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Novel radiation-resistant glass fiber/epoxy composite for cryogenic insulation system

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ABSTRACT

A new radiation-resistant epoxy resin system was developed that has low viscosity and long working time at 45 °C. The system consists of triglycidyl-p-aminophenol (TGPAP) epoxide, isopropylidenebisphenol bis[(2-glycidyloxy-3-n-butoxy)-1-propylether] (IPBE) epoxide and diethyl toluene diamine (DETD). Boron-free glass fiber composites of epoxy resin with different ratio of TGPAP/IPBE/DETD were prepared by vacuum press impregnation. The ratio of TGPAP/IPBE affected the working time and the viscosity at the impregnation. The mechanical properties of the composites at 300 K and at 77 K were measured before and after ^{60}Co γ-ray irradiation of 1 MGy at ambient temperature. The γ-ray radiation scarcely affected the properties of the composites.

1. Introduction

Within superconducting magnet systems, the insulation systems are subjected to a critical situation as radiation environment at cryogenic temperatures. If any component of the insulation systems is seriously damaged owning to the high radiation dose level or the high mechanical stresses, the performance of the entire magnet system could not be ensured. Therefore, the insulation material must exhibit a certain mechanical strength and radiation resistance at cryogenic temperatures.

In principle, the insulation materials are glass fiber reinforced plastics (GFRPs) consisting of boron-free glass fibers and matrix materials [1]. In the past decades, extensive work has been done to investigate processing techniques of the insulation materials and the radiation effect on the mechanical properties of GFRP composites at cryogenic temperatures. Based on these studies [1–18], advanced epoxy based GFRPs with improved mechanical properties and radiation hardness were introduced into fusion technology, and certain chemical structure have been noted to result in enhanced radiation tolerance. In addition, vacuum press impregnation (VPI) are generally selected to fabricate insulation systems. Impregnating resins in fusion magnetic technology are required to be stable for radiation, and have low viscosity, long usable life, and high toughness. In some recent magnet structures, the resin systems for VPI process are usually based upon diglycidyl ether of bisphenol A (DGEBA) or diglycidyl ether of bisphenol F (DGEBF) cured by acid anhydride hardeners such as methyl tetrahydrophthalic anhydride (MTHPA). However, previous studies showed that with regards to epoxy systems, radiation tolerance increases with resin functionality, and aromatic amine curing agents are superior to anhydride systems [2,5]. Multi-functional epoxy resins with aromatic amine hardeners can withstand radiation doses of up to 200 MGy with only a 25% loss of strength. Unfortunately most aromatic amine curing agents are solid at room temperature and multifunctional epoxies tend to have relatively high viscosities or short working time that do not permit their application for VPI process. Therefore, it is important to develop new multi-functional epoxy resin system which is suitable for VPI process.

In the present study, a blend of a low viscosity tri-functional epoxide TGPAP and an aromatic flexible epoxide IPBE was used. The addition of IPBE improved resin toughness. The resins were hardened with a liquid aromatic amine. Moreover, the radiation resistance of GFRP with various ratios of TGPAP to IPBE was evaluated by γ-ray irradiation of 1 MGy at ambient temperature.

2. Experiment

2.1. Materials

The base resin, TGPAP (triglycidyl-p-aminophenol; AFG-90: Institute of Synthetic Resin, Shanghai), is a low viscosity tri-functional epoxide, known as a radiation stable material. The aromatic flexible epoxide, IPBE (isopropylidenebisphenol bis[(2-glycidyloxy-3-n-butoxy)-1-propylether]; PY 4122 of Huntsman), is an flexible molecule. The hardener, DETD (diethyl toluene diamine; HY 5200 of Huntsman), is a liquid aromatic amine. The chemical structures are shown in Fig. 1. The glass fiber cloth is boron free, 240 g/m^2 plain weave, with 18 ± 1 threads/cm in the warp (length),

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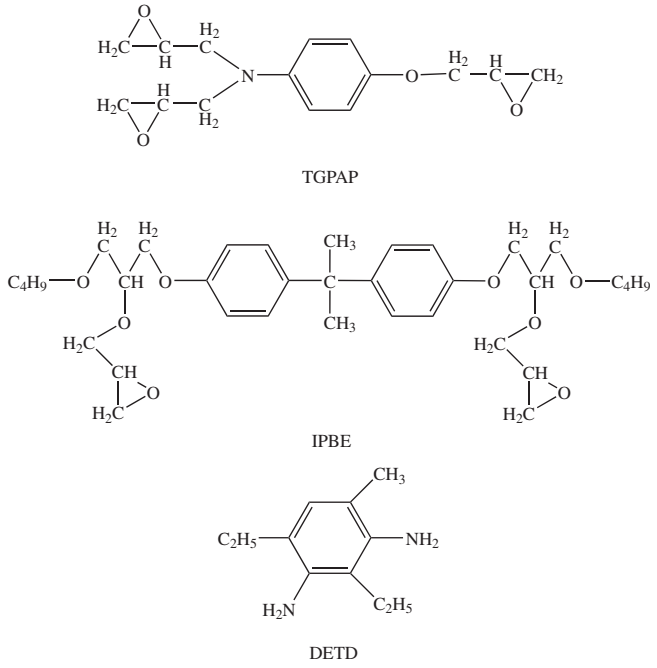

