

Curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin

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Abstract. Curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin were investigated. The cure behavior of benzoxazine with cyanate ester resin was monitored by model reaction using nuclear magnetic resonance (NMR). As a result of the model reaction, the ring opening reaction of benzoxazine ring and thermal self-cyclotrimerization of cyanate ester group occurred, and then the phenolic hydroxyl group generated by the ring opening reaction of benzoxazine ring co-reacted with cyanate ester group. The properties of the cured thermosetting resin were estimated by mechanical properties, electrical resistivity, water resistance and heat resistance. The cured thermosetting resin from benzoxazine and cyanate ester resin showed good heat resistance, high electrical resistivity and high water resistance, compared with the cured thermosetting resin from benzoxazine and epoxy resin.

Keywords: thermosetting resins, benzoxazine, cyanate ester resin

1. 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 microvoids. Moreover acid or base compounds as catalysts must be used to synthesize novolac or resole precursors of cured phenolic resin, which result in corrosion of the processing equipment. Another problem is that the cured phenolic resin is brittle.

It is well known that the benzoxazine ring is stable at low temperature, but a ring opening reaction occurs at high temperature, and novolac type oligomers having both phenolic hydroxyl group and tertiary amine group are produced [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.

Ishida and co-workers [2–24] synthesized a lot of types of oxazines and studied their cure kinetics, molecular structures, mechanical and dynamic mechanical properties, and so on. Jang and Shin also studied the cure kinetics of a benzoxazine-based phenolic resin [25]. Jang and Seo studied the performance improvement of rubber-modified polybenzoxazine [26]. Recently, maleimide-modified [22–23, 27–28] and furan-modified [29] benzox-

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azines have been synthesized, and the properties of the cured resins have been investigated. Nanocomposites using benzoxazines also recently have been reported [30–33].

We also have already investigated the curing behavior of the bisphenol-A, terphenol or poly(*p*-vinylphenol) based benzoxazines with epoxy resin or bisoxazoline and the properties of the cured resins [34–41]. Consequently, the molding compound from bisphenol-A based benzoxazine and epoxy resin or bisoxazoline showed good flowability below 140°C, curing reaction proceeded above 180°C rapidly. And the cured thermosetting resins from benzoxazine compounds and epoxy resin or bisoxazoline had superior heat resistance, electrical resistivity, mechanical properties and water resistance to the cured thermosetting resins from conventional bisphenol-A type novolac and epoxy resin or bisoxazoline.

In this report, we investigated the curing behavior of benzoxazine resin with cyanate ester resin and the properties of the cured thermosetting resin.

Cyanate ester resin has drawn a great deal of attention as one of the high-performance thermosets, comparable to epoxy resins and polyimide. The cyanate ester monomer undergoes thermal self-cyclotrimerization to form a three-dimensional net-

work structure of polycyanurate containing triazine groups [42, 43]. Polycyanurate possesses several superior properties including high heat resistance, low moisture absorption, high electrical resistivity, low dielectric constant, and low shrinkage. Therefore it is also expected that the cured thermosetting resin from benzoxazine resin and cyanate ester resin has high heat resistance, high electrical resistivity and low moisture absorption. 2,2-bis(4-cyanatophenyl) propane (bisphenol-A based cyanate ester resin) is a widely accepted cyanate ester monomer used in wide range applications. In this study, we investigated the curing behavior of bisphenol-A based benzoxazine with bisphenol-A based cyanate ester resin and the properties of the cured thermosetting resin.

