

Studies on New Type of Phenolic Resin (IX) Curing Reaction of Bisphenol A-Based Benzoxazine with Bisoxazoline and the Properties of the Cured Resin. II. Cure Reactivity of Benzoxazine

HAJIME KIMURA,¹ SHUICHI TAGUCHI,² AKIHIRO MATSUMOTO¹

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

² Himeji Institute of Technology, 2167, Syosha, Himeji, 671-2201 Japan

Received 19 April 2000; accepted 12 June 2000

ABSTRACT: Bisphenol A-based benzoxazine that contained oligomers (oligo-Ba) was prepared from bisphenol A, formaline, and aniline. Curing reaction of oligo-Ba with bisoxazoline and the properties of the cured resin were investigated. Consequently, the ring-opening reaction of benzoxazine ring occurred, and then the phenolic hydroxyl group generated by the ring-opening reaction of benzoxazine ring reacted with oxazoline ring. It was found that the cure induction time and cure time of the molten mixture from oligo-Ba and bisoxazoline could be reduced and also the cure temperature could be lowered, compared with those from bisphenol A-based benzoxazine, which contained no oligomers (Ba), and bisoxazoline. The melt viscosity of the molten mixture from oligo-Ba and bisoxazoline was kept 0.1–10 [Pas] at 140°C even after 40 min, the molten mixture from oligo-Ba and bisoxazoline showed good flowability below 140°C as well as that from Ba and bisoxazoline. However, above 160°C the curing reaction of oligo-Ba with bisoxazoline proceeded more rapidly than that of Ba with bisoxazoline. The cured resin from oligo-Ba and bisoxazoline showed good heat resistance and water resistance, compared with the cured resin from Ba and bisoxazoline. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2331–2339, 2001

Key words: bisphenol A; benzoxazine; bisoxazoline; cured resin

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, 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 microvoid. And acid or base compounds as catalysts, which result in corrosion of the processing equipment, 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.

Correspondence to: H. Kimura.

Journal of Applied Polymer Science, Vol. 79, 2331–2339 (2001)
© 2001 John Wiley & Sons, Inc.

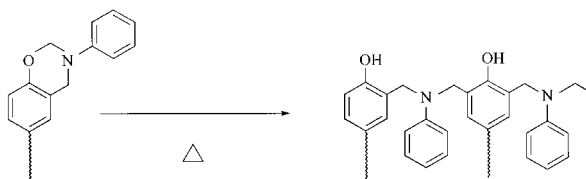


Figure 1 Ring-opening reaction of a benzoxazine ring.

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 the phenolic hydroxyl group and the tertiary amine group, are produced¹ (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 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. Jang et al.²⁰ studied the performance improvement of rubber-modified polybenzoxazine. However, the reactivity of compounds that have benzoxazine ring with other compounds has hardly been investigated. We have already investigated the curing behavior of the bisphenol A, terpenedi-phenol or poly(*p*-vinylphenol)-based benzoxazines with epoxy resin or bisoxazoline, and the properties of the cured resins.^{21–24} Consequently, the molding compound from bisphenol A-based benzoxazine that contained no oligomers (Ba) and bisoxazoline showed good flowability below 140°C, curing reaction proceeded above 180°C rapidly. And the cured resins from benzoxazine compounds and epoxy resin or bisoxazoline had superior heat resistance, electrical insulation, and water resistance to the cured resins from conventional bisphenol A-type novolac and epoxy resin or bisoxazoline.

Despite their high performance (e.g., heat and water resistance) of the benzoxazine-based resin, it is believed that the benzoxazine-based resins show surprisingly low crosslink densities in comparison to ordinary thermosetting resin.⁸ Then, another problem is that the cure induction time and cure time of the benzoxazine compounds are long, and also the cure temperature is high.

In this report, to achieve a higher crosslink density of the cured resin from benzoxazine-based resin, to reduce the cure induction time and cure

time of the benzoxazine compound, and to lower the cure temperature of the benzoxazine compound, we synthesized bisphenol A-based benzoxazine, which contained oligomers (oligo-Ba), and investigated the curing behavior of oligo-Ba with bisoxazoline and the properties of the cured resin.

It was reported²⁵ that phenolic resin cured by bisoxazoline had low cure shrinkage and good toughness while retaining high heat resistance, low flammability, and 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 2. Therefore, it is also expected that the cured resin from oligo-Ba and bisoxazoline has good toughness, high heat resistance, etc.

