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Silver nanoparticles/graphene oxide decorated carbon fiber synergistic reinforcement in epoxy-based composites

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ABSTRACT

A novel two-layer reinforced carbon fiber (CF), i.e., Ag nanoparticles (Ag NPs)/graphene oxide (GO) reinforced CF (named as CF/Ag/GO) was prepared by an electrochemical deposition and electrophoretic deposition (EPD) consequently. The modified fiber showed an increased interfacial shear strength (IFSS) and tensile strength. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectrometer, atomic force microscopic (AFM) and dynamic contact angle analysis (DCA) were carried out to investigate CF reinforced composites. And test results demonstrated that the presence of Ag NPs and GO sheets increased the surface roughness and surface energy of CFs significantly. IFSS of CF/epoxy and the tensile strength of CFs were increased by 86.1% and 36.8%, respectively. Ag NPs filled in the cracks in CF effectively to enhance the tensile strength, while GO sheets improved the wettability of resin on CFs and formed mechanical interlocking between CFs and epoxy resin. These Ag NPs and GO sheets worked together in a ferocious synergy on the interface of CF and epoxy to cause the enhanced mechanical properties.

1. Introduction

In recent decades, carbon fibers (CFs), which worked as an ideal reinforcing phase in polymer composites, have attracted tremendous attentions due to their low weight, high stiffness, excellent tensile strength and high thermal stability [1–3]. However, certain drawbacks of CFs/polymer composites, which are the poor wettability and weak adhesion between CF and matrix, limit their wide applications [4,5]. And weak interfacial strength leads to deteriorating performance of composite materials. Therefore, enhancing the interfacial adhesive properties between CF and matrix such as epoxy via surface modification with various nanoscale materials is critical [6,7]. Graphene or graphene oxide (GO) has been demonstrated as an ideal candidate for selective reinforcement of fiber-matrix interface regions or hydrogels [8,9] owing to its outstanding thermal, electrical and mechanical performance [10–13]. The combination of CFs and graphene would help the stress transfers from weak matrix to strong fibers [14]. For example, the mechanical properties of graphene or GO reinforced CF/epoxy composites are enhanced dramatically [15]. However, the improvement of fiber tensile strength is relatively disappointing, for example, −9.8% in PBO fibers/epoxy composites [16], 7.9% in CF/

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epoxy composites [17] and 12.4% in CF/polyethersulfone composites [15].

Metal or metallic oxide nanoparticles were usually used to reinforce epoxy composites [18,19]. Metal nanoparticles have been also used to functionalize CFs, which exhibited greatly enhanced tensile strength [20], it was speculated that the metal nanoparticles could fill in the surface cracks of fibers and increase the radius of the crack tip to avoid the stress concentration. Among metal nanoparticles, Ag nanoparticles (Ag NPs) are popular due to their high electrical and thermal conductivities [21,22]. Besides, electrodeposition method with many advantages, for example, good uniformity, high efficiency, high yield, thickness controllable, binder-free and easy to scale up can be used to deposit metal, phosphors or catalysis coatings from a stable solution [23]. Analogously, electrophoretic deposition (EPD) is also a versatile technique that can be used to deposit any powdered solid (from micro- to nano-particles) from a stable suspension. Now EPD has been developed to deposit nanotube, graphene and graphene-based materials for field emitters or energy storage applications. However, to combine both nanoparticles and GO onto CFs has not been reported.

In this paper, we presented new Ag NPs and GO modified CF reinforcement to strengthen the mechanical property of CF/epoxy composites. Efficient electrophoretic deposition (EPD) and electrodeposition were carried out to deposit Ag NPs and GO onto the surface of CF layer by layer, respectively. Ag NPs and GO sheets were able to fill in the surface cracks on fibers and increase the wettability between matrix and fiber, respectively. Epoxy matrix was selected to evaluate the performance of CF reinforced composites due to its widespread use as engineering materials. Mechanical properties and surface properties of CFs with and without surface treatments were compared. It has been found that after modification, the novel two-layer reinforced CF was able to enhance IFSS of CF/epoxy, as well as CF tensile strength. Besides, this easy and efficient modification method could be helpful to industrial application of high-performance CF reinforcements.

2. Materials and methods

2.1. Materials

CFs (T700SC) was provided by Toray (Japan). GO was produced by oxidation of scaly graphite through modified Hummer's method [24,25]. Silver nitrate ($AgNO_3$) and poly (vinylpyrrolidone) (PVP Mn = 30,000) were supplied by Sigma-Aldrich. Hydrochloric acid (36–38%), concentrated sulfuric acid (95–98%), concentrated nitric acid (68%), isopropyl alcohol, potassium permanganate ($KMnO_4$) and magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai).

