terpenediphenol-based benzoxazine; curing behavior; bisphenol A

INTRODUCTION

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

Our objective in this study is to develop a new type of phenolic resin, which releases no volatiles and needs no catalysts.

It is well known that the benzoxazine ring is stable at low temperature, but the ring opening reaction occurs at high temperature, and novolac type oligomer having both the phenolic hydroxyl group and the tertiary amine group are produced[1] (Fig. 1). Using this benzoxazine compound as a phenolic resin, it is expected to develop a new type of phenolic resin that releases no volatiles during the curing reaction, and needs no catalysts.

Recently, Ishida et al.[2–18] synthesized a lot of types of oxazines, and studied the cure kinetics, molecular structures, mechanical, and dynamic mechanical properties, etc. Shin et al.[19] also studied the cure kinetics of a benzoxazine-based phenolic resin. J. Jang et al.[20] studied the performance improvement of rubber-modified polybenzoxazine. However, the reactivity of compounds that have benzoxazine rings with other compounds have hardly been investigated. We have already investigated the curing behavior of the
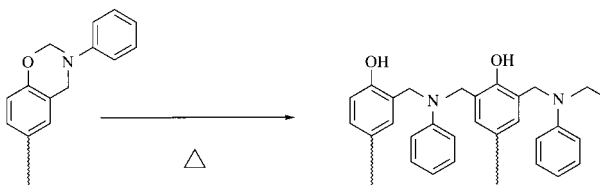
Figure 1 Ring-opening reaction of a benzoxazine ring.

bisphenol A-based benzoxazine with epoxy resin or bisoxazoline and the properties of the cured resin.[21,22] Consequently, the cured resin from benzoxazine compound and epoxy resin or bisoxazoline had superior heat resistance, electrical insulation, and water resistance to those of the cured resin from conventional bisphenol A-type novolac and epoxy resin or bisoxazoline.

In this report, to improve the mechanical properties and water resistance of the cured resin from the benzoxazine compound and epoxy resin further, we synthesized terpenediphenol-based benzoxazine and investigated the curing behavior of terpenediphenol-based benzoxazine with epoxy resin and the properties of the cured resin. The cured resins from reinforced resins with fused silica were prepared, and the properties of the cured resins were also evaluated.

Terpenediphenol is obtained by the reaction of excess phenol with terpene compounds that are contained in pine or orange rind. It is said that terpenediphenol is a useful material to improve the heat or water resistance of commercial polymers. For example, Matsumoto et al.[23] studied the synthesis and properties of terpenediphenol–formaldehyde resin. It was reported that terpenediphenol–formaldehyde resin had superior heat resistance, water resistance, and mechanical properties. Therefore, it is expected that the cured resin from terpenediphenol-based benzoxazine and epoxy resin has good heat resistance, water resistance, and mechanical properties.

EXPERIMENTAL

Materials

Bisphenol A, dioxane (98%), tetrahydrofuran (THF, 99.5%), aniline (99%), 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 was supplied from Shikoku Chemical Co., Ltd. Terpenediphenol (YP-90) was supplied from Yasuhara Chemical Co., Ltd. YP-90 contains two structural isomers (Fig. 2), i.e., 1,3-terpenediphenol (1,3-TP) and 2,8-terpenediphenol (2,8-TP) (1,3-TP : 2,8-TP = 2 : 1). o-Cresol novolac-type epoxy resin (OCNE, epoxy equivalent 211) was supplied from Dainihon Ink and Chemicals. Fused silica (smash type, average diameter 15 μm) was purchased from Tatsumori Ltd. All chemicals were used without further purification. The chemical structures of these compounds are shown in Figure 2.

