



## Material properties

## Preparation and characterization of functionalized graphene oxide/carbon fiber/epoxy nanocomposites



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## ABSTRACT

Graphene oxide (GO) was functionalized using three different diamines, namely ethylenediamine (EDA), 4,4'-diaminodiphenyl sulfone (DDS) and *p*-phenylenediamine (PPD) to reinforce an epoxy adhesive, with the aim of improving the bonding strength of carbon fiber/epoxy composite. The chemical structure of the functionalized GO (FGO) nanosheets was characterized by elemental analysis, FT-IR and XRD. Hand lay-up, as a simple method, was applied for 3-ply composite fabrication. In the sample preparation, the fiber-to-resin ratio of 40:60 (w:w) and fiber orientations of 0°, 90°, and 0° were used. The GO and FGO nanoparticles were first dispersed in the epoxy resin, and then the GO and FGO reinforced epoxy (GO- or FGO-epoxy) were directly introduced into the carbon fiber layers to improve the mechanical properties. The GO and FGO contents varied in the range of 0.1–0.5 wt%. Results showed that the mechanical properties, in terms of tensile and flexural properties, were mainly dependent on the type of GO functionalization followed by the percentage of modified GO. As a result, both the tensile and flexural strengths are effectively enhanced by the FGOs addition. The tensile and flexural moduli are also increased by the FGO filling in the epoxy resin due to the excellent elastic modulus of FGO. The optimal FGO content for effectively improving the overall composite mechanical performance was found to be 0.3 wt%. Scanning electron microscopy (SEM) revealed that the failure mechanism of carbon fibers pulled out from the epoxy matrix contributed to the enhancement of the mechanical performance of the epoxy. These results show that diamine FGOs can strengthen the interfacial bonding between the carbon fibers and the epoxy adhesive.

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## 1. Introduction

Carbon fiber/epoxy (CF/EP) nanocomposites with their favorable strength-to-weight and stiffness-to-weight ratios are replacing traditional metallic materials in a wide range of applications, such as aeronautical and astronautical structures (e.g., aircraft, space shuttle and satellite) [1–3], and ground vehicles and sports utilities [4,5]. The mechanical properties of CF/EP nanocomposites critically depend on the fiber-matrix interfacial adhesion, fiber amount, aspect ratio, orientation with respect to loading direction, etc [6]. Among these, fiber-matrix interfacial adhesion is extremely important since CFs have chemical inertness and poor wettability with most of the polymeric matrices [7]. Good interfacial properties are essential to ensure the efficient load transfer from matrix to fillers, which help reduce stress concentrations and improve overall

mechanical properties [8]. Hence, it is necessary to improve the fiber-matrix adhesion to enhance mechanical properties.

Many methods have been developed for improving the CF-polymer matrix interfacial adhesion, including electrochemical, chemical, thermal, grafting, coating (sizing) and discharge plasma treatments, etc [9,10]. Graphene oxide (GO) as a potential multi-functional sizing agent can be uniformly dispersed and firmly adsorbed on the surface of CFs to prepare a new hierarchical reinforcement. The GO can be produced in large quantities at a relatively low cost and possesses excellent mechanical properties [7]. It has attracted a great deal of scientific interest because of its large surface area (2630 m<sup>2</sup>/g), high intrinsic mobility (200,000 cm<sup>2</sup>/Vs), high Young's modulus (~1.0 TPa), high thermal conductivity (~5000 W/mK), and high optical transmittance (~97.7%) [2,11]. The GO contains various oxygenated functional groups such as epoxide, hydroxyl and carbonyl groups. It is expected that GO coating on CFs will enhance the CF-matrix interfacial adhesion, and thus the applied load can be more effectively

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transferred from matrix to CFs to enhance composite mechanical properties [12]. However, functionalization of the GO nanosheets is usually required to improve their solubility in organic solvents or compatibility with polymers [13]. The GO is heavily oxygenated, bearing hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxyl groups located at the sheet edges [14,15]. The presence of these groups makes the functionalization of GO sheets much easier [5,16]. Among various functional groups, the amine group has a relatively high reactivity and can easily react with many chemicals [17]. Stankovich et al. [18] made the hydrophilic GO nanosheets hydrophobic using isocyanates as modifiers. Niyogi et al. [19] functionalized GO (FGO) with octadecylamine. The GO first reacted with  $\text{SOCl}_2$  and then the acylated GO was grafted with long-chain aliphatic amine.

