Glass Fiber-Reinforced Composite Based on Benzoxazine Resin

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ABSTRACT: In this study, we aimed to prepare and characterize glass fiber-reinforced composites (GFRP) based on benzoxazine resins. Therefore, the molten resin from benzoxazine and bisoxazoline with the latent curing agent was used as the matrix resin, and the properties of GFRP based on the molten resins were investigated. The properties of GFRP were estimated by mechanical properties, heat resistance, and flame resistance. As a result, it was found that GFRP based on the molten resins from benzoxazine and bisoxazoline with the latent curing agent showed good heat resistance, flame resistance, and mechanical properties compared with those of the conventional GFRP. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1256–1263, 2009

Key words: glass fiber-reinforced composite; benzoxazine; bisoxazoline; latent curing agent

INTRODUCTION

Epoxy resins (EPs) are widely used as an advanced composite matrix in the electronic or electrical industries because of their high mechanical properties, low shrinkage in cure, good adhesion properties, superior electrical insulation properties, and good processability. The main problem of EPs is their flammability. Although halogenated flame retardants give good flame retardancy and have been used widely for several decades, these materials including halogen compounds such as Br would be difficult to use because of the production of dioxane derivatives, which are harmful to the environment when combusted. For this reason, developing the new halogen-free, flame-retardant materials instead of the halogenated EPs is becoming important.

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 oligomers (benzoxazine-based resin) having both the phenolic hydroxyl group and the tertiary amine groups are produced[1] (Fig. 1). We think that this benzoxazine-based resin has attracted significant attention as a new halogen-free, flame-retardant material instead of a halogenated EP.

Benzoxazine-based resin has unique characteristics, such as dimensional stability, near-zero shrinkage, in addition to good heat resistance, water resistance, electrical insulation properties, mechani-

cal properties, and flame resistance.[2–8] Furthermore, this benzoxazine-based resin does not need strong acid catalysts for curing, and does not produce by-products during curing reaction.[9] We also have already investigated the curing behavior of the bisphenol-A, terpenediphenol, or poly(p-vinylphenol)-based benzoxazines with EP or bisoxazoline and the properties of the cured resins.[10–14]

Despite the high performance (e.g., good heat and flame resistance) of benzoxazine-based resin, it is believed that benzoxazine-based resins show surprisingly low crosslink densities in comparison with the ordinary thermosetting resin.[15] Then, the most important problem is that the cure time of the benzoxazine compounds is long, and also that the cure temperature is high. We have been studying to reduce the cure time and to lower the cure temperature of the benzoxazine compound. Therefore, we prepared heat latent curing agents from acids and amines and investigated the catalytic effects of the latent curing agents on the curing reaction of benzoxazine with bisoxazoline or EP and the properties of the cured resins.[16–18] As a result, the cure time of molten resins from benzoxazine and bisoxazoline or EP with latent curing agent was reduced, and the cure temperature was lowered, in comparison with those of resins from benzoxazine and bisoxazoline or EP without latent curing agent. Cured resins from benzoxazine and bisoxazoline or EP with latent curing agent showed good heat resistance, flame resistance, mechanical properties, and electrical insulation, in comparison with cured resins from benzoxazine and bisoxazoline or EP without latent curing agent.

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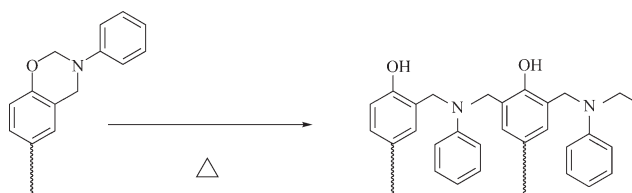
Figure 1 Ring-opening reaction of a benzoxazine ring.

To date, a few papers have reported on glass fiber-reinforced composite (GFRP) based on the benzoxazine resin. In this study, we aimed to prepare and characterize GFRPs based on benzoxazine resins. Therefore, the molten benzoxazine resins from benzoxazine and bisoxazoline with the latent curing agent were used as the matrix resin, and the properties of GFRP based on the molten benzoxazine resins were investigated.

EXPERIMENTAL

Materials

Glass cloth (WEA 22F 105BXN, amino silane coupling agent treated, plain woven cloth) used as reinforcement was supplied by Nittobo (Tokyo, Japan).