Synthesis of Benzoxazines

Three kinds of terpenediphenol based benzoxazine (2,8-Ta, 1,3-Ta, and Ya) were synthesized according to the method explained by Ishida et al.[2] (Fig. 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 ice bath. The mixture was stirred for 10 min, 0.1 mol 2,8-terpenediphenol in 100 mL dioxane was
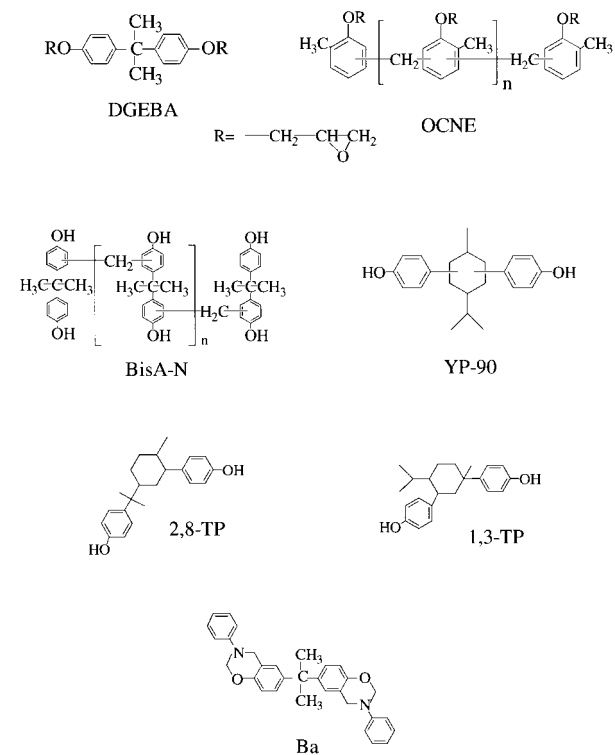

Figure 2 Chemical structures of DGEBA, OCNE, BisA-N, 2,8-TP, 1,3-TP, YP-90, and Ba.
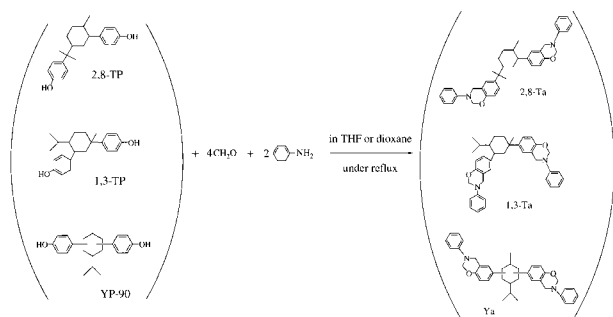
Figure 3 Synthesis of 2,8-Ta, 1,3-Ta, and Ya.

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.

Curing Condition of Neat Resin

Samples containing 50 mol% 2,8-Ta or 1,3-Ta, and 50 mol % DGEBA were prepared and cured in

a mold at a specified temperature in the oven. The curing condition was determined as 170°C/2 h + 190°C/2 h +200°C/2 h + 220°C/2 h from the results of model reaction.[21]