EXPERIMENTAL

Materials

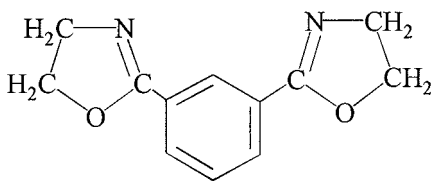
Bisphenol A, dioxane (98%), aniline (99%), and formaldehyde (37% in water) were purchased from Nacalai Tesque Co., Ltd. Triphenylphosphite used as a catalyst for the reaction of an oxazoline ring with a phenolic hydroxyl group was purchased from Yoneyama Chemical Co., Ltd. 2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) as bisoxazoline (1,3-PBO) was supplied by Mikuni Pharmaceutical Industrial Co., Ltd.. All chemicals were used without further purification. The chemical structure of 1,3-PBO is shown in Figure 3.

Synthesis and Characterization of Benzoxazines

Oligo-Ba and Ba were synthesized according to the method explained by Ishida et al.⁸ (Fig. 4). A 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 an 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



Figure 2 Ring-opening reaction of an oxazoline ring with a phenolic hydroxyl group.



1,3-PBO

Figure 3 Chemical structure of 1,3-PBO.

solution is refluxed for 6 h. The solvent is then evaporated and the viscous fluid is dissolved in ethyl acetate. The ethyl acetate solution is washed with water several times. Ethyl acetate is evaporated to give oligo-Ba. Ba was prepared by repeatedly washing its ethyl acetate solution with 3 N NaOH solution to eliminate oligomers having phenolic hydroxyl groups in the reaction product. The structures of oligo-Ba and Ba were analyzed by $^1\text{H-NMR}$ measurement. $^1\text{H-NMR}$ measurement was carried out on Japan Electron Company JMN-GSX-270 instrument operating at 270 MHz. Deuterated chloroform was used as a solvent, and tetramethylsilane was used as an internal standard. The number average molecular weight (M_n) was measured by Gel Permeation Chromatography (GPC). GPC was carried out on Waters ALC/GPC 150C instrument with a refractive index (RI) detector. Tetrahydrofuran was used as an eluent, and polystyrene was used as a standard.

Curing Condition

Samples containing 50 mol % oligo-Ba and 50 mol % 1,3-PBO with 1 wt % triphenylphosphite as a catalyst were prepared and cured in a mold at a specified temperature in the oven. The curing condition was determined as $170^\circ\text{C}/2\text{h} + 200^\circ\text{C}/2\text{h} + 230^\circ\text{C}/2\text{h} + 250^\circ\text{C}/2\text{h}$ from the results of a previous article.²² For comparison, the curing reaction of 50 mol % Ba with 50 mol % 1,3-PBO was also carried out on the same condition.

Properties of the Molding Compound and the Cured Resin

The structure of the cured resin was analyzed by Fourier Transform Infrared Spectrophotometer (FTIR). FTIR measurement was carried out on Nicolet Impact 420 instrument. The spectral range was $4000\text{--}400\text{ cm}^{-1}$. One hundred twenty-

eight scans were coadded at a resolution of 4 cm^{-1} . Samples were prepared as KBr pellets.

To investigate the thermal stability of the molding compound, gelation time was estimated according to JIS K6910. Namely, 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 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. Dynamic mechanical analysis was measured by a three-point bending method at 1 Hz, with a heating rate of $2^\circ\text{C}/\text{min}$ on a Seiko Instruments Co., Ltd. DMS-110 Dynamic Mechanical Analysis Spectrometer. The peak temperature of $\tan \delta$ by dynamic mechanical analysis was considered as T_g .²⁶ 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.

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

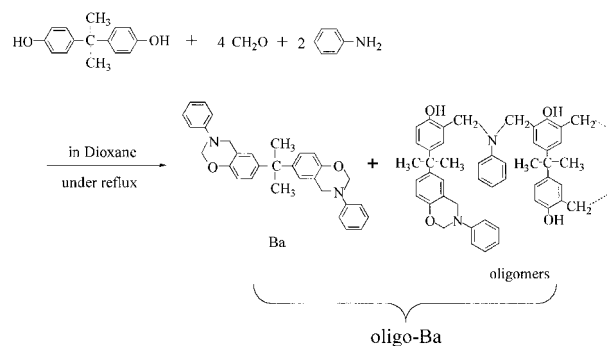


Figure 4 Synthesis of oligo-Ba.

