Improving fiber/matrix interfacial strength through graphene and graphene-oxide nano platelets

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Abstract. Fiber/matrix interfacial shear strength (ISS) is a key factor determining the mechanical properties of structural composites. In this manuscript the positive effects of both graphene and graphene oxide in improving the ISS value of glass-fiber reinforced composites are experimentally demonstrated. Two strategies will be presented: i) uniform dispersion of the nanofillers in the polymer matrix or ii) selective deposition of the nanofillers at the fiber/matrix interface. Both thermoplastic (polypropylene) and thermosetting (epoxy) matrices are investigated and the effects of nanoparticles on the fiber/matrix interface are determined through micromechanical tests on single-fiber composites. Finally, the beneficial effects of the investigated nanofillers on both mechanical and functional (strain monitoring) properties of multiscale macrocomposites are experimentally proved for the cases of polypropylene-based composites reinforced with short glass fibers and on epoxy-based composites reinforced with continuous unidirectional glass fibers.

1. Introduction

The fiber/matrix interphase is a fundamental issue in composites due to its major role in determining the mechanisms of stress transfer from the matrix to the ‘load-bearing’ fibrous phase [1]. Several approaches have been proposed in the last 15 years to improve the fiber/matrix adhesion and to design the interphase of polymer composites [2]. The main strategies can be distinguished 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) interphase formation by matrix modifications [3]. In more recent years, a remarkable attention have been devoted to the usage of nanofillers for the interphase engineering of fiber-reinforced polymer composites [4]. In fact, nanofillers may improve the stress transfer ability at the fiber/matrix interface and allow the creation of (multi)functional interphase in polymer composites. Added functionalities provide sensing, self-healing and damping properties [5].
Depending on their morphology, nanofillers can be classified as i) isodimensional (3D, nanoparticles with a characteristic dimension less than 100 nm), ii) bi-dimensional (2D, nanofibres or nanotubes with a diameter less than 100 nm), iii) mono-dimensional (1D, lamellar nanoplatelets with a thickness less than 1 nm). Among 1D lamellar nanoplatelets a remarkable case is represented by graphene [6]. Graphene sheets, one-atom-thick two-dimensional layers of sp²-bonded carbon, manifest a range of unusual properties. Their thermal conductivity and mechanical stiffness may reach the remarkable in-plane values of graphite, i.e. 3000 Wm⁻¹K⁻¹ and 1060 GPa, respectively; their fracture strength should be comparable to that of carbon nanotubes for similar types of defects. Moreover, recent studies have shown that individual graphene sheets have extraordinary electronic transport properties [7].

One possible way to harness these properties for applications would be to incorporate graphene sheets in a polymer matrix. The manufacturing of such composites requires not only that graphene sheets are produced in a sufficient quantity, but that they also are homogeneously distributed in the polymer matrix [7-9]. The current available methods for the mechanical exfoliation of graphite are not suitable for large scale production. On the other hand, chemical oxidation of graphite into graphite oxide may offer an easy path to obtain graphene oxide (GO) in a large quantity that can be eventually reduced (chemically, electrochemically or thermally [10]) into graphene. The bulk production of GO and reduced graphene oxide (rGO) has created opportunities to explore this flat structure of carbon with polymer and nanoparticles in composites.

The aim of this work is to demonstrate how both graphene and graphene-oxide nanofillers can be used to improve the fiber/matrix adhesion of glass-fiber reinforced composites, as assessed by micromechanical (single-fiber fragmentation and microdebonding) tests. To prove this concept, two cases studies will be presented: i) uniform dispersion of graphene nanoplatelets in the matrix of polypropylene/glass fiber and epoxy/glass fiber composites or ii) selective deposition of graphene oxide and reduced graphene oxide at the fiber/matrix interface in epoxy/glass-fiber composites. Moreover, the positive role of both GO and rGO on both mechanical and functional (electrical conductivity) properties of (real) composites is investigated on polypropylene-based composites reinforced with short glass fibers composites and on epoxy-based composites reinforced with continuous glass fibers.