Fig. 1. Chemical structure of TGPAP (a), IPBE (b), DETD (c).

14 ± 1 threads/cm in the fill (width), and treaded by silane agent (RW220-90, Sinoma Science and Technology Co., China). The thickness of the cloth is quoted as 0.2 ± 0.022 mm.

2.2. Specimen preparation

The GFRP composites were prepared by VPI process. The formulation of epoxy resin is listed in Table 1. The GFRP panels were 10 mm and 20 mm thickness consisting of 50 layers and 100 layers of glass fiber cloth, respectively. Prior to the impregnation process, the metal mould filled with the required number of glass fiber layers need a heat treatment at 45 °C for 10 h. In addition, the release agent was smeared on the surface of the metal mould to enable easy detachment of the laminate after the VPI process. TGPAP, IPBE and DETD were completely mixed by a mechanical stirrer and degassed with a vacuum pump to eliminate air bubbles at 45 °C. The bubble-free mixtures were then impregnated into the preheated mould at 45 °C and cured at 80 °C for 10 h, then 120 °C for 10 h.

2.3. Irradiation and test procedures

In order to investigate the influence of irradiation on the properties of the prepared GFRP, half of the samples were irradiated by ^{60}Co γ-ray irradiation at ambient temperature with a dose rate of 100 Gy/min. The total dose was 1 MGy.

The viscosity of the epoxy resin was measured using a viscometer (Brookfield DV 2) equipped with a thermostatically controlled water bath for temperature control.

Table 1
Formulation of epoxy resin (pbw: parts by weight).

Epoxy resin type	Epoxide		Hardener DETD (pbw)
	TGPAP (pbw)	IPBE (pbw)	
1	100	0	44
2	85	15	39
3	75	25	36
4	60	40	31

Both the short-beam shear (SBS) tests and the compression tests were carried out at 77 K and 300 K using a universal testing machine in combination with a cryostat (MTS-SANS 100 kN). The cryogenic condition was achieved by dipping samples inside a cryostat filled with liquid nitrogen. The entire test was conducted while the specimen and its loading fixture were submerged in liquid nitrogen.

The apparent interlaminar shear strength (ILSS) was determined by short-beam bending test according to the ASTM D2344. A cross-head speed of 1 mm/min, and a sample thickness of 10 mm were used. Through-thickness compression strength was assessed on small specimens with outer dimensions of 7 mm × 7 mm × 20 mm (length × width × thickness) according to ASTM D695.

3. Results and discussion

3.1. Processing characteristics

In order to determine the useful working life of epoxy resin formulations, we have measured the viscosity of TGPAP/IPBE/DETD composites with different ratios at 45 °C as a function of time shown in Fig. 2. IPBE reduces the rate of chemical reactions to result in extending the effective working life. If the viscosity at 'end point' for vacuum press impregnation is taken as 500 mPa s, the usable life for this system is around 17 h at 45 °C for the TGPAP/DETD alone and around 24 h for IPBE 30 pbw added.

The contents of glass fiber, epoxy resin and void were determined for the GFRP composites. The contents by volume percentage are shown in Table 2. These values are derived from the density of epoxy resin, glass fiber and composite by measurement of the weight fraction. The calculation of volume percentage for glass fiber (V_f), and the void (V_v) are as following:

$$V_f(\%) = \frac{W_f \times \rho_c}{\rho_f} \tag{1}$$

$$\rho_t = \frac{100}{\frac{W_f}{\rho_f} + \frac{W_r}{\rho_r}} \tag{2}$$

$$V_v(\%) = 100 \times \frac{\rho_t - \rho_c}{\rho_t} \tag{3}$$

where W_f and W_r are the weight percentage of the glass fiber and epoxy resin, respectively, ρ_f, ρ_r and ρ_c are the density of the glass