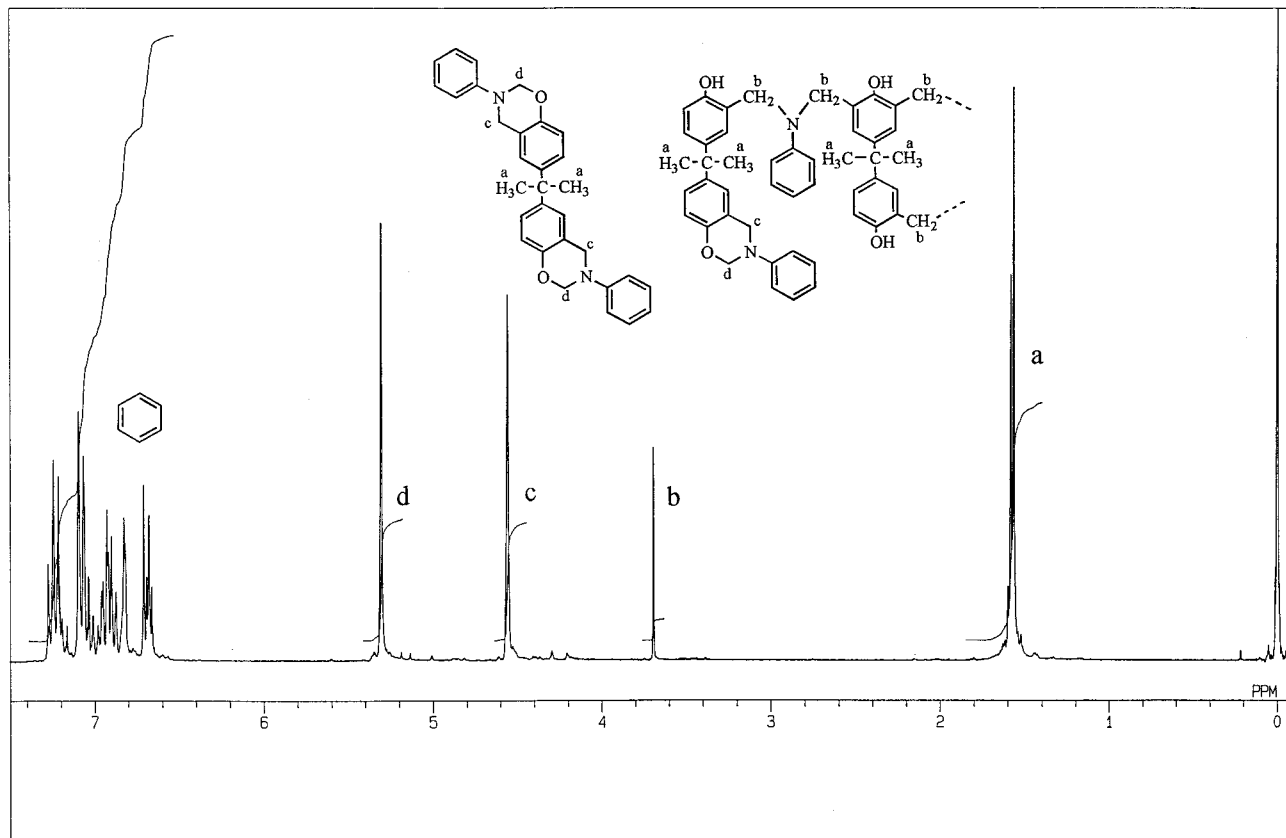


Figure 5 $^1\text{H-NMR}$ spectrum of oligo-Ba (solvent, chloroform-d).

where ρ_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.

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

Measurements for melt viscosity and storage modulus (G') were conducted on a UBM Co., Ltd. Dynamic Mechanical Spectrometer (Rheosol-

G3000) by using a 40-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 (140, 160, and 180°C) at a rate of 30°C/min. The melt viscosity and G' for the isothermal test at the measuring temperature were measured as a function of time.

RESULTS AND DISCUSSION

Synthesis of Oligo-Ba

The synthesis of oligo-Ba was carried out using 1,4-dioxane as a solvent. Any yield was 80–90%. $^1\text{H-NMR}$ spectrum of oligo-Ba is shown in Figure 5. The peaks (c, d) assigned to the methylene proton of benzoxazine ring were detected. And the peak (b) assigned to the methylene proton attached to the tertiary amine group, which was produced by the ring opening reaction of benzoxazine ring, was also detected. This means that the