2. Experimental methods

2.1. Materials

2.1.1. Polypropylene and epoxy matrices. The polypropylene (PP) matrix used in this work was an isotactic homo-polypropylene matrix (code PPH-B-10-FB) produced by Polychim Industrie (Loon-Plage, France) and kindly provided by Lati Industria Termoplastici (Varese, Italy). This PP matrix was characterized by a melt flow index value of 6.9 g/10’ (190 °C, 2.16 Kg). The mechanical properties of neat PP compression moulded plaques are reported in Table 1. Fusabond_ P M-613-05 maleic anhydride modified polypropylene (PPgMA) was supplied by DuPont™ de Nemours (Geneva, Switzerland).

Two types of bicomponent epoxy resins were used: i) epoxy_1, consisting of an epoxy base EC 252 and a hardener W241 mixed at a weight ratio of 100:40, was provided by Elantas Italia S.r.l.; while ii) epoxy_2, consisting of a mixture of 635 thin epoxy and a 556 slow aminic hardener at a weight ratio of 200:100, was supplied by US Composites. Epoxy_1 resin was cured at room temperature for 3 h followed by 15 h at 60 °C, while epoxy_2 was cured at T = 80 °C for 1 h, followed by post-curing at T = 100 °C for 4 h. The physical properties of both epoxy resins are reported in Table 1.
2.1.2. Glass fibers. Depending on the polymer matrix involved, two types of glass fibers (GF) were used: i) PP-compatible RO99 P319 GF supplied by Saint-Gobain - Vetrotex (average diameter 15.3 ± 1.5 µm), named as GF_1; ii) epoxy-compatible XG 2089 GF supplied by PPG Industries (average diameter 16.0 ± 0.1 µm), named as GF_2. The scale and shape parameters of the Weibull strength distribution of GF are summarized in Table 1. Continuous glass fibers were chopped in short-glass fibers (average length of 6.50 ± 0.44 mm) by using a chopper gun CDA-08 provided by GlasCraft (Graco®, Bury, England).

| Material       | E (MPa)   | σ_b (MPa) | σ_0  (MPa) | m       | T_g (°C) | T_m (°C) |
|----------------|-----------|-----------|------------|---------|---------|---------|
| PP             | 1546 ± 24 | 37.1 ± 0.11 | -          | -       | 9.9     | 165.1   |
| Epoxy_1        | 795 ± 28  | 26.1 ± 1.1  | -          | -       | 28.0    | -       |
| Epoxy_2        | 2917 ± 37 | 59.6 ± 0.7  | -          | -       | 64.8    | -       |
| GF_1 - (PP-compatible) | - | 3206 | 6.2 | - | - |
| GF_2 - (Epoxy-compatible) | 3551 | 4.4 | - | - | - |

2.1.3. Graphene and graphene oxide. Exfoliated graphite nanoplatelets (GNP) type M-5 with an average diameter of 5 µm and thickness in the range of 10–20 nm were supplied by XG Sciences Inc. (East Lansing, USA). Details on the exfoliation process as well as on the morphology of GP can be found elsewhere [11].

Graphene oxide (GO) was synthesized using an approach derived from the Hummer’s method [12]. 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 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 hours to obtain GO powder.

2.1.4. Electrophoretic deposition of graphene oxide on glass fiber. A stable suspension is the key for uniform deposition of graphene on GF. Initially, graphite oxide powder was added in water at a concentration of 1 mg/ml and the dispersion was subjected to bath-sonication for 1 h. Since GF are non-conductive materials, two copper plates were used as electrodes in the EPD process. The GF (fixed on a window frame) were placed in contact with the anode. Since GO display negative potential due to functionalities attached during the oxidation reaction, during the EPD process GO migrated towards the anode and deposited on the GF. EPD was carried out at various applied voltages up to 10 V/cm with a constant deposition time of 5 min and a gap between the electrodes of 2 cm. A second EPD cycle was performed under the same conditions while reversing the window frame with GF, 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. A schematic of the EPD process used to deposit GO nanosheets on GF_2 is depicted in Figure 1 [13]. To chemically reduce the GO coating into rGO, the dried fibers were exposed to hydrazine hydrate vapors at 100°C for 24 hours, as reported elsewhere [14].
2.2. Processing techniques

2.2.1. Preparation of polypropylene-based composites. Square sheets (thickness of around 0.7 mm) of neat PP and PP-GNP nanocomposites were prepared by melt mixing in a Thermo Haake internal mixer (temperature = 190 °C, rotor speed = 50 rpm, time = 10 min) followed by compression moulding in a Carver laboratory press (temperature = 190 °C, pressure = 0.76 MPa, time = 10 min). Thin (70–80 µm) matrix films used for the preparation of the microcomposites were obtained by a further hot pressing stage (temperature = 200 °C, pressure = 3.4 MPa, time = 10 min).