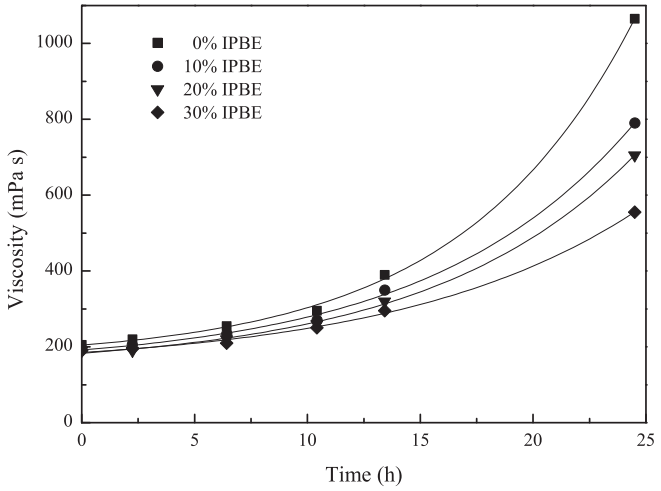

Fig. 2. Viscosity versus time at 45 °C for various TGPAP/DETD/IPBE compounds.

Table 2
Volume% of glass fiber, epoxy resin and void for GFRP with different epoxy resin formulation.

Epoxy resin type	Glass fiber	Resin	Void
1	42.5	57.0	<0.5
2	41.8	56.7	<0.5
3	41.9	56.6	<0.5
4	42.4	57.1	<0.5

fiber, epoxy resin and GFRP composites, respectively, and ρ_t is the theoretical density of GFRP. The experimental error may be less than ±0.5%, therefore the void content is calculated to be around 0.5 vol.%.

3.2. Interlaminar shear strength

The interlaminar shear strength (ILSS) is defined as the resistance of a layered composite to internal forces that tend to induce relative motion parallel to, and between, the layers, and is widely used to evaluate the radiation resistance [10,19–21]. The short-beam shear test (ASTM D2344) is one of the useful methods for characterizing the interlaminar failure resistance of fiber-reinforced composites. For shear failure, the ratio of test span to specimen thickness should lie within the range from 2.5 to 5. Furthermore, since the increase in shear strength may be larger than that in tensile strength when a specimen is cooled to low temperature, a value of the span-to-thickness ratio less than 5 may be necessary to produce shear failure. In this work, to ensure interlaminar shear failure mode, a span-to-thickness ratio was 5:1 for room-temperature and 4:1 for low-temperature. All specimens failed with a single interlaminar shear failure along the centre line of the specimen and the typical photo of actual failure mode is illustrated in Fig. 3a. The ILSS for various GFRP specimens observed at 300 K and 77 K are presented in Fig. 4. The increase of IPBE content tends to decrease the ILSS at 300 K, but shows constant ILSS at 77 K. After ^{60}Co γ-ray irradiation, no distinct changes of the ILSS was observed.

3.3. Compressive strength

As shown in Fig. 3b, a 45° failure mode was observed in all through-thickness compression tests. The angular splitting was caused by the matrix crack and fiber breakage. The compressive

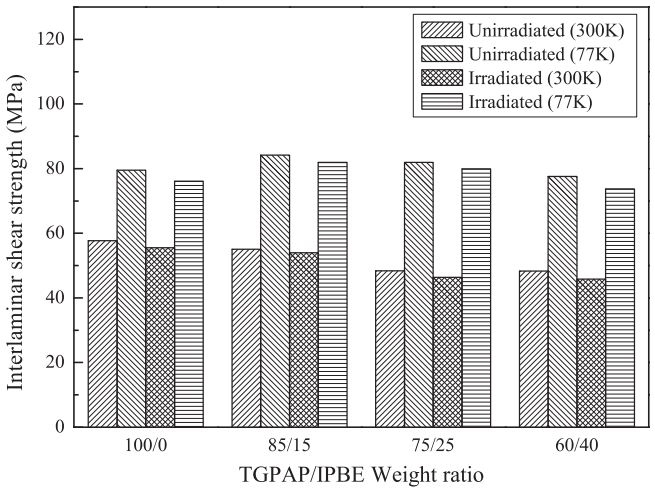

Fig. 4. ILSS of GFRP with different epoxy resin at 300 K and 77 K before and after 1 MGy γ-ray irradiation.

strength of GFRP with different epoxy resins are showed in Fig. 5. The strength of GFRP at 300 K decreases slightly with increase of IPBE, but the strength at 77 K shows the decrease by 20% for the GFRP with TGPAP/IPBE 60/40. Except the GFRP with TGPAP/IPBE 60/40, our GFRP is similar mechanical properties to that of G-10 CR and G-11 CR [22]. For γ-ray irradiation effects up to 1 MGy, as same as ILSS testing, no significant degradation of the compressive strength was observed at room temperature and at 77 K.

