

New Thermosetting Resin from Poly(*p*-vinylphenol) Based Benzoxazine and Epoxy Resin

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ABSTRACT: Poly(*p*-vinylphenol) (VP) based benzoxazine was prepared from VP, formaline, and aniline. The curing behavior of the benzoxazine with the 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 reaction induction time or cure time of the molten mixture from VP based benzoxazine and epoxy resin was found to decrease, compared with those from conventional bisphenol A based benzoxazine and epoxy resin. The curing reaction rate of VP based benzoxazine and epoxy resin increased more than that of conventional bisphenol A based benzoxazine and epoxy resin. The properties of the cured resin from neat resins and from reinforced resins with fused silica were evaluated. The cured resins from VP based benzoxazine and epoxy resin showed good heat resistance, mechanical properties, electrical insulation, and water resistance compared to the cured resin from VP and epoxy resin using imidazole as the catalyst. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 555–565, 2001

Key words: phenolic resin; benzoxazine; poly(*p*-vinylphenol); thermal stability; curing reaction rate

INTRODUCTION

Phenolic resin is widely used 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 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 are released because of the condensation reaction. These vola-

tiles sometimes reduce the properties of the cured phenolic resin because of the formation of microvoids. In addition, acid or base compounds, which result in corrosion of the processing equipment, must be used as catalysts to synthesize novolac or resole precursors of cured phenolic resins. Another problem is that the cured phenolic resin is brittle.

Our objective in this study was to develop a new type of phenolic resin that 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 a novolac type oligomer with a phenolic hydroxyl group and a tertiary amine group is produced¹ (Fig. 1). Us-

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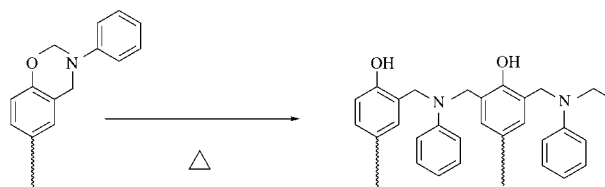


Figure 1 The ring-opening reaction of a benzoxazine ring.

ing this benzoxazine compound as a phenolic resin, we 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 numerous types of oxazines and studied the cure kinetics, molecular structures, mechanical and dynamic mechanical properties, and so on. Jang and Shin¹⁹ also studied the cure kinetics of a benzoxazine based phenolic resin. Jang and Seo²⁰ studied the performance improvement of rubber-modified polybenzoxazine. However, the reactivity of compounds that have a benzoxazine ring with other compounds were scarcely investigated. We previously investigated the curing behavior of bisphenol A or terpenediphenol based benzoxazine with epoxy resin or bisoxazoline and studied the properties of the cured resin.^{21–23} Consequently, the molding compound from bisphenol A based benzoxazine (Ba) and bisoxazoline showed good flowability below 140°C and the curing reaction proceeded rapidly above 180°C. The cured resins from the benzoxazine compound and epoxy resin or bisoxazoline also had heat resistance, electrical insulation, and water resistance that were superior to those of the cured resins from conventional bisphenol A type novolac and epoxy resin or bisoxazoline.

Despite the high performance (e.g., good heat or water resistance) of the benzoxazine based resin, it is believed that the benzoxazine based resin shows surprisingly low crosslink densities in comparison to an ordinary thermosetting resin.⁸ Another problem is that the reaction induction time for curing of the benzoxazine compound is long and the reaction rate is slow.

To achieve a higher crosslink density of the cured resin from the benzoxazine based resin or to decrease the reaction induction time and increase the reaction rate for curing of the benzoxazine compound, we synthesized poly(*p*-vinylphenol) (VP) based benzoxazine and investigated the curing behavior of VP based benzoxazine with epoxy resin and the properties of the cured resin. Cured

resins from reinforced resins with fused silica were prepared, the properties of the cured resins were evaluated.

Moreover, the molding compound prepared from VP and epoxy resin using imidazole as a catalyst has poor thermal stability (viz., a short pot life at the molding temperature and ease of cure), so the processability of the molding compound is very poor. Fujiwara et al. improved the processability of the molding compound by means of a latent curing agent.²⁴ We also improved the processability of the phenolic resin-bisoxazoline molding compound by means of the benzoxazine ring.²² Therefore, we expected that the molding compound prepared from VP based benzoxazine and epoxy resin would have good processability, because the phenolic hydroxyl group that contributes to the curing reaction is protected by the benzoxazine ring that is stable below the molding temperature.