Single-fiber microcomposite samples for the single fiber fragmentation tests were prepared by the following procedure [15]. About 10 fibers were aligned between two films of the selected PP matrix, sandwiched between two Mylar sheets (thickness of 0.5 mm) and two aluminum plates. The mould was placed in a vacuum oven at a temperature of 165 °C and at a pressure of about 10 kPa for about 20 min and then it was let to cool in air. The specimens were obtained by cutting strips containing one single fiber longitudinally aligned in the centerline. The dimensions of microcomposites were roughly 5 mm in width and 25 mm in length.

Single-fiber microcomposite samples for the microdebonding test were prepared by depositing a molten PP microdrop onto a single fiber filament supported on a paper tab [16]. In order to avoid the formation of asymmetric droplets with respect to the filament, a PP fiber was tied around the filament prior to heating [17]. PP microdrops were distributed symmetrically around the filament during melting in a hot-stage equipment (Instec HCS302, Boulder, CO, USA) while observing under an optical microscope Leica DMRM (Leica Microsystems Inc., Buffalo Grove, USA). Prior to testing, the microbond samples were examined using the optical microscope in order to determine the fiber diameter (d), embedded fiber length (L), and the maximum droplet diameter (D).

Composites reinforced with short GF_1 (up to 30 wt%) with and without GNP (up to 7 wt%) were made by melt mixing and injection moulding using a vertical, co-rotating, bench-top twin-screw microextruder (DSM Micro 15 cm³ Compounder) connected to a micro-injection moulding unit (DSM). The compound was mixed for 3 min, at 190 °C and 250 rpm. After the polymer compound had melted and homogenized, short GF_1 strands were directly added to the melt and further mixed for 2 min before injection moulding. The mould temperature was 80 °C and the injection pressure was 800 kPa. ASTM D638 dumbbell specimens were obtained.
2.2.2. Preparation of epoxy-based composites. GNP nanoplatelets were dispersed in isopropanol by sonication using a Misonix S-4000-010 for 1 h (30% amplitude, 8 W power) equipped with a probe of 12.5 mm diameter. Once the isopropanol was filtered away, the GNP powder was mixed with the epoxy_2 at 800 rpm and T = 60 °C for 40 min using a magnetic stirring plate.

The composites were made as follows: first the GNP were dispersed in isopropanol by sonication using the same procedure as mentioned above. GF_1 were then added to the solution and stirring was continued for 20 min followed by addition of the curing agent and subsequent stirring at 800 rpm for 30 min. The mixture was degassed in a vacuum oven and cured with the thermal cycle described in par. 2.1 for epoxy_2.

Microcomposite samples for microdebonding tests were prepared by depositing a microdrop of epoxy_2 (and corresponding nanocomposites) onto a single GF_1 filament supported on a paper tab. Epoxy microdrops were distributed symmetrically around the filament while observing under an optical microscope. The drops were cured with the thermal cycle described in par. 2.1 for epoxy_2. Prior to testing, the samples were examined using an optical microscope (Leica DMRM, Buffalo Grove, IL, USA) in order to determine the fiber diameter (d), embedded fiber length (L), and the maximum droplet diameter (D).

Single GO or rGO coated GF_2 were axially aligned in a silicon mould and epoxy_1 resin was poured into the mould to fabricate single fiber model composites for the single fiber fragmentation tests. The samples were cured according to the thermal cycle described in par. 2.1 for epoxy_1.

Unidirectional composites consisting of rGO coated glass fibers were created by a hand lay-up method. Briefly, strands of rGO coated GF_2 were aligned in a silicon mould in layers and each layer was infused with epoxy_1 resin and cured according to the thermal treatment described in par. 2.1 for epoxy_1. The processed composites manifested an approximate fiber volume fraction of 34% as evaluated on the basis of the measured (by displacement in water) density of the composites. On the cured specimens (100 mm × 13 mm × 2 mm), silver paste was applied on the cross section at a distance of 30 mm and thin aluminum sheet was also covered over the silver paste to avoid ohmic resistance of electrical contacts.