Diethanolamine, isopropanolamine, and p-toluenesulfonic acid were purchased from Nacalai Tesque (Kyoto, Japan). 2,2-Bis(3,4-dihydro-3-phenyl-1,3-benzoxazine)propane (bisphenol-A-based benzoxazine; Ba) was supplied by Shikoku Chemicals (Kagawa, Japan). 2,2′-(1,3-Phenylene)-bis(4,5-dihydro-oxazoles) as a bisoxazoline (1,3-PBO) was supplied by Mikuni Pharmaceutical Industrial (Osaka, Japan). Bisphenol A-based EP (EPIKOTE 828, epoxy equivalent 186) as an EP, and tetrabromobisphenol A-based EP (EPIKOTE 5046B80, epoxy equivalent 472, Br content 20.6%) as a flame-retardant EP (TBBA) were supplied by Japan Epoxy Resins (Tokyo, Japan). And triethylene tetramine (TETA) and dicyandiamide (DICY) were used as the curing agents for EP and TBBA. All chemicals were used without further purification. The chemical structures of Ba and 1,3-PBO are shown in Figure 2.

Preparation of the heat latent curing agent

The preparation of the heat latent curing agent was carried out by using the reaction of the acids and amine compounds.[16–18] In a typical experiment, diethanolamine as an amine compound (5.26 g, 0.05 mol) was charged to a beaker, and p-toluenesulfonic acid (9.5 g, 0.05 mol) was added to the beaker. The product was the neutral salt obtained from the acid and amine, and it was used as the heat latent curing agent without purification.

Preparation of the matrix resins for GFRP

Two kinds of matrix resin samples (Sample No. 1 and No. 2) containing 50 mol % Ba and 50 mol % 1,3-PBO with latent curing agents were prepared.

Sample (No. 1) containing 50 mol % Ba and 50 mol % 1,3-PBO was heated to about 150°C, and a clear molten mixture was obtained. After the temperature of the molten mixture was cooled down to 100°C, 10 wt % latent curing agent (Cat. 1, neutral salt obtained from diethanolamine and p-toluenesulfonic acid) was added into the molten mixture and stirred. The clear molten mixture (Ba/1,3-PBO/Cat. 1) obtained was used as a matrix resin for GFRPs.

Sample (No. 2) containing 50 mol % Ba and 50 mol % 1,3-PBO was heated to about 150°C, and a clear molten mixture was obtained. After the temperature of the molten mixture was cooled down to 100°C, 5 wt % latent curing agent (Cat. 2, neutral salt obtained from isopropanolamine and p-toluenesulfonic acid) was added into the molten mixture and stirred. The clear molten mixture (Ba/1,3-PBO/Cat. 2) obtained was used as another matrix resin for GFRPs.

Preparation of GFRP

The preparation of GFRPs was carried out by using the prepreg method. Namely, glass cloth was impregnated with a solution of the matrix resins in methyl ethyl ketone and dried at room temperature for about 18 h. After that, 10 plies of the prepregs were stacked and molded using compression molder at 150°C for 2 h + 170°C for 1 h under the pressure
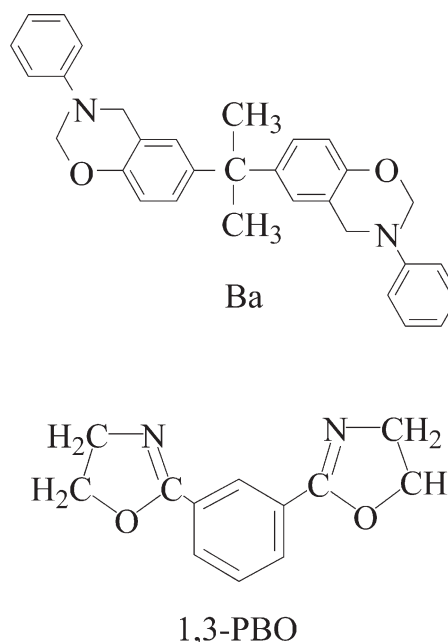
Figure 2 Chemical structures of Ba and 1,3-PBO.
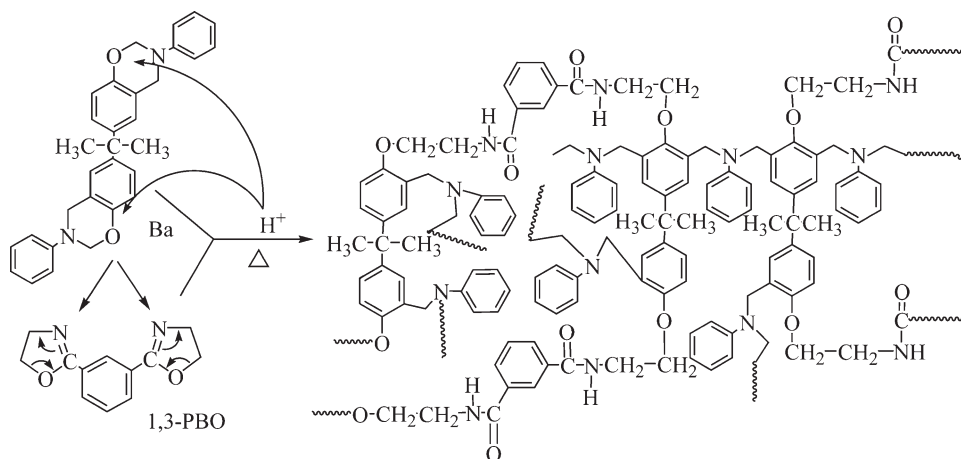
Figure 3 Curing reaction (copolymerization) of Ba with 1,3-PBO.