Although substantial research has been conducted on improving the interface performance of CF composites, only a small portion has focused on the effect of interface performance on GO/CF/EP nanocomposite [2,20]. Therefore, the purpose of the current investigation was to: (1) prepare and characterize FGO using ethylenediamine (EDA), 4,4'-diaminodiphenyl sulfone (DDS), and *p*-phenylenediamine (PPD), (2) fabricate FGO/CF/EP nanocomposites, and (3) determine the role of different functionalization of GO on the mechanical and morphological properties of the nanocomposites.

## 2. Materials and methods

### 2.1. Materials

Graphite powder was used as the starting material for the preparation of graphite oxide (GO). The graphite had a particle size of  $\sim 70 \mu\text{m}$ , a purity of 99.9% and a density of  $2.25 \text{ g/cm}^3$ . Graphite powder, ethylenediamine ( $\text{C}_2\text{H}_4(\text{NH}_2)_2$ ), dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ) and thionyl chloride ( $\text{SOCl}_2$ ) were purchased from Loba Chemie Co. Ltd., India. All other chemicals, such as 4,4'-diaminodiphenyl sulfone ( $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ ), *p*-nitroaniline ( $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%) and nitric acid ( $\text{HNO}_3$ , 65%) were obtained from Merck Co. (Germany) and were of reagent grade.

Unidirectional CF used in the research was T700S (with density of  $1.8 \text{ g/cm}^3$ , average diameter of  $7 \mu\text{m}$ , and filament number of 12 k), which was purchased from Toray Industries, Inc (USA).

The matrix system used in this study was a cold-curing bisphenol-A-based epoxy resin Araldite LY 5052 (a novolac epoxy containing 1,4-butanediol diglycidylether) and an aromatic amine hardener HY 5052 (Huntsman Petrochemical Co., USA). Resin-to-hardener ratio of 100:38 by weight was used as recommended by the supplier. Physical properties of the used resin and its hardener are presented in Table 1.

Release agent QZ 13 was a product of Huntsman Petrochemical Co. (USA). It should be noted that the mold was coated with release agent to ensure that the carbon fibers did not adhere to the mold.

### 2.2. Synthesis of GO

The GO was prepared by oxidizing graphite powders based on a

modified Staudenmaier method [21]. In brief,  $\text{H}_2\text{SO}_4$  (18 mL) and  $\text{HNO}_3$  (9 mL) were slowly added into a 250-mL round bottom flask and cooled by immersion in an ice bath. Then, raw graphite (1 g) was added under vigorous stirring. After the graphite powder was well dispersed,  $\text{KClO}_3$  (11 g) was added slowly over a 2 h period to avoid sudden increase in temperature. The oxidation was allowed to proceed for 7 days at room temperature. On completion of the reaction, the mixture was poured into deionized water (100 mL) and filtered. The graphite oxide was re-dispersed and washed in a 5% solution of HCl. Then, the product was washed repeatedly with deionized water, until the pH of the filtrate reached 6. Subsequently, the GO was obtained by sonicating for 3 h in a mixture of water and ethanol (50 mL), and was finally dried in a vacuum desiccator (Fig. 1a).