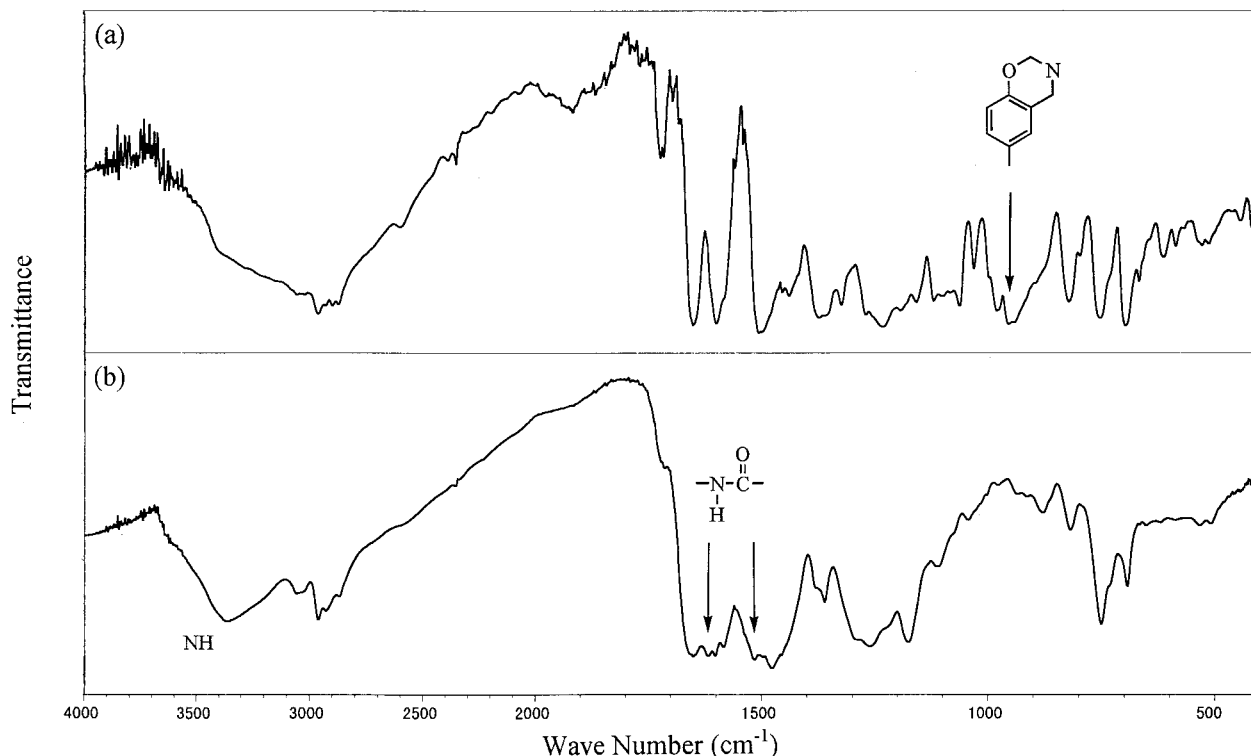


Figure 6 FTIR spectra of the compound from curing reaction of 50 mol % oligo-Ba with 50 mol % 1,3-PBO: (a) before curing reaction; (b) after curing reaction.

reaction product contains not only Ba but also oligomers, as shown in Figure 4. As a result of GPC, M_n of oligomers in oligo-Ba was about 1300. Then, by examining the ratio between the integrated intensities of the resonance peaks in $^1\text{H-NMR}$, the benzoxazine ring content in oligo-Ba was calculated. The ratio between the integrated intensity of the methylene units in the benzoxazine ring (peaks c and d), and the integrated intensity of the methylene units (peak b) in the oligomers was 1 : 6. Consequently, the benzoxazine ring content in oligo-Ba was calculated as 75%. The presence of the phenolic hydroxyl groups (about 25% in oligo-Ba) with free *ortho*-positions in the oligomers may have an accelerative effect on the curing reaction, that is, it may reduce the cure induction time and cure time, and lower the cure temperature.

Curing Reaction of Oligo-Ba with 1,3-PBO

To investigate the curing reaction of oligo-Ba with 1,3-PBO, FTIR measurement was carried out. FTIR spectra of the compound before and after the curing reaction of oligo-Ba with 1,3-PBO are shown in Figure 6. As a result, the absorption at

949 cm^{-1} assigned to the tri-substituted benzene ring in the benzoxazine ring structure disappeared. The broad absorption at ca. 3360 cm^{-1} assigned to the secondary amine group and very small amount of phenolic hydroxyl group that could not react with oxazoline ring appeared. And the absorption at $1520, 1620\text{ cm}^{-1}$ assigned to the amide group also appeared [Fig. 6(b)]. It was found the ring opening reaction of benzoxazine ring occurred, and then the phenolic hydroxyl groups generated by the ring-opening reaction of benzoxazine ring reacted with oxazoline ring as shown in Figure 7. And it was considered that the amide groups generated by the ring-opening reaction of oxazoline ring could not be associated with the curing reaction, because the resonance effect of amide group could lessen the nucleophilicity of nitrogen and the reactivity of secondary amine group (amide group) to oxazoline ring was lower than that of phenolic hydroxyl group to oxazoline ring.

