Irradiation effect of the insulating materials for fusion superconducting magnets at cryogenic temperature

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Abstract. In ITER, superconducting magnets should be used in such severe environment as high fluence of fast neutron, cryogenic temperature and large electromagnetic forces. Insulating material is one of the most sensitive component to radiation. So radiation resistance on mechanical properties at cryogenic temperature are required for insulating material. The purpose of this study is to evaluate irradiation effect of insulating material at cryogenic temperature by gamma-ray irradiation. Firstly, glass fiber reinforced plastic (GFRP) and hybrid composite were prepared. After irradiation at room temperature (RT) or liquid nitrogen temperature (LNT, 77 K), interlaminar shear strength (ILSS) and glass transition temperature (Tg) measurement were conducted. It was shown that insulating materials irradiated at room temperature were much degraded than those at cryogenic temperature.

1. Introduction
In ITER, high temperature plasma is confined by strong magnetic field of superconducting magnets. The superconducting magnets are operated under such severe environment as high fluence of fast neutron (10^{22} n/m^2, E > 0.1 MeV), cryogenic temperature (liquid helium temperature, 4.2 K) and large electromagnetic forces, especially large shear strength up to 45 MPa [1] [2]. It has been reported that insulating materials are the most sensitive to the irradiation among the components of superconducting magnets. So, radiation resistance on mechanical properties at cryogenic temperature is required for insulation materials.

The insulating materials are hybrid composites which consist of glass cloth, polyimide film and organic polymer. Previous studies have investigated irradiation effect of hybrid composite and glass fiber reinforced plastic (GFRP) which consists of glass cloth and organic polymer. As a result, it was shown that the insulating material using compound of cyanate ester and epoxy resin have favorable radiation resistance on mechanical strength even after the irradiation simulated in ITER design [3] [4]. However, most of those studies have investigated the irradiation effect of insulating materials after room temperature (RT) irradiation. In ITER, actual irradiation environment of insulating materials is cryogenic temperature. In addition, it is considered that the temperature of the magnet components including the insulating materials change intermittently for magnets maintenance. The purpose in this study is to evaluate the irradiation effects of insulating materials at cryogenic temperature and those of temperature change after irradiation.
2. Experiment

2.1. Materials
To evaluate the mechanism of the irradiation induced degradation, we used the epoxy resin which is relatively sensitive against radiation compared with the compound of cyanate ester and epoxies, in this study. Epikote828 (Diglycidyl Ether of Bisphenol-A, DGEBA, Mitsubishi Chemical Corporation) as an epoxy resin and Baxxodur EC301 (Polyetheramin D230, Mitsui Fine Chemicals, Inc.) as a hardener were prepared. Figure 1 shows the chemical structures of Epikote828 and D230. GFRP and hybrid composite were fabricated by using the resins. Boron-free S-glass cloth was used in GFRP and hybrid composite.

![Chemical structure of DGEBA and D230](image1.png)

**Figure 1.** Chemical structure of DGEBA and D230

2.2. Sample preparation
Epikote828 and D230 were mixed at the epoxy equivalent (100 : 32.3). In the case of GFRP, 45 glass cloth sheets were laminated and impregnated with the resin under vacuum. In the case of hybrid composite, 29 glass cloth sheets and 28 polyimide film sheets were laminated. After vacuum impregnation, they were cured at 70 °C for 3 hours and then at 110 °C for 2 hours. Composites were cut into double-notch specimens for interlaminar shear strength (ILSS) test after curing. Figure 2 shows the shape of speciemen for ILSS test. As the double-notch specimen’s thickness was about 6 mm, there were 7 or 8 layers of the glass cloth per millimeter thickness in the case of GFRP, and about 4 or 5 layers in the case of hybrid composite. Volume fiber content ($V_f$) was 41.09 % in the case of GFRP, and 26.22 % in the case of hybrid composite as observed value, respectively. By similar method, epoxy plate which consists of only matrix resin was made for Dynamic Mechanical Analysis (DMA). The plate was cut into 50 mm $\times$ 10 mm $\times$ 1.5 mm in size.

![Shape of specimen for ILSS test](image2.png)

**Figure 2.** Shape of specimen for ILSS test
2.3. Irradiation and test procedures

Those specimens were irradiated by gamma-ray in $^{60}$Co gamma-ray irradiation facility, Research Laboratory for Quantum Beam Science, Institute of Scientific and Industrial Research, Osaka University. Irradiation was conducted at RT under air atmosphere or at liquid nitrogen temperature (LNT, 77 K) in liquid nitrogen. Dose rate was 71.4 kGy/h and absorbed dose was 10 MGy. Figure 3 shows the double-notch specimens of GFRP and hybrid composite before and after irradiation.

ILSS test was performed by Shimadzu Autograph AG-X10kN (Shimadzu Corporation). Table 1 shows the irradiation temperature and thermal history of specimens. In condition A, the samples was irradiated at RT. After irradiation, they were cooled down to LNT and then ILSS was conducted at LNT. In condition B, the samples was irradiated at LNT. After irradiation, they were warmed up to RT and then cooled down to LNT again. ILSS test was conducted at LNT. In condition C, the samples was irradiated at LNT. After irradiation, they were kept at LNT and then ILSS test was conducted at the same temperature. ILSS was calculated by following formula;

$$\tau = \frac{W}{bL}$$

where, $\tau$ is interlaminar shear stress, $W$ is load, $b$ is depth of specimen and $L$ is notch distance, respectively.