of 50 kg/mm^2. Then, the laminate was postcured in an oven at 170°C for 1 h + 200°C for 2 h. This curing condition was determined from the results of previous reports.[16–18]

For comparison, the conventional fiber-reinforced epoxy composites were prepared using the same glass cloth with amino silane coupling agent by prepreg method. TETA (12.8 phr) was used as the curing agent for EP, and DICY (6 phr) was used as the curing agent for TBBA. Curing condition of EP was at room temperature for 1 day under the pressure of 50 kg/mm^2, and that of TBBA was at 160°C for 1 h + 180°C for 20 min under the pressure of 50 kg/mm^2. Ten plies of the prepregs were stacked and molded using compression molder.

Resin-content determination

The resin content was determined by pyrolysis of specimens in air at 600°C for 4 h and by estimating the mass loss. The resin content of any GFRP was in the range of 50–51% by weight.

Properties of the GFRP

The properties of GFRP were characterized by their heat resistance, tensile, flexural, and impact properties, and flame resistance.

The heat resistance was estimated via the glass-transition temperature (T_g) by dynamic mechanical analysis (DMA). DMA was measured by a three-point-bending method at 1 Hz, with heating rate of 2°C/min on a Seiko Instruments (Tiba, Japan) DMS-110 DMA spectrometer. The peak temperature of tan δ by DMA was considered to be T_g.[19]

The tensile properties were measured on a type B test piece according to JIS K7054. After attaching the test piece to the two holders, a load was applied on the test piece and measured at the break of test piece at the nearest

0.1 kgf. If the break has taken place outside the mid parallel portion, the measurement shall be discarded and a retest shall be made. The tensile strength (σ_t) was calculated with the following equation:

$$\sigma_t = P_t/A$$

where P_t is the load at break of test piece, and A is the original minimum sectional area of test piece.

The flexural properties were measured on rectangular samples according to JIS K7055. 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 (σ_b) was calculated with the following equation:

$$\sigma_b = 3P_bL/2Wh^2$$

where P_b is the load at break of test piece, L is the support span, W is the width of test piece, and h is the depth of test piece.

The impact strength was measured on flatwise samples according to JIS K7061. Test piece is held as a simply supported beam and is impacted by a swinging pendulum. The energy lost by the pendulum is equated with the energy absorbed by the test
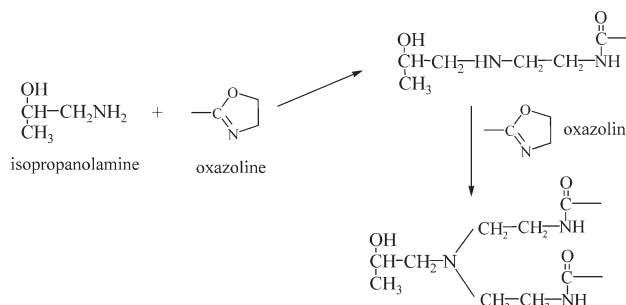
Figure 4 Curing reaction of amines liberated with oxazoline.
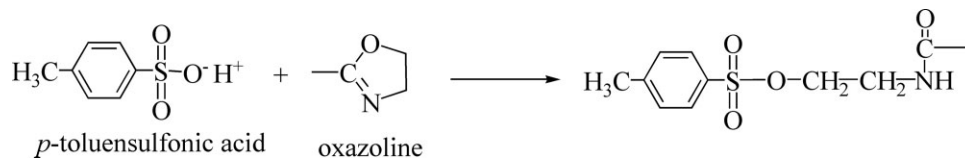
Figure 5 Curing reaction of acids liberated (p-toluenesulfonic acid) with oxazoline ring.