Thermal Stability of the Molten Mixture from Oligo-Ba and 1,3-PBO

Table I shows the gelation time of the molten mixtures from 50 mol % oligo-Ba or Ba and 50 mol

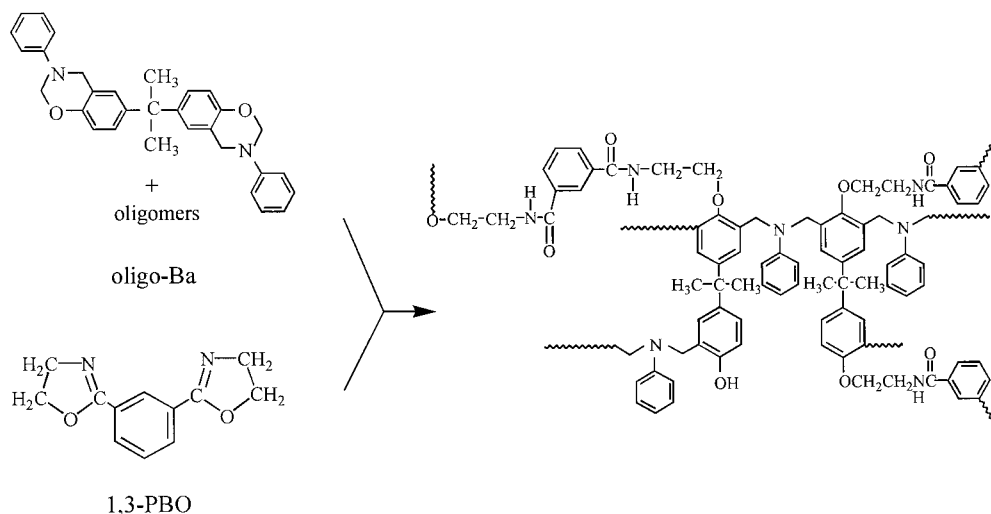


Figure 7 Curing reaction of oligo-Ba with 1,3-PBO.

% 1,3-PBO. Both molten mixtures were thermally stable under 120°C for more than 60 min, because the curing reaction could not occur. This was because the ring-opening reaction of benzoxazine ring was difficult to occur under 120°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 that contributed to the curing reaction were produced easily. Compared oligo-Ba with Ba, gelation time of oligo-Ba was more shortened than that of Ba, especially at 180°C. The reason was considered that oligo-Ba contained oligomers that had phenolic hydroxyl groups, and the presence of the phenolic hydroxyl groups with free *ortho*-position in oligo-Ba might have an accelerative effect on the gelation reaction.^{1,2,4}

Table I Gelation Time of Oligo-Ba/1,3-PBO and Ba/1,3-PBO Molten Mixtures

Temp. (°C)	Gelation Time (min)	
	Oligo-Ba/1,3-PBO	Ba/1,3-PBO
120	> 60	> 60
150	46	> 60
170	18	43
180	7	22
190	4	14
200	2	7
210	2	5
220	1	4

Melt Viscosity and Storage Modulus of the Molten Mixture from Oligo-Ba and 1,3-PBO

Results of the dynamic mechanical analysis at 160 and 180°C, which is the typical cure temperature for phenolic resin, are shown for oligo-Ba/1,3-PBO and Ba/1,3-PBO molten mixtures in Figure 8. The storage modulus (G') value of Ba/1,3-PBO molten mixture did not increase much for a relatively long time (30 min) at 160°C, and then increased gradually, because curing reaction could not occur adequately at 160°C. Namely, it was found that the reaction induction time for curing of Ba/1,3-PBO molten mixture was long, and also cure speed was slow. On the other hand, G' value of oligo-Ba/1,3-PBO molten mixture at

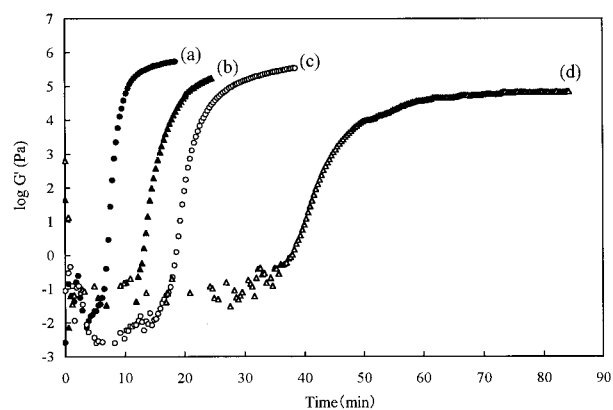


Figure 8 Dynamic mechanical analysis of oligo-Ba/1,3-PBO and Ba/1,3-PBO molten mixtures. (a) oligo-Ba/1,3-PBO at 180°C, (b) Ba/1,3-PBO at 180°C, (c) oligo-Ba/1,3-PBO at 160°C, (d) Ba/1,3-PBO at 160°C.

