Development of high radiation-resistant glass fiber reinforced plastics with cyanate-based
resin for superconducting magnet systems

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Abstract

Glass fiber reinforced plastics (GFRPs) with cyanate ester resin/epoxy resin, bismaleimide
resin/epoxy resin, and bismaleimide-triazine resin as matrices were developed for the

superconducting magnet systems used in high intensity accelerators. The radiation resistance of these GFRPs was evaluated based on their gas evolution and changes in their mechanical properties after gamma-ray irradiation with dose of 100 MGy in vacuum at ambient temperature. After irradiation, a small amount of gas was evolved from all of the GFRPs, and a slight decrease in mechanical properties was observed compared with the conventional epoxy resin-GFRP, G10. Among the GFRPs, the smallest amount of gas (6×10^{-5} mol/g) was evolved from the GFRP with the bismaleimide-triazine resin, which also retained more than 88 % of its flexural strength after 100 MGy irradiation; this GFRP is thus considered the most promising material for superconducting magnet systems.

Keywords: Superconducting magnet, Glass fiber reinforced plastics, Cyanate-based resin, Gamma-ray irradiation, Gas evolution, Mechanical properties

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1. Introduction

In high intensity accelerators such as the Japan Proton Accelerator Research Complex (J-PARC) jointly operated by Japan Atomic Energy Agency (JAEA) and High Energy Accelerator Research Organization (KEK) and the Large Hadron Collider (LHC) at the European Organization for Nuclear Research (CERN), superconducting magnet systems that work stably under high radiation field are indispensable to realize future projects [1-3]. For the LHC upgrade project, the total dose of radiation on superconducting magnet system during operating period has been estimated to be a few tens of MGy [2, 4, 5]. The performance of a superconducting magnet system depends on the radiation resistance of the organic materials that are used as electrical insulators and/or structural materials in the system, because the radiation resistance of organic materials is inferior to that of inorganic materials. Conventionally, epoxy resin glass fiber reinforced plastics (GFRPs) have been used as the electrical insulators and/or structural materials of superconducting magnet systems because of their excellent mechanical, electrical, and thermal properties. However, the mechanical properties of epoxy resin-GFRP deteriorate above approximately 10 MGy [6, 7]. Therefore, it is necessary to develop organic materials with higher radiation resistance of more than several tens of MGy to develop superconducting magnet systems for future projects at various accelerators.

Epoxy/cyanate-based blended resins have been proposed as novel alternatives to

conventional epoxy resin-GFRPs for the superconducting magnet system in the International Thermonuclear Experimental Reactor (ITER) [8-14]. Cyanate-based resins, which exhibit high radiation resistance, high thermal stability, and low dielectric constant, modify the radiation resistance of the GFRP. Many reports have evaluated the radiation resistance of epoxy/cyanate-based blended resins and their GFRPs; the effects of combination and composition of epoxy/cyanate-based blended resins as well as irradiation conditions such as the radiation source (gamma-rays, neutrons, electron beam) and/or irradiation temperature have been reported. Recently, a laminate film composed of glass cloth, polyimide film, and an epoxy/cyanate-based blended resin with a radiation resistance of 10^{22} neutrons (10 MGy) was developed [15]. For ITER, the GFRP is fabricated by a vacuum pressure impregnation (VPI) process, where the resins are impregnated into glass cloth that is wound around a superconducting coil [16-19]. In the VPI process, the initial viscosity of resin is one of the most important issues. To achieve an optimum initial viscosity, compounding of the epoxy resin is indispensable because the viscosity of cyanate-based resin is high. However, it has been reported that the ether linkage introduced by epoxy component is predominantly decomposed by radiation, which may cause deterioration of the GFRP [20]. This finding suggests that it is useful to reduce the compounding ratio of epoxy resin to develop a GFRP with high radiation resistance.