2. Experimental

2.1. Materials

2,2-bis(3,4-dihydro-3-phenyl-1,3-benzoxazine) propane (bisphenol-A based benzoxazine, Ba) and 2-(3,4-dihydro-3-phenyl-1,3-benzoxazine) butane (mono functional benzoxazine, BuPa) was supplied by Shikoku Chemicals Co., Ltd. (Kagawa, Japan). 2,2-bis(4-cyanatophenyl) propane (bisphenol-A based cyanate ester, BADCy) and 2-phenyl-2-(4-cyanatophenyl) propane (mono functional cyanate

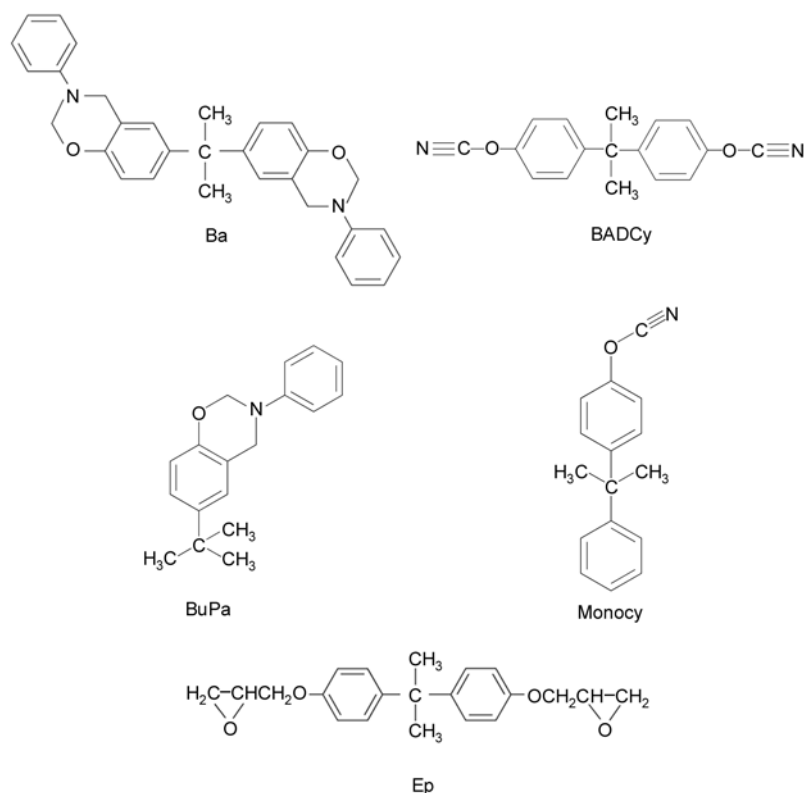


Figure 1. Chemical structures of Ba, BuPa, BADCy, Monocy and Ep

ester, Monocy) was supplied by Mitsubishi Gas Chemical Company, Inc. (Tokyo, Japan). Bisphenol A based epoxy resin (EPIKOTE 828, epoxy equivalent 186) as an epoxy resin (Ep) was supplied by Japan Epoxy Resins Co., Ltd. (Tokyo, Japan). All chemicals were used without further purification. The chemical structures of Ba, BuPa, BADCy, Monocy and Ep are shown in Figure 1.

2.2. Model reaction and characterization

It is difficult to investigate the curing reaction of Ba with BADCy in detail because both Ba and BADCy have two functionalities and gelation occurs easily, and so the compound from the reaction is partially insoluble in solvents used for the measurement of nuclear magnetic resonance (NMR) such as CDCl_3 , acetone-D, CD_3OD and so on. In this way, BuPa and Monocy were used as each model compounds in order to investigate curing behavior of benzoxazine (Ba) with cyanate ester resin (BADCy), because both BuPa and Monocy have mono functionality and gelation does not occur, and it is easy to investigate the curing reaction. The structures of the compounds obtained by model reaction (reaction of BuPa with Monocy) were analyzed by ^{13}C -NMR measurement. ^{13}C -NMR measurement was carried out on Japan Electron Company (Tokyo, Japan) JMN-GSX-270 instrument operating at 67.8 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane was used as an internal standard.

