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Gamma irradiation effects on cyanate ester/epoxy insulation materials for superconducting magnets

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HIGHLIGHTS

- Irradiation resistance of glass fiber reinforced cyanate ester/epoxy composite was investigated.
- The cyanate ester/epoxy resin system has a low viscosity and long pot life.
- The T_g of the matrix resin decreased slightly with the increase of irradiation dose.
- The ILSS of GFRP composite increased slightly when exposed to 10 MGy of gamma irradiation.

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ABSTRACT

Cyanate ester/epoxy resin was used as a cryogenic-grade polymer matrix and glass fiber reinforced polymer (GFRP) composite was manufactured. The processing properties of matrix resin in terms of the isothermal viscosity at 45 °C were investigated. The specimens were exposed with gamma irradiation of 1 MGy, 5 MGy and 10 MGy, respectively. The effect of gamma irradiation on thermal properties and structure of cyanate ester/epoxy matrix was investigated. The interlaminar shear strength (ILSS) of the composites before and after irradiation were investigated at room temperature, 77 K and 4.2 K. Results showed that cyanate ester/epoxy system had a low viscosity and a long pot life at 45 °C. The glass transition temperature of the matrix resin decreased with the increasing irradiation dose. Moreover, the ILSS of GFRP composite slightly increases after irradiation and toughening mechanism was also discussed.

1. Introduction

Glass fiber reinforced polymer (GFRP) composites have been employed as insulation materials of superconducting magnets such as the International Thermonuclear Experimental Reactor (ITER) [1–5]. With the development of superconducting magnets, GFRP composites were proposed higher requirements. Because of their specific applications in a radiation and cryogenic environment, GFRP composites were required to simultaneously effects of high mechanical loads, extremely cryogenic temperatures and intense nuclear radiation. In case of ITER, the electrical insulation system of TF magnet system is required its irradiation resistance of 10 MGy. Meanwhile, the insulation systems in superconducting magnets were commonly manufactured by a vacuum pressure impregnation (VPI) which requires the resin system should have a low viscosity and a long pot life to make sure an efficient impregnation. In our pervious study [6–9], GFRP composites based on epoxy resin matrix with improved process and irradiation resistance were published.

Cyanate ester/epoxy resin systems have attracted much attention owing to their excellent resistance against the nuclear irradiation. Although extensive researches were carried out to investigate irradiation effects on the mechanical properties of GFRP composites [10,11], little was known the effects of irradiation on thermal properties and structure of polymer matrix. Since polymer matrix are usually sensitive to irradiation, the structure and thermal properties could be significantly affected by irradiation contributed to degrading properties, which leads to degradation and then serious engineering problems. Investigation of irradiation effects on thermal properties and structure of polymer matrix could help us better understand the change mechanisms of mechanical properties.

In this study, a blend system of cyanate ester/epoxy was selected as the matrix resin and the GFRP composites were manufactured by

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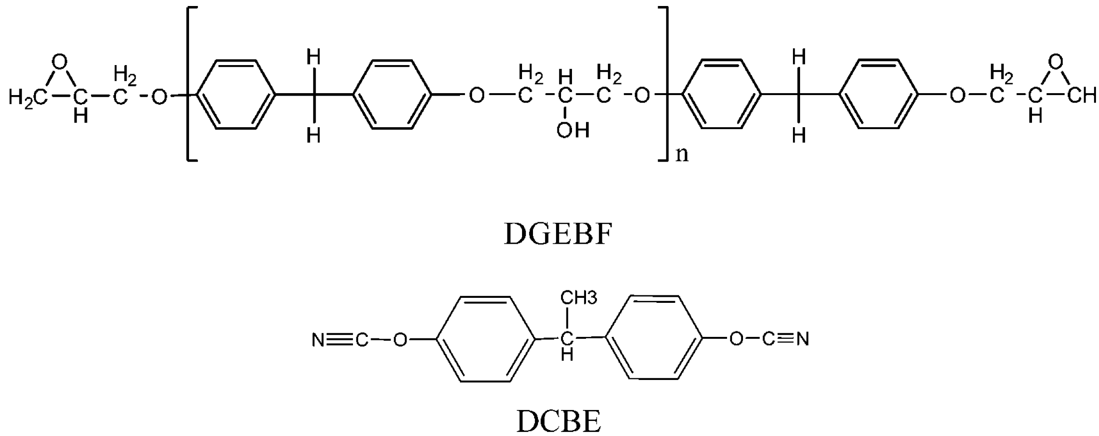

Fig. 1. Chemical structures of DGEBF and DCBE.