specimen. The absorbed energy is calculated by the use of the following equation:

$$E = WR[(\cos\beta - \cos\alpha) \\ - (\cos\alpha' - \cos\alpha)(\alpha + \beta/\alpha + \alpha')$$

where E is the absorbed energy, WR is the moment of pendulum about its rotary axis, α' is the swing up angle of pendulum when it is allowed to swing without the test specimen from its lifting angle α, and β is the swing up angle of pendulum after it made test piece to fracture.

The charpy impact strength (a_c) is obtained by dividing the absorbed energy by the original sectional area:
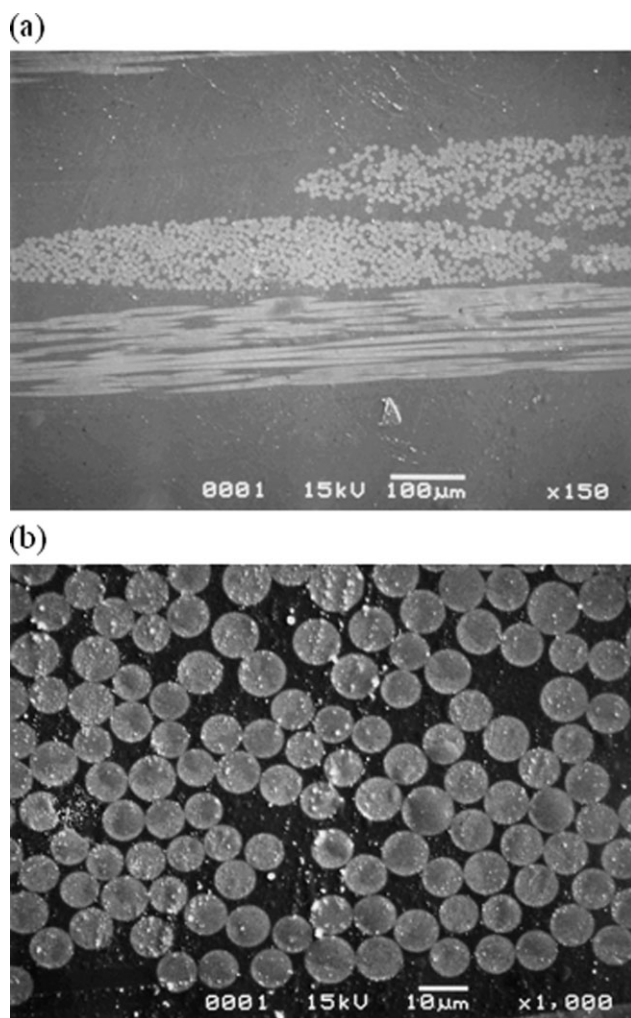