EXPERIMENTAL

Materials

Dioxane (98%), aniline (99%), and formaldehyde (37% in water) were purchased from Nakarai Tesuku Co., Ltd. Diglycidyl ether of bisphenol A (DGEBA, epoxy equivalent 186) was supplied by Yuka–Shell Epoxy Co., Ltd., and 2-ethyl-4-methylimidazole (2Et4Mz) was supplied by Shikoku Chemicals Co., Ltd. Maruzen Petrochemical Co., Ltd. supplied the VP ($M_n = 800$, $M_w = 1100$) and poly(*p*-vinylphenol-*co*-butyl acrylate) (VBP, $M_n = 4600$, $M_w = 11,600$, VP molar fraction = 56%). *o*-Cresol novolac type epoxy resin (OCNE, epoxy equivalent 211) was supplied by Dainippon Ink and Chemicals. Fused silica (smash type, 15- μ m average diameter) was purchased from Tatsumori Ltd. All chemicals were used without further purification. The chemical structures of these compounds are shown in Figure 2.

Synthesis and Characterization of Benzoxazines

Two kinds of VP based benzoxazines (Va and VBa) were synthesized according to the method of Ning and Ishida² (Fig. 3). The general procedure is as follows: 0.1 mol of aniline in 20 mL of dioxane was added slowly to 0.2 mol of formaldehyde (37% in water) in 80 mL of dioxane, keeping the temperature below 10°C in an ice bath. The mixture was stirred for 10 min, 0.1 mol of VP in 100

The properties of the cured epoxy resin were characterized by heat resistance, fracture toughness, electrical insulation, and water absorption. The heat resistance was estimated by the glass-transition temperature (T_g) from dynamic mechanical analysis (DMA). The DMA was performed by the three-point bending method at 1 Hz with a heating rate of 2°C/min on a Seiko Instruments Co., Ltd. DMS-110 DMA spectrometer. The peak temperature of the $\tan \delta$ by DMA was considered as the T_g .²⁵ The fracture toughness was estimated by the critical stress intensity factor (K_{IC}) according to ASTM D5045. The electrical insulation was estimated by the volume resistivity. The volume resistivity was measured by a Yokogawa–Hewlett-Packard Co., Ltd. HP4339A instrument according to JIS K6911. The disk test pieces (approximately 50-mm diameter and 3-mm thickness) were charged with electricity (500 V), and after 1 min the volume resistance was measured. The 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 resistance.

The water absorption was estimated according to JIS K7209. 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. The test pieces were taken out of the water and weighed to the nearest 0.1 mg, and the mass was taken as M_2 . The water absorption was calculated by the following equation:

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

Measurements for the melt viscosity and storage modulus (G') were conducted on a Rheometric Scientific F. E. Ltd. dynamic mechanical spectrometer (ARES-2KFR1N1) by using a 40-mm parallel plate fixture at various temperatures. The plates were preheated to 100°C before the test. Next, the plates were heated from 100°C to the measuring temperature (140 or 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.

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 equations:

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

where σ is the flexural 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; and

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

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.

The deflection temperature under load was measured on the rectangular sample according to JIS K6911. The test piece was laid horizontally on the supports (100-mm span). Next, a load determined to produce a bending stress of 18.5 kgf/cm² was put on the test piece for 5 min, and the zero point of the dial gauge was recorded. The temperature was raised at a rate of 2°C/min, and the temperature when the deflection of the test piece reached 0.26 mm to the first decimal place was measured. This was taken as the deflection temperature under load of the sample.

RESULTS AND DISCUSSION

Synthesis of VP Based Benzoxazine

The synthesis of Va and VBa was carried out using 1,4-dioxane as a solvent. The yield was 80–90%. ¹H-NMR spectra of VP and Va are shown in Figure 4. The peaks assigned to the proton of the benzoxazine ring were detected (peaks c and d), and the structure of Va was confirmed. The structure of VBa was also confirmed by ¹H-NMR and ¹³C-NMR measurements. Then, by examining the ratio between the integrated intensities of the resonance peaks in the ¹H-NMR, the benzoxazine