2.3. Testing methods

2.3.1. Single-fiber fragmentation test. Single fiber fragmentation tests (SFFT) tests were performed at room temperature by using a custom-made apparatus represented by a small tensile tester (Minimat, by Polymer Laboratories) placed under a polarized optical stereomicroscope (Wild M3Z by Leica). A schematic of the device is reported in Figure 2.
Samples of single-fiber microcomposites were 5 mm in width and 25 mm in length. A cross-head speed of 10 mm/min was applied up to a strain of 10%, necessary to assure the saturation of the fragmentation process. The mean fiber length at saturation, L_s, was measured by an image analysis software (Image J). The value of critical fiber length, L_C, was considered to be equal to 4/3 of L_s. ISS values were evaluated in accordance to the simplified micromechanical model proposed by Kelly and Tyson. The static equilibrium between the tensile force acting on a fiber and the shear force transferred through the fiber-matrix interface provides an average value of ISS according to the following equation:

\[ \text{ISS} = \frac{\sigma_{fb}(L_C) d}{2 L_C} \]  

(1)

where d is the fiber diameter and \( \sigma_{fb}(L_C) \) is the fiber tensile strength at the critical length. This latter value can be estimated by assuming a Weibull distribution for the fiber strength, i.e.:

\[ \sigma_{fb}(L_C) = \sigma_0 \left( \frac{L_C}{L_0} \right)^m \Gamma \left( 1 + \frac{1}{m} \right) \]

(2)

where \( \Gamma \) is the Gamma function, while \( \sigma_0 \) and m are the scale and shape parameters of the Weibull strength distribution (reported in Table 1) at the reference length L_0, respectively.

2.3.2. Microdebonding test. Microdebonding tests were conducted at a crosshead speed of 1 mm/min by an Instron 33R 4466 (Norwood, USA) tensile tester equipped with a 500 N load cell. During testing the paper tab attached to one end of the glass fiber was slowly pulled up, while the droplet was constrained by a shearing plate, which was fixed on a stationary support. A nominal interfacial shear strength (ISS) value was computed by using the following expression:
where $F_{\text{max}}$ is the maximum applied load recorded during the test, $d$ the fiber diameter, and $L$ the embedded fiber length. When a critical load is reached, the fiber-matrix interface fails and the load dramatically decreases.

2.3.3. Mechanical tests on composites. Tensile tests were performed according to ASTM D638 with an Instron model 33R 4466 tensile tester equipped with a 10 kN load cell at a crosshead speed of 5 mm/min. Each data point is an average of at least five measurements. Axial strain was recorded by using a resistance extensometer Instron model 2630-101 with a gauge length of 10 mm. The elastic modulus was measured as a secant value between longitudinal deformations of 0.05% and 0.25%.

2.3.4. Electrical resistivity and strain monitoring measurements. Two different resistivity measurement methods were employed depending on the electrical behaviour of the investigated materials. For specimens having resistivity levels exceeding $10^6 \, \Omega \text{cm}$, the electrical resistivity was measured using a Keithley 8009 resistivity test chamber coupled with a Keithley 6517A high-resistance meter. In the other case of more conductive samples, a 6-1/2-digit electrometer/high resistance system (Keithley model 6517A) was used and a 2-points electrical measurement was chosen as test configuration.

The possibility to monitor the strain in epoxy_1 composites containing rGO coated fibers by measuring the variation of electrical resistivity was investigated under various loading conditions such as tensile quasi-static (ramp) and dynamic (loading-unloading). Tests were performed by an Instron 5969 testing machine equipped with a 50 kN load cell simultaneously recording the applied strain (by an electrical extensometer Instron model 2620) and the variations of electrical resistivity by a electrometer/high resistance system (Keithley model 6517A) [18, 19].

2.3.5. Electron microscopy. Scanning electron microscopy (SEM) observations of the fracture surfaces of the composites were obtained by a Phenom G2 Pro (Phenom-World BV) microscope, at an acceleration voltage of 5 kV. A thin gold coating was applied onto the surface by plasma sputtering to minimize the charging effects.

A field emission scanning electron microscope (FESEM, Zeiss SUPRA 40) was also utilized to observe the morphology of coatings of GO and rGO nanosheets on glass fibers. Approximately 5 nm thick layer of platinum was deposited on samples prior to FESEM observations.

