Composites Part A 108 (2018) 12–22

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

Micro-crack behavior of carbon fiber reinforced Fe_3O_4/graphene oxide modified epoxy composites for cryogenic application

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ARTICLE INFO

Keywords:
Epoxy
Carbon fiber
Graphene oxide
Cryogenic temperature

ABSTRACT

The epoxy nanocomposites with Fe_3O_4 modified graphene oxide (Fe_3O_4/GO) were used to influence the micro-cracks resistance of carbon fiber reinforced epoxy (CF/EP) laminate at 77 K. Fe_3O_4/GO with good paramagnetic properties were prepared by co-precipitation method and used to modify epoxy for cryogenic applications. Fe_3O_4/GO modified CF/EP laminates were also prepared through vacuum-assisted resin transfer molding (VARTM). The results show that the Fe_3O_4/GO can effectively improve the mechanical properties of epoxy (EP) matrix at 77 K and reduce the coefficient of thermal expansion (CTE) of EP matrix. It also can obviously improve the micro-cracks resistance of CF/EP composites at 77 K. Compared to neat EP, the CTE of Fe_3O_4/GO modified EP composite is decreased 51.6%. Compared to CF/EP composite, the micro-cracks density of Fe_3O_4/GO modified CF/EP composite at 77 K is decreased 60.0%.

1. Introduction

Carbon fiber reinforced epoxy (CF/EP) composite material with its high specific strength and modulus, anti fatigue and corrosion, easy designed and suitable for be prepared in large area is considered to be the most promising structural materials in cryogenic propellant tank for space shuttles [1]. When CF/EP composite is used for cryogenic liquid storage and suffered the process of low-temperature aging and the cycling from room temperature (RT) to cryogenic temperature (77 K), micro-cracks will be produced and grow in the epoxy (EP) matrix. It is due to the different performance of carbon fiber (CF) and EP matrix, especially thermal properties, such as coefficient of thermal expansion (CTE) of EP is about $65 \times 10^{-6}\,°C^{-1}$ and the CTE of CF is about $-12 \times 10^{-6}\,°C^{-1}$ [2]. This vast difference will introduce a high internal stress in the composites during the temperature cycle, leading to the formation and growth of micro-cracks in the epoxy matrix. Therefore, the resistance to micro-crack of the CF/EP composites is largely determined by the performance of epoxy matrix, which is closely related to the property of the filler dispersed in the resin except the molecular structure of the epoxy resin.

The two dimensional (2-D) one-atom-carbon thick graphene oxide (GO) shows excellent physical properties, such as high mechanical stiffness (130 GPa) [3], thermal conductivity (4.84×10^3 to 5.30×10^3 W/mK) [4], large specific surface area (2600 m^2/g) [5] and intrinsic carrier mobility (200,000 cm^2/V) [6], which allow GO serve as efficient nanofillers to enhance the mechanical and conductive properties of polymers including epoxy resin [7]. For instance, epoxy based composites with GO platelets by SiO_2 have showed a reduced tensile strength though an increased Young's modulus from 4.53GPa (neat epoxy) to 6.21 GPa and fracture toughness from 1.42 MPa·$m^{1/2}$ (neat epoxy) to 2.59 MPa $m^{1/2}$ at 77 K (with 1.0 wt% modified GO platelets) is observed [8]. The silanized GO (SGO) reinforced carbon fiber/epoxy composites have been fabricated for the interfacial shear strength (IFSS) from 40.3 MPa to 64.8 MPa and interlaminar shear strength (ILSS) from 70.35 MPa to 83.46 MPa in the composites with a loading of 0.5 wt% SGO [9].

Though GO decorated with metal or metal oxide particles have been studied due to their potential wide applications in microwave absorption, energy storage [10] and environmental remediation [11]. For instance, the microwave absorption values of Fe_3O_4 modified GO

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https://doi.org/10.1016/j.compositesa.2018.02.014
Received 5 December 2017; Received in revised form 4 February 2018; Accepted 8 February 2018
Available online 15 February 2018
1359-835X/