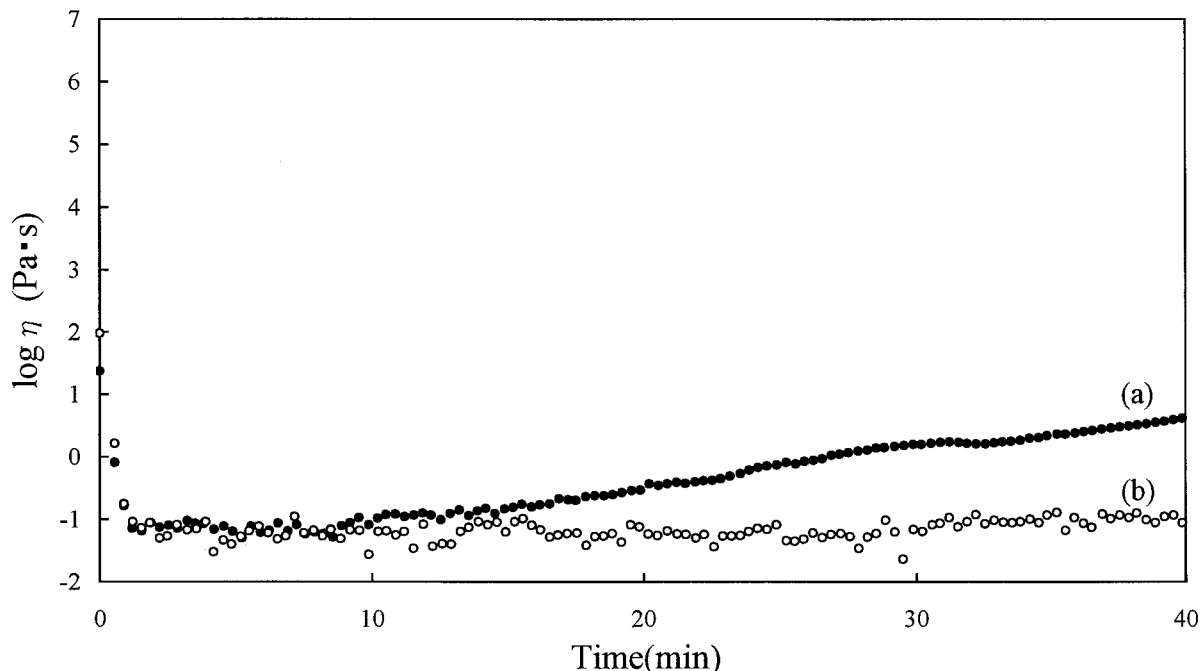


Figure 9 Melt viscosity of oligo-Ba/1,3-PBO and Ba/1,3-PBO molten mixtures at 140°C: (a) oligo-Ba/1,3-PBO, (b) Ba/1,3-PBO.

160°C increased rapidly within 15 min, and then reached a plateau. The slopes of G' curve at the inflection point and the intersecting point of the slopes of G' curve were considered as cure rate (V_c) and cure time (T_c), respectively.²⁷ As a result, V_c value of oligo-Ba/1,3-PBO molten mixtures was higher than that of Ba/1,3-PBO apparently at 160°C. Next, T_c values at 160°C were taken as follows: oligo-Ba/1,3-PBO, 25 min and Ba/1,3-PBO, 45 min. Oligo-Ba/1,3-PBO molten mixture had a much shorter cure time than Ba/1,3-PBO at 160°C. And T_c value at 180°C of Ba/1,3-PBO molten mixture was taken as 20 min. Consequently, the T_c value at 160°C of oligo-Ba/1,3-PBO was very close to that at 180°C of Ba/1,3-PBO. Namely, cure temperature of oligo-Ba/1,3-PBO was about 20°C lower than that of Ba/1,3-PBO. From these results, it showed that the cure induction time and cure time of the molten mixture from oligo-Ba and 1,3-PBO could be reduced, and also the cure temperature could be lowered, compared with those from Ba and bisoxazoline. The cure rate of oligo-Ba with bisoxazoline could increase more than that of Ba with bisoxazoline. The presence of the phenolic hydroxyl groups with free *ortho*-positions in the oligomers might have an accelerative effect on the curing reaction.^{1,2,4}

Figure 9 shows the plot of melt viscosity (η) of oligo-Ba/1,3-PBO and Ba/1,3-PBO molten mixtures vs. time at 140°C. The melt viscosity of both molten mixtures was kept a low value 0.1–10 [Pas] at 140°C even after 40 min. The molten mixtures showed good flowability under 140°C as expected from the results of gelation time in Table I, because the ring-opening reaction of benzoxazine ring was difficult to occur at low temperature, 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 160°C, the G' value increased rapidly, as shown in Figure 8.