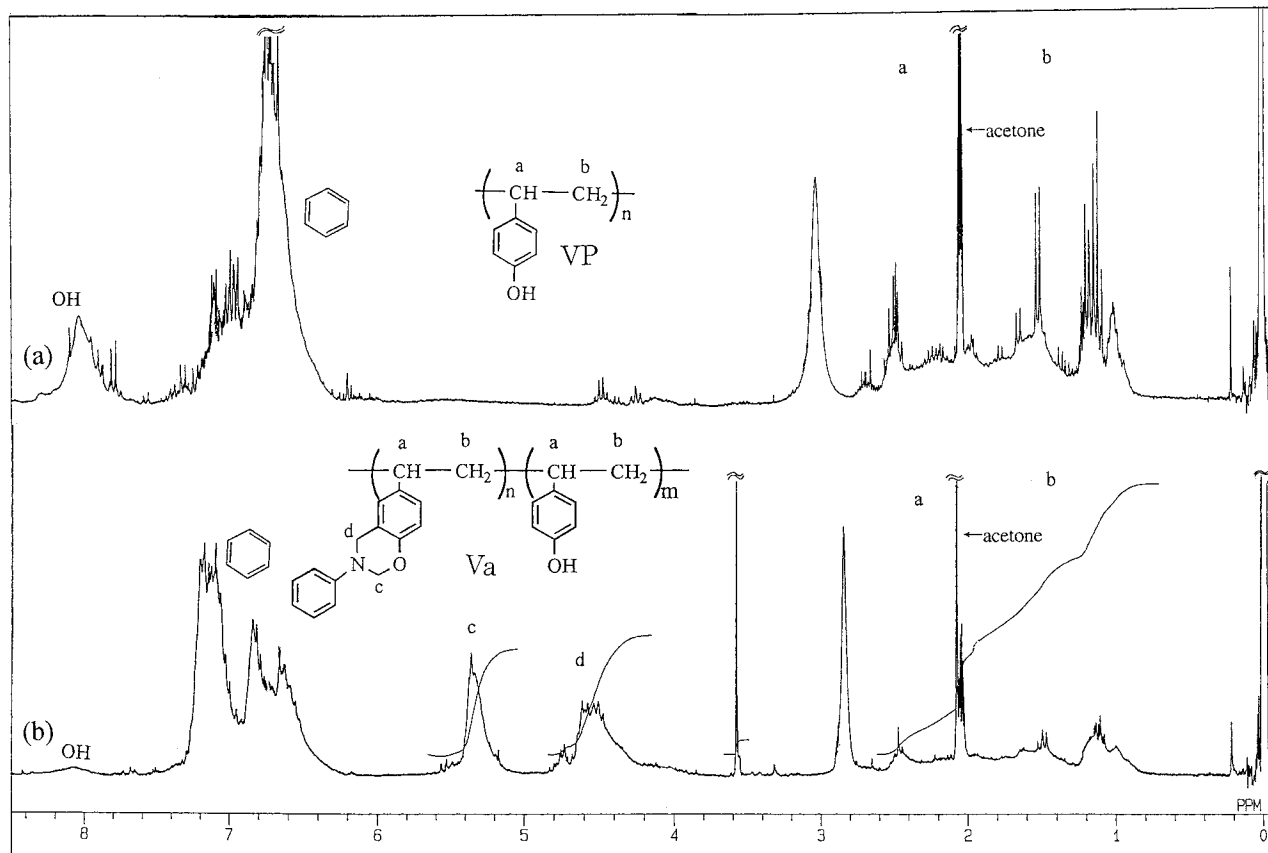


Figure 4 The $^1\text{H-NMR}$ spectra of (a) VP and (b) Va with acetone- d^6 as a solvent.

ring content in Va or VBa was calculated. The ratio between the integrated intensity of the methylene units in the benzoxazine ring [Fig. 4(b), peak d] and the integrated intensity of the methine and methylene units [Fig. 4(a), peaks a and b, respectively] in the Va polymer chain was calculated to be 0.64. Consequently, the benzoxazine ring content in the Va was calculated as 64%. In the same way, the benzoxazine content in the VBa was calculated as 72%. The presence of the phenolic structures with free ortho positions in the polymer chain may have an accelerative effect on the curing reaction: it may reduce the reaction induction time and increase the reaction rate.

Curing Reaction of VP Based Benzoxazine with Epoxy Resin

To investigate the curing reaction of Va or VBa with DGEBA in detail, the FTIR measurement was carried out. FTIR spectra of the compound prepared from the curing reaction of Va with DGEBA are shown in Figure 5. 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 both started to disappear within 2 h at 170°C [Fig. 5(b)]. When the curing condition was 170°C for 2 h and 190°C for 2 h [Fig. 5(c)], both absorptions disappeared. We 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, but at higher temperatures (above 170°C) it proceeded rapidly.

