Study on irradiation effect of insulating materials for fusion superconducting magnets: temperature dependence of mechanical strength

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Abstract. Insulating materials used in the superconducting magnets of fusion reactors are exposed to cryogenic temperatures, intense radiations, and strong electromagnetic forces. In the experimental fusion reactor ITER, resin mixed with epoxy resin (EP) and cyanate ester (CE) (CE content: 40 wt.%) is used as a matrix of glass reinforced plastics (GFRP) as an insulating material to maintains mechanical strength and insulating performance in such environments. This composition ratio is basically determined by strength tests at room temperature or liquid nitrogen temperature, so the study at liquid helium temperature is required. In this study, the effects of the resin composition of GFRP on interlaminar shear stress (ILSS) at room temperature, liquid nitrogen temperature, and liquid helium temperature before and after γ-ray irradiation were evaluated. The ILSS after γ-ray irradiation of EP showed a maximum value at liquid helium temperature, while the addition of CE caused the ILSS after irradiation to show a maximum value at liquid nitrogen temperature. It was also shown that the temperature dependence of the ILSS decreased with increasing CE content. The results showed that the addition of CE to EP contributes to the improvement of radiation resistance, but excessive addition of CE promotes embrittlement at LHeT.

1. Introduction

The insulating material used in superconducting magnets for fusion reactors is a hybrid composite of a resin matrix, glass cloth, and polyimide film, which is exposed to intense radiation such as fast neutrons and secondary radiation such as γ-ray at liquid helium temperature (LHeT) and strong electromagnetic forces during fusion reactor operation [1]. In the experimental fusion reactor ITER, a 3:2 mixture of epoxy resin (EP) and cyanate ester (CE) with excellent radiation resistance (CE content: 40 wt.%) is used as the matrix as an insulating material capable of maintaining mechanical strength and insulating performance in such an environment. This composition ratio was determined through strength tests at room temperature (RT) and liquid nitrogen temperature (LNT) [2], not at the actual environment of

LHeT. However, it has been shown that the freezing of molecular motion in epoxy resins occurs at temperatures below LNT [3], suggesting the importance of studying at LNT.

In our previous study, we prepared GFRPs using two different base materials: EP resin and mixture of EP and CE (CE content: 40 wt.%), and investigated the temperature dependence, from room temperature to liquid helium temperature, of ILSS before and after γ-ray irradiation of up to 10 MGy at room temperature [4]. As a result, in the case of EP and hardener, the ILSS after irradiation showed a maximum value at LHeT, whereas in the case of the CE mixed resin, the ILSS showed a maximum value at LNT and a slight decrease at LHeT. We have also studied the changes in ILSS and glass transition temperature (T_g) of these resins due to irradiation in liquid nitrogen [5], and have found that the decrease in ILSS and T_g was less for irradiation in liquid nitrogen than for irradiation at room temperature, which was not due to the elimination of the effect of oxygen but rather to the fact that irradiation was at a low temperature. These results indicate that whether the irradiation and test conditions are room temperature or low temperature has a significant effect on the properties of GFRP.

In this study, focusing on the test temperature, we prepared four types of insulating materials with four types of resin compositions, and measured the interlaminar shear strength (ILSS) at RT, LNT, and LHeT after γ-ray irradiation at room temperature, where the effect on the ILSS is more significant. Our objective is to evaluate the effect of resin composition on the dose and temperature dependence of ILSS, and to obtain a guideline to consider the optimal resin composition for high mechanical strength at LHeT. Although the actual composite materials used for ITER include polyimide films in addition to glass cloths, GFRP prepared by the vacuum impregnation method with glass cloths and resin matrix was used in this study to simplify the system.

2. Experimental methods

2.1. Overview of the Experiments

The radiation resistance differs depending on the main ingredient and curing agent. Many studies have been conducted for resin and insulation systems of fusion plasma containment [6],[7],[8]. These studies showed that the cyanate ester systems are more radiation resistant than the epoxy systems, and cyanate ester-epoxy blends have been proposed to reduce the cost. In this study, to investigate the effect of adding cyanate esters, we used a non-aromatic curing agent for the epoxy resin and a varying amount of cyanate ester in the epoxy resin for cyanate ester-epoxy blends.