$$a_c = E/bh \times 10^3$$
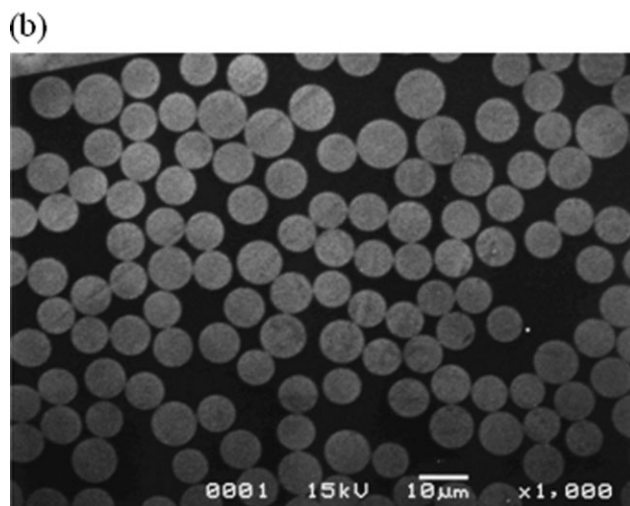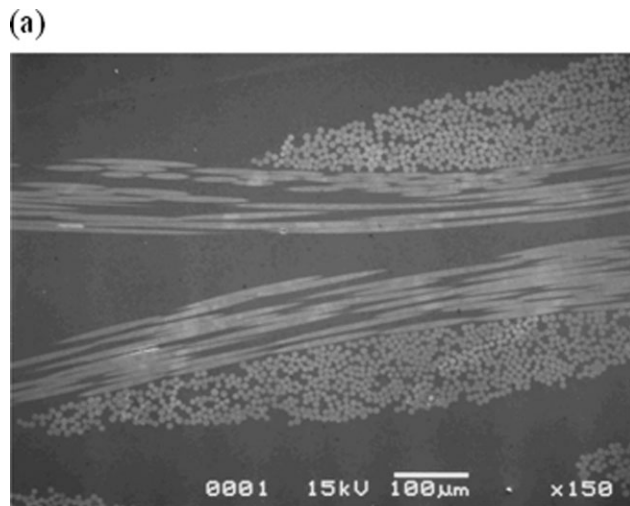
Figure 6 SEM micrographs of cross-sections on GFRP using Ba/1,3-PBO/Cat. 1 as a matrix resin: (a) ×150 and (b) ×1000.
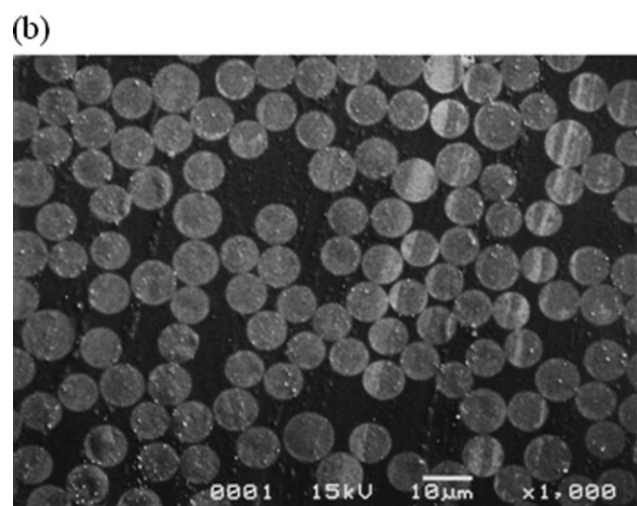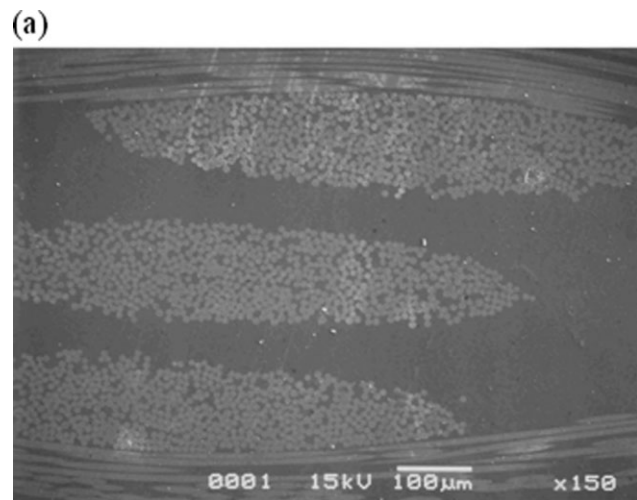
Figure 7 SEM micrographs of cross-sections on GFRP using Ba/1,3-PBO/Cat. 2 as a matrix resin: (a) ×150 and (b) ×1000.

Figure 8 SEM micrographs of cross-sections on GFRP using EP as a matrix resin: (a) ×150 and (b) ×1000.

where b is the width of test piece and h is the depth of test piece.