Thermal Stability of Molten Mixture from Va or VBa and DGEBA

Table I shows the gelation time of the molten mixture from 50 mol % Va or VBa and 50 mol % DGEBA and the gelation time of the molten mixture from 50 mol % VP or VBP, 50 mol % DGEBA, and 2Et4Mz as a catalyst. The molten mixtures from 50 mol % Va or VBa and 50 mol % DGEBA were thermally stable under 120°C for more than 30 min, because the curing reaction could not

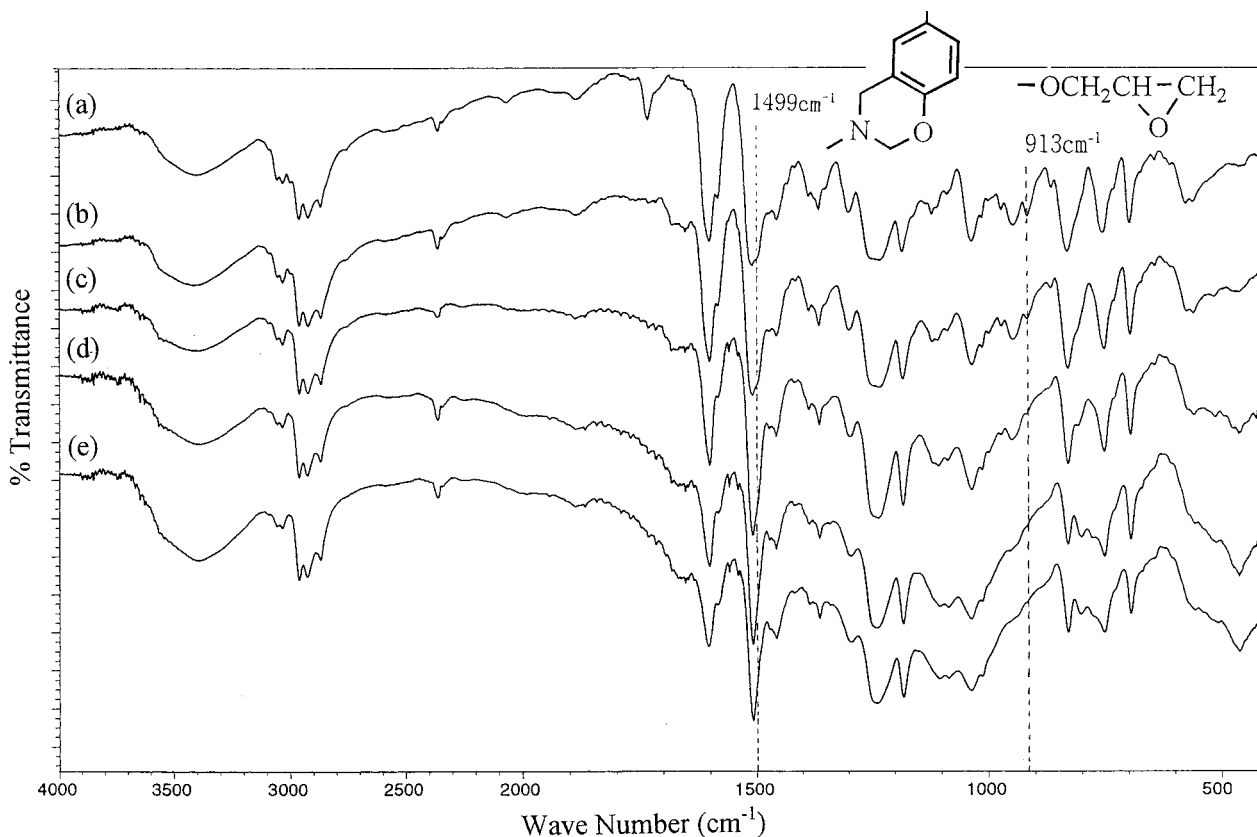


Figure 5 FTIR spectra of the molten mixture from 50 mol % Va and 50 mol % DGEBA, (a) Before reaction, (b) 170°C/2h, (c) 170°C/2h + 190°C/2h, (d) 170°C/2h + 190°C/2h + 200°C/2h, (e) 170°C/2h + 190°C/2h + 200°C/2h + 220°C/2h.

occur. This is because the ring-opening reaction of the benzoxazine ring is difficult under 120°C, and the phenolic hydroxyl groups and the tertiary amine group that are contributed to the curing reaction are not produced. However, the gelation

time was shortened with the rise of the molding temperature, because the phenolic hydroxyl groups and the tertiary amine group that were contributed to the curing reaction were produced easily. The molten mixtures from 50 mol % VP or

Table I Gelation Time of Va/DGEBA, VBa/DGEBA, VP/DGEBA, and VBP/DGEBA

Temperature (°C)	Gelation Time (min)			
	Va/DGEBA	VBa/DGEBA	VP/DGEBA ^a	VBP/DGEBA ^a
100	>90	67	6	6
120	>90	33	3	2
150	66	15	0.9	0.8
170	32	8	0.5	0.5
180	20	5	0.4	0.4
190	13	3	0.3	0.3
200	8	2	0.2	0.2
210	5	2	0.1	0.2
220	3	1	0.1	0.1

^a The catalyst was 2Et4Mz.