2.3. Curing condition

Samples containing 50 mol% Ba and 50 mol% BADCy were prepared and cured in a mold at a specified temperature in the oven. The curing condition of Ba with BADCy was determined as $180^\circ\text{C}/2\text{ h} + 200^\circ\text{C}/2\text{ h} + 220^\circ\text{C}/2\text{ h}$ from the results of Fourier Transform Infrared Spectrophotometer (FT-IR). For comparison, the curing reaction of 50 mol% Ba with 50 mol% Ep was also carried out. The curing condition of Ba with Ep was determined as $170^\circ\text{C}/2\text{ h} + 190^\circ\text{C}/2\text{ h} + 200^\circ\text{C}/2\text{ h} + 220^\circ\text{C}/2\text{ h}$ from the results of previous paper [34].

2.4. Properties of the molding compound and the cured resin

The structure of the cured thermosetting resin was analyzed by Fourier Transform Infrared Spectrophotometer (FT-IR). FT-IR measurement was carried

out on Nicolet Impact 420 instrument (Thermo Fisher Scientific K.K, Yokohama, Japan). 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.

Differential scanning calorimetry (DSC) was applied to evaluate the cure behavior. DSC was measured with heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere on a Seiko Instruments Co., Ltd., (Chiba, Japan) STI EXSTAR 6000.

Thermal gravimetric analysis (TGA) was applied to evaluate the thermal stability. TGA was measured with heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere on a Seiko Instruments Co., Ltd. (Chiba, Japan) TGA 5200 Thermal Gravimetric Analyzer.

In order 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 thermosetting 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 points bending method at 1 Hz, with a heating rate of $2^\circ\text{C}/\text{min}$ on a Seiko Instruments Co., Ltd (Chiba, Japan) DMS-110 Dynamic Mechanical Analysis Spectrometer. The peak temperature of $\tan\delta$ by dynamic mechanical analysis was considered as T_g [44].

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 (Tokyo, Japan) 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 Equation (1):

$$\rho_V = \frac{\pi d^2}{4t} \cdot R_V \quad (1)$$

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 50mm 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 Equation (2):

$$\text{Water absorption [\%]} = \frac{M_2 - M_1}{M_1} \cdot 100 \quad (2)$$

3. Results and discussion

3.1. Model reaction

^{13}C -NMR spectrum of the product obtained by model reaction (reaction of BuPa with Monocy) at 200°C for 1 hr is shown in Figure 2. As a result, both