However, the VPI process is not always necessary for superconducting magnet systems in

accelerators; that is, the bulk of the GFRP that is fabricated from laminae of prepreg sheets can be cut into desirable parts [21]. Therefore, we developed three types of GFRPs with cyanate-based resins as the main matrix material: cyanate ester resin/epoxy resin, bismaleimide resin/epoxy resin, and bismaleimide-triazine resin (epoxy resin-free). In this work, the radiation resistance of the GFRPs was evaluated based on their gas evolution and mechanical properties, and the feasibility of using GFRPs for superconducting magnet systems was discussed.

2. Experimental procedure

The conditions used to prepare the GFRPs in this work are summarized in Table 1. Cyanate ester resin/epoxy resin (CE-GFRP), bismaleimide resin/epoxy resin (BMI-GFRP), and bismaleimide-triazine resin (BT-GFRP) were used as the matrices. A plane-woven, amino silane-treated S-2 glass cloth (thickness of 0.18 mm) was used as reinforcement. The glass cloth was impregnated by the resins and then hot-pressed for curing. The full curing temperatures of the CE-GFRP, BMI-GFRP, and BT-GFRP were 150 °C, 230 °C and 220 °C, respectively. The number of glass cloth ply was 197, 260, and 177 for CE-GFRP, BMI-GFRP, and BT-GFRP, respectively to obtain a thickness of 30 mm; the GFRPs were cut to a thickness of 2 or 4 mm for subsequent tests. The density of the obtained GFRP was 1740, 1990, and

1740 kg/m³ for CE-GFRP, BMI-GFRP, and BT-GFRP, respectively. These GFRPs were manufactured by Arisawa Manufacturing Co., Ltd. In this work, epoxy resin-GFRP, G10, was subjected to experiments as a reference sample.

The following thermal and electrical properties of the GFRPs were evaluated: coefficient of thermal expansion (compressive load of 0.5 g, temperature range of -150 to 200 °C, heating rate of 2 °C/min, atmosphere of nitrogen; Rigaku, Thermomechanical analyzer), specific heat at 25 °C (heating rate of 10 °C/min, atmosphere of nitrogen; Perkin Elmer, DSC-7), thermal diffusivity at 25 °C (xenon lamp, air atmosphere; NETZSCH, LFA447), volume resistivity (applied voltage of DC 500 V, test temperature at 21 °C; Advantest, R8340), dielectric breakdown voltage and strength (DC voltage increasing rate of 2 kV/sec, test temperature at 23 °C; Tokyo Transformer, standard type of dielectric strength testing system), relative permittivity and loss tangent (applied voltage of 1 V, frequencies of 100 Hz and 1 MHz, test temperature at 21 °C; Agilent Technology, 4284A).

To evaluate the radiation resistance, GFRPs were placed into glass ampoules, which were evacuated and sealed. The samples were irradiated with ⁶⁰Co gamma-rays to a dose of 100 MGy as a maximum with a dose rate of 15 kGy/h at ambient temperature. After the irradiation, the gases accumulated in the glass ampoule were analyzed using gas chromatography (Shimadzu, GC-8A) at room temperature (25 °C). Three-point flexural tests were conducted in air at room temperature (23 °C) according to JIS K7055. The span was 64 mm and the

crosshead speed was 2 mm/min (Shimadzu, AG-5000A). After the flexural test, the fracture part of specimen was observed by an optical microscope (Keyence, VHX-1000). Tensile and compression tests (Instron, Model1185) were conducted in air at room temperature (23 °C) according to JIS K7164 and JIS K7018, respectively. A crosshead speed of 1 mm/min was applied for both tests. The results of mechanical tests were obtained by averaging the values of three specimens.

For the measurement of the thermal properties and flexural property, the anisotropy of the glass fiber in the specimens was considered; that is, directions perpendicular (V-direction) and parallel (H-direction) to laminae were tested, as illustrated in Fig. 1.

3. Results and discussion

Table 2 lists the thermal and electrical properties of the GFRPs developed in this work. The thermal properties were measured perpendicular (V-direction) and parallel (H-direction) to laminae. For all of the GFRPs, the coefficients of thermal expansion in the V-direction and thermal diffusivities and conductivities in the H-direction were higher. This result was caused by the anisotropy of the glass fiber. In the direction along the laminae, expansion was suppressed and thermal conduction was enhanced by the glass fiber with lower coefficient of thermal expansion and higher thermal conductivity than those of the resins. No difference was

observed based on the different types of resins. These results were similar to the electrical property results. Although the thermal and electrical properties of G10 vary widely depending on the composition of the resin, and the treatment of the glass fiber, the values of the properties are almost the same as those of the GFRPs developed in this work [22]. This finding suggests that the GFRPs developed in this work are applicable for electrical insulators and/or structural materials based on their thermal and electrical properties.