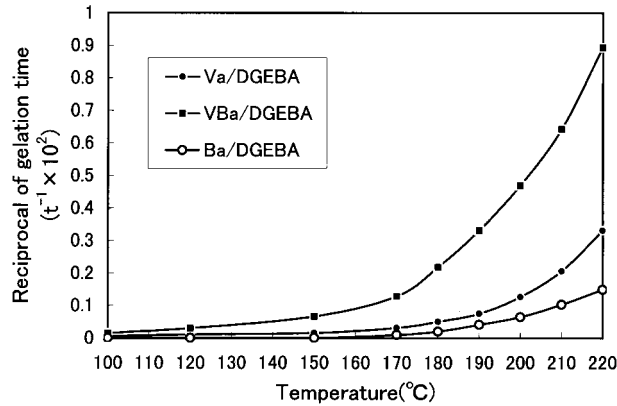


Figure 6 The reciprocal plot of the gelation time versus the temperature for (circ) Va/DGEBA, (■) VBa/DGEBA, and (○) Ba/DGEBA.

VBP, 50 mol % DGEBA, and 2Et4Mz as a catalyst cured rapidly for about 2 min, even at 120°C. We realized that the molding compound from VP and the epoxy resin using imidazole as a catalyst had poor thermal stability, which is a short pot life at the molding temperature and ease of cure, and so the processability of the molding compound was very poor. On the other hand, the molding compound from VP based benzoxazine and epoxy resin had good processability, because the phe-

nolic hydroxyl group that contributed to the curing reaction was protected by the benzoxazine ring that was stable at the molding temperature.

Furthermore, the reciprocal plot of the gelation time as a function of temperature is shown in Figure 6. The reaction rate of the molten mixture from VBa/DGEBA or Va/DGEBA was faster than that of the molten mixture from conventional Ba/DGEBA (Fig. 2), especially above 170°C, as shown in Figure 6. The reason was thought to be that Va or VBa was the polymer with high molecular weight, and so the gelation reaction of Va or VBa with DGEBA was faster than that of Ba with DGEBA.

Melt Viscosity or Storage Modulus of Molten Mixture from Va or VBa and DGEBA

Figure 7 presents the results of the DMA at 180°C, which is the typical cure temperature for phenolic resins, for Va/DGEBA, VBa/DGEBA, and Ba/DGEBA molten mixtures. The G' value of the conventional Ba/DGEBA molten mixture did not increase much for 110 min and then increased gradually, because the curing reaction was not adequate at 180°C: the reaction induction time for curing of the conventional benzoxazine compound was long, and the cure speed was slow. On the

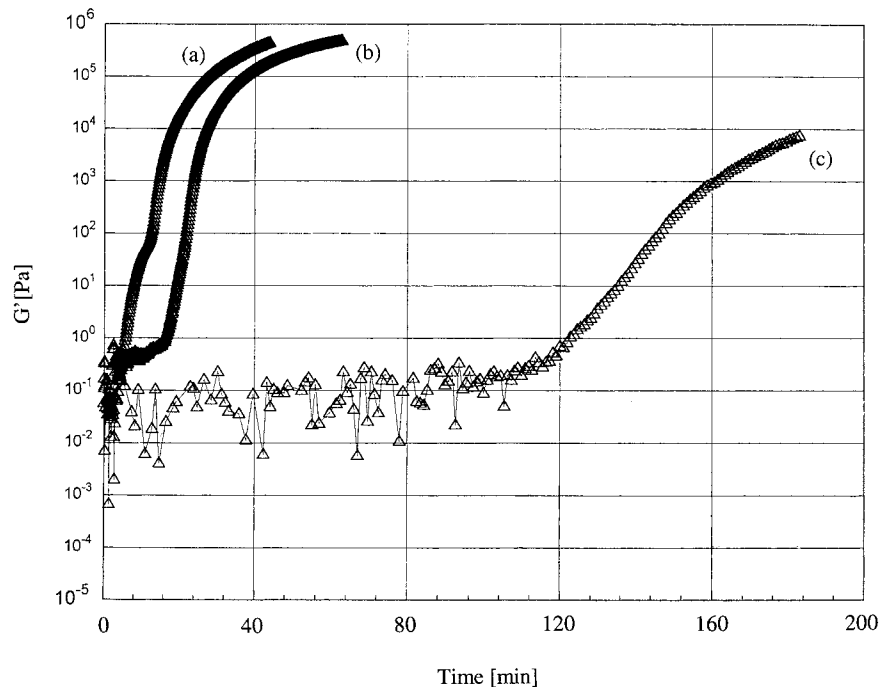


Figure 7 The plot of the G' of the molten mixture from 50 mol % Va, VBa, or Ba and 50 mol % DGEBA at 180°C: (a) VBa/DGEBA, (b) Va/DGEBA, and (c) Ba/DGEBA.

