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Modifying glass fibers with graphene oxide: Towards high-performance polymer composites

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ABSTRACT

Graphene oxide (GO) sheets were covalently grafted onto glass fibers (GFs) to improve the interfacial properties of GFs/polymer composites. It was confirmed that GO sheets were chemically grafted onto GFs via amido bond. The surface configuration of GFs changed by GO sheets could enhance strength and toughness of the interfacial region between GFs and polymer matrix. This strategy has the potential to be applied in high performance polymer matrix composites.

1. Introduction

Fibers reinforced polymer (FRP) composites are extremely important in industries and have attracted tremendous attention [1–3]. Glass fibers (GFs) have stimulated tremendous interest as reinforcement for polymer matrix due to its very low cost, high mechanical property, good heat resistance, etc. For GFs/polymer composites, the interface between GFs and polymer plays an important role in controlling some of the mechanical properties. In order to obtain high-performance FRP composites, high interfacial strength is the key issue [4]. However, the interfacial adhesion between GFs and polymer tends to be weak due to poor wettability and adsorption. In this paper, we propose a new way to enhance the interfacial adhesion between GFs and polymer.

Graphene (G) and graphene oxide (GO) have attracted enormous attention in recent years due to their remarkable properties and large specific surface area [5–8]. As carbon materials, G and GO have demonstrated higher performance and lower production cost than carbon nanotube [9]. GO sheets could be easily acquired from natural graphite flakes by strong oxidation and subsequent exfoliation [10]. The as obtained GO sheets bear various oxygen-containing groups, mainly epoxides and hydroxyls on their basal planes and carboxyls on the edges, which can facilitate the dispersion of GO in water [11,12]. In addition, GO sheets show a wrinkled structure and each GO sheet can be regarded as a single, ''soft'', two-dimensional macromolecule [13]. GO surface is usually negatively charged due to the ionization of carboxyl functional groups. Thus, it can be co-assembled with some positively charged particles such as silica particles and others via mutual electrostatic interaction [14]. This strategy has been widely applied in various fields [15–19], including the field of polymer composites [20–22]. Meanwhile, GO with carboxyl groups can be fixed to the surface of particles with amino groups by amidation reaction. Liu et al. [23] developed new solid-phase extraction (SPE) adsorbents by covalently binding G and GO sheets to silica. Whether can it be extended? Can this method be used to fix GO onto GFs surface to realize the improvement of interface bonding between GFs and polymer matrix? GO sheets may adhere to GFs surface more firmly due to the covalent bond connection which makes it more efficient for the modification of GFs.

In this work, a facile method to enhance the interfacial bonding between GFs and polymer has been developed by covalently grafting GO sheets on GFs. Firstly, GO was synthesized by a modified Hummers method [24,25]. Next, GFs surface was modified by silane coupling agent with amino group. Finally, GO was covalently grafted onto GFs by amidation reaction between the carboxy groups of GO and the amino groups of amino-terminated GFs. The overall procedure is shown in Fig. 1.

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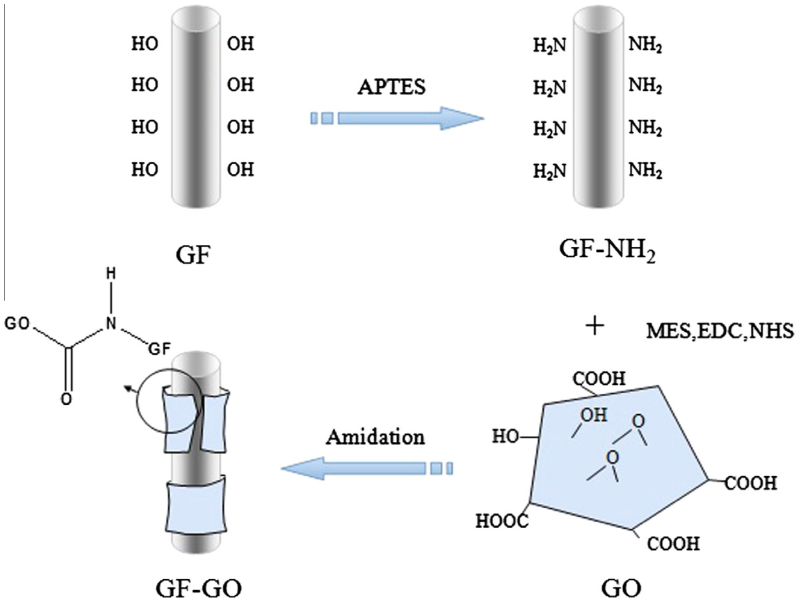

Fig. 1. Chemical routes to the synthesis of GO-g-GF.