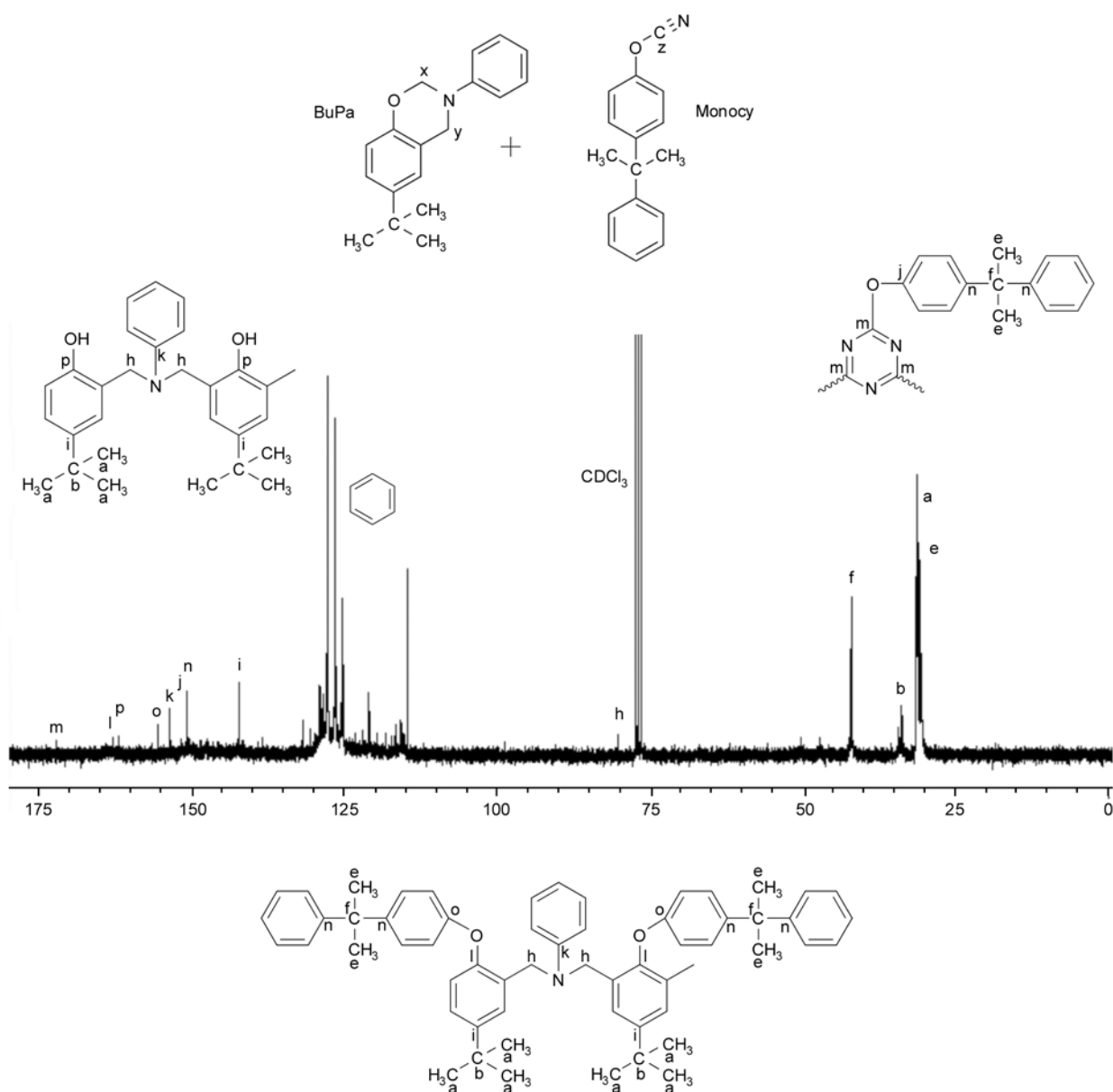


Figure 2. ^{13}C -NMR spectrum of the product obtained by model reaction at 200°C for 1 hr

two peaks (x, 79.1 ppm and y, 50.7 ppm) assigned to the carbon of benzoxazine ring and a peak (z, 108.8 ppm) assigned to the carbon of cyanate ester group were not detected. The peak (p) assigned to C1 carbon of the benzene ring adjacent to phenolic hydroxyl group generated by the ring opening reaction of benzoxazine ring was detected. The peak (h) assigned to methylene carbon of



which was produced by the ring-opening reaction of benzoxazine ring, was also detected. It was found that the ring-opening reaction of the benzoxazine ring occurred (Figure 3). And the peak (m) assigned to C1 carbon of the benzene ring adjacent to triazine group generated by the thermal self-cyclotrimerization of cyanate ester group was detected. It was found that thermal self-cyclotrimerization of cyanate ester group occurred (Figure 3). Furthermore, the peak (l) assigned to C1 carbon of the benzene ring adjacent to ether bond was detected. It was suggested that the phenolic hydroxyl group produced by the ring opening reaction of BuPa reacted with cyanate ester group of Monocy. Namely, shown in Figure 4, the phenolic hydroxyl group produced by the ring opening reaction of benzoxazine co-reacted with cyanate ester group to form the intermediate iminocarbonate, which further induce curing reaction of cyanate ester to form polycyanurate.