Preparation of Molding Compound and Compression Molding

The molding compound were prepared by hot roll-kneading of a mixture of 50 phr Ya, 50 phr OCNE, wax (1 phr of OCNE) as lubricant, and 100 phr fused silica as filler. Test pieces of the molding compounds were prepared by compression molding at 190°C for 20 min after preheating to required moldability for compression molding. All test pieces were postcured at 190°C/1 h + 200°C/2 h + 220°C/2 h so that the curing reaction could proceed completely, and they were used for the various measurements. For comparison, both the molding compound of 50 phr bisphenol A-based benzoxazine (Ba, Fig. 2), 50 phr OCNE, 100 phr fused silica and wax, and that of 50 phr BisA-N, 50 phr OCNE, 100 phr fused silica, wax, and 2-ethyl-4-methylimidazole as a curing accelerator were prepared on the same conditions. Test pieces
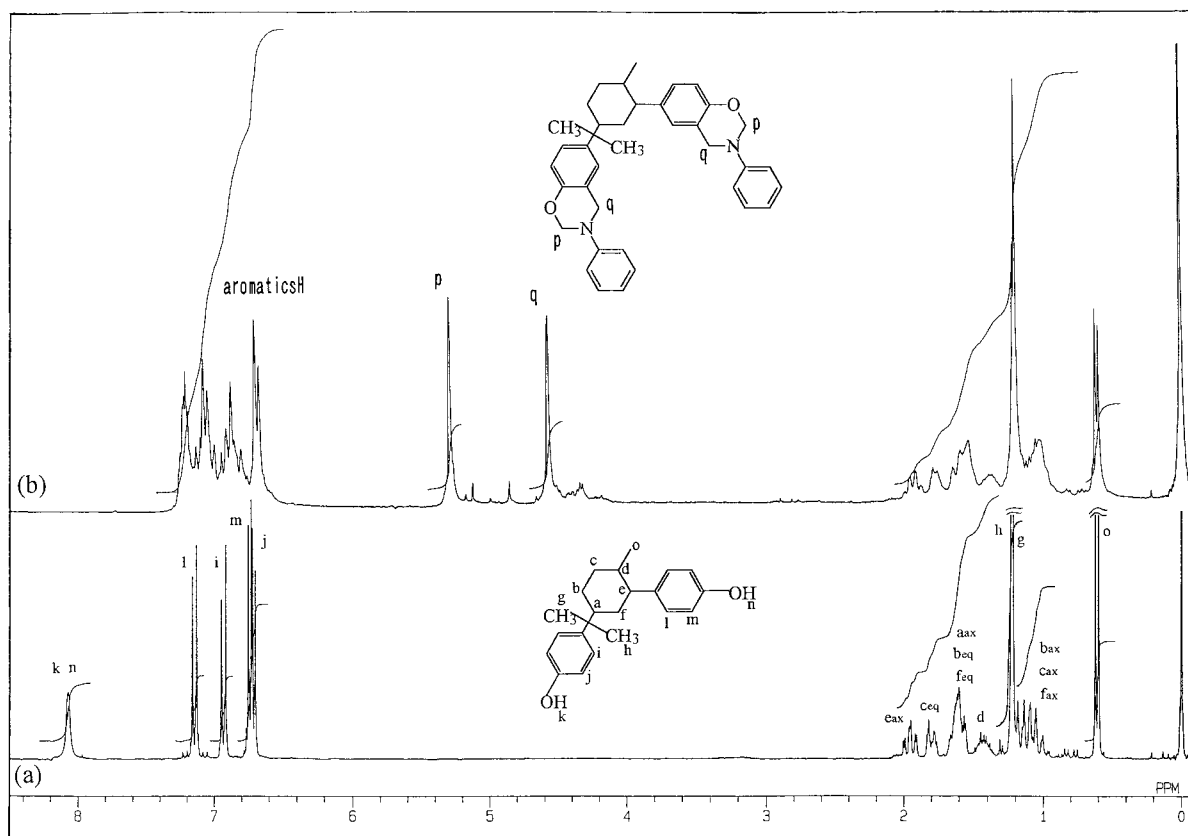

Figure 4 ^{1}H-NMR spectra of 2,8-TP and 2,8-Ta. (a) 2,8-TP; (b) 2,8-Ta.
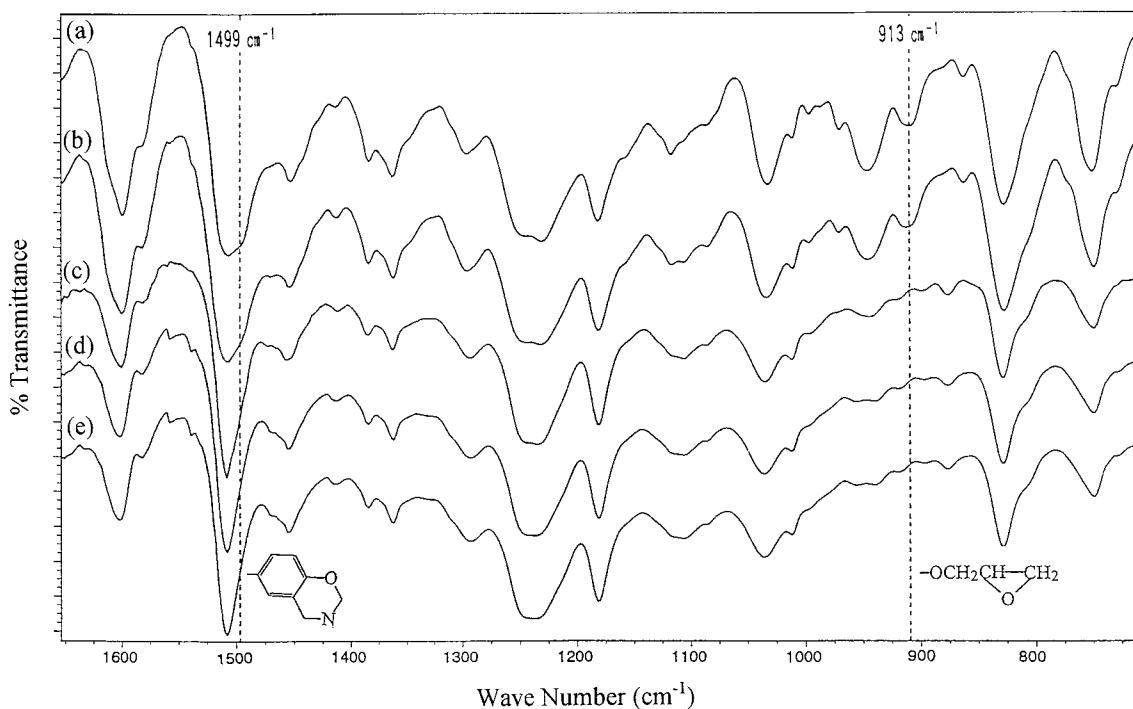
Figure 5 FTIR spectra of the molten mixture from 50 mol % 2,8-Ta and 50 mol % DGEBA. (a) Before reaction, (b) 170°C/2 h, (c) 170°C/2 h + 190°C/2 h, (d) 170°C/2 h + 190°C/2 h + 200°C/2 h, (e) 170°C/2 h + 190°C/2 h +200°C/2 h + 220°C/2h.