GFRP with a base resin consisting of a mixture of polyetheramine and epoxy resin (hereafter referred to as PEAEP) and GFRP with a base resin made of a mixture of cyanate ester and epoxy resin (hereafter referred to as CEEP) were prepared by vacuum impregnation. GFRPs were then irradiated with γ-rays at room temperature and in air, and then subjected to ILSS tests at three temperatures of RT, LNT and LHeT. The composition of CEEP was adjusted so that the cyanate ester content in the resin was 20, 40, and 60 wt.%. The resin matrix samples before and after irradiation were analyzed by dynamic viscoelasticity measurements to investigate the glass transition temperature. Details of each experiment are described below.

2.2. Fabrication of Glass Fiber Reinforced Resin (GFRP) by Vacuum Impregnation Method

First, plain-woven S-glass cloth (Arisawa Mfg. Co., Ltd., Japan) was cut along the fiber into 65 mm × 105 mm pieces. 45 pieces were stacked in an aluminum impregnation container coated with mold release agent and fixed from the top and bottom using metal plates and bolts and nuts. The glass clothes were then vacuum-dried at 100°C for 24 hours in an electric furnace in order to prevent a decrease in strength due to moisture absorption in the glass cloth. Next, a mixture of polyetheramine (Baxxodur EC 301, Mitsui Fine Chemicals, Inc., Japan) and bisphenol A epoxy resin (JER-828, Mitsubishi Chemical Corporation, Japan) was prepared. The weight ratio of the epoxy resin to the curing agent was defined as the ratio of the equivalent amount of epoxy to that of reactive functional groups in the curing agent. Based on the equivalent amount, 32.2 g of polyetheramine was used per 100 g of epoxy resin.

Similarly, mixed resins of bisphenol E cyanate ester (Primaset® LeCy, Lonza, Swiss) and bisphenol A epoxy resin with cyanate ester content of 20, 40, and 60 wt.% were prepared. These mixed resins were stirred and defoamed in a vacuum de-aerator (VD-VLH, As-One Corporation, Japan), and then poured into an impregnation vessel with a fixed glass cloth while pulling a vacuum. GFRP sheets were then heated and cured in an electric furnace (AVO-200NS, As-One Corporation, Japan). The structural formulas of the resins and the hardener used are shown in figure 1, and the temperature program for each resin is shown in figure 2.

The prepared GFRP plate was removed from the container and processed into the ILSS specimen shown in figure 3. In this specimen shape, grooves were dug in the through-layer direction, overlapping each other by about 0.2 mm to ensure that interlaminar shear failure occurs between the grooves during the ILSS test.

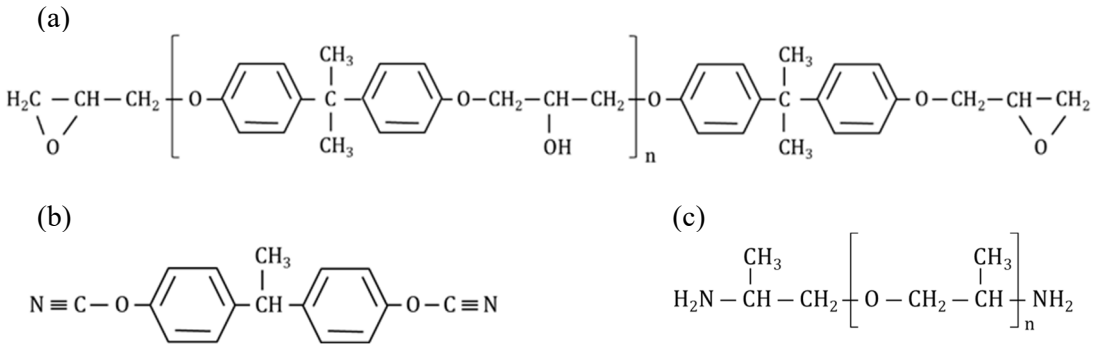

Figure 1. Chemical structures of the resins and the hardener:
(a) (Bisphenol A) epoxy resin, (b) (Bisphenol E type) cyanate ester, and (c) polyetheramine.