3.2. Curing reaction of Ba with BADCy

To investigate the curing reaction of Ba with BADCy, FT-IR measurement was carried out. FT-IR spectra of the compound before and after the curing reaction of Ba with BADCy are shown in Figure 5. As a result, the absorption at 949 cm^{-1} assigned to the tri-substituted benzene ring in the benzoxazine ring structure disappeared after 2 h at 180°C (Figure 5b). And the absorptions at 2266 and 2230 cm^{-1} assigned to cyanate ester group also disappeared after 2 h at 180°C (Figure 5b). The new absorptions at 1565 and 1370 cm^{-1} assigned to the triazine group appeared after 2 h at 220°C (Figure 5d). It was found the ring opening reaction of benzoxazine ring and thermal self-cyclotrimerization of cyanate ester group occurred, and then the phenolic hydroxyl groups generated by the ring-opening reaction of benzoxazine ring might react with cyanate ester as shown in Figure 4 from the results of model reaction.

From the results of FT-IR measurement, the curing condition was determined as follows: after the molding compound softened at 150°C to remove any bubbles containing in it sufficiently, curing reaction was carried out stepwise at $180^\circ\text{C}/2\text{ hr} + 200^\circ\text{C}/2\text{ hr}$. Finally, at $220^\circ\text{C}/2\text{ hr}$ the cured thermosetting resin was postcured so that the curing reaction could proceed completely. In this way, the curing condition of Ba with BADCy was determined as $180^\circ\text{C}/2\text{ hr} + 200^\circ\text{C}/2\text{ hr} + 220^\circ\text{C}/2\text{ hr}$.

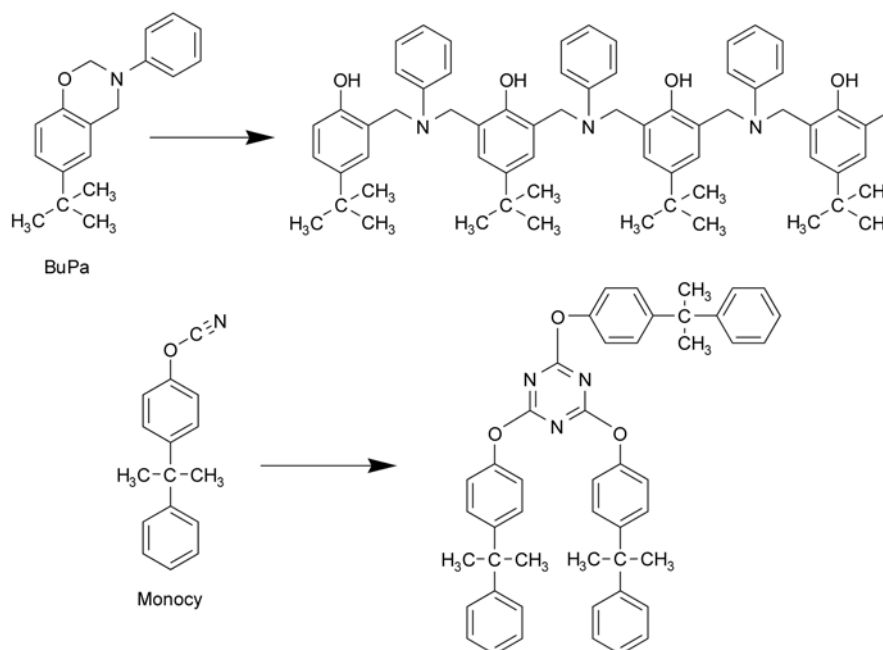


Figure 3. Ring-opening reaction of benzoxazine (BuPa) and thermal self-cyclotrimerization of cyanate ester (Monocy)