Properties of the Cured Resin

The properties of the cured resin from oligo-Ba or Ba and 1,3-PBO are shown in Table II. As a result, glass transition temperature (T_g) of the cured resin from oligo-Ba and 1,3-PBO was much higher than that of the cured resin from Ba and 1,3-PBO. Both cured resins from oligo-Ba or Ba and 1,3-PBO had extremely high volume resistivity of commercial resins. K_{IC} of the cured resin from oligo-Ba and 1,3-PBO was also slightly smaller than that of the cured resin from Ba and

Table II Properties of the Cured Resin

Sample	T_g^a (°C)	K_{IC} (MPa m ^{1/2})	Volume Resistivity (Ω cm)		Water Absorption ^b (wt %)
			Before Boiling	After 2 h Boiling	
Oligo-Ba/1,3-PBO	232	0.75	1.1×10^{16}	3.2×10^{15}	0.23
Ba/1,3-PBO	195	0.93	3.5×10^{16}	7.2×10^{15}	0.28

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

1,3-PBO. But water absorption after 2 h boiling of the cured resin from oligo-Ba and 1,3-PBO was slightly superior to that of the cured resin from Ba and 1,3-PBO. The reason for these results was considered that crosslink density might be augmented by molecular entanglement of oligomers in oligo-Ba during curing reaction.²⁸

This idea was supported by dynamic mechanical analysis. Dynamic mechanical properties of the cured resins from oligo-Ba/1,3-PBO and Ba/1,3-PBO are shown in Figure 10. Crosslink density $\rho(E')$ can be calculated using the equation of state for rubbery elasticity.²⁹

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

where ϕ is the front factor, T is the absolute temperature, R is the gas constant, and E' is the storage modulus of the sample at temperature T .

This equation is applicable to polymer networks that have a rubbery plateau region.²⁹ Although the adoption of this equation to the highly crosslinked systems is over the applicability of the rubber elasticity theory, there is no theoretical equation to calculate crosslink density for highly crosslinked polymers. Therefore, in our study, the value of $\rho(E')$ of the samples was calculated at $T_g + 40^\circ\text{C}$ according to this equation, so as to compare crosslink density of each sample.^{10,30,31} The results are shown in Table III, assuming that ϕ is equal to 1.³² The value of $\rho(E')$

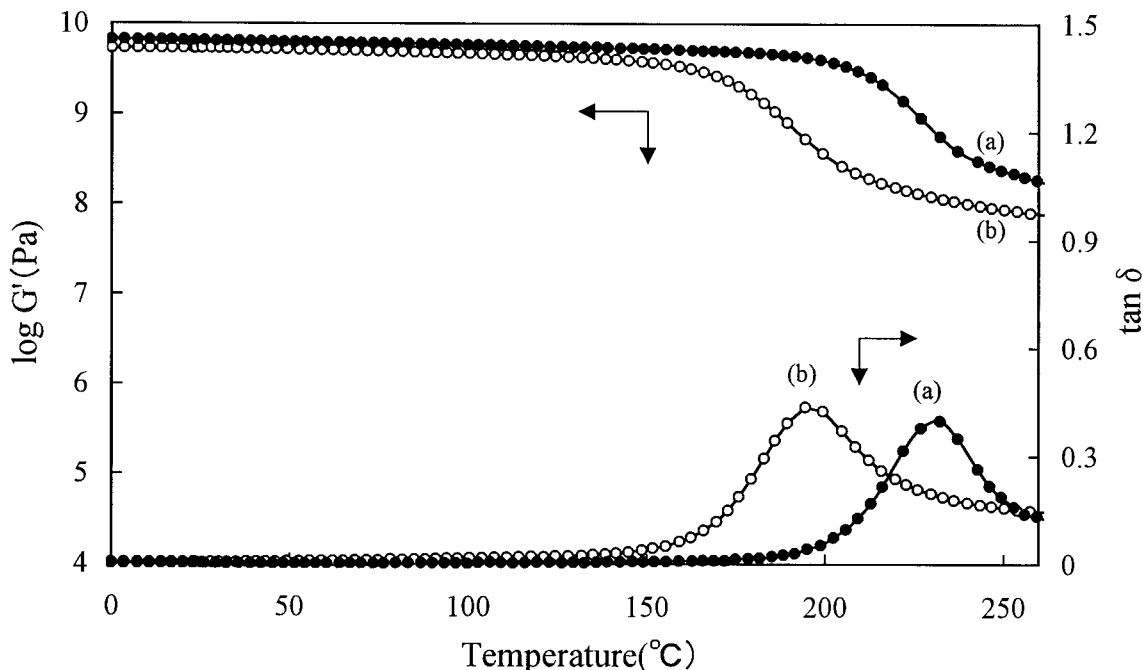


Figure 10 Dynamic mechanical analysis of the cured resins from oligo-Ba or Ba and 1,3-PBO: (a) oligo-Ba/1,3-PBO, (b) Ba/1,3-PBO.