When polymeric materials are irradiated by radiation, decomposed gases are produced. The amount of evolved gases can be an indicator for judgment of radiation resistance of the material, that is, a material which evolves low amount of gases can be evaluated as a high radiation-resistant material. On the other hand, components including GFRPs in the superconducting magnet system are exposed to liquid helium temperature ($-269\text{ }^{\circ}\text{C}$ (4K)). It has been reported that the total amount of evolved gases from a GFRP with poly(methyl methacrylate) (PMMA) by gamma-ray irradiation at $-196\text{ }^{\circ}\text{C}$ (77K) is less than that by the irradiation at room temperature (the gas analysis was conducted at room temperature) [23]. This is caused by restriction of molecular motion in the polymeric material at $-196\text{ }^{\circ}\text{C}$ (77K). And besides, the molecular motion is extremely restricted at $-269\text{ }^{\circ}\text{C}$ (4K) which suggests the amount of decomposed gases after the irradiation would be much lowered. In this sense, evaluation of evolved gases by the irradiation at room temperature gives results in safe side in terms of evaluation of radiation resistance. Thus, gas evolution from the GFRPs after

gamma-ray irradiation at room temperature was investigated in this work (Fig. 2). The main components of the evolved gases were hydrogen (H_2), carbon dioxide (CO_2), and carbon monoxide (CO). Methane (CH_4) and ethane (C_2H_6) gases were detected as minor components with amounts of 10^{-7} – 10^{-6} mol/g at 100 MGy (the results are not shown). The H_2 , CO_2 , and CO gases were produced by the cleavage of C–H bonds and ether linkage ($-C-O-C-$) [20, 24, 25]. It has been reported that radiolysis of epoxy/cyanate-based blended resins occurs at crosslinking sites that are formed between epoxy resin and cyanate-based resin [20]. For cyanate-based resins, cyclic $-N=C-(O)-N=$ structures are formed during the curing treatment. The cyclic $-N=C-(O)-N=$ structures are more stable than ether linkage ($-C-O-C-$) in terms of bond-dissociation energy (C–N bond: 745 kJ/mol, C–H bond: 335 kJ/mol, C–O bond: 530 kJ/mol, and C–C bond: 599 kJ/mol) [26], which is considered a reason for the suppressed radiolysis of GFRPs containing cyanate-based resin. Compared with G10, the amount of total gas from the GFRPs developed in this work was suppressed by 40–70 % (Fig. 2 (a)). After 100 MGy irradiation, the amount of total gas evolved from BT-GFRP, whose matrix is epoxy resin-free, was the smallest at 6×10^{-5} mol/g which is approximately 38 % of that for CE-GFRP and approximately 47 % of that for BMI-GFRP. Figure 2 (b) shows the amount of evolved H_2 gas. As mentioned above, it is important to select GFRPs which evolve low amount of decomposed gases by the irradiation. Particularly, the amount of H_2 gas should be paid attention because H_2 , which is an impurity of the liquid helium used as the coolant in

superconducting magnet systems, may affect on operation of the helium cooling plant. Thus, the evolution of H₂ should be prevented as much as possible to maintain stable control of the helium cooling plant. On this viewpoint, BT-GFRP evolved the smallest amount of H₂ gas among the GFRPs developed in this work. The amount of CO₂ gas from CE-GFRP and BMI-GFRP were more than that from BT-GFRP because CE-GFRP and BMI-GFRP contain epoxy resin component (Fig. 2 (c)). While behavior of CO gas evolution was similar to that of CO₂ gas evolution, the amount of CO gas decreased in the high dose range (Fig. 2 (d)). Such decreasing in the amount of CO gas is considered to be caused by the oxidation of CO gas ($\text{CO} + \text{O} \rightarrow \text{CO}_2$), which means that the amount of CO₂ gas from CE-GFRP and BMI-GFRP includes the amount of CO₂ gas produced by the oxidation of CO gas. According to the results of gas analysis, BT-GFRP is the most suitable for a superconducting magnet system with helium cooling plant.