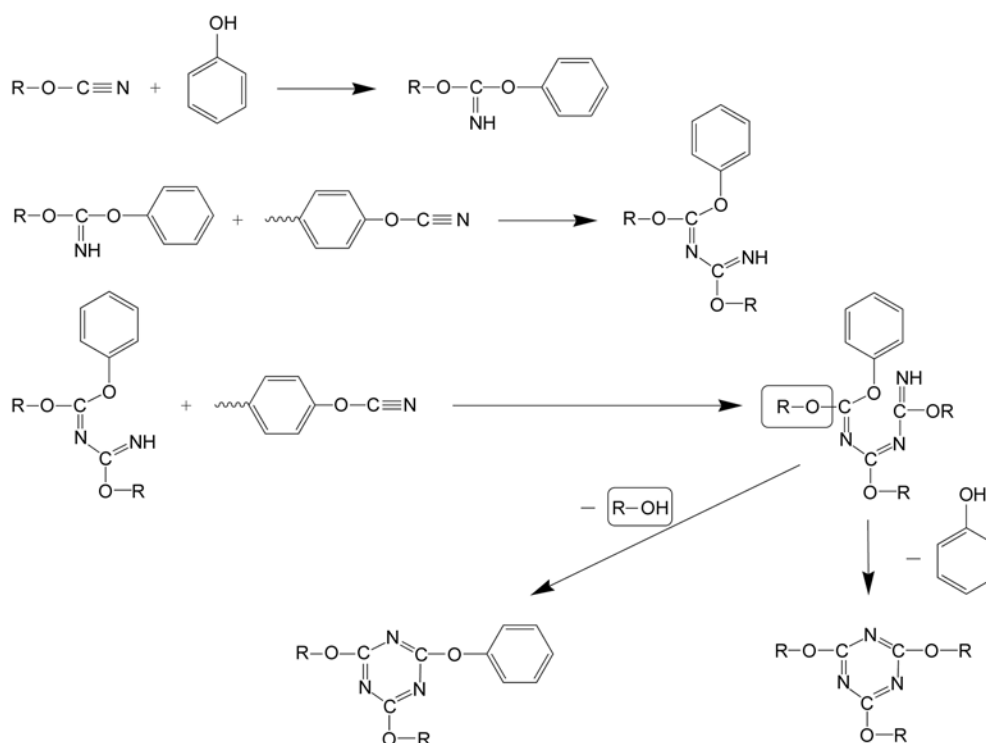


Figure 4. Co-reaction of benzoxazine (BuPa) with cyanate ester (Monocy)

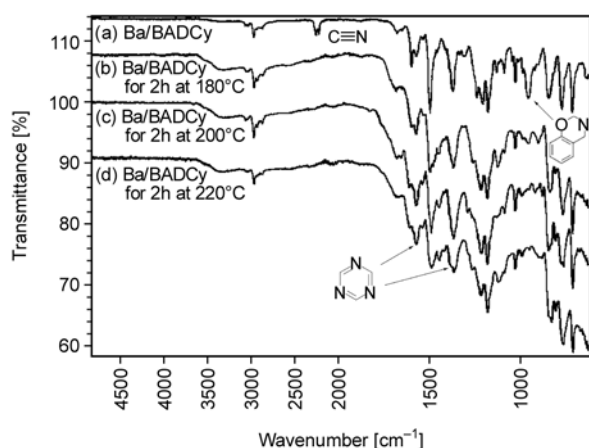


Figure 5. FT-IR spectra of the compound from curing reaction of 50 mol% Ba with 50 mol% BADCy. (a) before curing reaction, (b) after 180°C/2 hr, (c) after 180°C/2 hr + 200°C/2 hr, (d) after 180°C/2 hr + 200°C/2 hr + 220°C/2 hr.