2. Experimental section

2.1. Materials

Graphite powder (8000 meshes, 99.95%) was purchased from Aladdin Industrial Corporation. Concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-Hydroxysulfosuccinimide (NHS), 2-(N-morpholino)ethanesulfonic acid (MES) and ethanol were of analytical grade and purchased from Sinopharm Chemical Reagent (Shanghai, China). GFs and 3-Triethoxysilylpropylamine (APTES) were kindly provided by Taishan Glass fiber INC.

2.2. Preparation of GO

GO was prepared by the modified Hummers method [24,25]. Exfoliation of GO was realized by sonication for 1 h in an aqueous solvent. The non-exfoliated GO sheets were removed by centrifuge (4000 rpm, 10 min). A well dispersed GO colloid solution was obtained and used to immobilize onto GFs surface in the subsequent process.

2.3. Preparation of GO grafted GFs(GO-g-GF)

Prior to assembly, the long GFs were thoroughly washed with distilled water and dried under vacuum. Then GFs were surface treated with 4 wt% APTES. In a typical process, APTES (2 g) was added into a ethanol–water solution with pH 5–6 by drop. The solution was stirred for 3 h for the hydrolysis of APTES. Next, GFs (50 g) were immersed into it. The grafting reaction of APTES on GFs surface was realized by sonication for 50 min at 60 °C. Then, the APTES modified GFs(NH_2-GF) was taken out from the mixture, washed with ethanol and deionized water for several times, dried under vacuum.

The covalent immobilization of GO sheets onto GFs surface involves the formation of NHS ester with the carboxylate-terminated GO using the water-soluble EDC. Amino groups of APTES remaining on the GFs surface displace the terminal NHS groups, resulting in covalent immobilization of GO and GFs. A certain amount of GO solution was mixed with 0.1 M of MES buffer solution. The pH of the solution was adjusted to 6.0 by 0.1 M sodium hydroxide (NaOH). EDC was added and NHS was joined after 10 min. Magnetic stirring 1–2 h was used to make it activated. NH_2-GF was immersed in the solution for 24 h to proceed the amidation reaction. Then it was collected and washed with water for three times to remove the unbound GO. The concentrations of GO solution varied from 1.0 to 2.0 mg/mL (1.0, 1.5 and 2.0 mg/mL). The samples were marked as GO-g-GF1.0, GO-g-GF1.5 and GO-g-GF2.0, respectively.

2.4. Characterizations

The morphology property of GO sheets was performed on an atomic force microscope (AFM) system (Veeco NsIV, USA) and a JEM 2010 transmission electron microscopy (TEM). The scanning electron microscopy (SEM) images of GF were obtained on a FEI QUANTA FEG 250 field emission SEM system. Fourier transform infrared (FTIR) measurements were conducted on a Nicolet 380 infrared spectrometer (Thermo electron corporation, United States). Vacuum bag molding technology was used in the preparation of GFs/epoxy resin composites. Interlaminar shear strength (ILSS) of composites was measured by the three-point short-beam shear test according to ASTM D-2344 at WDW-30 type universal testing machine (Shanghai Shenli Testing Machine Company, China).

3. Results and discussion

3.1. The morphology and structure of GO sheets

GO nanosheets were obtained through oxidation, simple sonication and centrifugal separation. In contrast to black hydrophobic graphite, GO nanosheets exhibit slight golden color, and form a homogeneous and stable dispersion in aqueous media (as shown in the digital photo of colloid suspension of GO (1 mg/mL), Fig. 2(a)). Through an oxidation process, hydrophilic groups (carboxyl, hydroxyl and epoxy groups) are introduced onto the edge sites and basal planes of GO, which make GO partially hydrophilic and guarantee the stable existence in aqueous medium [26]. TEM