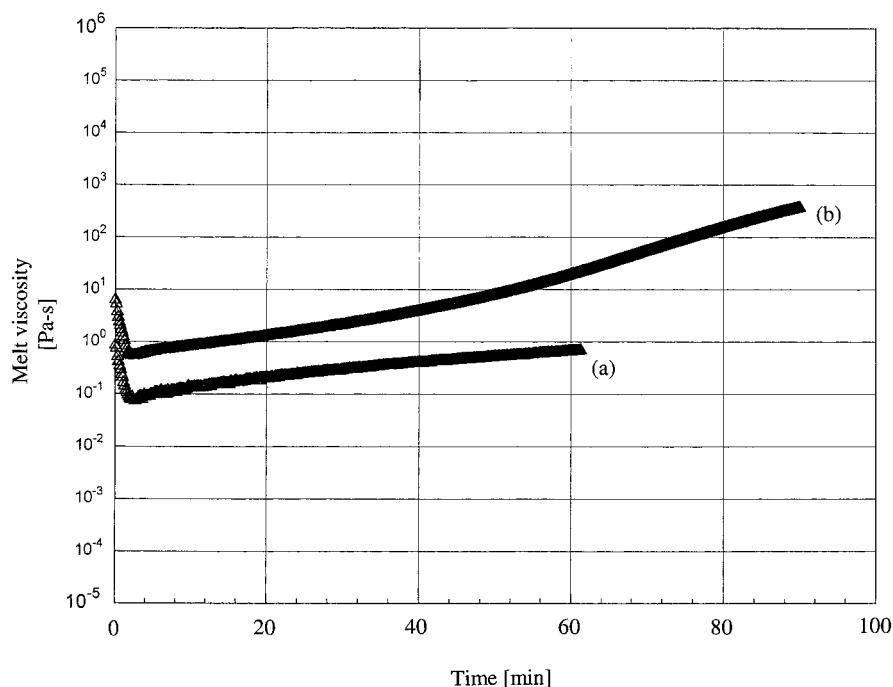


Figure 8 The plot of the melt viscosity of the molten mixture from 50 mol % Va or VBa and 50 mol % DGEBA at 140°C: (a) Va/DGEBA and (b) VBa/DGEBA.

other hand, the G' value of Va/DGEBA and VBa/DGEBA molten mixtures increased rapidly within 15 min and then reached a plateau. The slope of the G' curve at the inflection point and the intersecting point of the slopes of the G' curve were considered as the cure rate (V_c) and cure time (T_c), respectively.²⁶ As a result, the V_c values of Va/DGEBA and VBa/DGEBA molten mixtures were apparently higher than that of Ba/DGEBA. Next, the T_c values were assumed as 30 min for Va/DGEBA, 20 min for VBa/DGEBA, and 160 min for Ba/DGEBA. The Va/DGEBA and VBa/DGEBA molten mixtures had a much shorter cure time than conventional Ba/DGEBA. These results showed that the reaction induction time or cure time of the molten mixture from VP based benzoxazine and epoxy resin could decrease, compared with those from conventional Ba and epoxy resin. The curing reaction rate of VP based benzoxazine and epoxy resin could increase more than that of conventional Ba and epoxy resin. The presence of the phenolic structures with free ortho positions in the polymer chain might have an accelerative effect on the curing reaction.

Figure 8 shows the plot of the melt viscosity of Va/DGEBA and VBa/DGEBA molten mixtures versus time at 140°C. The melt viscosity of both molten mixtures was kept at a low value of 0.1–10

Pa s at 140°C, even after 1 h. 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 the benzoxazine ring was difficult at low temperature and the phenolic hydroxyl groups that contribute to the curing reaction were not produced. However, because the benzoxazine ring opened and the phenolic hydroxyl groups were easily produced above 180°C, the G' value increased rapidly as shown in Figure 7.