Figure 3 shows results of flexural test of the GFRPs after gamma-ray irradiation. Figures 3 (a) and (b) show typical displacement-load curves of BT-GFRP and G10 in V-direction and H-direction, respectively. Different fracture modes were observed between the test directions: ductile-like and monolithic-like fracture for V-direction and H-direction, respectively. In the V-direction, the displacement-load curves exhibited zig-zag-shape just before fracture which indicates that bedonding between resin and glass cloth occurs gradually. On the contrary, in the H-direction, the displacement-load curves exhibited sudden decreasing in the load just

before fracture which indicates that debonding occurs momentarily. The displacement-load curves of CE-GFRP and BMI-GFRP before and after the irradiation were almost similar to those of BT-GFRP. In case of G10 after 50 MGy irradiation, ductile-like fracture was observed in both V-direction and H-direction where the specimen was fractured by slight deformation. This is caused by deterioration of adhesiveness between the resin and glass cloth due to decomposition of the resin by the irradiation, as described later. As shown in Fig. 3 (c), the initial strengths of the GFRPs in the V-direction were 518, 492, and 612 MPa for CE-GFRP, BMI-GFRP, and BT-GFRP, respectively. Their retention after 100 MGy irradiation was 105 %, 83 % and 88 % for CE-GFRP, BMI-GFRP, and BT-GFRP, respectively. In the H-direction, the initial strengths were 581, 722, and 693 MPa, and the retention after 100 MGy irradiation was 101 %, 80 %, and 93 % for CE-GFRP, BMI-GFRP, and BT-GFRP, respectively (Fig. 3 (d)). For CE-GFRP, the retention of strength of more than 100 % may be caused by the crosslinking of molecules in the resin even after 100 MGy irradiation. However, the initial flexural strengths of G10 in the V-direction and H-direction were 526 and 446 MPa, and the retention after 50 MGy irradiation was 17 % and 31 %, respectively. This decrease in the flexural strength of the GFRPs after the irradiation was caused by the deterioration of adhesiveness between the resin and glass cloth. Figure 4 shows the GFRPs after the flexural test in V-direction. In case of the specimens before irradiation, macroscopic delamination was not observed for all of the GFRPs. After the irradiation, obvious delamination was found for

G10. On the contrary, all of the GFRPs developed in this work did not show macroscopic delamination even after the irradiation with dose of 100 MGy. The bottom parts of specimen (stressed by tensile load during the flexural test) were observed by an optical microscope in order to investigate debonding between resin and glass cloth (Fig. 5). The debonding region between the resin and glass cloth is traced by a white line. For CE-GFRP (Fig. 5 (a)), BMI-GFRP (Fig. 5 (b)), and BT-GFRP (Fig. 5 (c)), debonding was observed in some parts. However, long debonding region in almost all the layers was observed for G10 (Fig. 5 (d)). This result indicates that the deterioration of the adhesiveness between the resin and glass cloth in the CE-GFRP, BMI-GFRP, and BT-GFRP was suppressed, which is supported by that the GFRPs developed in this work evolving smaller amounts of gases than G10 (as indicated in Fig. 2). Thus, the GFRPs developed in this work exhibited high retention of flexural strength. According to the gas evolution and flexural strength results, BT-GFRP, which exhibited the smallest amount of gas evolution and relatively high retention of its flexural strength, is the most promising material among the GFRPs developed.

