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Enhancement of interfacial adhesion in glass fiber/epoxy composites by electrophoretic deposition of graphene oxide on glass fibers

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ABSTRACT

Graphene oxide (GO) can increase the fiber/matrix interfacial shear strength (ISS) in glass fibers (GF) reinforced epoxy composites. To validate our argument, GO was synthesized and deposited over GF through electrophoretic deposition. Tuned voltage lead to different thickness of deposited GO steadily increasing with the electric field up to 10 V/cm. Coated fibers were aligned in a mold and an epoxy matrix was used to create a single-fiber microcomposite. Fragmentation test showed significantly higher ISS values for coated over bare fibers with increments up to a factor of about 2 and proportional to the amount of GO deposited on the GF. Tribological tests were performed at nanoscale by atomic force microscopy to measure the delamination strength between GO and GF. This latter resulted to be much higher than the ISS thus proving the efficiency of the new GO fiber coating method here proposed for producing advanced graphene based composites. The failure of the composite at the GO/matrix rather than at the GO/GF interface was also confirmed by scanning electron microscopy observation of the fracture surfaces of microcomposites.

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1. Introduction

The use of composite materials has grown in almost every engineering sector over the past 35 years. This increasing interest is mostly due to the unique properties of polymer composites in terms of lightness, rigidity, strength, easy formability, damage tolerance and corrosion resistance. Notably, there is an enormous potential for growth on the global market since both advanced and commodity composites still only own a relatively small market percentage in contrast to competing materials such as steel and aluminum [1]. Properties of composite materials are largely determined by the fiber/matrix interfacial adhesion [2,3]. In fact, an effective interface is necessary to guarantee the stress transfer from the matrix to the load-bearing fibers. The fiber-matrix interface transfers stresses via combination of mechanical interlocking, chemical bonding and physical adhesion [4]. However, due to limitations such as the lack of reactive functional groups on the fiber surface and poor wettability, effective transfer of load between fibers and matrix is a difficult task. Hence it has been of prime concern in the research areas of both academia and industries to enhance the interfacial adhesion between fiber and matrix.

Adhesion strength between fibers and matrices can be improved by various approaches. As described in a recent review paper by Karger-Kocsis et al. [5], the most common methods can be classified on the basis of the selected strategies distinguishing between i) interphase tailoring via sizing/coating on fibers, ii) creation of hierarchical fibers by nanostructures, iii) fiber surface modifications by polymer deposition and iv) potential effects of matrix modifications on the interphase formation. In particular, development of hierarchical micro/nano composites and its theoretical investigation [6] has been explored with great interest in recent years, specifically on the integration of nanoscale reinforcement on fibers [7,8]. Growth or deposition of carbon nanotubes (CNTs) on reinforcements for better interfacial adhesion has been reported in numerous articles. The use of chemical vapor deposition (CVD) [9],

grafting technique [10,11], electrophoretic deposition (EPD) [12] has been successfully implemented for the growth/deposition of nanomaterials on various fibers. Wang e*t al.* used multi-walled carbon nanotubes (MWCNTs) as an interphase between GF and vinyl ester composites. They reported improved bonding between the GF and the resin matrix [13]. Similarly Zhang et al. found an increase of 30% ISS by EPD to deposit MWCNTs on the surface of GF [14]. The electrical conductivity of fibers also improved due to deposited MWCNT. Exfoliated graphite nanoplatelets were deposited by Park et al. [15] using EPD onto single carbon fibers.

Graphene, being a superlative nanomaterial, has been considered to be a promising and exciting research area [16] because of its outstanding ideal properties including electron mobility at room temperature (250000 cm^2/V), thermal conductivity (5000 W m^{-1} K^{-1}) and mechanical properties, with a Young's modulus of 1 TPa and a record-breaking strength of 130 GPa [17–19]. Hu et al. have recently discussed in detail the use of graphene polymer nanocomposites for structural and functional applications [20]. The incorporation of graphene in polymer based composites has resulted in improved performance due to the interfacial interactions between polymers and graphene-based materials [21–23]. It has been reported that with polymers, the molecular interactions of graphene consist of either hydrophobic-hydrophobic interactions, weak van der Waal's forces and π-π stacking [24–28]. The use of oxidized form of graphene in polymer matrix gives more versatility of interactions due to the presence of oxygen-containing polar functionalities like carboxyl, carbonyl, epoxide and hydroxyl groups [29]. The elastic modulus of the polymer composites increases greatly due to the interfacial cross-linking [30] whereas electrostatic interactions are also important which result in nanocomposites much stronger and tougher [31].

This research group previously evaluated the role of graphene nanoplatelets in GF/epoxy matrix composite either by sonication in the epoxy matrix or dip coating the fibers in graphene dispersion [32]. An increase of elastic modulus, without compromising the impact strength and with an enhancement of the viscoelastic properties of composites, was reported.