Properties of Cured Resin

Table II shows the properties of the cured resin from Va or VBa and DGEBA and the properties of the cured resin from VP or VBP, DGEBA, and 2Et4Mz as a catalyst. As a result, the T_g of the cured resin from Va or VBa and DGEBA was higher than that of the cured resin from VP or VBP and DGEBA. This was because the movement of molecular chain was hindered by the rigid and bulky N-Ph group between the bridging points in the cured resin. The cured resin from VBa and DGEBA had a lower T_g than that from Va and DGEBA. The lower T_g may result from the presence of a flexible butyl acrylate group. VBP was used for the purpose of improving the tough-

Table II Properties of Cured Resin from Va or VBa and DGEBA

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	
Va/DGEBA	174	0.63	1.7×10^{16}	7.5×10^{15}	0.32
VBa/DGEBA	143	0.60	1.9×10^{16}	3.4×10^{15}	0.54
VP/DGEBA ^c	165	0.64	4.7×10^{15}	1.0×10^{15}	0.50
VBP/DGEBA ^c	118	0.60	1.7×10^{16}	8.6×10^{14}	1.39

^a The peak temperature of the $\tan \delta$ by DMA.

^b After 2-h boiling.

^c The catalyst was 2Et4Mz.

ness (K_{IC}) of the benzoxazine based resin because of the flexible butyl acrylate group, but the K_{IC} of all the cured resins was almost the same value. The volume resistivity of the cured resin from Va or VBa and DGEBA was higher than that of the others, and the cured resin from Va or VBa and DGEBA had the relatively high volume resistivity of commercial conventional resins. The water absorption after 2-h boiling of the cured resin from Va or VBa and DGEBA was especially superior to those of the cured resin from VP or VBP and DGEBA. The reason was thought to be that the cured resin from Va or VBa and DGEBA had more aromatic rings and the crosslink density was augmented by the ring-opening reaction of the benzoxazine ring, as reflected by the shift in the T_g .

These results were supported by DMA. The dynamic mechanical properties of the cured res-

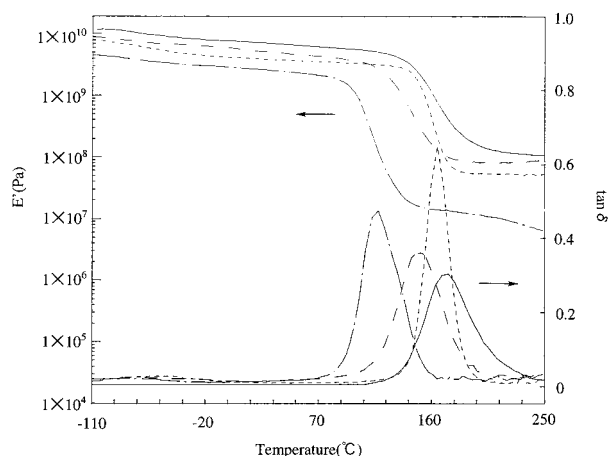


Figure 9 The dynamic mechanical properties of the cured resin from Va/DGEBA, VBa/DGEBA, VP/DGEBA, and VBP/DGEBA, (—) Va/DGEBA, (---) VBa/DGEBA, (-----) VP/DGEBA, (-.-.-) VBP/DGEBA.

ins from Va/DGEBA, VBa/DGEBA, VP/DGEBA, and VBP/DGEBA are shown in Figure 9. The crosslink density, $\rho(E')$, can be calculated using the equation of state for rubbery elasticity,²⁷

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

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.²⁸ 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 the crosslink density for highly crosslinked polymers. Therefore, in our study the $\rho(E')$ values of the samples were calculated at the T_g plus 40°C according to this equation in order to compare the crosslink density of each sample.^{10,28,29} The results are shown in Table III, assuming that ϕ is equal to 1.³⁰ The $\rho(E')$ values of the cured resin from Va or VBa and DGEBA were much higher than those of the cured resin from VP or VBP and DGEBA. This suggests that the crosslink density of the cured resin from Va or VBa and DGEBA is higher than that of the cured resin from VP or VBP and

Table III Values of $\rho(E')$ of Cured Resin from Va, VBa, VP, VBP, and Ba

Sample	$\rho(E')$ (mol/m ³)
Va/DGEBA	8.2×10^2
VBa/DGEBA	7.9×10^2
VP/DGEBA	4.5×10^2
VBP/DGEBA	1.2×10^2
Ba/DGEBA	2.6×10^2

Table IV Properties of Cured Resin from Va or VBa and OCNE

Sample	Flexural Strength (MPa)	Flexural Modulus (GPa)	T_g^a (°C)	T_{HDT}^b (°C)	Volume Resistivity (Ω cm)		Water Absorption ^c (wt %)
					Before Boiling	After 2-h Boiling	
Va/OCNE	77	7.8	209	214	6.8×10^{15}	3.2×10^{15}	0.11
VBa/OCNE	70	6.9	177	181	4.8×10^{15}	1.9×10^{15}	0.16
VP/OCNE ^d	71	6.6	209	206	6.7×10^{15}	2.1×10^{15}	0.16
VBP/OCNE ^d	69	5.1	160	156	7.1×10^{15}	2.6×10^{15}	0.28

^a The peak temperature of the $\tan \delta$ by DMA.