During the operation of a superconducting magnet system, the structural material is stressed by tensile and/or compressive stress as well as flexural stress because of the temperature and magnetic field. Thus, tensile and compression tests after gamma-ray irradiation under vacuum were conducted for BT-GFRP and G10. Figure 6 (a) shows typical displacement-load curves in the tensile test. In case of BT-GFRP, the displacement-load curve did not changed greatly

before and after the irradiation which suggests that adhesiveness between resin and glass cloth was retained well. For G10 after the irradiation, the displacement-load curve indicating debonding was found. As shown in Fig. 6 (b), the initial tensile strength and modulus of BT-GFRP were 453 MPa and 29 GPa, respectively, and their retention after 50 MGy irradiation were 95 % and 93 %, respectively. For G10, the retention of the tensile strength and modulus after 50 MGy irradiation were 75 % and 65 %. In terms of the change in the compressive property, all of the specimens before and after the irradiation exhibited similar displacement-load curves (Fig. 7 (a)). In the compression test, delamination due to the debonding between the resin and glass cloth was predominant fracture mode, and the fracture occurred momentarily. As shown in Fig. 7 (b), BT-GFRP exhibited an initial compressive strength and modulus of 382 MPa and 27 GPa, and the retention of these values after 50 MGy irradiation was 91 % and 111 %, respectively. For G10, the retention of the compressive strength and modulus after 50 MGy irradiation was 23 % and 104 %, respectively. In our design of a superconducting magnet system, the criterion for the radiation resistance of the GFRP in terms of the mechanical properties was determined to be retention of more than 70 % after irradiation; that is, all of the GFRPs developed in this work satisfied the criterion. In particular, BT-GFRP is considered the most promising material for superconducting magnet systems.

4. Conclusion

In this study, several GFRPs were developed using different resin matrices for application in the superconducting magnet systems used in high intensity accelerators, and their radiation resistances were evaluated based on gas evolution and changes in their mechanical properties.

All of the developed GFRPs exhibited a small amount of gas evolution and a slight decrease in their mechanical properties after irradiation compared with the conventional epoxy resin-GFRP (G10). BT-GFRP evolved the smallest amount of gas (6×10^{-5} mol/g) and retained 88 % of its flexural strength after 100 MGy gamma-ray irradiation as well as 95 % of its tensile strength and 91 % of its compressive strength after 50 MGy gamma-ray irradiation; this GFRP is considered the most promising material for superconducting magnet systems.

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Figure and table captions

Figure 1 Scheme of test specimens.

Figure 2 Evolved gases from GFRPs after gamma-ray irradiation: (a) total gas, (b) H₂, (c) CO₂, and (d) CO.

Figure 3 Change in flexural property of GFRPs after gamma-ray irradiation: displacement-load curves ((a) V-direction and (b) H-direction) and flexural strength ((c) V-direction and (d) H-direction).

Figure 4 Photographs of GFRPs after flexural test in V-direction.

Figure 5 Microscopic photographs of fractured part (bottom side of specimen in Fig. 4) of GFRPs after flexural test: (a) CE-GFRP (100MGy), (b) BMI-GFRP (100MGy), (c) BT-GFRP (100MGy), and (d) G10 (50MGy).

Figure 6 Change in tensile properties of BT-GFRP and G10 after gamma-ray irradiation: (a) displacement-load curve and (b) tensile strength and modulus.

Figure 7 Change in compressive properties of BT-GFRP and G10 after gamma-ray irradiation: (a) displacement-load curve and (b) compressive strength and modulus.

Table 1 Preparation conditions of GFRPs.

Table 2 Thermal and electrical properties of GFRPs developed in this work.

Figure

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	CE-GFRP	BMI-GFRP	BT-GFRP
Resin	Cyanate ester / Epoxy	Bismaleimide / Epoxy	Bismaleimide-Triazine
Press condition	100 ° C×23min×1.8kg/cm ²	120 ° C×60min×40kg/cm ²	130 ° C×25min×1.8kg/cm ²
(Post-curing)	→130 ° C×10min×5.4kg/cm ² →130 ° C×8hr×35kg/cm ²	→180 ° C×120min×40kg/cm ²	→160 ° C×10min×3.6kg/cm ² →160 ° C×8hr×35kg/cm ²
Curing condition	130 ° C×11hr	200 ° C×3hr	160 ° C×16hr
(Full curing)	→150 ° C×28hr	→230 ° C×12hr	→180 ° C×12hr →220 ° C×12hr

Table 1 Preparation conditions of GFRPs.