VPI. The viscosity and pot life of the blend system were measured. Effect of irradiation on the molecule structure and thermal properties of the polymer matrix was investigated. Moreover, mechanical properties with different irradiation doses were measured and toughening mechanisms were also discussed.

2. Experimental

2.1. Materials

The epoxy resin and the cyanate ester used in this work were diglycidyl ether of bisphenol-F (DGEBF, GY285 from Huntsman) and 1,1-bis(4-cyanatophenyl)ethane (DCBE, Primaset LECy from Lonza), respectively. Their chemical structures are shown in Fig. 1. The catalyst, acetylacetone cobalt(II) (Co(acac)$_2$), was provided by Alfa Aesar. The glass fiber woven is a boron free, 240 g/m^2 plain weave, with 18 threads/cm in the warp (length), 14 threads/cm in the fill (width), treated by a silane agent (RW220-90 from Sinoma Science and Technology Co. Ltd, China).

2.2. Specimen preparation

GFRP composites were prepared with a thickness of 4 mm were prepared with a VPI process. First, woven glass fiber with a dimension of 6 × 18 cm were cut and sealed into a metal mould coated with releasing agent. The metal mould together with woven glass fiber was dried at 100 °C for 10 h. The 60 wt% epoxy resin and 40 wt% cyanate ester with 0.01 wt% Co(acac)$_2$ were mixed in a 250 ml beaker and then the bubble freed suspensions were impregnated into the preheated mould followed by curing at 100 °C for 6 h, 120 °C for 4 h and then 150 °C for 16.5 h.

2.3. Irradiation and test procedures

The specimens were irradiated by ^{60}Co γ-ray irradiation in air at ambient temperature with a doses rate of 300 Gy/min. The total doses were 1 MGy, 5 MGy and 10 MGy, respectively.

The viscosity of cyanate ester/epoxy resin was measured by a Brookfield DV 2 Pro viscometer equipped with a small sample container (6.7 ml). The temperature was kept at 45 °C by a re-circular water around the sample container.

UV–vis spectra of cyanate ester/epoxy matrix were obtained with on a Cary 5000 (Varian, American) spectrometer. The spectra were measured from 190 nm to 1100 nm with a scanning speed of 400 nm/min. Three specimens of each type were tested.

Fourier transform infrared spectroscopy (FTIR) was measured with an Excalibur 3100 (Varian, American) spectrometer using KBr pastille. The spectra were collected from 4000 cm^{-1} to 500 cm^{-1} with the co-addition of 32 scans providing a spectral resolution of 4 cm^{-1}. Three specimens of each type were tested.

Glass transition temperature (T_g) was measured using NETZSCH DSC 404 F3 differential scanning calorimeter (DSC) with a heating rate of 10 K/min and a temperature range from 25 °C to 250 °C. Three specimens were tested and the average value of T_g was obtained.

Short-beam shear (SBS) tests were carried out on a SUNS 4202 test machine (capacity, 20 kN) with a cross-head speed of 1.5 mm/min. The tests at 77 K were carried out by immersing the specimens and the clamps into liquid nitrogen. The specimen was prepared with dimensions of 4 × 8 × 24 mm and the span was set to 16 mm. Five samples of each type were tested and the average value was determined.

Interlaminar shear strength (ILSS) was determined by a SBS test according to standard ASTM D2344. The ILSS of these composites can be calculated according to the following formula:

$$\text{ILSS} = \frac{0.75P_B}{b \times h} \quad (1)$$

where P_B is the maximum load, b is the specimen width and h is the specimen thickness.

The fracture surface of the composites after SBS tests was studied by using a Hitachi S-4800 SEM. A thin evaporated layer of gold was functionalized on the fracture surface to improve conductivity and thus resolution.

3. Results and discussion

3.1. Viscosity

A long pot life and low viscosity of resin matrix are essential to a VPI process to ensure a complete impregnation of a large superconducting coil [12]. The viscosity of the cyanate ester/epoxy (DGEBF/CE) system at 45 °C as a function of time is shown in Fig. 2. It is observed that the initial viscosity of the cyanate ester/epoxy system is about 50 mPa s and the viscosity remain unchanged within 50 h. For comparison, epoxy resin systems of DGEBF/DETD and TGPAP/DETD [9] were incorporated in Fig. 2. Obviously, compared with other two conventional epoxy resin systems, the cyanate ester/epoxy system exhibits lower initial viscosity and longer pot life which demonstrated that the cyanate ester/epoxy system is suitable for VPI process to impregnate large-scale superconducting magnets.