^b The deflection temperature under load.

^c After 2-h boiling.

^d The catalyst was 2Et4Mz.

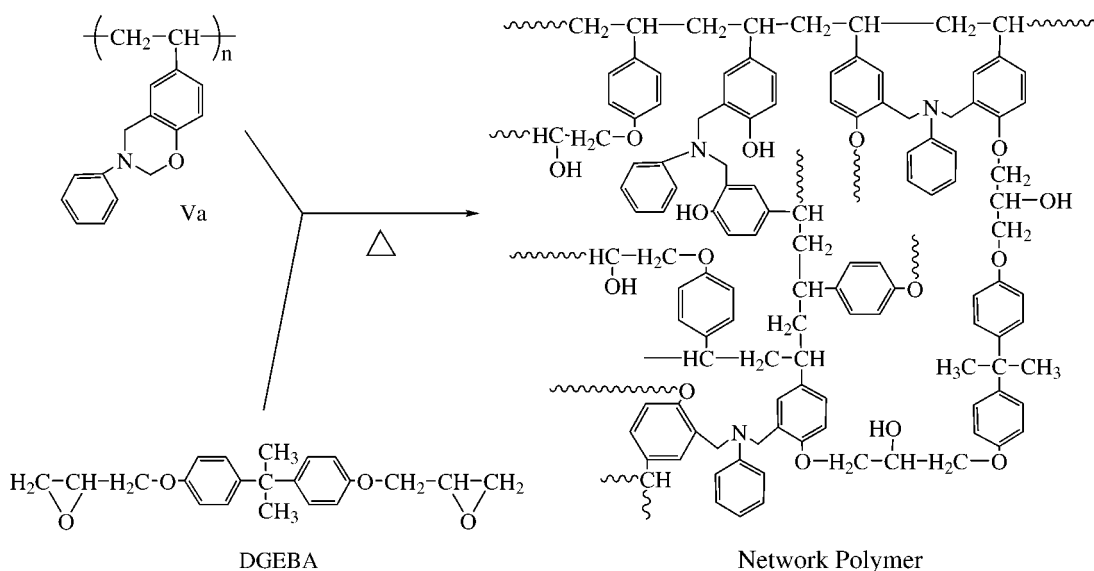
DGEBA. This high crosslink density may be due to the ring-opening reaction of the benzoxazine ring, and the $\rho(E')$ values of the cured resin from VP based benzoxazine and epoxy resin were much higher than that of the cured resin from conventional Ba (Fig. 2) and epoxy resin.

Table IV shows the properties of the cured resin from the molding compounds of Va or VBa and OCNE using silica as the filler. The flexural strength and flexural modulus of the moldings from Va or VBa and OCNE were higher than those of the others. This shows that the cured resin from the molding compounds from Va or VBa and OCNE is much stronger and harder, and the T_g and deflection temperature under load of the cured resin from the molding compounds of Va or VBa and OCNE were especially higher than

those of the cured resin from the molding compounds of VP or VBP and OCNE. Also, water absorption after 2-h boiling of the moldings from Va or VBa and OCNE was superior to that of the others. The cured resin from the molding compounds of Va and OCNE showed the highest value in all items. The crosslink density might be augmented by the ring-opening reaction of the benzoxazine ring, as shown in the DMA.

CONCLUSION

The purpose of this study was the development of a new phenolic resin, which releases no volatiles during the curing reaction and needs no catalysts. We investigated the curing reaction of VP based

**Figure 10** The curing reaction of Va with DGEBA.

benzoxazine with epoxy resin as shown in Figure 10 and the properties of the cured resin. The curing reaction did not proceed at low temperature, but it proceeded quantitatively without curing accelerators at higher temperature. The molten mixture from VP based benzoxazine and epoxy resin showed good thermal stability and good flowability under 140°C; above 180°C the curing reaction proceeded rapidly. We also found that the reaction induction time or cure time of the molten mixture from VP based benzoxazine and epoxy resin was able to decrease compared to those of the molten mixture from conventional Ba and epoxy resin, and the curing reaction rate of VP based benzoxazine and epoxy resin was also able to increase. The cured resin from VP based benzoxazine and epoxy resin had heat resistance, electrical insulation, and water resistance that was superior to those of the cured resin from VP and epoxy resin using imidazole as a catalyst.

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