3.3. Thermal stability of the molding compound from Ba and BADCy

The gelation time of the molding compounds from 50 mol% Ba and 50 mol% BADCy was measured. Furthermore, the reciprocal plot of gelation time as a function of temperature is shown in Figure 6. The molding compound was thermally stable under 120°C for about 45 min, because the curing reaction could not occur. This was because the ring opening reaction of benzoxazine ring was difficult to occur

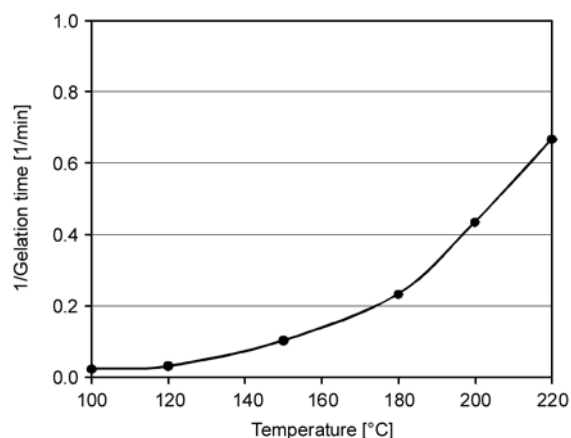


Figure 6. Reciprocal plot of gelation time as a function of temperature

under 120°C, especially under dilution by BADCy, 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, and thermal self-cyclotrimerization of cyanate ester group occurred.

3.4. DSC analysis of the molding compound

Figure 7 shows the DSC curves of the molding compounds from Ba and BADCy or Ep. From the

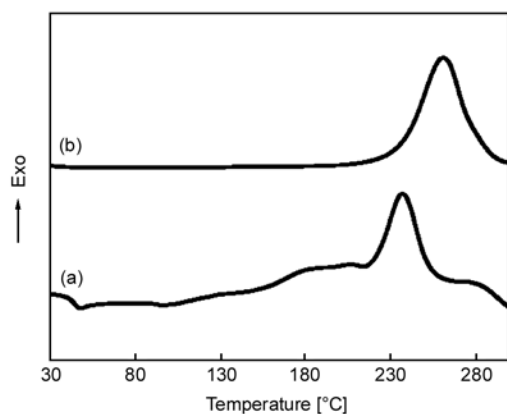


Figure 7. DSC curves of the molding compounds from Ba and BADCy or Ep. (a) Ba + BADCy, (b) Ba + Ep.

results of DSC, the maximum exotherm temperature (peak temperature) of the molding compounds from Ba and BADCy shifted to lower temperature side by about 20°C, compared with that of the molding compounds from Ba and Ep. It was found that the curing reaction of Ba with BADCy could proceed more rapidly than that of Ba with Ep. The reason might be considered that the co-reaction of the phenolic hydroxyl group produced by the ring opening reaction of benzoxazine with cyanate ester group occurred more rapidly than that of the phenolic hydroxyl group produced by the ring opening reaction of benzoxazine with epoxy group.

3.5. TGA analysis of the molding compound

Figure 8 shows the TGA curves of the molding compounds from Ba and BADCy or Ep. For the molding compounds from Ba and BADCy, the initial decomposition that was defined as 5 wt% of mass loss occurred about 330°C and the char yield at 600°C was 44 wt%. For the molding compounds from Ba and Ep, the initial decomposition that was defined as 5 wt% of mass loss occurred about 310°C and the char yield at 600°C was 27 wt%. In terms of the thermal gravimetric results, the thermal decomposition stability of the molding compounds from Ba and BADCy was superior to that of the molding compounds from Ba and Ep.

Table 1. Properties of the cured thermosetting resins

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	
Ba/BADCy	223	0.61	$5.5 \cdot 10^{16}$	$5.2 \cdot 10^{15}$	0.26
Ba/Ep	175	0.54	$4.0 \cdot 10^{16}$	$1.2 \cdot 10^{15}$	0.46

^aPeak temperature of $\tan \delta$ by DMA.

^bAfter 2 h boiling.