of the molding compounds were prepared by compression molding and postcuring on the same conditions.

Properties of the Cured Epoxy Resin

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

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 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 to 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.[24] 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.

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

where ρ_v is the 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 rsistance.

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,
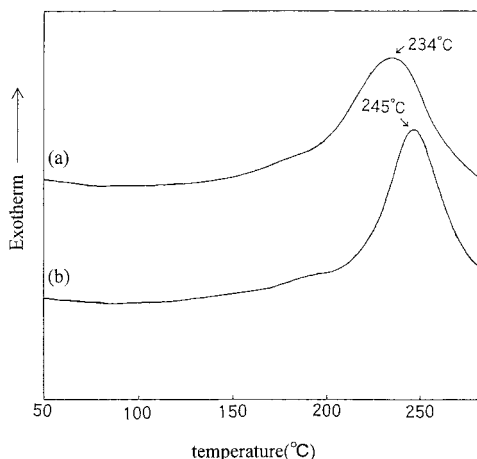
Figure 6 DSC curves of the molten mixture from 50 mol % 2,8-Ta or 1,3-Ta and 50 mol % DGEBA. (a) 2,8-Ta/DGEBA, (b) 1,3-Ta/DGEBA.

the test pieces were taken out of the boiling water and cooled down by putting them in water kept at the temperature of the testing room for 15 min. After taking the test pieces out of the water, they were weighed to the nearest 0.1 mg, and the mass was taken as M_2. Water absorption was calculated by the following equation.

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

Flexural properties were measured on the 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 and modulus were calculated by the following equation.

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

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

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

where E is the flexural modulus, 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.

Characterization

^{1}H- and ^{13}C-NMR measurement was carried out on Japan Electron Company JMN-GSX-270 instrument operating at 270 MHz and at 67.8 MHz. Deuterated chloroform was used as a solvent, and tetramethylsilane was used as an internal 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. Differential scanning calorimetry was measured with a heating rate of 10°C/min under N_2 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.

RESULTS AND DISCUSSION

Synthesis of Terpenediphenol-Based Benzoxazine

The synthesis of 2,8-Ta was carried out using 1,4-dioxane as a solvent. However, the syntheses of 1,3-Ta and Ya were carried out using tetrahydrofuran (THF) as a solvent because of the insolubility in 1,4-dioxane. Any yield was $50-60\%$. ^{1}H-NMR spectra of 2,8-TP and 2,8-Ta are shown in Figure 4. The peak (p,q) assigned to the proton of benzoxazine ring was detected, and the structure of 2,8-Ta was confirmed. The structures of 1,3-Ta and Ya was also confirmed by ^{1}H-NMR measurement. Then, by examining the ratio between the integrated intensities of the resonance peaks in ^{1}H-NMR, the benzoxazine ring content in 2,8-Ta or 1,3-Ta was calculated. The ratio between the integrated intensity of the methylene