Fig. 6 showed the typical examples of the compressive load–displacement curves for GFRP measured at 300 K and 77 K. The load–displacement curves show also, that, there is no significant difference in compressive behavior by γ-ray irradiation up to 1 MGy. Moreover, the compressive strength at cryogenic temperature is higher than that at room temperature, which is relating to increase the modulus at low temperature.

3.4. Swelling

Swelling is one of indicators to measure radiation induced effect of GFRP laminates. In this work, the changes of sample dimension and weight of GFRP specimens were measured. As can be seen from Table 3, the changes by irradiation are very small for any

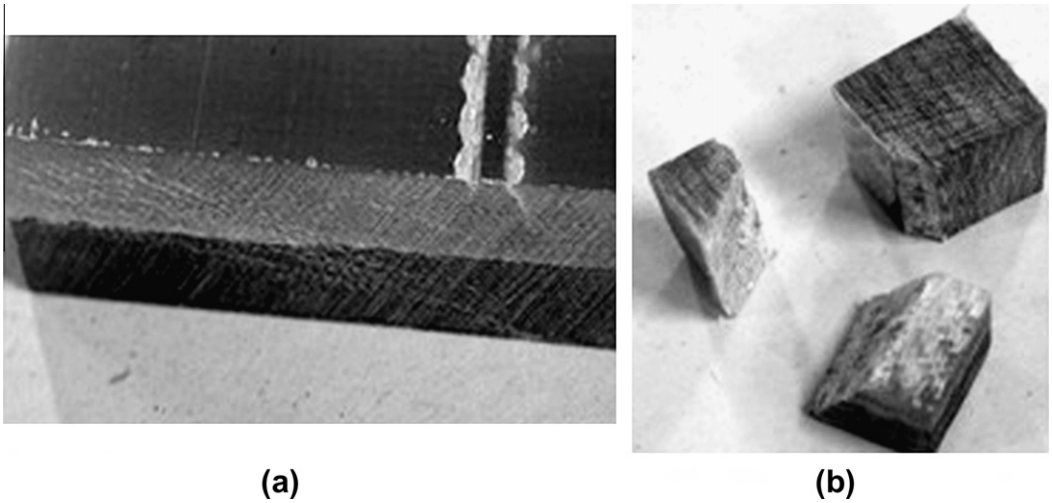

Fig. 3. Photographs of GFRP specimens after ILSS test (a) and compression test (b).

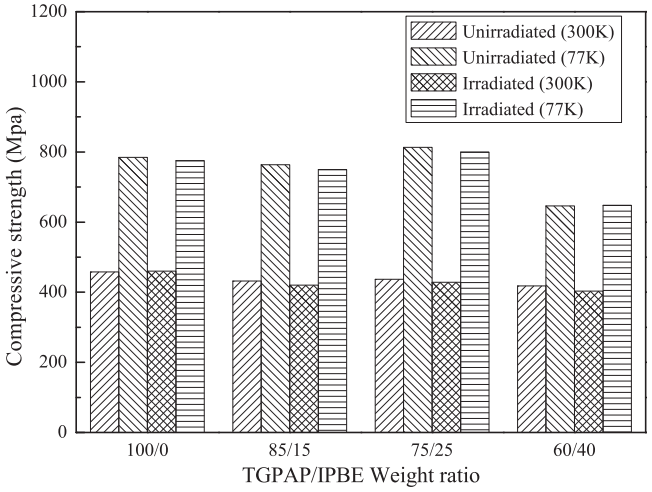

Fig. 5. Compressive strength of GFRP with different epoxy resins at 300 K and 77 K before and after 1 MGy γ-ray irradiation.

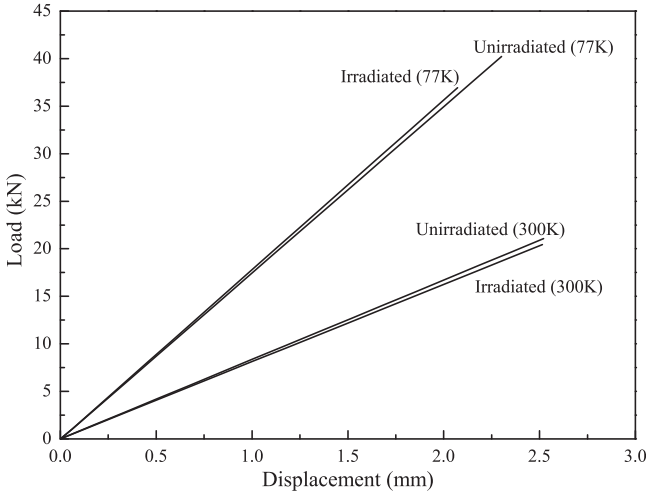

Fig. 6. Compressive load–displacement curves at 300 K and 77 K, non-irradiated and irradiated 1 MGy.