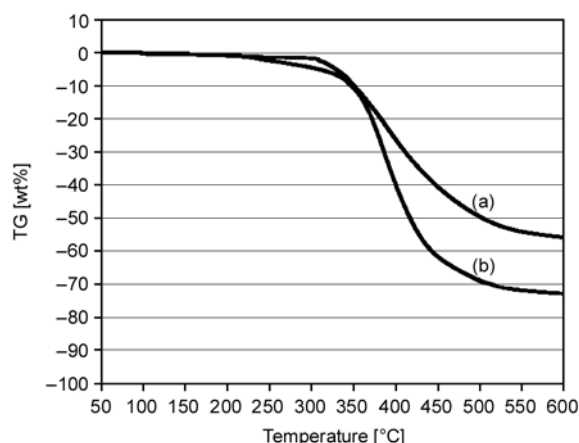


Figure 8. TGA curves of the molding compounds from Ba and BADCy or Ep. (a) Ba + BADCy, (b) Ba + Ep.

3.6. Properties of the cured thermosetting resin

The properties of the cured thermosetting resins from Ba and BADCy or Ep are shown in Table 1. And the curves of Dynamic mechanical analysis (DMA) are shown in Figure 9. As a result, glass transition temperature (T_g) of the cured thermosetting resin from Ba and BADCy was much higher than that of the cured thermosetting resins from Ba and Ep. The cured thermosetting resin from Ba and BADCy had extremely high volume resistivity of commercial resins, and volume resistivity of the cured thermosetting resin from Ba and BADCy was a little higher than that of the cured thermosetting

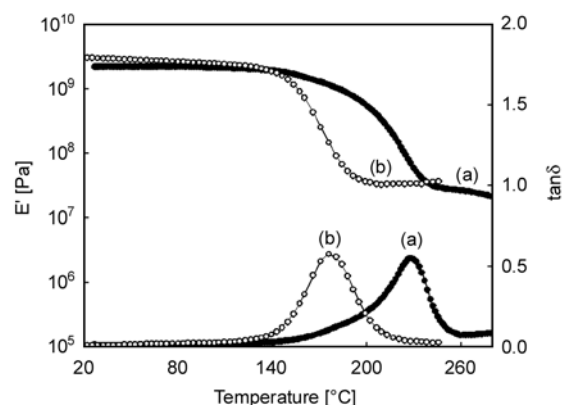


Figure 9. DMA curves of the cured thermosetting resins from Ba and BADCy or Ep. (a) Ba/BADCy, (b) Ba/Ep.

resins from Ba and Ep. K_{IC} of the cured thermosetting resin from Ba and BADCy was also slightly higher than that of the cured thermosetting resin from Ba and Ep. Water absorption after 2 h boiling of the cured thermosetting resin from Ba and BADCy was superior to that of the cured thermosetting resin from Ba and Ep. The reason of these results (good heat resistance, high electrical resistivity and high water resistance) might be due to the formation of rigid and hydrophobic triazine ring by thermal self-cyclotrimerization of cyanate ester group [43].

4. Conclusions

In this study, we investigated the curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin. As a result of model reaction, it was found that the ring opening reaction of benzoxazine ring and thermal self-cyclotrimerization of cyanate ester group occurred. Furthermore, it was suggested that the phenolic hydroxyl group produced by the ring opening reaction of benzoxazine co-reacted with cyanate ester group to form the intermediate imonocarbonate, which further induce curing reaction of cyanate ester to form polycyanurate containing triazine groups. The molding compound from benzoxazine and cyanate ester resin showed good thermal stability below 120°C, but above 160°C the curing reaction of benzoxazine with cyanate ester resin proceeded more rapidly. From the thermal gravimetric results, the thermal decomposition stability of the molding compounds from benzoxazine and cyanate ester resin was superior to that of the molding compounds from benzoxazine and epoxy resin. The cured thermosetting resin from benzoxazine and cyanate ester resin had superior heat resistance, electrical resistance and water resistance to those from benzoxazine and epoxy resin. This might be because rigid and hydrophobic triazine ring structure was incorporated into the backbone of the cured thermosetting resin by thermal self-cyclotrimerization of cyanate ester group.

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