Table I   Gelation Time of 2,8-Ta/DGEBA and 1,3-Ta/DGEBA

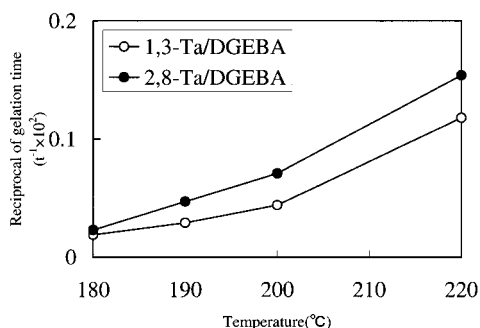| Temp. (°C)	Gelation Time (min)	
	2,8-Ta/DGEBA	1,3-Ta/DGEBA
150	>60	>60
180	43	53
190	21	35
200	14	23
220	7	9

Figure 7 Reciprocal plot of gelation time vs. temperature. (●, 2,8-Ta/DGEBA; ○, 1,3-Ta/DGEBA).

units in the benzoxazine ring [Fig. 4(b), peaks p and q], and the integrated intensity of the aromatic protons was 1:3.5. Consequently, the benzoxazine ring content in 2,8-Ta was calculated as 60%. In the same way, the benzoxazine ring content in 1,3-Ta was calculated as 60%.

Curing Reaction of Terpenediphenol-Based Benzoxazine with Epoxy Resin

To investigate the curing reaction of 2,8-Ta or 1,3-Ta with DGEBA in detail, FTIR measurement was carried out. FTIR spectra of the compound prepared from the curing reaction of 2,8-Ta with DGEBA are shown in Figure 5. Both the absorption at 1499 cm^{-1} assigned to the trisubstituted benzene ring in the benzoxazine ring structure and the absorption at 913 cm^{-1} assigned to the epoxy ring started to disappear within 2 h at 170°C [Fig. 5(b)]. When the curing condition is 170°C/2 h + 190°C/2 h [Fig. 5(c)], both the absorptions disappeared. It was realized that the benzoxazine and epoxy ring opened, and the curing reaction proceeded quantitatively without curing accelerators. The curing reaction did not proceed

at low temperatures, at higher temperatures, it proceeded rapidly.

DSC curves of the molten mixture prepared from 50 mol % 2,8-Ta or 1,3-Ta and 50 mol % DGEBA are shown in Figure 6. An exothermic peak derived from the curing reaction was observed in both cases of (a) 2,8-Ta/DGEBA and (b) 1,3-Ta/DGEBA. However, the curve of the molten mixture of 2,8-Ta/DGEBA shifted to the lower peak temperature than that of 1,3-Ta/DGEBA. It was realized that curing reaction of 2,8-Ta/DGEBA proceeded more rapidly than that of 1,3-Ta/DGEBA. The steric hindrance of 1,3-Ta may be higher than that of 2,8-Ta because of the rigid structure.

Table I shows the gelation time of the molten mixture from 50 mol % 2,8-Ta or 1,3-Ta and 50 mol % DGEBA. Furthermore, the reciprocal plot of gelation time as a function of temperature is shown in Figure 7. The molten mixture was thermally stable for a long time, and curing reaction could not occur under 150°C. It was because the ring-opening reaction of benzoxazine ring was difficult to occur under 150°C, and the phenolic hydroxyl groups that were 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 produced easily. And the reaction rate of the molten mixture of 2,8-Ta/DGEBA was faster than that of the molten mixture of 1,3-Ta/DGEBA, especially above 190°C, as shown in Figure 7. The reason was considered that the steric hindrance of 1,3-Ta might be higher than that of 2,8-Ta because of the rigid structure, and so the gelation reaction of 1,3-Ta with DGEBA was more difficult to proceed.

Table II   Properties of the Cured Resin from 2,8-Ta or 1,3-Ta and DGEBA

| | | | Volume Resistivity (Ω cm) | | |
| | | | Before Boiling | After 2 h Boiling | Water Absorption[b] (wt %) |
Sample	$T_g{}^{a}$ (°C)	K_{IC} (MPa m$^{1/2}$)			
2,8-Ta/DGEBA	180	0.64	2.7×10^{16}	1.0×10^{16}	0.28
1,3-Ta/DGEBA	180	0.55	1.8×10^{16}	8.7×10^{15}	0.31
Ba/DGEBA[21]	175	0.54	4.0×10^{16}	1.2×10^{16}	0.54
BisA-N/DGEBA[21]	149	0.51	3.0×10^{16}	3.1×10^{15}	0.51

[a] Peak temp. of tan δ by DMA.
[b] After 2 h boiling.