Table 3
Change of swelling and weight loss of GFRP by 1 MGy γ-ray irradiation.

Epoxy resin type	Change of swelling (%)	Weight loss (%)
1	0.0	0.0
2	0.1	0.03
3	0.05	0.024
4	0.15	0.031

specimens. The weight loss may be caused by hydrogen evolution during irradiation.

4. Conclusion

A novel radiation stable epoxy resin of TGPAP/IPBE/DETD composition for GFRP matrix was developed. The viscosity can be controlled by varying the ratio of TGPAP to IPBE to adapt to vacuum press impregnation process. After ^{60}Co γ-ray irradiation up to 1 MGy, the mechanical properties of GFRP retained high level for the epoxy resin composition above the ratio 75/25 of TGPAP/IPBE. Irradiation affected scarcely to the mechanical properties, in addition, the swelling and weight loss of the GFRP specimens were so small that can be neglected. In summary, IPBE improves the GFRP processing characteristics but does not have a significant influence on the mechanical properties as well as the radiation resistance.

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References

[1] K. Bittner-Rohrhofer, K. Humer, H. Fillunger, R.K. Maix, H.W. Weber, Cryogenics 42 (2002) 697–704.
[2] J.B. Schutz, R.P. Reed, D. Evans, Adv. Cryog. Eng. 46 (2000) 197–204.
[3] E.K. Tschegg, K. Humer, H.W. Weber, Cryogenics 31 (1991) 312–318.
[4] H.W. Weber, E. Kubasta, W. Steiner, H. Benz, K. Nylund, J. Nucl. Mater. 115 (1983) 11–15.
[5] S. Egusa, J. Mater. Sci. 23 (11) (1988) 2753–2760.
[6] R.E. Schmunk, G.R. Imel, Y.D. Harker, J. Nucl. Mater. 103 (1981) 723–727.
[7] K. Humer, H.W. Weber, E.K. Tschegg, Cryogenics 35 (1995) 871–882.
[8] S. Nishijima, T. Okada, T. Hirokawa, J. Yasuda, Y. Iwasaki, Cryogenics 31 (1991) 273–276.
[9] P.E. Fabian, R.P. Reed, J.B. Schutz, T.S. Bauer-McDaniel, Cryogenics 35 (1995) 689–692.
[10] K. Humer, S. Spieβberger, H.W. Weber, E.K. Tschegg, H. Gerstenberg, Cryogenics 36 (1996) 611–617.
[11] E.R. Hodgson, J. Nucl. Mater. 258–263 (1998) 226–233.
[12] D. Evans, R.P. Reed, Adv. Cryog. Eng. 46 (2000) 211–218.
[13] K. Humer, H.W. Weber, R. Hastik, H. Hauser, H. Gerstenberg, Cryogenics 40 (2000) 295–301.
[14] K. Bittner-Rohrhofer, K. Humer, H.W. Weber, K. Hamada, M. Sugimoto, K. Okuno, J. Nucl. Mater. 307–311 (2002) 1310–1313.
[15] P.E. Fabian, J.A. Rice, N.A. Munshi, K. Humer, H.W. Weber, Fusion Eng. Des. 61–62 (2002) 795–799.
[16] R. Prokopec, K. Humer, R.K. Maix, H. Fillunger, H.W. Weber, Fusion Eng. Des. 82 (2007) 1508–1512.
[17] H. Zhang, R.J. Huang, L.F. Li, D. Evans, Adv. Cryog. Eng. 54 (2008) 174–181.
[18] R. Prokopec, K. Humer, R.K. Maix, H. Fillunger, H.W. Weber, Fusion Eng. Des. 84 (2009) 1544–1547.
[19] P.E. Fabian, N.A. Munshi, S.W. Feucht, K. Bittner-Rohrhofer, K. Humer, H.W. Weber, Adv. Cryog. Eng. 50 (2004) 289–296.
[20] R.P. Reed, J.B. Darr, J.B. Schutz, Cryogenics 32 (1992) 9–13.
[21] H. Becker, Adv. Cryog. Eng. 30 (1984) 33–40.
[22] M.B. Kasen, G.R. MacDonald, D.H. Beekman, R.E. Schramm, Adv. Cryog. Eng. 26 (1980) 235–243.