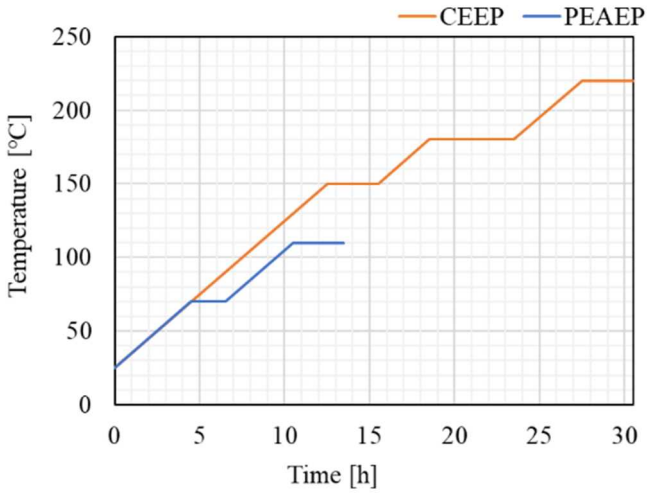

Figure 2. Curing condition of CEEP and PEAEP.

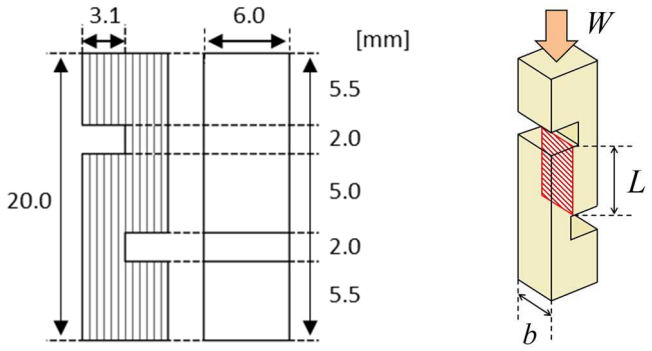

Figure 3. Dimensions of double-notch specimen.

2.3. Gamma-ray irradiation

The processed GFRP specimens were irradiated with γ-ray at the ^{60}Co γ-ray irradiation facility in the Quantum Beam Science Laboratory of the Institute of Scientific and Industrial Research, Osaka University, under the irradiation conditions shown in table 1.

Table 1. Irradiation conditions of γ-ray.

Absorbed dose	0, 5, 10 MGy
Dose rate	42 kGy/h
Irradiation time	120, 240 h
Irradiation distance	2.5 cm
Temperature	Room temperature (about 300 K)
Irradiation atmosphere	Air atmosphere

Interlaminar shear strength (ILSS) test

ILSS tests at room temperature and liquid nitrogen temperature were performed on γ-ray irradiated GFRP at the Graduate School of Engineering, Osaka University, and at liquid helium temperature at the National Institute for Fusion Science (NIFS), respectively. The test jig shown in figure 4 and universal tester (Autograph AG-10kNX for RT and LNT, and Autograph AGS-10kNX for LHeT, both manufactured by Shimadzu Corp., Japan) was used for the tests. For the liquid nitrogen temperature ILSS tests, the specimens were placed inside glass Dewar jar filled with liquid nitrogen. On the other hand, ILSS tests at liquid helium temperature were performed inside the double glass Dewar jars shown in figure 4, with the inner glass Dewar jar filled with liquid helium and the outer Dewar jar filled with liquid nitrogen. The crosshead speed was 1 mm/min, and the maximum test force during the ILSS test was used as the load at specimen failure. As shown in right figure in figure 3, if the width of the specimen is b (mm), the distance between the two grooves is L (mm), and the load at which the specimen fails is W (N), ILSS; τ (MPa) can be expressed by Equation (1).

$$\tau = \frac{W}{bL} \tag{1}$$

ILSS tests were conducted on nine specimens per condition for PEAEP and four specimens per condition for CEEP.