3. Results and Discussion

3.1. Effects of graphene homogeneously dispersed in the polymer matrix

3.1.1. Polypropylene-based composites. Both single-fiber fragmentation test [15] and microdebond tests [20] clearly evidenced how a homogeneous dispersion of GNP in the PP matrix improve the fiber-matrix adhesion. In fact, as evidenced in Figure 3, the ISS values increases with the GNP content in the polymer matrix. It is worthwhile to note that both micromechanical testing methods provided comparable results and that ISS value is improved by a factor of about 6 when 7 wt% of GNP is dispersed in the polymer matrix.
Figure 3. ISS values as determined by both the fragmentation and microdebonding tests on PP-based microcomposites containing GNP homogeneously dispersed in the matrix.

The observed effects of GNP on the interfacial adhesion are comparable to those induced by the addition of more common compatibilizers used to improve the fiber/matrix adhesion in PP/glass fiber composites, such as maleic anhydride modified polypropylene (PPgMA). In fact, as documented in Figure 4, the fiber/matrix adhesion levels reached by dispersing GNP in the PP matrix are quite similar to those observed when PPgMA is dispersed in the same polymer matrix.

Figure 4. ISS values as determined by the fragmentation test on PP-based microcomposites containing GNP nanoplatelets or PPgMA compatibilizer homogeneously dispersed in the matrix.
A possible reason for the positive role of both GNP and PPgMA on the fiber/matrix interfacial interaction can be explained by analyzing the energetics of the surfaces involved. In fact, as reported by Pedrazzoli and Pegoretti [15], wettability measurements in two different liquids (water and ethylene glycol) evidenced that the thermodynamic work of adhesion of the polymer matrix with respect to glass fiber, was improved by the presence of GNP or PPgMA. In particular, the polar component of the matrix surface tension ($\gamma_p$) increased considerably due to the addition of PPgMA, probably due to the presence of hydrophilic maleic anhydride groups with high surface energy. PP/GNP systems manifested a similar increase in $\gamma_p$ likely because of the possible presence of functional groups at the edges of GNP [21]. The dispersive component ($\gamma_d$) is slightly higher for all nanocomposites with respect to unfilled PP and increases proportionally to the content of PPgMA or GNP [15].

It is interesting to investigate how the positive effects of GNP on the fiber/matrix interfacial interactions can reflect on the properties of PP-composites reinforced with large quantities of short glass fibers. For this reason, PP-based injection moulded composites reinforced with various amounts of short GF_1 and GNP were mechanically tested in tension. First of all, as manifested in Figure 5 the appearance of the fracture surfaces of the composites with and without GNP appeared to be markedly different. SEM micrographs of fracture surfaces for PP composites reinforced with 10 wt% GF_1 are shown in Figure 5(a). The GF appeared to be quite homogeneously dispersed in the PP matrix but several fibers were pulled out from the matrix. Interfacial debonding resulted to be the dominant failure mechanism, indicating a rather low adhesion level. This observation is consistent with the outcome of the micromechanical tests. On the other hand, a different situation can be noticed for hybrid PP composites containing 5 wt% GNP and 10 wt% GF whose fracture surface is reported in Figure 5(b). In this case, very few debonded fibers can be observed, thus indicating a significantly better fiber–matrix adhesion. Furthermore, the improved fiber/matrix compatibility is documented by the presence of matrix fragments on the fiber surface after pull-out.

![Figure 5.](image)

Figure 5. SEM micrographs of fracture surfaces of a) PP composites reinforced with 10 wt% of short glass fibers, b) PP composites reinforced with 10 wt% of short glass fibers and 5 wt% of GNP.
The tensile modulus of composites with 10, 15 and 30 wt% of short GF\_1 and various amounts of GNP is plotted in the following Figure 6. The presence of GNP in the polymer matrix plays a beneficial effect of PP-based composites reinforced with 10 wt% of short GF\_1, whose elastic modulus continuously increased until an increment of about 38% was reached when 7 wt% of GNP were added. It is also worthwhile to note that the addition of 5 wt% of GNP in a PP-based composite reinforced with 15 wt% of short glass fibers generated a material whose elastic modulus was comparable to that of a composite loaded with 30 wt% of short GF\_1. The inserts of Figure 6 some additional properties measured on the investigated composites are reported, such as the tensile strength $\sigma_t$, the Izod impact strength and the density values [20]. The addition of GNP improved the strength values of composites reinforced with 10 and 15 wt% of short GF\_1 at levels higher than that of a composite reinforced with 30 wt% of short GF\_1 without GNP. Moreover, the Izod impact strength was preserved and the density decreased. In fact the density of the composites with 10 wt% of short GF\_1 and 7 wt% of GNP was about 12% lower than that of the composites reinforced with 30 wt% of short GF\_1 without GNP. Therefore, the presence of GNP lead to improved multiscale composites both in term of mechanical properties and lightness.