Table III   Properties of the Cured Resin from Ya and OCNE

Sample	Flexural Strength (MPa)	Flexural Modulus (GPa)	Volume Resistivity (Ω cm)		Water Absorption[a] (wt %)
			Before Boiling	After 2 h Boiling	
Ya/OCNE	76	7.8	4.8×10^{15}	2.6×10^{15}	0.08
Ba/OCNE	70	8.2	5.2×10^{15}	3.9×10^{15}	0.12
BisA-N/OCNE	68	6.7	7.5×10^{15}	3.2×10^{15}	0.19

[a] After 2 h boiling.

Properties of The Cured Resin

Table II shows the properties of the cured resin from 2,8-Ta or 1,3-Ta and DGEBA. The curing reaction of Ba or BisA-N with DGEBA was also carried out on the same conditions as that of 2,8-Ta or 1,3-Ta and DGEBA (170°C/2 h + 190°C/2 h + 200°C/2 h + 220°C/2 h). As a result, glass transition temperature (T_g) of the cured resin from 2,8-Ta or 1,3-Ta and DGEBA was higher than that of the cured resin from Ba or BisA-N and DGEBA. This was because the movement of molecular chain was hindered by rigid and bulky cyclohexane ring arising from terpene backbone in the cured resin. The volume resistivity of the cured resin from 2,8-Ta or 1,3-Ta and DGEBA was almost the same as that of the cured resin from Ba or BisA-N and DGEBA, but the cured resin from 2,8-Ta or 1,3-Ta and DGEBA had relatively high volume resistivity of commercial conventional resins. K_{IC} of the cured resin from 2,8-Ta and DGEBA was slightly higher than that of the other cured resins. The cured resin from 2,8-Ta and DGEBA might have longer distance between bridging points than the others. Especially, water absorption after 2 h boiling of the cured resin from 2,8-Ta or 1,3-Ta and DGEBA was superior to that of the cured resin from Ba or BisA-N and DGEBA. The reason was considered as follows: the cured resin from 2,8-Ta or 1,3-Ta and DGEBA had rigid and hydrophobic cyclohexane, and the density of the crosslinking was augmented by hydrogen bonding[10] derived from nitrogen atom between phenolic nuclei, as reflected by the shift in T_g.

Table III shows the properties of the cured resin from the molding compound of Ya and OCNE. Frexural strength of the moldings from Ya and OCNE was better than that of the others. Especially, water absorption after 2 h boiling of the moldings from Ya and OCNE was superior to that of the others. This was because the cured resin from Ya and OCNE had rigid and hydrophobic cyclohexane rings arising from the terpene backbone.

CONCLUSION

The purpose of this study was the development of a new phenolic resin, which releases no volatiles during curing reaction and needs no catalysts. We investigated the curing reaction of terpenediphenol-based benzoxazine with epoxy resin, as shown in Figure 8, and the properties of the cured resin. As a result, the curing reaction did not proceed below 150°C, but it proceeded quantitatively without curing accelerators above 180°C. The cured resin from terpenediphenol-based benzoxazine and epoxy resin had superior heat resistance, electrical insulation, and especially water resistance to those of the cured resin from bisphenol A-based benzoxazine or bisphenol A-type novolac and epoxy resin.

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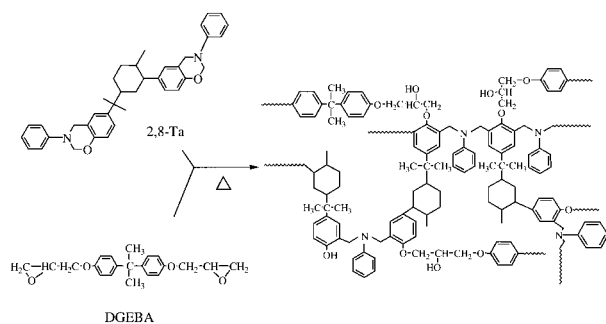

Figure 8   Curing reaction of 2,8-Ta with DGEBA.

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