Flame resistance was estimated by cone calorimeter and the limited oxygen index (LOI). A cone calorimeter was used at an incident heat flux of 50 kW/m^2 in an air atmosphere under free convective air flow conditions according to ISO 5660. Composite samples (100 mm × 100 mm) were wrapped in aluminum foil and placed in a specimen holder over ceramic blanket at least 13 mm thick. A spacing of 25 mm was maintained between the bottom of the cone and top of the specimen. LOI was tested according to ASTM D 2863. The percentage in the oxygen/nitrogen mixture deemed sufficiently to sustain the flame was taken as the LOI.

Scanning electron microscope (SEM; accelerating voltage was 15 kV) was used to confirm good resin distribution and interfacial adhesion between the resin and the fiber on a JEOL (Tokyo, Japan) JSM-5800.
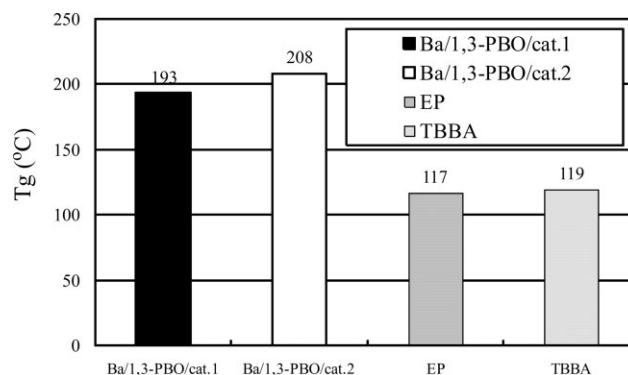
Figure 9 Glass transition temperature (T_g) of GFRP.

RESULTS AND DISCUSSION

Curing reaction of Ba with 1,3-PBO using the latent curing agents

The latent curing agent in this study consisted of the salt of the acid and amine compounds that would liberate the free acids and amines by high-temperature decomposition. Therefore, acids and amines that were liberated at the high temperature could act as curing agents in the curing reaction of benzoxazines (Ba) and bisoxazoline (1,3-PBO).

As previously reported,[16,18] we might suggest the curing reaction mechanism of Ba and 1,3-PBO with the latent curing agents as follows. In the presence of acids liberated, a rapid proton transfers and generates a phenolate ion. This phenolate ion can then react with another benzoxazine or bisoxazoline groups, and the curing reaction (copolymerization) of Ba with 1,3-PBO proceeded as shown in Figure 3. And also, amines liberated at the high temperature can react with oxazoline ring as shown in Figure 4. Acids liberated (*p*-toluenesulfonic acid) can react with oxazoline ring as shown in Figure 5. In this way, the curing reaction of benzoxazines (Ba) and bisoxazoline (1,3-PBO) with the latent curing agent
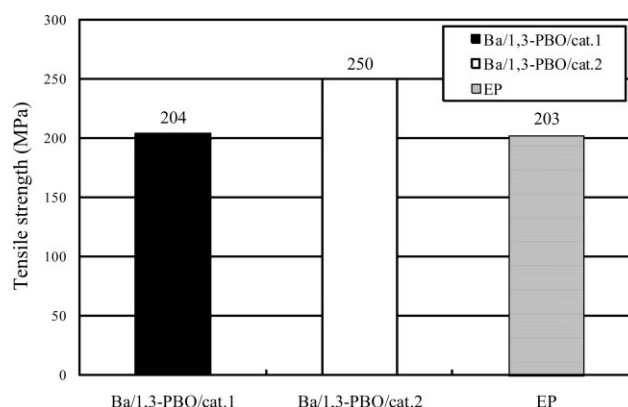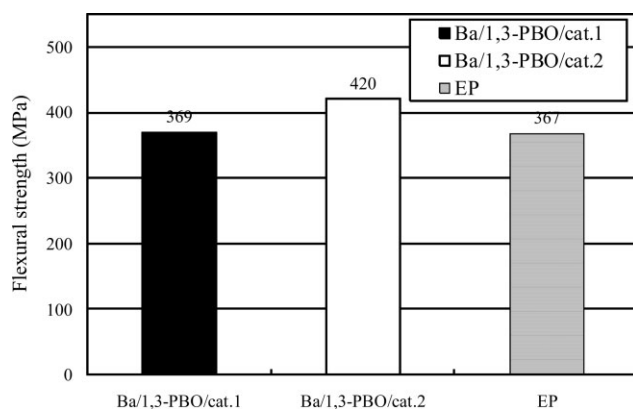

Figure 10 Tensile strength of GFRP.