2.2. Experimental procedures

2.2.1. Electrodeposition, EPD and preparation of modified CFs/epoxy microdroplets

As-received CFs were firstly desized in refluxed acetone for 48 h, marked as untreated CF. Then, Ag NPs were prepared to fill in the surface cracks on fibers and improve the tensile strength of CF by electrodeposition. Briefly, an electrophoresis apparatus was connected with conductive substrates, the untreated CF bundle used as cathode, and a stainless steel tubing served as anode. $AgNO_3$ and PVP were used as support electrolyte. The concentration of $AgNO_3$ was 6 mmol L^{-1}, and the mole ratio of PVP to $AgNO_3$ in the electrolyte was 3:1. Electrodeposition was performed with the applied voltage (E) of 30 V, and the parallel arrangement with spacing (d) of 1 cm. After varying the deposition time of 10 s, 30 s, 60 s and 90 s, the Ag-loaded CFs were cleaned with excess water, and let it in the air for 24 h, marked as CF/Ag-10, CF/Ag-30, CF/Ag-60 and CF/Ag-90, respectively. Subsequently, GO was deposited on the surface of CF/Ag-30 by EPD process. These GO sheets could increase the specific surface area of CF and stick into the matrix to enhance the mechanical interlocking. Briefly, EPD was performed within 200 mL electrophoretic ink, which was a mixture of GO (0.1 mg/mL) and $Mg(NO_3)_2{\cdot}6H_2O$ (0.1 mg/mL render the graphene sheets positively charged) ultrasonic-dispersed in isopropyl alcohol. After that, CF/Ag-30 was used as cathode, and stainless steel tubing was served as anode. EPD performed in condition of d = 1 cm, E = 160 V for 30 s, 60 s or 120 s, respectively. Then all the modified CFs were cleaned with excess water and isopropyl alcohol, and let them in air for 24 h. The resulted modified CFs are marked as CF/Ag/GO-30, CF/Ag/GO-60 and CF/Ag/GO-90, respectively. The scheme of preparation of CF/Ag/GO was shown in Fig. 1.

Resin microdroplets were mixed by epoxy resin and the hardener, which contains the WSR618 and methyl tetrahyelrophthalic anhydride (weight ratio 100:32), and then the mixture was applied on a single CF to form resin microdroplet. The curing process took place for 2 h at 90 °C, 2 h at 120 °C and 4 h at 150 °C. The prepared specimens were used to evaluate interfacial properties.

2.2.2. Characterizations of CFs

IFSS of CF and epoxy was assessed by micro-bond test via the interfacial evaluation equipment (FA620, Japan). The test was carried out by a moving trestle together with a single fiber at a displacement rate of 0.05 μm/s. Then the prepared specimens were tested and the maximum loads during the test were noted down. The IFSS was counted using Equation (1) [16].

$$IFSS = \frac{F}{\pi d l} \tag{1}$$

where F is the recorded maximum load, d is the diameter of CF, and l is the effective length of CF that embedded in the matrix.

SEM measurements of GO and modified CFs were performance (200FEG, Quanta FEI Inc. USA) used to access, by operating at 20 kV. Gold sputtering was applied before SEM observation to improve the conductivity for better imaging. TEM (Hitachi H-7650) was carried out to investigate the microstructures of GO and CF/Ag/GO, by operating at 200 kV accelerating voltage. AFM was carried out to examine the thickness of GO and the surface roughness (Ra) of different CFs, using NT-MDT Solver-P47H in the tapping mode of operation. The chemical compositions of CFs were analyzed quantitatively by XPS, using ESCALAB 220i-XLVG instrument at a monochromatic Al Kα source (energy 1486.6 eV). The chemical groups on CFs surface were measured by FTIR spectrum (Nicolet, Avatar360, USA) with the wavenumber range of 400–3600 cm^{-1}. Raman spectra were collected by Renishaw 2000 Raman spectrometer.

Monofilament tensile test was performed based on the ASTM

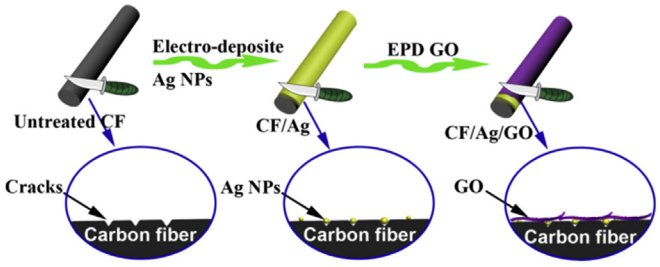

Fig. 1. Schematic diagram of the procedure for the fabrication of CF/Ag/GO.