§11. Study on Degradation Process of Organic Insulation Materials for Fusion Superconducting Magnet by Exposure to Radiation

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The polymeric materials used for the electric insulation are one of the most radiosensitive materials in the superconducting fusion magnet. It is important to evaluate the irradiation effect of the insulation materials and improve the radiation durability for safety and durability of the reactor system. In this study, cyanate ester (CE) was used in order to prepare the radiation-durable resin, and the radiation effects on the resins with different percentages of cyanate ester in the mixed resin with epoxy resin were investigated.

CE resin (CA200, Mitsubishi Gas Chemical Company Inc.) and epoxy resin (Epikote828, Mitsubishi Chemical Corporation) were mixed in 100, 40, 30 wt% and the test samples were fabricated by heat treatment. The samples were with 60-Co gamma ray in the absorbed dose of 5MGy at dose rate of 1MGy/day under air atmosphere and room temperature. The radical species generated by the gamma irradiation in the samples were measured using electron spin resonance (ESR) every day. In the test period, the samples were stored in the desiccator at 23°C.

ESR spectra of CE/epoxy mixed resin samples immediately after irradiation are shown Fig.1. The spectrum of 100 wt.% CE showed higher signal intensity than those of 40 wt.% and 30wt.%. The relation between the main signal strength of ESR and the lapsed days after irradiation are shown in Fig.2. The signal intensities were decreased with time in all the samples, whereas initial intensity differed depending on the rate of the cyanate ester.

It is considered that the radicals generated in 40wt.% and 30wt.% CE samples decreases promptly, which causes the scission of polymer chain. In contrast, the radicals generated in the 100 wt.% CE sample exist in relatively stable state. It is reported that cyanate ester forms the triazine rings by cyclotrimerization which form the three-dimensional network with high stability. It is considered that there are two reasons why the radicals are stable in the 100wt.% CE sample. Firstly, a triazine ring has many pi bondings which makes radicals delocalized and stable. Secondly, it is also expected that the three-dimensional networks of the triazine rings protect the orbitals containing the unpaired electrons. The generated radical and following reaction is considered to be the same regardless of the composition of the resin, but the concentration of reaction site differs depending on the percentage of CE.

It is considered because radical existing in the samples decreases by the chemical reactions. To investigate the influence of radical reactions on the molecular structure, glass-transition points of 100wt% and 40wt% CE sample immediately after irradiation and seven days after were measured, but the significant difference among these samples was not observed.

The previous studies show that the glass transition temperature shows a correlation with the crosslinking density of the polymers, and it indicates that the chemical reaction of the radicals remaining in the sample after irradiation hardly affects the molecular structure of the polymer.

We are currently preparing the jig for the mechanical testing at the cryogenic temperature. In the future, we will conduct a strength test of insulating material in the liquid nitrogen and helium, in order to evaluate the performance of the material in the conditions close to the actual conditions of use. We are also planning to measure the linear expansion coefficient of the resins before and after irradiation to examine the relationship between the molecular structure and the mechanical strength which changes by the irradiation.

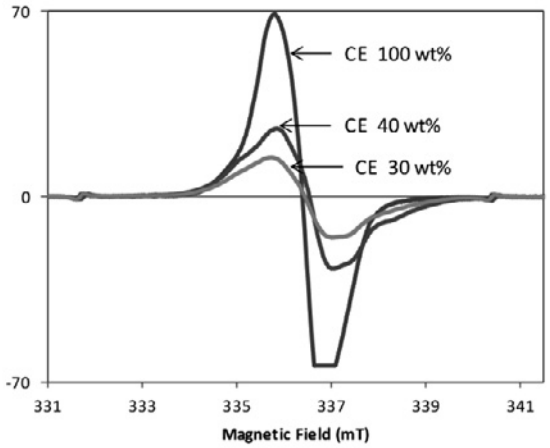

Fig. 1. ESR spectrum of CE/epoxy composite materials irradiated at 5 MGy in air.

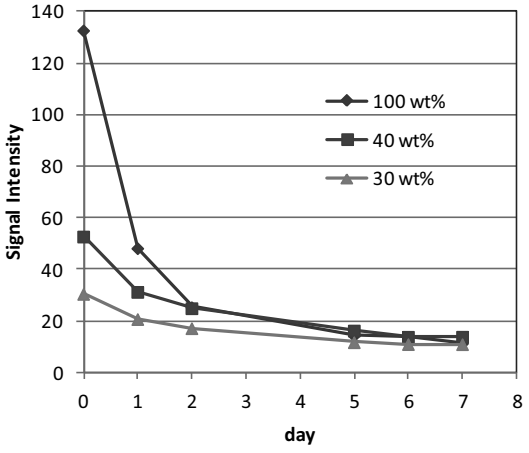

Fig. 2. ESR signal intensity vs. storage day for CE/epoxy composite materials irradiated and stored in air.