Figure 11 Flexural strength of GFRP.

Figure 12 Impact strength of GFRP.

could proceed. It was considered that acids and amines, which the latent curing agents liberated by high-temperature decomposition, might be incorporated in the curing system of benzoxazine and bisoxazoline.

Properties of glass-reinforced composites

Two kinds of matrix resins (Ba/1,3-PBO/Cat. 1 and Ba/1,3-PBO/Cat. 2) were used for preparation of GFRP based on benzoxazine resin. The morphology of GFRP was investigated by SEM. SEM images of GFRP cross-sections of benzoxazine-based resins (Ba/1,3-PBO/Cat. 1 and Ba/1,3-PBO/Cat. 2) and conventional EP as a matrix resin are shown in Figures 6–8. It can be observed that any GFRP shows good resin distribution and interfacial adhesion between the resin and the fiber.

The heat-resistant properties of GFRP based on benzoxazine resin and conventional epoxy GFRP are shown in Figure 9. Glass transition temperature (T_g) of GFRP based on benzoxazine resin was much higher than that of the conventional epoxy and flame-retardant epoxy GFRP.

The mechanical properties of GFRP based on benzoxazine resin and conventional epoxy GFRP are shown in Figures 10–12. As a result, the mechanical properties (tensile, flexural, and impact strength) of GFRP based on benzoxazine resin were higher than those of the conventional epoxy GFRP. These higher heat resistance and mechanical properties might be because more benzene rigid structure components
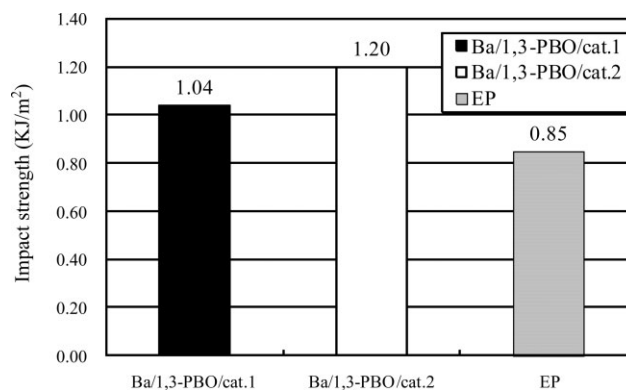
from benzoxazine and bisoxazoline were incorporated into the curing system, and because the cross-link density was augmented.[16,18] And the mechanical properties (tensile, flexural, and impact strength) of GFRP based on benzoxazine resin (Ba/1,3-PBO/Cat. 2) were higher than those of GFRP based on benzoxazine resin (Ba/1,3-PBO/Cat. 1). The reason considered was that crosslink density might be augmented by the bivalent amine of isopropanolamine more effectively than the univalent-amine of diethanolamine.[16]

The cone calorimeter properties of GFRP are given in Table I and Figure 13. From the results of cone calorimeter tests, time to ignition (TTI), peak heat release rate (PHRR), time to peak (TTP), total heat release rate (THR), and CO or CO_2 yield were estimated (Table I).

TTI may be defined as the ease of ignition. TTIs of the conventional and flame-retardant epoxy GFRPs were 40 s and 31 s, respectively; TTIs of GFRPs based on benzoxazine resin were 45–46 s. It was found that GFRPs based on benzoxazine resins were more difficult to ignite than the conventional or flame-retardant epoxy GFRPs. Heat release rate (HRR) is the heat generated per unit time by the burning sample divided by the surface area of the sample. Hence, it is a measure of the HRR to the surroundings per unit surface area of the burning material. The important parameters for assessing the fire performance of a material are the PHRR and THR. HRR curves as a function of time are given in Figure 13. As can be seen from Table I and Figure 13, GFRPs based on benzoxazine resin showed