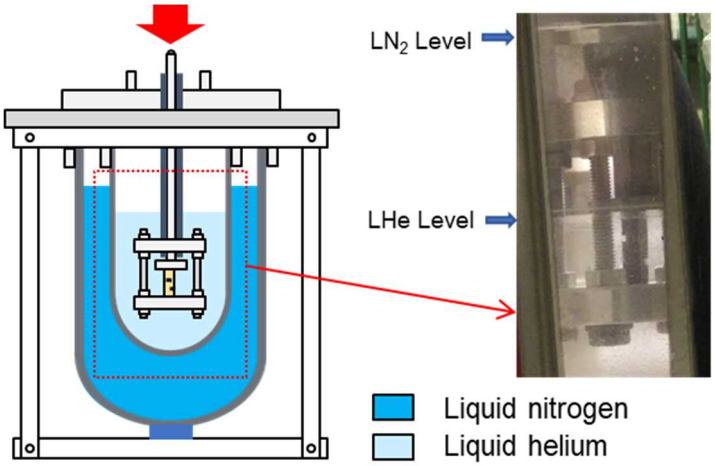

Figure 4. ILSS test system in liquid helium.

2.4. Dynamic Viscoelasticity Measurement

Dynamic viscoelasticity measurements were performed on PEAEP and CEEP with CE contents of 20, 40, and 60 wt.%. First, PEAEP and CEEP resins without glass cloth were prepared as described in Section 2.3, cured, and machined to approximately 1 mm × 10 mm × 40 mm. Specimens for dynamic viscoelasticity measurements were then prepared by irradiation with γ-rays at absorbed doses of 0, 5, and 10 MGy, as described in section 2.1. Dynamic viscoelasticity measurements were performed on these specimens using a dynamic viscoelasticity measuring device (AR2000, TA Instruments Co., Ltd., USA). The specimens were heated from room temperature to a maximum of 250°C at a rate of 5 °C/min while constant torsional vibration (1 Hz, ε = 0.5%) was applied.

3. Results and discussions

3.1. Absorbed dose and temperature dependence of interlaminar shear strength (ILSS)

The ILSS test results for GFRP samples with different resin compositions, measurement temperatures, and absorbed doses of γ-ray irradiation are shown in figures 5 and 6. First, the absorbed dose dependence is discussed. As shown in figure 5, the average ILSS of PEAEP at 10 MGy tends to be lower than that at 0 MGy at all temperatures, although significant differences are seen only in LNT. This suggests that the mechanical strength of PEAEP is degraded by γ-ray irradiation. On the other hand, the ILSS of CEEP tended not to change significantly after γ-ray irradiation, confirming its high radiation resistance of CE, even in LHeT.

Most reactions such as molecular chain scission or crosslinking induced by γ-ray irradiation are thought to be caused by unstable radicals. In general, aromatic compounds, which are more abundant in cyanate esters, stabilize radicals by delocalizing electrons [9]. In addition, epoxy resins cured with polyether amines have a structure in which linear molecules are bonded together, whereas mixed resins of cyanate esters and epoxy resins have many cyclic structures, such as triazine ring, isocyanate, oxazoline ring, and oxazolidinone. Cyclic structures increase the rigidity of the matrix, and rich benzene rings delocalize the radicals generated by γ-rays. Therefore, main chain of PEAEP is relatively easily broken by γ-rays, whereas CEEP is considered to have high radiation resistance because of rigidity of the matrix and delocalization of electrons.

Next, the temperature dependence is discussed. figure 6 shows that as the cyanate ester content increases, the ILSS at room temperature becomes higher, while the ILSS at cryogenic temperature (LNT and LHeT) becomes lower, although these trends are not always monotonous and significant. This indicates that the temperature dependence of ILSS becomes smaller as CE content increases, and the effect of CE addition shows an opposite trend at room temperature and cryogenic temperatures.