**Figure 6.** Tensile modulus of PP-based composites with various amounts of short glass fibers (i.e. 10 wt%, 20 wt% and 30 wt%) and GNP.

### 3.1.2. Epoxy-based composites.

The beneficial effect of the homogeneous dispersion of 5 wt% of GNP in epoxy\_2 was tested by microdebonding test on microcomposites in which small epoxy droplets are deposited on GF\_1 fibers (see Figure 7a), and the obtained results are reported in Figure 7b.
Similarly to what was observed for the PP-based composites, even for epoxy/glass composites a positive effect of GNP on the fiber/matrix interfacial shear strength was clearly detected. In fact, the dispersion of 5 wt% of GNP in the polymer matrix induced an increase of ISS values by about 40%.

Concurrently, the mechanical properties of the neat epoxy_1 resin resulted to be improved by the presence of GNP, as documented by the data reported in Figure 8. In fact, for a GF content of zero (corresponding to the neat epoxy), an improvement of tensile modulus (E, in Figure 8a), tensile strength ($\sigma_b$, in Figure 8b) was observed, while the Izod impact strength (in Figure 8c) was practically not affected. From the data reported in Figure 8, it can be observed that improvement of E, $\sigma_b$ and also of the impact strength are caused by the presence of GNP in epoxy_1 composites with various amounts of short glass fibers. In particular, it can be observed that a composite filled with 15 wt% of short GF_1 (PP-15%GF-5%GNP) exhibited tensile modulus and impact strength values similar to the corresponding values of a epoxy_1 composite containing 30 wt% of short GF_1 (PP-30%GF). At the same time, for the hybrid composite PP-15%GF-5%GNP an higher tensile strength value (70.4 MPa) with respect to the sample PP-30%GF (67.8 MPa) was measured. In the plots of Figure 8 the density of each composite tested is also reported. It is worthwhile to note that the hybrid composite PP-15%GF-5%GNP had a density lower by $\sim$ 7% compared to the density of 30 wt% of short GF_1/epoxy.
Figure 8. Effect of 5wt% of GNP on a) the tensile modulus, b) the tensile strength and c) the Izod impact strength of epoxy_1 composites reinforced with various amounts of short GF_1.

3.2. Effects of graphene-oxide and reduced graphene oxide deposited on the glass fibers

The electrophoretic deposition (EPD) process of graphene oxide on GF_2 fibers lead to a compact and quite homogeneous coating. The appearance of GF_2 fibers coated with both GO at two different deposition voltages can be observed in the SEM pictures reported in Figure 9. Figure 9c the appearance of fiber coated with reduced graphene oxide can also be observed.
b) Scanning electron micrographs of bare GF_2 fiber (a), and GF_2 fibers electrophoretically coated with GO deposited at 7.5 V/cm (b) or 10 V/cm (c) and subsequently reduced to rGO (d).

The thickness (weight) of the deposited coatings resulted to linearly increase with the intensity of the applied voltage adopted during the electrophoretic deposition process [13].

The adherence of the GO coating on the glass fiber surface was investigated by tribological tests performed at a nanoscale level by atomic force microscopy (AFM) [13]. Calibrated tip was slid from bare GF to GO covered region at a fixed normal force (FN). This method was capable of measuring substrate-coating adhesion energy by debonding the deposited GO. The analysis and modeling of the obtained force data allowed us to assign a value of about 130 MPa to the shear stress required for the debonding of GO coating from the glass fiber. As reported in Figure 9c, even after the chemical reduction process the rGO coating appears to be tightly bounded on the glass fiber surface.

