Composites: Part A 90 (2016) 433–440

Contents lists available at ScienceDirect

Composites: Part A

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

Effect of a multiscale reinforcement by carbon fiber surface treatment with graphene oxide/carbon nanotubes on the mechanical properties of reinforced carbon/carbon composites

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ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form 12 August 2016
Accepted 13 August 2016
Available online 13 August 2016

Keywords:
A. Carbon fiber
B. Mechanical properties
Interface/interphase
E. Surface treatments

ABSTRACT

An effective carbon fiber/graphene oxide/carbon nanotubes (CF-GO-CNTs) multiscale reinforcement was prepared by co-grafting carbon nanotubes (CNTs) and graphene oxide (GO) onto the carbon fiber surface. The effects of surface modification on the properties of carbon fiber (CF) and the resulting composites was investigated systematically. The GO and CNTs were chemically grafted on the carbon fiber surface as a uniform coating, which could significantly increase the polar functional groups and surface energy of carbon fiber. In addition, the GO and CNTs co-grafted on the carbon fiber surface could improve interlaminar shear strength of the resulting composites by 48.12% and the interfacial shear strength of the resulting composites by 83.39%. The presence of GO and CNTs could significantly enhance both the area and wettability of fiber surface, leading to great increase in the mechanical properties of GO/CNTs/carbon fiber reinforced composites.

1. Introduction

Carbon fiber (CF), as an ideal reinforcement, has been widely used in advanced structural materials due to its exceptional mechanical properties and excellent thermal properties. There has been an increasing demand of carbon fiber composites in sports, automotive and aerospace industries [1–3]. However, the smooth and chemically inert surface of inorganic carbon fiber may lead to poor matrix compatibility and weak adhesion of fiber-matrix, which in turn negatively affects the mechanical properties of carbon fiber reinforced composites. To overcome the limitations imposed by impediments of the smooth and inert fiber surface, many researches concerning surface modification of carbon fiber have been reported [4,5]. Recently, the introduction of carbon nanotubes (CNTs) in the composites has been developed as an effective reinforcement for enhancement of composite properties [6,7]. Therefore, hybridizing carbon fiber with carbon nanotubes arises as a novel method to produce high mechanical performance of composites, because CNTs could increase carbon fiber surface area and mechanical interlocking between fiber and epoxy [8–10]. Although directly grafting CNTs onto fiber surface is an effective method to improve the properties of fiber-matrix interface, the lack of chemical bonding limits the further increase of the interfacial properties of the resulting composites [11,12].

Graphene oxide (GO) with excellent mechanical properties could uniformly disperse and firmly adsorb on the carbon fiber surface to develop a new hierarchical reinforcement [13,14]. As a novel carbon materials, graphene oxide (GO) possesses a two-dimension structure and exhibits extraordinary mechanical, thermal [15,16] properties. Specially, GO with various oxygen functional groups [17] can be prepared in large quantities at a relatively low cost [18]. GO grafted on the fiber surface, which can offer both intralaminar and interlaminar reinforcement, could greatly improve the mechanical properties of carbon fiber reinforced composites [19]. In a previous study, our group has reported that GO directly grafted on the carbon fiber surface could effectively increase the interfacial adhesion of the resulting composites [14].

In the work reported here, we further modified GO/carbon fiber with CNTs by amidation reaction between amine groups of CNTs and acyl chloride groups of GO on the carbon fiber surface. This new reinforcement was aimed to investigate the effects of the newly introduced component on the interfacial properties of

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http://dx.doi.org/10.1016/j.compositesa.2016.08.012
1359-835X/

carbon fiber-epoxy matrix. The surface chemical composition, wettability and morphologies of carbon fiber were characterized by X-ray photoelectron spectroscopy (XPS), dynamic contact angle analysis (DCA), scanning electron microscopy (SEM), respectively. Mechanical properties of the composites were investigated by interlaminar shear strength (ILSS) and interfacial shear strength (IFSS).

2. Experiments

2.1. Materials

Thionyl chloride ($SOCl_2$), ethylenediamine (EDA), dimethylformamide (DMF) were all purchased from Sigma-Aldrich. The matrix system used in this work were WAR618 epoxy resin (molecular weight 350–400, molecule structure is shown in Fig. 1) and hardener H-256 (3,3′-diethyl-4,4′-diaminodiphenyl methane, DEDDM). The commercial carbon fiber (JT-400A-3K, average diameter 6.8 μm, the linear density 0.175 ± 6 g/m, the density 1.76 g/cm^3) was procured from Jilin Shen Zhou Carbon Fiber Co., LTD and the multi-walled CNTs (purity > 95%, diameter 10–30 nm) were provided by Shenzhen Nanotech Port Co., Ltd. All chemicals were used as received unless stated otherwise.