Another important feature in the temperature dependence is that the ILSS after γ-ray irradiation of PEAEP showed a maximum value at liquid helium temperature, while the addition of CE caused the ILSS after irradiation to show a maximum value at liquid nitrogen temperature. The ILSS of irradiated GFRP with PEAEP increased monotonously with decreasing temperature. The reason for this is thought to be that irradiated EP have increased molecular degrees of freedom due to chain scission, which facilitates stress relaxation even at LHeT. On the other hand, the higher CE content, the higher ILSS at RT, whereas the lower ILSS at LNT and LHeT, compared to PEAEP. Furthermore, ILSS decreased as the temperature dropped from LNT to LHeT. The reason for this is thought to be that the formation of cyclic structure described above by addition of CE makes the resin matrix rigid and increases ILSS at RT compared to PEAEP, while promoting low-temperature embrittlement by reducing toughness. The decrease in ILSS from LNT to LHeT clearly demonstrates this feature. The mechanism is discussed again in section 3.2.

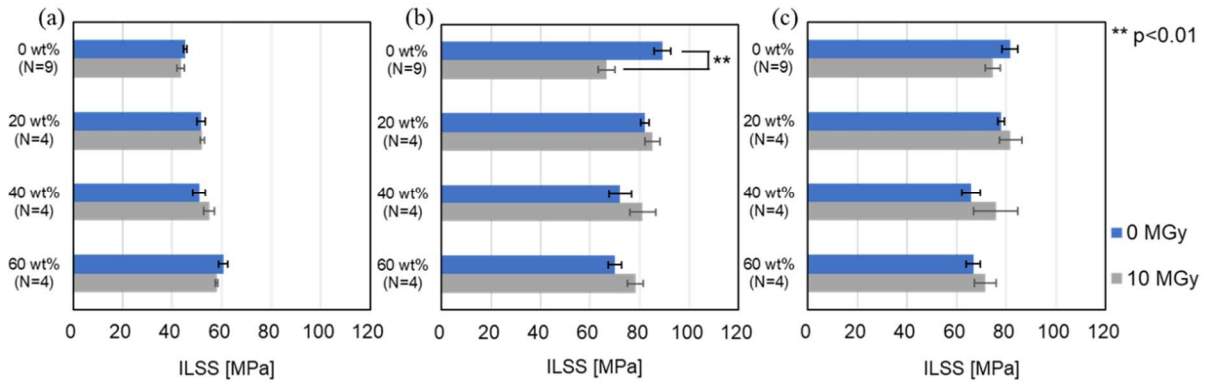

Figure 5. ILSS of GFRPs at (a) RT, (b) LNT, (c) LHeT. *N* indicates the number of samples. 0 wt% is PEAEP sample and 20-60 wt% is CEEP sample, where the percentage indicates the ratio of CE. The p-value indicates significant probability. Error bars indicate the standard deviation.