	Test direction	Coefficient of thermal expansion ($10^{-5} \text{ }^{\circ}\text{C}^{-1}$)	Specific heat (J/kg·K)	Thermal diffusivity ($10^{-7} \text{ m}^2/\text{s}$)	Thermal conductivity (W/m·K)	Volume resistivity ($10^{15} \Omega \cdot \text{cm}$)	Dielectric breakdown voltage (kV)	Dielectric breakdown strength (kV/mm)	Relative permittivity at 100Hz	Relative permittivity at 1MHz	Loss tangent at 100Hz	Loss tangent at 1MHz
CE-GFRP	V	4.4	953	2.44	0.404	4.43 ± 0.13	31.1 ± 0.2	29 ± 0.6	4.71 ± 0.06	4.46 ± 0.04	0.0095 ± 0.0005	0.0139 ± 0.0004
	H	1.0	953	3.26	0.541							
BMI-GFRP	V	2.5	897	3.39	0.605	1.52 ± 0.11	28.2 ± 0.7	27 ± 1.0	5.77 ± 0.01	5.41 ± 0.01	0.0097 ± 0.0011	0.0168 ± 0.0001
	H	0.6	897	3.99	0.711							
BT-GFRP	V	4.2	941	2.46	0.402	3.59 ± 0.12	26.3 ± 1.7	25 ± 1.5	4.45 ± 0.07	4.29 ± 0.06	0.0061 ± 0.0001	0.0112 ± 0.0007
	H	0.8	941	3.83	0.626							

Table 2 Thermal and electrical properties of GFRPs developed in this work.

Table 1 Preparation conditions of GFRPs.

	CE-GFRP	BMI-GFRP	BT-GFRP
Resin	Cyanate ester / Epoxy	Bismaleimide / Epoxy	Bismaleimide-Triazine
Press condition	100 ° C×23min×1.8kg/cm ²	120 ° C×60min×40kg/cm ²	130 ° C×25min×1.8kg/cm ²
(Post-curing)	→130 ° C×10min×5.4kg/cm ² →130 ° C×8hr×35kg/cm ²	→180 ° C×120min×40kg/cm ²	→160 ° C×10min×3.6kg/cm ² →160 ° C×8hr×35kg/cm ²
Curing condition	130 ° C×11hr	200 ° C×3hr	160 ° C×16hr
(Full curing)	→150 ° C×28hr	→230 ° C×12hr	→180 ° C×12hr →220 ° C×12hr

Table 2 Thermal and electrical properties of GFRPs developed in this work.

	Test direction	Coefficient of thermal expansion ($10^{-5} \text{ }^{\circ}\text{C}^{-1}$)	Specific heat (J/kg·K)	Thermal diffusivity ($10^{-7} \text{ m}^2/\text{s}$)	Thermal conductivity (W/m·K)	Volume resistivity ($10^{15} \Omega \cdot \text{cm}$)	Dielectric breakdown voltage (kV)	Dielectric breakdown strength (kV/mm)	Relative permittivity at 100Hz	Relative permittivity at 1MHz	Loss tangent at 100Hz	Loss tangent at 1MHz
CE-GFRP	V	4.4	953	2.44	0.404	4.43 ± 0.13	31.1 ± 0.2	29 ± 0.6	4.71 ± 0.06	4.46 ± 0.04	0.0095 ± 0.0005	0.0139 ± 0.0004
	H	1.0	953	3.26	0.541							
BMI-GFRP	V	2.5	897	3.39	0.605	1.52 ± 0.11	28.2 ± 0.7	27 ± 1.0	5.77 ± 0.01	5.41 ± 0.01	0.0097 ± 0.0011	0.0168 ± 0.0001
	H	0.6	897	3.99	0.711							
BT-GFRP	V	4.2	941	2.46	0.402	3.59 ± 0.12	26.3 ± 1.7	25 ± 1.5	4.45 ± 0.07	4.29 ± 0.06	0.0061 ± 0.0001	0.0112 ± 0.0007
	H	0.8	941	3.83	0.626							