Improving fracture toughness of epoxy resin composites by magnetic particles modified short glass fiber

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Abstract. In this paper, magnetic nanoparticles were loaded on the surface of short glass fibers by solvent thermal method to prepare magnetic short glass fibers (MSGF) that have orientation response to a weak magnetic field (0.12T), and further MSGF/epoxy resin (EP) composites were prepared. Scanning electron microscope, X-ray diffractometer, infrared spectroscopy and vibration sample magnetometer were used to characterize the samples before and after loading magnetic nanoparticles on the surface of SCF. The effects of MSGF particle content and magnetic field on the fracture toughness of MSGF/EP composites and the toughening mechanism were investigated. The results show that γ-Fe₂O₃ nanoparticles surface loaded MSGF are successfully achieved using solvothermal synthesis method under the 240 °C with ferric acetylacetonate as iron source and ethanol as solvent. With the optimum MSGF content of 3wt%, when MSGF are oriented along the direction perpendicular to the crack growth under magnetic field, compared to that of pure epoxy resin, the fracture toughness KIC and GIC of the composite materials with magnetic orientation are increased by 54.4% and 138.5%, respectively, and increased by 20% and 43.9% than that of MSGF/EP composites without magnetic orientation, respectively. The main mechanisms of toughening epoxy resin by MSGF include debonding, pulling-out, bridging and deflecting crack.

1. Introduction

Epoxy resin (EP) is widely used in coatings, insulating materials, adhesives, reinforced composites and other fields because of its excellent properties. However, cured epoxy resin is prone to brittle fracture due to the nature characteristics such as molecular structure and cured cross-linking network structure. Especially in low-viscosity resin systems cured at room temperature and in low temperature environment, the problem is particularly serious, which greatly limits its application in the fields of mechanical engineering [1]. In general, some fillers are added to epoxy resin to improve its poor fracture toughness. There are many kinds of fillers, including traditional tougheners such as inorganic particles and elastomers [2, 3], as well as some nanomaterials that have attracted extensive attention in recent years, such as nano-SiO₂ [4], carbon nanotubes [5] and graphene [6], which have been widely studied to enhance the fracture toughness of epoxy resins. Short cut fibers such as glass fibers (SGF) and carbon fibers (SCF) have good physical and chemical properties such as light weight, high strength, excellent heat resistance and chemical stability. They also have the advantages of low price and easy availability as raw materials. Addition of short cut fibers in EP can improve the fracture toughness of composites [7] mainly because they have excellent mechanical strength, when the composites are subjected to
external force, the composite material transfers the external force to the fibers through matrix resin, and the fibers toughen EP by pulling out from the matrix, rupturing and deflecting the crack. Some studies show that [6, 8, 9], fillers with a certain aspect ratio can achieve more efficient toughening effect when they are aligned along the direction perpendicular to the crack growth under electric field, magnetic field or stress field. Due to particularly low magnetic sensitivity, SGF cannot be oriented under a magnetic field supplied by a common NdFeB permanent magnet. Inspired by modification of carbon nanotubes by magnetic nanoparticles [10], in this work, magnetic nanoparticles surface-modified SGF will be prepared using solvothermal method, and then are subject to being orientated in EP under magnetic field, and then the effect of the orientation on fracture toughness of epoxy resin and related toughening mechanism will be investigated, expecting to obtain a kind of modified SGF with simple process, low cost and effective toughening of epoxy resin.

2. Materials and Methods

2.1. Materials
SGF with 6-7 μm in diameter and 50-70 μm in length were purchased from Shenzhen Fiber Valley Technology Co., Ltd. Iron acetylacetonate (Fe(acac)_3) with purity of analytical reagent was provided by Shanghai Aladdin Biochemical Technology Co., Ltd. Anhydrous ethanol with grade of analytical reagent was supplied by Xilong Chemical Co., Ltd. Epoxy resin RIMR-135 and curing agent RIMR-134 were obtained from HEXION Inc.

2.2. Sample preparation
After mixing 10ml absolute ethanol, 10g SCF and 1g Fe(acac)_3 evenly, the mixture was added to the pressure reactor and reacted at 240 °C for 4h. After washing and drying the mixture, magnetic short cut glass fibers (MSGF) were obtained. According to the sample preparation method reported by Ma et al. [11], MSGF and SGF with different mass fractions were added into RIMR-135, dispersed by high-speed homogenizer for 5 minutes, then the curing agent was added at the ratio of 20% resin mass. After mechanical stirring for 10 minutes, the mixtures were poured into a silicone rubber mould and placed under the magnetic field of 0.12T supplied by two parallel Nd-Fe-B permanent magnets. The corresponding composites were obtained after the curing process of first room temperature for 3h and then 80 °C for 15h.