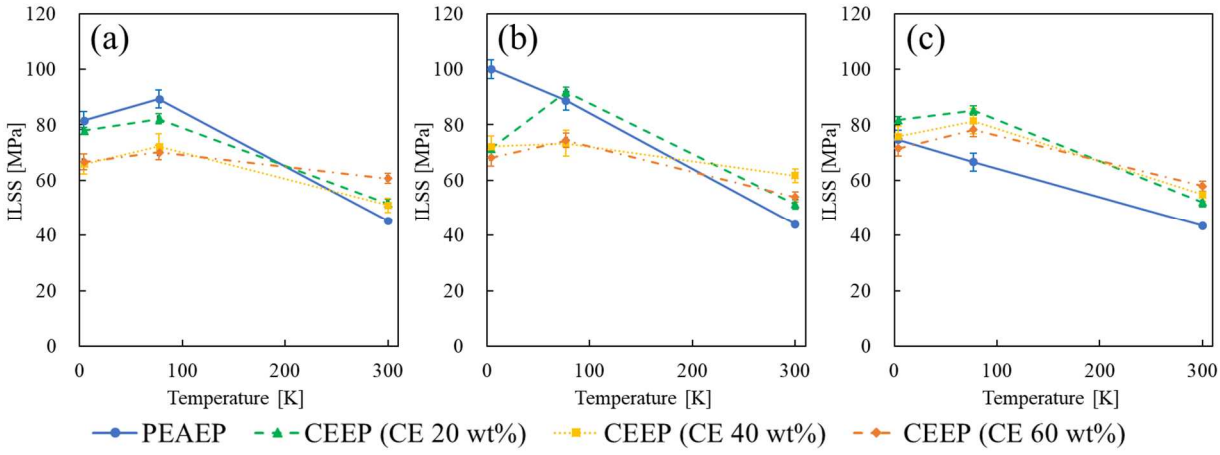

Figure 6. ILSS of GFRPs at (a) 0 MGy, (b) 5 MGy, (c) 10 MGy. The original data is as same as in figure 5. Error bars indicate the standard deviation.

So far we have discussed the resin matrix, but the actual material is a composite with glass fibers, and the discussion of the glass-resin interface should not be ignored. We observed the fracture surface of all samples by SEM observation. None of the samples showed complete interfacial fracture or complete cohesive fracture, but a characteristic phenomenon was a wavy pattern (river pattern) [4,10], indicating

brittle fracture, which was observed in all samples except the 0 MGy PEAEP resin. This indicates the importance of preventing further embrittlement of the matrix by the addition of CE.

These results suggest that the addition of cyanate esters improves radiation resistance, but excessive addition promotes embrittlement. It is also considered that the optimal percentage of cyanate esters in the resin may be less than the 40 wt.% adopted in ITER for mechanical strength at LHeT.

3.2. Investigation of the crosslink density of the base resin by dynamic viscoelasticity measurements

The relationship between T_g' and absorbed dose for PEAEP and CEEP was evaluated by dynamic viscoelasticity measurement, as shown in figure 7. Here, tan δ is defined as tan $\delta = G''/G'$, where G' and G'' are storage shear modulus (Pa) and loss shear modulus (Pa), respectively. T_g' is the temperature at which the peak tan δ temperature, correlates with the glass transition temperature T_g. It was found that the higher the cyanate ester content, the higher the peak tan δ temperature. This indicates that the more cyanate ester in the resin, the higher the glass transition temperature. Here in figure 7 (a), two peaks corresponding to the two phases are seen for CEEP 60 wt.%, but the peak on the higher temperature side with higher peak height is adopted and plotted in figure 7 (b).