Table III Values of $\rho(E')$ of the Cured Resin

Sample	$\rho(E')$ (mol/m ³)
Oligo-Ba/1,3-PBO	1.1×10^4
Ba/1,3-PBO	9.0×10^3

of the cured resin from oligo-Ba and 1,3-PBO was about 20% higher than that of the cured resin from Ba and 1,3-PBO. This suggests that crosslink density of the cured resin from oligo-Ba and 1,3-PBO is higher than that of the cured resin from Ba and 1,3-PBO. This high crosslink density may be due to more molecular entanglement of oligomers in oligo-Ba.²⁸

CONCLUSION

The purpose of this study is to achieve a higher crosslink density of the cured resin from benzoxazine based resin, to reduce the cure induction time and cure time of the benzoxazine compound, and to lower the cure temperature of the benzoxazine compound. We investigated the curing reaction of bisphenol A-based benzoxazine that contained oligomers (oligo-Ba) with bisoxazoline and the properties of the cured resin. As a result, the molten mixture from oligo-Ba and bisoxazoline showed good thermal stability, and good flowability below 140°C as well as that from bisphenol A-based benzoxazine that contained no oligomers (Ba) and bisoxazoline. However, above 160°C the curing reaction of oligo-Ba with bisoxazoline proceeded more rapidly than that of Ba with bisoxazoline. It was found that the cure induction time and cure time of the molten mixture from oligo-Ba and bisoxazoline could be reduced, and also the cure temperature could be lowered, compared with those from Ba and bisoxazoline. The cured resin from oligo-Ba and bisoxazoline had superior heat resistance and water resistance to that from Ba and bisoxazoline because of higher crosslink density.

REFERENCES

- Riess, G.; Schwob, J. M.; Guth, G.; Roche, M.; Lande, B. In *Advances in Polymer Synthesis*; Culbertson, B. M.; Mcgrath, J. E., eds.; Plenum: New York, 1985.
- Ning, X.; Ishida, H. *J Polym Sci Polym Phys* 1994, 32, 921.
- Ning, X.; Ishida, H. *J Polym Sci Polym Chem* 1994, 32, 1121.
- Ishida, H.; Rodriguez, Y. *J Appl Polym Sci* 1995, 58, 1751.
- Ishida, H.; Rodriguez, Y. *Polymer* 1995, 36, 3151.
- Dungers, J.; Ishida, H. *Spectrochim Acta* 1995, 51A, 1061.
- Dungers, J.; Ishida, H. *Spectrochim Acta* 1995, 51A, 855.
- Ishida, H.; Allen, D. J. *J Polym Sci Polym Phys* 1996, 34, 1019.
- Shen, S. B.; Ishida, H. *J Appl Polym Sci* 1996, 61, 1595.
- Ishida, H.; Allen, D. J. *Polymer* 1996, 37, 4487.
- Shen, S. B.; Ishida, H. *Polym Compos* 1996, 17, 710.
- Dunkers, J.; Zarate, E. A.; Ishida, H. *J Phys Chem* 1996, 100, 13514.
- Ishida, H.; Low, H. Y. *Macromolecules* 1997, 30, 1099.
- Russel, V. M.; Koenig, J. L.; Low, H. Y.; Ishida, H. *J Appl Polym Sci* 1998, 70, 1401.
- Russel, V. M.; Koenig, J. L.; Low, H. Y.; Ishida, H. *J Appl Polym Sci* 1998, 70, 1413.
- Kim, H. J.; Brunovska, Z.; Ishida, H. *J Appl Polym Sci* 1999, 73, 857.
- Brunovska, Z.; Ishida, H. *J Appl Polym Sci* 1999, 73, 2937.
- Shen, S. B.; Ishida, H. *J Polym Sci Polym Phys* 1999, 37, 3257.
- Jang, J.; Shin, S. *Polym J* 1995, 27, 601.
- Jang, J.; Seo, D. *J Appl Polym Sci* 1998, 67, 1.
- Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1998, 68, 1903.
- Kimura, H.; Matsumoto, A.; Hasegawa, K.; Fukuda, A. *J Appl Polym Sci* 1998, 72, 1551.
- Kimura, H.; Murata, Y.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1999, 74, 2266.
- Kimura, H.; Matsumoto, A.; Sugito, H.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci*, to appear.
- Culbertson, B. M.; Tiba, O.; Deviney, M. L. 34th International SAMPE Symp 1989, 2483.
- Kwei, K.T. *J Polym Sci A-2* 1966, 8, 943.
- Meacham, R. M. *Ind Eng Chem Res* 1991, 30, 798.
- Matsumoto, A.; Uchiyama, K.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Adhesion Soc Jpn* 1996, 32, 86.
- Murayama, T.; Bell, P. J. *J Polym Sci A-2* 1970, 8, 437.
- Hasegawa, K.; Fukuda, A.; Tonogai, S. *J Appl Polym Sci* 1989, 37, 3423.
- Matsumoto, A.; Hasegawa, K.; Fukuda, A. *Polym Int* 1993, 30, 65.
- Kamon, T.; Saito, K.; Miwa, Y.; Saeki, K. *Kobunshi Kagaku* 1973, 30, 279.