The single-fiber fragmentation test indicated a positive effect of the GO coating on the stress transfer ability at the fiber/matrix interface. In fact, as reported in Figure 10, the ISS values improved as the intensity of the voltage applied for the GO deposition increased. It is noteworthy to observe that for GO-coated fiber at the maximum EPD voltage of 10 V/cm an increment of the ISS value of about 220% was obtained with respect to the uncoated fibers. The effect of a chemical reduction of GO coating into rGO on the ISS values was also investigated by single-fiber fragmentation tests whose results are reported in Figure 10. It is interesting to observe that the rGO coating electrophoretically deposited on the glass fibers played a positive effect on the fiber/matrix ISS values which displayed an improvement of about 70% at the maximum EPD voltage of 10 V/cm. At the same time, it is clear that the beneficial effect of rGO coating was lower than that observed for GO coating. This difference can be attributed to the much lower amount of oxygenated functional groups in rGO with respect to GO, as experimentally proven by Fourier transformation infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) [22].
Figure 10. ISS values as determined by the fragmentation test performed on microcomposites containing GF_2 fiber coated with GO or rGO applied by electrophoretic deposition (EPD) under various applied voltages.

Electrical resistivity measurements on unidirectional composites containing GO or rGO coated glass fibers are reported in Figure 11 and compared with the case of uncoated glass fibers. It clearly emerges that the GO coating did not significantly modify the electrical resistivity of epoxy/glass composites. On the other hand, the electrical conductivity value of composites containing rGO coated glass fibers markedly decreased (by 12 orders of magnitude) with respect to the resistivity value of composites with uncoated fiber.

Figure 11. Electrical resistivity of composites reinforced with continuous uncoated glass fibers (epoxy/GF), continuous glass fibers coated with GO (epoxy/GO/GF) and continuous glass fibers coated with rGO (epoxy/rGO/GF).
Therefore, composites containing rGO coated fibers were subjected to various (both static and dynamic) mechanical loading conditions, and the strain was monitored (by an axial extensometer) simultaneously to electrical resistance variations along axial direction. For shake of brevity, only two cases are reported on Figure 12, regarding the obtained results under quasi static and the dynamic loading conditions. It is interesting to note that the variations in the electrical resistivity of the investigated composites quite carefully reflected the applied strain histories under both loading conditions. This experimental result clearly indicates that the rGO coating can extend to epoxy/glass composites the possibility of a strain monitoring based on the control of the electrical resistance variations.

**Figure 12.** Electrical resistivity variations of composites reinforced with continuous rGO coated glass fibers under a) quasi static and b) dynamic loading conditions.
4. Conclusions

In this manuscript an overview is presented on some possible strategies for improving the mechanical and functional properties of glass fiber reinforced composites through graphene and graphene-oxide nano platelets.

A homogenous dispersion of graphene nanoplatelets in a thermoplastic polymer such as polypropylene induced a remarkable improvement in the fiber/matrix adhesion with interfacial shear strength values improved up to a factor of about 6 when 7 wt% of GNP is dispersed in the polymer matrix. As a consequence, the presence of GNP played also a role in determining the mechanical properties of short-glass fiber reinforced PP. For instance, in PP-based composites reinforced with 10 wt% of short glass fibers an elastic modulus increment of about 38% was observed when 7 wt% of GNP were added. Moreover, the addition of 5 wt% of GNP in a PP-based composite reinforced with 15 wt% of short glass fibers generated a material whose elastic modulus was comparable to that of a composite loaded with 30 wt% of short glass fibers, with a significative reduction of the material specific weight.

The beneficial effects on the fiber/matrix adhesion of a the dispersion of GNP in the matrix resin had been also experimentally proved by microdebonding test on epoxy-based microcomposites. In fact, the dispersion of 5 wt% of GNP in the matrix resin induced an increase of ISS values by about 40%. Concurrently, improvements of tensile modulus, tensile strength and Izod impact strength were promoted by the presence of GNP in epoxy composites reinforced with various amounts of short glass fibers.

Another investigated strategy for the fiber/matrix interphase engineering was the electrophorectic deposition of graphene oxide on the glass fiber surface and the chemical reduction of the obtained coating into rGO. It is noteworthy to observe that ISS value for GO-coated fiber at the maximum EPD voltage of 10 V/cm an increment of the ISS value of about 220% was obtained with respect to the uncoated fibers. Noteworthy, the chemical reduction of the GO coating in rGO allowed to increase the electrical conductivity of unidirectional epoxy/glass composites by 12 orders of magnitude with respect to the typical values of composites with uncoated glass fibers. The piezoresistive response of composites reinforced with rGO coated glass fibers was monitored by measuring the electrical resistance change on specimens subjected to mechanical loading under quasi static and dynamic loading conditions. In this way, the possibility of strain monitoring due to the presence of an engineered fiber/matrix interphase was experimentally proved.

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