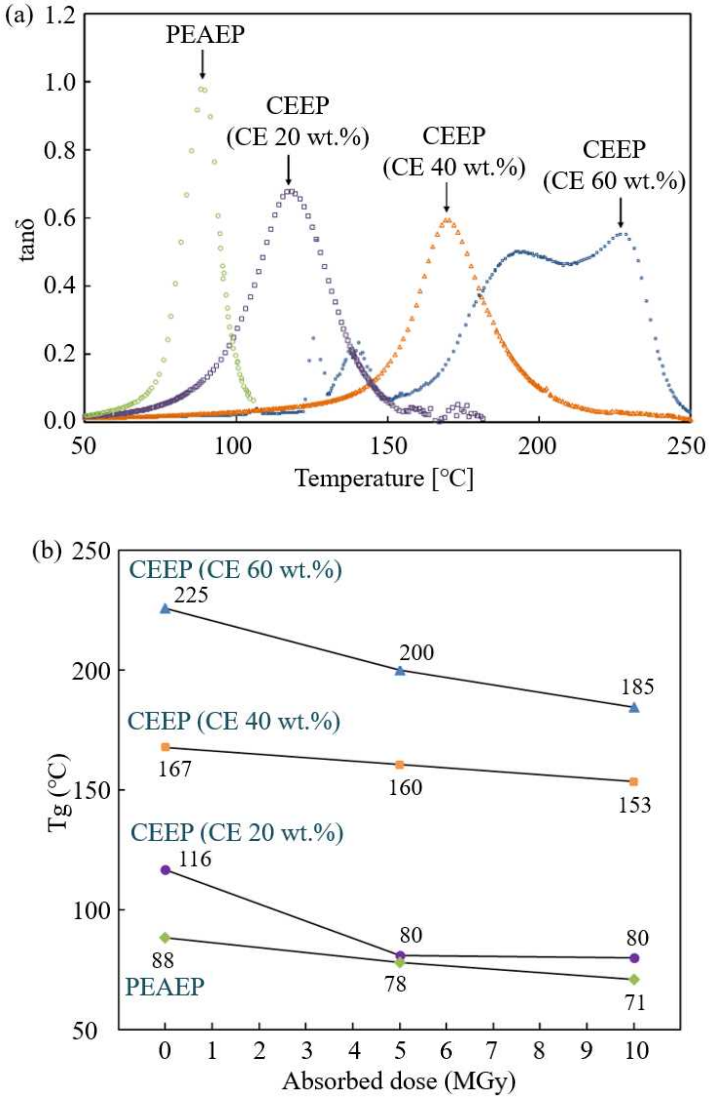

Figure 7. The results of dynamic viscoelasticity measurements in PEAEP and CEEP samples not including glass cloth: (a) temperature dependence of tan δ, and (b) absorbed dose dependence of T_g'.

Since polymeric materials with higher glass transition temperatures tend to have higher crosslink densities [11],[12], it can be inferred from the present results that the higher the cyanate ester content in the resin, the higher the crosslink density. In addition, a tendency for T_g' to decrease with increasing absorbed dose was observed for all resins. This indicates that the crosslink density decreased with γ-ray irradiation for all resins. It is suggested that molecular chain scission rather than cross-linking was the predominant reaction induced by γ-ray irradiation, regardless of the resin composition.

Despite the fact that the γ-ray irradiation mainly caused molecular chain scission, the average ILSS tended to increase in CEEP, and a stress relaxation model can be considered as the mechanism. When the molecular chains are broken by γ-ray irradiation, the molecular degrees of freedom become larger, and stress relaxation is more likely to occur, which may have improved the ILSS. In the case of CEEP, however, low-temperature brittleness due to freezing of molecular motion in LHeT may have been a more significant effect. On the other hand, PEAEP showed a characteristic phenomenon of maximum ILSS at LHeT after irradiation. This can also be explained by stress relaxation; PEAEP has a larger degree of freedom of molecular motion than CEEP, and thus the effect of stress relaxation is more pronounced at LHeT.

These results suggest that the addition of CE contributes to radiation resistance, but excessive addition may lead to embrittlement under irradiation at liquid helium temperatures. On the other hand, the large degree of freedom of molecular motion of EP suggests that stress relaxation is likely to occur at LHeT. Based on these results, the optimal CE/EP ratio at LHeT should be investigated.

4. Conclusion

ILSS tests were carried out on four types of GFRPs with different resin compositions at three temperatures (RT, LNT, and LHeT) after γ-ray irradiation. It was found that the higher the CE content in the resin, the lower the temperature dependence and the grater the embrittlement tendency at LHeT. These phenomena were attributed to the difference between CE and EP in the degree of freedom of motion of the molecular chains of the base resin and their change due to molecular chain scission by γ-ray irradiation. These results indicate that the addition of CE to EP contributes to the improvement of radiation resistance, but excessive addition of CE promotes embrittlement at liquid helium temperature, so the component ratios of the resins should be considered by making good use of the high degree of freedom of movement of the molecular chains of EP, not simply reinforce the rigidity of the chain by addition of CE.

The present results suggest that the optimum percentage of cyanate ester in the resin may be lower than the 40 wt.%, adopted in ITER, when considering ILSS at liquid helium temperature. However, when simulating a more realistic system, the effects of low-temperature irradiation and temperature history need to be considered in future studies. Furthermore, from the viewpoint of dielectric breakdown voltage, it has been suggested that dielectric breakdown may occur due to micro-breakage before macro-breakage occurs under stress [13], and further study is needed in this regard.

5. References

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