TABLE I
Cone Calorimeter Properties of GFRP

Resin	TTI (s)	PHRR (kW/m²)	TTP (s)	THR (MJ/m²)	CO (kg/kg)	CO₂ (kg/kg)
EP	40	1032	52	36.5	0.075	0.80
TBBA	31	476	43	17.3	0.069	0.14
Ba/1,3-PBO/Cat. 1	46	496	62	38.8	0.014	0.69
Ba/1,3-PBO/Cat. 2	45	501	55	37.4	0.005	1.04

smaller PHRR than the conventional epoxy GFRP and almost the same PHRR as the flame-retardant epoxy GFRP. And then, as can be seen from TTI and TTP values in Table I and Figure 13, the HRR curves of GFRP based on benzoxazine resin are shifted toward longer times, indicating that they ignite slowly and burn for longer times. This indicates that its degradation and volatilization may be delayed. It was found that GFRPs based on benzoxazine resins were much more flame-retardant than the conventional epoxy GFRP, and almost the same as the flame-retardant epoxy GFRP. Average CO and CO_2 productions in 5 min are given in Table I. It was found that GFRPs based on benzoxazine resins produced CO less than the conventional epoxy or flame-retardant epoxy GFRP.

LOI results for GFRP are given in Figure 14. LOI of GFRP based on benzoxazine resin was much higher than that of the conventional epoxy GFRP. And especially, LOI of GFRP based on benzoxazine resin was higher than that of flame-retardant epoxy GFRP.

The reason for these good flame-retardant properties was considered that more benzene rigid structure components from benzoxazine and bisoxazoline were incorporated into the curing system, and because the crosslink density was augmented.[16,18] This high crosslink density might be due to several reactions, including the reactions such as Figures 3–5. We might associate this good performance with high benzene content and crosslink density in the cured resin. Another possibility is that the high aromatic content of benzoxazine based resins leads to a high char yield[16] at the burning surface. Increasing char formation could limit the production of combustible gases, decrease the thermal conductivity of the resins, and decrease the exothermacity of the pyrolysis reactions, consequently to limit the resins' flammability.[20–22] And benzoxazine-based resin have nitrogen-rich structures. This nitrogen-rich structure
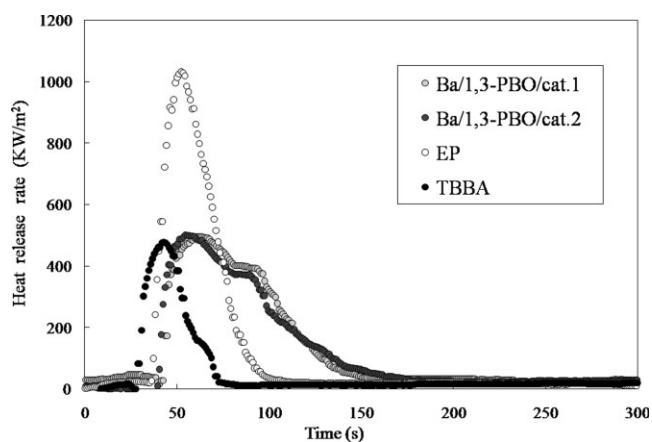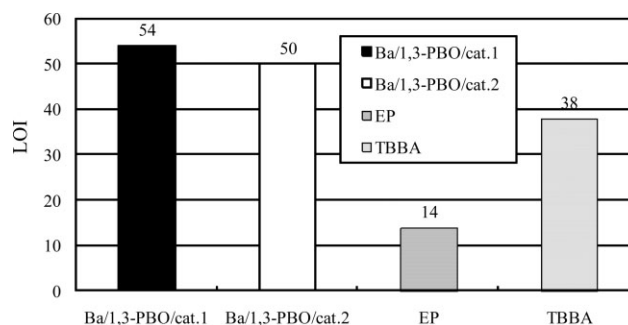

Figure 14 LOI of GFRP.

might be expected to impart flame retardancy. The incombustible ammonia gas from the nitrogen-rich structure of benzoxazine-based resin degradation might have a significant effect on reducing flammability of the materials.[23,24]

CONCLUSIONS

The purpose of this study was to prepare and characterize GFRP based on benzoxazine resins. We investigated the properties of GFRP based on the molten benzoxazine resins from benzoxazine and bisoxazoline with the latent curing agent as the matrix resin. As a result, GFRP based on the molten resins from benzoxazine and bisoxazoline with the latent curing agent showed good heat resistance, flame resistance, and mechanical properties compared with those of the conventional glass fiber-reinforced epoxy or flame-retardant epoxy composites. The reason was considered that the matrix resin from benzoxazine and bisoxazoline with the latent curing agent had a lot of benzene rigid structure components, high crosslink density, high char yield, and nitrogen-rich structures.

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Figure 13 Cone calorimeter properties of GFRP.

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