2.2. Experimental procedure

The CF-GO-CNTs multiscale reinforcement was prepared by several steps of chemical reactions. Graphene oxide (GO) was prepared by the acid oxidation of graphite powders using the Hummers method [20] and was functionalized with thionyl chloride. The CNTs were functionalized with EDA. These methods of functionalized GO and CNTs are similar to the procedure described in the literature [21]. The carbon fiber was extracted with supercritical ace-tone/water at 633 K for 20 min, followed being oxidized by concentrated nitric acid at 60 °C for 3 h. After that, the carbon fiber was put into the mixture solution of 100 mL $SOCl_2$ and 5 mL DMF at 78 °C for 48 h and was then reacted with 100 mL ethylenediamine (EDA) at 80 °C for 24 h, generating the ethylenediamine (EDA) functionalized carbon fiber ($CF\text{-}NH_2$).

The carbon fiber/graphene oxide/carbon nanotubes (CF-GO-CNTs) multiscale reinforcement was achieved by two steps. $CF\text{-}NH_2$ was reacted with 0.2 g thionyl chloride functionalized GO in DMF at 50 °C for 48 h in the first place. After being washed with DMF, the carbon fiber grafted with GO (CF-GO) was reacted with 0.2 g CNTs in DMF at 50 °C for 48 h, yielding the carbon fiber co-grafted with GO and CNTs (CF-GO-CNTs). The formation procedure of hybrid reinforcement was illustrated in Fig. 2.

2.3. Manufacture of hybrid composites

The multiscale carbon fibers grafted with GO and CNTs were used as the base material to synthesize the CNTs/GO/CF/epoxy resin hybrid composites by compression molding method. The epoxy resin and hardener H-256 (weight ratio: 100:32) were mixed and stirred for 5 min. The carbon fiber composites were placed with a controlled environment (363 K for 1 h under 5 MPa, 393 K for 2 h under 10 MPa and 423 K for 3 h under 10 MPa). Composites laminates were obtained with final fiber volume fraction in the range from 60% to 65 %. Composite specimens were adopted for test specimens and thickness of specimens were 6.5 and 2 mm, respectively.

2.4. Characterizations

2.4.1. Scanning electron microscopy

Scanning electron microscopy (SEM) (VE-8800, Keyence, Japan) was operated at an operating voltage of 20 kV to characterize the surface morphology of carbon fiber as well as the fracture surface of carbon fiber reinforced composites. The gold sputtering was used to improve the conductivity

2.4.2. Surface area measurements

The specific surface areas of desized carbon fiber, GO/CF hybrid fiber and CNTs/GO/CF hybrid fiber were calculated by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption at −196 °C. An automated adsorption apparatus (NOVA-2000) was employed for the measurement.

2.4.3. Fourier transform infrared spectra

Fourier transform infrared spectra (FTIR) was performed to evaluate the chemical structures on a Perkin Elmer spectrometer (Spectrum one, USA). The samples were characterized with a resolution of 2 cm^{-1} and 32 scans.

2.4.4. Raman spectra

Raman spectra were recorded on a SPEX 1403 (SPEX, USA) microscopic confocal Raman spectrometer by employing a laser of 514 nm as incident light. The time for each measurement was 30 s and the spectra were recorded by accumulating the measurement for five times.

2.4.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, VG, UK) was performed to study the surface element of carbon fibers using a monochromated Al Ka source (1486.6 eV) at a base pressure of 2×10^{-9} mbar. The high resolution spectra was acquired with a pass energy of 20 eV and an energy step size of 0.05 eV.

2.4.6. Thermogravimetric analysis

The specimens were investigated with simultaneous thermal analyzer (TGA/1600LF, Switzerland). Samples of 10–15 mg were sealed in aluminium pans and heated from 100 to 550 °C at 10 °C/min with the flow rate of 50 mL/min nitrogen atmosphere.

2.4.7. Dynamic contact angle test

Dynamic contact angle tests were measured using a dynamic contact angle meter (DCAT21, Data-physics Instruments, Germany) at an immersion speed of 0.05 mm/s. Deionized water ($\gamma^d = 21.8$ mN m^{-1}, $\gamma = 72.8$ mN m^{-1}) and diiodomethane ($\gamma^d = 50.8$ mN m^{-1}, $\gamma = 50.8$ mN m^{-1}) were used as the test liquids [22]. The surface free energy, and its dispersive and polar components can be derived as the following equations:

$$\gamma_1(1+\cos\theta) = \frac{4\gamma_1^d\cdot\gamma_s^d}{\gamma_1^d+\gamma_s^d} + \frac{4\gamma_1^p\cdot\gamma_s^p}{\gamma_1^p+\gamma_s^p}$$

$$\gamma_{Total} = \gamma_s^d + \gamma_s^p$$

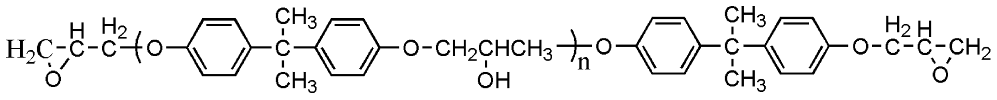

Fig. 1. The molecule structure of WSR618 epoxy resin.