This current work was aimed to assess the interfacial shear strength between an epoxy matrix and GFs coated with electrophoretically deposited graphene oxide. In addition, atomic force microscope (AFM) tribological studies were performed using diamond probe. Delamination of GO was performed with optimized normal force to calculate the shear strength of the GO/GF interface.

2. Experimental section

2.1. Materials and samples preparation

All chemicals were of analytical grade and used without further purification. Graphite powder, sodium nitrate, potassium permanganate, sulfuric acid and hydrogen peroxide were purchased from Sigma Aldrich while hydrochloric acid was from Codec Chemical Co. Ltd.. E-glass fibers (manufactured by PPG, trade name: 2001) having a diameter of 25.1 ± 0.4 μm were used as reinforcement. This GF had an epoxy-compatible sizing and it was used as received. A bicomponent epoxy resin (epoxy base EC 252 and hardener W 241) was provided by Elantas Italia S.r.l. The physical properties of epoxy resin cured at room temperature for 3 h followed by 15 h at 60 °C are summarized in Table 1.

Graphene oxide was synthesized using an approach similar to Hummer's method [33]. Briefly, 1 g graphite powder was added into 46 ml of H_2SO_4 cooled in an ice bath, followed by the addition of 1 g of $NaNO_3$ and stirred for 15 min. In the next step, 6 g of $KMnO_4$ were slowly added in order to avoid a spontaneous exothermic reaction. The mixture was then stirred for at least 24 h

Table 1
Physical properties of epoxy resin.

Physical property	Value
Glass transition temperature (T_g)	28 °C
Thermal degradation	340 °C
Yield stress (σ_y)	22.8 ± 2.4 MPa
Tensile strength (σ_T)	26.1 ± 1.1 MPa
Young's Modulus	795 ± 28 MPa

at 35 °C. Finally, excess of distilled water was added to the above mixture while the temperature was kept under 80 °C. In the end, 30% H_2O_2 was added to the mixture to stop the reaction. The resulting suspension was thoroughly washed using HCl solution and distilled water to remove Mn ions and acid respectively. The obtained brown solution was dried in a vacuum oven at 50 °C for at least 36 h.

A schematic description of the EPD process used to deposit GO nanosheets on GFs is depicted in Fig. 1. A stable suspension is the key for uniform deposition of graphene on GFs. Initially, graphite oxide powder was added in water with a concentration level of 1 mg/ml and the dispersion was subjected to bath-sonication for 1 h. Since GFs are non-conductive materials, two copper plates were used as electrodes in the EPD process. The GFs (fixed on a window frame) were placed near the anode since GO display negative potential due to functionalities attached during the oxidation reaction. Hence, during the EPD process GO migrated towards the anode and deposited on the GFs. EPD was carried out at various applied voltages up to 10 V/cm with a constant deposition time of 5 min and electrodes gap of 2 cm. A second EPD cycle was performed under the same conditions while reversing the GFs so that a homogenous deposition could be achieved on the fiber surface. The coated samples were dried in a vacuum oven at 40 °C for 12 h.

2.2. Testing methods

The morphology of GO nanosheets coatings were investigated by field emission scanning electron microscopy (FESEM) by a Zeiss SUPRA 40 microscope. Approximately 5 nm thick layer of platinum was deposited on samples prior to FESEM observations. Thickness (z-direction) and roughness of GO coatings on GF were measured by AFM with a NT-MDT solver P47h device operated in intermittent contact mode (tapping mode).

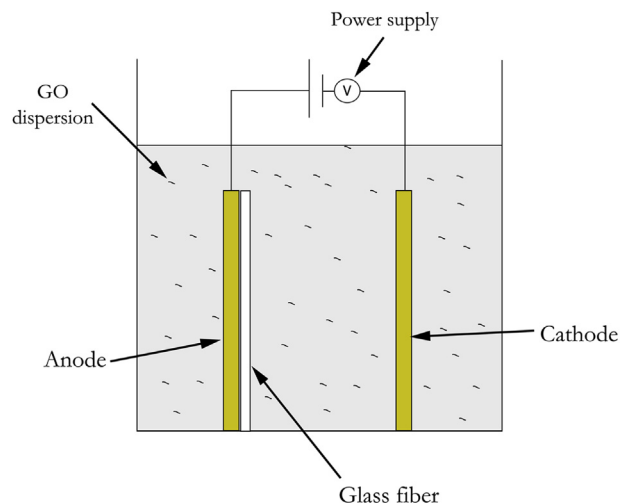The oxidation level of graphite was evaluated using X-ray

Fig. 1. Schematics of the electrophoretic deposition process of GO on GF.