2.3. Characterization
Scanning electron microscopy (SEM, JSM-5610LV, JEOL, Ltd. Japan) was used to characterize the surface morphology of SGF and MSGF and the fracture morphology of the composites. The magnetic properties of the samples were characterized by vibration sample magnetometer (VSM, 7400-S, Lake Shore, USA). The possible functional groups on SGF surface before and after loading nanoparticles were analysed by Fourier transform infrared spectroscopy (FTIR, TENSOR27, Bruker, Germany). The crystal structure and phase composition of the samples were measured and analysed by X-ray diffraction (XRD, D8-2-Advance, Bruker, Germany). According to Scherrer formula, the grain size of magnetic particles was estimated. According to ASTM D5045-2014 test standard, composite material specimens were prepared. Three-point bending tests were carried out on universal testing machine (WDW-E100, Jinan Shijin Group Co., Ltd., China). Then the critical stress intensity factor K_{IC} was calculated using the experimental data. The strain energy release rate G_{IC} of composites was calculated by formula (1).

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G_{IC} = \frac{K_{IC}^2}{E} \left(1 - \nu^2\right)
\]

Where the Poisson ratio \( \nu \) is 0.36 and the Young modulus \( E \) is 3.16 GPa.
3. Result and discussions

3.1. Characterization of MSGF

The XRD patterns of SGF and MSGF are shown in figure 2. The diffraction peaks at $2\theta = 35.46$ and $62.60$ correspond to the (311) and (440) plane of $\gamma$-Fe$_2$O$_3$ with cubic spinel crystal structure recorded in standard card XRD24-0081, respectively. However, due to the small content of $\gamma$-Fe$_2$O$_3$ in the sample, the intensity of the diffraction peaks is weak, and the diffraction peaks corresponding to (400) and (511) are even submerged by background noise. According to the formula (1), the crystal size of (311) was calculated to be around 12nm. In comparison, the crystal size of Fe$_3$O$_4$ nanoparticles loaded on carbon nanotubes is than 6-8nm in the literature reported by Wan [12], which should be related to the difference in the selected solvent and dispersant in the solvothermal reactions. Figure 2 shows FTIR spectra of SGF and MSGF. There are significant absorption peaks at 3423 cm$^{-1}$ attributed to the abundant hydroxyl groups on the surface of glass fibers. Compared with SGF, the absorption peaks of MSGF loading the particles appear at 510 cm$^{-1}$, 567 cm$^{-1}$, 576 cm$^{-1}$ and 597 cm$^{-1}$, corresponding to the vibration peaks of Fe-O-Fe bond, which further confirms that there are $\gamma$-Fe$_2$O$_3$ nanoparticles on the surface of SGF. Figure 3 presents the SEM images of SGF and MSGF. SGF are approximately 6-7μm in diameter, and about 50-70 μm in length. The size of MSGF is almost the same as SGF without any change. The surface of SGF is smooth with minor impurities. In comparison, there are many small particles on the surface of MSGF and the surface roughness of MSGF increases. According to the XRD analysis, these particles are undoubtedly $\gamma$-Fe$_2$O$_3$ particles loaded on the surface of SGF by solvothermal method. From the local magnification, it is observed that the magnetic particles are spherical with the particle size range of 10-
20 nm that is similar to the crystal size of $\gamma$-Fe$_2$O$_3$ (311) determined by XRD analysis, which indicates that the $\gamma$-Fe$_2$O$_3$ particles mainly exist in the form of single crystal. Figure 4 shows the magnetic properties of SGF and MSGF. The hysteresis loops of SGF and MSGF are all S-shaped curves, indicating that both of them are paramagnetic materials. With the increase of magnetic field intensity, both SGF and MSGF reach saturation state quickly, and the saturation magnetization of SGF is close to 0.18 emu/g, while the saturation magnetization of MSGF increases to about 0.72 emu/g due to the loading of $\gamma$-Fe$_2$O$_3$. Figure 4 (b) shows that MSGF in the left bottle are attracted near the NdFeB permanent magnet (surface magnetic field intensity 0.12T), and all MSGF are attracted to the bottle wall near the magnet, indicating that all SGF are loaded with $\gamma$-Fe$_2$O$_3$. From figure 4 (c) and (d), the SGF are still disorderly dispersed under magnetic field, while the MSGF can be deflected under magnetic field and arranged in parallel the direction of magnetic field as shown by the red arrow, which indicates that MSGF can respond to the weak magnetic field by loading magnetic nanoparticles.

3.2. Fracture toughness of composite

Figure 5 presents effect of MSGF content on fracture toughness of MSGF/EP composites with or without magnetic field orientation with different MSGF contents.

Figure 5. Curves of $K_{IC}$ (a) and $G_{IC}$ (b) of MSGF/EP composites with or without magnetic field orientation with different MSGF contents.