### 2.3. Chemical functionalization of GO

#### 2.3.1. Functionalization with ethylenediamine (EDA)

The prepared GO (500 mg) was initially dispersed in thionyl chloride (30 mL). Then, the mixture was transferred to an oil bath ( $70^\circ\text{C}$ ) with reflux and stirring for 24 h. The resulting suspension was centrifuged and washed twice with dry tetrahydrofuran (THF) to remove the remaining thionyl chloride. Subsequently, the product (GO-Cl) was dried at  $50^\circ\text{C}$  for 3 h in a vacuum desiccator.

The resulting powder was dispersed in EDA (20 mL) and sonicated for 4 h at  $50^\circ\text{C}$ . Subsequently, the suspension was stirred for 24 h, and then centrifuged and washed thrice with THF to make sure that the residual of EDA was thoroughly removed. Finally, the product (EDA-FGO) was dried at  $50^\circ\text{C}$  for 6 h in a vacuum oven (Fig. 1b).

#### 2.3.2. Functionalization with 4,4'-diaminodiphenyl sulfone (DDS)

The GO-Cl powder was mixed with DDS (2 g) and dispersed in dry dimethylformamide (DMF, 20 mL). After that, the resultant mixture was sonicated for 4 h at  $40^\circ\text{C}$ . Then, the suspension was centrifuged and washed twice with DMF to remove the remaining trace of DDS. Subsequently, it was washed thrice with methanol and dried at  $50^\circ\text{C}$  overnight in vacuum oven. The final product was obtained by exfoliation of DDS-FGO via ultrasonic homogenizer (Misonix model 4000) at 400 W for 20 min (Fig. 1c).

#### 2.3.3. Functionalization with *p*-phenylenediamine (PPD)

The GO-Cl powder was mixed with *p*-nitroaniline (PNA) (1 g) and then dispersed in dry diethyl ether (60 mL). The mixture was sonicated in the ultrasonic bath for 3 h at  $35^\circ\text{C}$ . After sonication, this mixture was stirred for 24 h and then centrifuged and washed thrice with diethyl ether to ensure the residual of PNA was removed. To reduce nitro groups, PNA-FGO was mixed with stannous chloride ( $\text{SnCl}_2$ , 2 g) and then dispersed in DMF (30 mL) and refluxed for 18 h. Subsequently, the mixture was centrifuged and washed twice with DMF to remove all the remaining  $\text{SnCl}_2$ . Finally, the powder (PPD-FGO) was dried overnight in a vacuum oven (Fig. 1d).

### 2.4. Preparation of composites

Composites were prepared by a hand lay-up process, using a fiber-to-resin ratio of 40:60 (w:w). Composite panels ( $20 \times 20 \text{ cm}^2$ ) with thicknesses of  $0.40 \pm 0.02 \text{ mm}$  (each ply was approximately 0.13 mm thick) were fabricated. Before the hand lay-up process, the mold was coated with a release agent to ensure that the fibers would not adhere to the mold. Reinforcement fibers were cut and laid on the mold surface. The fiber orientation (angles) of  $0^\circ$ ,  $90^\circ$ , and  $0^\circ$  were used for all the experiments. The GO-EP and FGO-EP samples were prepared by mixing and ultrasonic dispersion for

**Table 1**  
Physical properties of the used resin and hardener.

| Properties                      | Araldite <sup>®</sup> LY 5052 | Aradur <sup>®</sup> 5052 | ISO     |
|---------------------------------|-------------------------------|--------------------------|---------|
| Appearance                      | Clear liquid                  | Clear liquid             | –       |
| Color (Gardner)                 | $\leq 2$                      | $\leq 4$                 | 4630    |
| Viscosity at $25^\circ\text{C}$ | 1000–1500 cps                 | 40–60 cps                | 12058-1 |
| Density at $25^\circ\text{C}$   | $1.17 \text{ g/cm}^3$         | $0.94 \text{ g/cm}^3$    | 1675    |
| Flash point                     | $\geq 140^\circ\text{C}$      | $\geq 110^\circ\text{C}$ | 2719    |

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