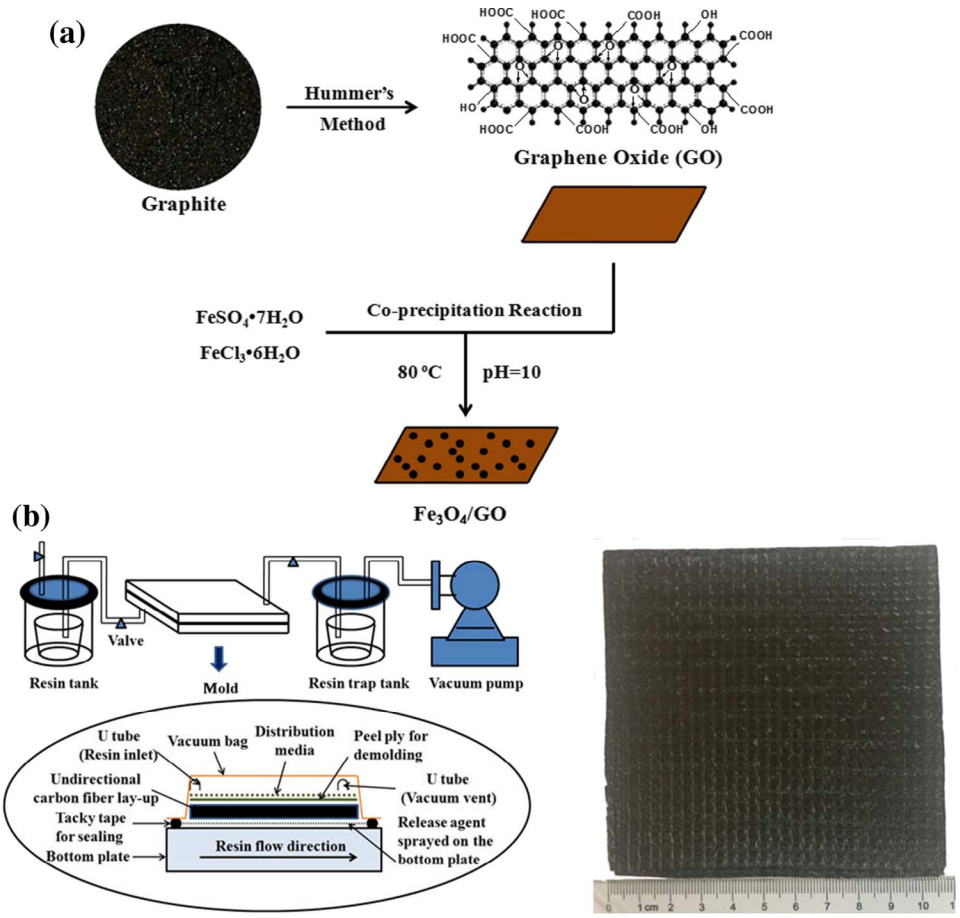

Fig. 1. (a) Scheme for preparation of Fe_3O_4/GO, (b) Scheme for preparation of Fe_3O_4/GO/CF/EP laminate (left) and photograph of Fe_3O_4/GO/CF/EP laminate (right) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

(Fe_3O_4/GO) composites less than -5 dB is in the range of 7.78–10.36 GHz [12]. Fe_3O_4/GO composites show an excellent electrocatalytic reduction toward H_2O_2 at a wide, linear range from 4×10^{-6} to 1×10^{-3} M ($R^2 = 0.994$) as examined by amperometry, and with a detection limit of 2×10^{-6} M [13]. These materials have potential promising applications including cloaking, superlens, wave filters, remote aerospace applications, and superconductors [14]. In this work, Fe_3O_4/GO and GO were introduced into the CF/EP composites. It is expected that Fe_3O_4/GO and GO not only enables the interfacial interactions between fillers and matrix stronger but also increases the micro-cracks resistance behavior of CF/EP composites at 77 K.

In this paper, CF/EP composites with two kinds of fillers, i.e., GO and Fe_3O_4/GO, were prepared at the same loading levels. The optimized formulation of diglycidyl ether of bisphenol-A (DGEBA)/polyoxypropylenediamine (Jeffamine D-230) with a low viscosity is selected as epoxy matrix. The tensile and impact properties of modified epoxy composites at 77 K were studied and compared with those at RT. The effect of GO and Fe_3O_4/GO fillers on the cryogenic toughening and micro-cracks resistance behavior of modified CF/EP laminates under cryogenic thermal cycling will be investigated.

2. Experimental

2.1. Materials

The epoxy YD-128 (DGEBA, Kukdo Chemical Ltd., Korea) with an epoxide equivalent weight (EEW) of 185–190 eq^{-1} was used for the present study. The curing agent was polyoxypropylenediamine (Jeffamine D-230) (New Seoul Chemical Ltd., Korea). The reagents used for the oxidation treatment were Potassium permanganate ($KMnO_4$, 99.0 wt%), hydrochloric acid (HCl, 95.0 wt%), Hydrogen peroxide solution (H_2O_2, 30.0 wt%) and sulfuric acid (H_2SO_4, 95.0 wt%). Expanded graphite, ammonia solution (25.0 wt%), ethanol (99.5 wt%), iron chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99.0 wt%), iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99.0 wt%) and monodispersed magnetite microspheres (Fe_3O_4, 99.0 wt%,) were purchased from Aladdin regent Co. Ltd, Shanghai, China. All the reagents were used as received and solutions were prepared using de-ionized (DI) water. Unidirectional carbon fiber (CARBONEX CF-730, Hankuk Carbon Ltd., Korea) was used as reinforcement for the composites.

2.2. Preparation of GO and Fe_3O_4/GO composite

2.2.1. Graphene oxide (GO)

The modified Hummers method was used to oxidize expanded graphite [15]. About 3 g of graphite was mixed with 150 mL of H_2SO_4 in a 500 mL three-neck flask and stirred in an ice-water bath. Potassium permanganate (15 g) was added to the suspension slowly and stirred for 2 h at 0–5 °C. About 150 mL of deionized (DI) water was slowly added under vigorous stirring followed by the addition of H_2O_2 drop by drop to the mixture until the color changed to bright yellow. For purification, the mixture was washed by DI-water and centrifuged with 5 wt% aqueous hydrochloric acid solution to remove the metal ions. The washing procedure was repeated with DI water until the solution was neutral. After filtration and freeze drying, solid GO was obtained.

2.2.2. Fe_3O_4 modified GO (Fe_3O_4/GO)

Fe_3O_4/GO was synthesized by a modified co-precipitation reaction