DMA was conducted by Advanced Rheometer AR1000 (TA Instruments). Dynamic storage modulus ($'G'$) and dynamic loss modulus ($"G"$) were measured, and then the ratio $"G"/'G'$ defined as tan $\delta$ was calculated. The temperature where the tan $\delta$ became maximum was defined as glass-transition temperature (Tg). The samples for DMA test irradiated at RT or LNT. The number of samples was 2 for each irradiation condition.

![Figure 3. Specimens before and after irradiation (left: GFRP, right: Hybrid composite)](image)

| Condition | Irradiation | Thermal History | ILSS test |
|-----------|-------------|----------------|----------|
| A         | RT          | cooled down    | LNT      |
| B         | LNT         | warmed up to RT, and then cooled down again | LNT |
| C         | LNT         | constant       | LNT      |

3. Results and discussion

3.1. ILSS test

Figure 4 shows the ILSS of GFRP and hybrid composite before and after irradiation. Concerning the GFRP, only the RT irradiated specimen shows the degradation. That is, the LNT irradiation does not degrade the ILSS of GFRP. The same phenomenon was observed in the hybrid composite specimens. This result indicated that the mechanical strength of the insulating material was not degraded by cryogenic irradiation whereas that was degraded by RT irradiation.
In the case of LNT irradiation, the significant difference was not induced between by raising temperature after irradiation (condition B) and by keeping at LNT (condition C). In addition, ILSS of hybrid composite specimens irradiated at RT shows larger degradation than those of GFRP. This result suggests that the interfacial strength between the resin and the polyimide film is more susceptible to radiation than those between the resin and the glass fiber. As a cause, it is considered that glass cloth has a larger adhesion area per unit area with the matrix resin compared with polyimide film, because the resin also flows into the gaps of the glass fibers by its permeability. Thereby the interface between the resin and the polyimide film had weaker strength, and then destruction occurred at the interface between the resin and the polyimide film.

![Figure 4. ILSS before and after irradiation (left : GFRP, right : Hybrid composite)](image)

### Figure 4. ILSS before and after irradiation (left : GFRP, right : Hybrid composite)

#### 3.2. DMA

Figure 5 shows the result of Tg measurement before and after irradiation. The Tg was slightly decreased by the LNT irradiation. The RT irradiation induced the large degradation in Tg. Generally, Tg decreases when the molecular chain scission occurs. Therefore, it indicates that the scission occurs more frequently by RT irradiation compared with LNT irradiation. In other words, it was shown that the molecular chain scission was hardly induced by the cryogenic irradiation, in contrast with RT irradiation.

![Figure 5. Tg before and after irradiation](image)
The reason why the degradation of the insulating material does not occur markedly at LNT compared with that at RT is considered that the molecular chain motion affects the irradiation effect. Tg is the temperature where Micro-Brownian motion starts and then the molecular motion is frozen lower than Tg. At higher than Tg, G-value follow the Arrhenius equation, whereas lower than Tg G-value shows constant, because the hydrogen radicals generated by irradiation recombine without attacking other molecular chains. This phenomenon is called a “cage effect.” Due to cage effect, it has been considered that G-value is constant lower than Tg [5]. However, as shown in Figure 5, insulating material is greatly degraded by RT irradiation although the Tg of the epoxy resin is higher than RT. Therefore, it is considered that the other molecular motion would affect the irradiation effect. In the epoxy resin, there is the temperature where the local molecular chain motion is taken place between RT and LNT [6]. That is, there is still local molecular chain motion at RT, though the molecular motion is frozen at LNT. In this study, insulating materials were degraded greatly by RT irradiation, but were hardly degraded by LNT irradiation. Therefore, it could be considered that the local molecular chain motion also affects the irradiation effect.

Another possible reason of degradation is oxygen effect. The irradiation at RT was performed in the air atmosphere. On the other hand, the irradiation at LNT was performed in liquid nitrogen where there was no oxygen. Oxygen is one of the factors affecting the irradiation effect. The experiments to evaluate the oxygen effect is now under planning.

In this study, DMA experiments were conducted only for matrix resin and we cannot discuss exactly if the local molecular motion affect the interface strength. But it is expected that local molecular motion will also affect the interfacial adhesion strength between resin and polyimide film. On the other hand, interface between the resin and glass fibres have strong bond by silane coupling agent that is independent from local molecular motion of the matrix resin. Above is considered as one of the reason why the irradiation effect on hybrid composite was larger than that on GFRP at RT. In future, we will validate the hypothesis by the experiment for irradiation effect on the interfacial bonding.

4. Conclusion
The purpose in this study is to evaluate the irradiation effect of insulating materials at cryogenic temperature especially the effect of temperature change after irradiation. Double-notch specimens made of GFRP or hybrid composite were irradiated at RT or LNT. The epoxy plate was prepared and also irradiated at RT or LNT. The ILSS test was made in GFRP and hybrid material, and Tg measurement was made in epoxy plate. By ILSS test, it was shown that ILSS was not degraded by LNT irradiation whereas ILSS was degraded by RT irradiation. In addition, it was also shown that ILSS was not changed by the temperature change between RT and LNT. Tg measurement showed that molecular chain scission in the matrix of insulating materials was not caused by LNT irradiation in contrast with RT irradiation. From these results, it was shown that insulating materials irradiated at cryogenic temperature was not degraded. As a cause of these results, it is considered that the local molecular motion could bring the deference. In order to verify the mechanism, the experiments eliminating the oxygen effects is now under planning.

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