When the content of MSGF is 3wt%, the fracture toughness of composites with magnetic field orientation is more prominent than that of the composites without magnetic field orientation. $K_{IC}$ and $G_{IC}$ of MSGF/EP composites without magnetic field orientation are 28.7% and 65.7% higher than pure epoxy resin, respectively. While $K_{IC}$ and $G_{IC}$ of MSGF/EP composites with magnetic field orientation are 54.4% and 138.5% higher than that of pure epoxy resin, and 20% and 43.9% higher than that of composites without magnetic field orientation, respectively. The toughening effect of magnetic oriented MSGF/EP composites is similar to that of carbon nanotubes reported in the literature [11]. More than 3wt% content, the fracture toughness of both composites begin to decrease with increase of MSGF content. The fracture toughness of the composites with 4wt% MSGF content is even lower than that of the composites with 2wt% MSGF content. When 5wt% MSGF are added, the fracture toughness of both composites with or without magnetic field orientation reaches the lowest value, but is still higher than that of pure epoxy resin. It may be that MSGF are prone to agglomeration at high content, which results in defects in matrix, stress concentration and poor fracture toughness of composites.
3.3. Toughening mechanism

To further confirm the toughening mechanism of MSGF, the fracture surface morphologies of pure epoxy resin and MSGF/EP composites with or without magnetic field orientation with MSGF content of 3wt% were analyzed by SEM, as shown in figure 6. It can be seen from figure 6(a) that the crack of pure epoxy resin initiates from the initial crack at the bottom and propagates internally. The crack initiation induces small plastic deformation crack. Propagation path of the crack is flat and simple, and the cracks become finer and shallower in a relatively short distance, and reach stable fracture zone with low surface roughness, which is the feature of a typical brittle fracture. In the absence of magnetic field orientation (figure 6(b), (c)), MSGF appears to be disorderly distributed in epoxy resin. As indicated by the arrows, some of the MSGFs are embedded in the matrix at different angles to the cross-section, and some of them leave tracks after debonding with the matrix. As surrounded by the circles, some MSGF perpendicular to the fracture surface show white bulges or black holes left after pulling out of fibers. At the crack initiation stage, the bridging effect of MSGF hinders crack propagation with debonding, peeling and pulling out, and the cracks are deflected around the fibers. Unlike that of pure EP, the crack propagation path of the composite is complex and irregular with more obvious plastic deformation of the matrix, deep cracks and more rough fracture surface. The crack propagation does not reach stable fracture zone at that short distance of pure EP. In the fracture zone (shown in figure 6(c)), obvious crack deflection and EP plastic deformation can still be observed around MSGF, which can absorb more fracture energy and improve the fracture toughness of the composite. These toughening mechanisms often occur in carbon nanotubes toughened EP composites [11]. With magnetic field orientation (figure 6(d), (e)), only white MSGF bulges and black holes left by MSGF pulling out as shown by the circles are observed on the fracture surface, which indicates that almost all MSGF are aligned in the direction perpendicular to the fracture surface under the magnetic field. The morphology of the fracture surface is similar to that of the composite without magnetic field orientation, presenting rough fracture surface, deep crack, prolonged crack growth zone and obvious EP plastic deformation around MSGF. Because of the small diameter, MSGF cannot induce crack deflection when they hinder the initiation and propagation of cracks. It is easy to find the difference between the both composites in the fracture zone (figure 6(c), (e)). Nevertheless, according to the fracture toughness data in figure 5, the fracture toughness of the composites with magnetic field orientation is significantly higher than that of the composite without magnetic field orientation, which implies that the pull-out behavior of MSGF can
absorb more fracture energy and contribute more to the improvement of fracture toughness than crack deflection, EP plastic deformation and debonding among these toughening mechanisms.

4. Conclusions
In this work, by ethanol solvothermal method, the magnetic $\gamma$-Fe$_2$O$_3$ particles can effectively be loaded on the short glass fibers. The magnetic short glass fibers (MSGF) can be well aligned in epoxy resin (EP) composites under weak magnetic field (0.12T). The method is simple in processing, environmentally friendly and low in cost. MSGF can effectively improve the fracture toughness of EP composites whether or not they are oriented by magnetic field. At the content of 3wt%, the magnetic field oriented MSGF/EP composites have the best properties. The $K_{IC}$ and $G_{IC}$ of MSGF/EP composites are 54.4% and 138.5% higher than that of pure epoxy resin, respectively. For the higher content of MSGF, further research is needed to more significantly enhance the fracture toughness of composites by improving the dispersion of MSGF. SEM analysis of fracture morphology shows that the toughening mechanisms of EP mainly include bridging effect of fibers, crack deflection, matrix plastic deformation, peeling off and pulling out of fibers. Among the mechanisms, pulling out of fiber plays a dominant role in toughening effect.

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