Original Article

Effect of graphene oxide coating on the ballistic performance of aramid fabric


Military Institute of Engineering — IME, Department of Materials Science, Praça General Tibúrcio 80, URCA, 22290-270 Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:
Received 24 October 2019
Accepted 19 December 2019
Available online 3 January 2020

Keywords:
Graphene oxide
Aramid
Nanocomposite
Ballistic test

ABSTRACT

Twaron® brand aromatic polyamide, commonly known as aramid fabric, was reinforced with a solution of graphene oxide (GO) followed by a heat treatment at 120 °C. The objective was to improve the ballistic properties of the material by increasing the friction coefficient of the fibers in the fabric. The GO produced by the modified Hummers method was characterized by Fourier transform infrared and Raman spectroscopy as well as by scanning electron microscopy (SEM) and atomic force microscopy. Both the as-received fabric and fabric coated with one and two filtrations of GO were characterized by the above-mentioned technique in addition to optical microscopy (OM). All samples were subjected to ballistic tests with 9 mm ammunition. The energy absorbed by the materials was calculated from the values of impact velocities and residual obtained by Doppler radar. The type of failure was characterized by means of SEM and OM visual analysis. The results show a better resistive force of the two filtrations GO coated fabric, up to 50%, when compared to the plain as-received fabric.

© 2019 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The gradual increase of armed conflicts between police and criminals in large urban centers is today associated with escalating changes in the characteristics of used armaments. In a scenario where criminals have access to increasingly powerful armaments, it becomes necessary to obtain ever more effective protection armor, as they become a key element in the personal and vehicular security of civil and military police [1].

Among the materials used in the manufacture of ballistic protection equipment, one can highlight those associated with fibers, both natural and synthetic. Natural fibers are a recent class investigated for possible substitution or hybridization with synthetic fibers in multilayered armor [2–7]. It is worth mentioning that, within this class, nanocellulose is a promising reinforcement for application requiring special properties [8–14]. However, synthetic fiber-based armors are still the most preferred worldwide in ballistic vests for personal protection. This is particularly the case of aramid...
mastic polyamide, also known as aramid, a synthetic fiber, which, has high strength and specific toughness, associated with low density and good mobility [15]. These specific fiber properties, added to the fabric architecture (weft and warp), contribute to the absorption of kinetic energy transferred from the projectile to the target in the form of elastic and plastic deformations [16–19]. The mechanisms of damage during the ballistic event coexist with these characteristics, contributing to the energy dissipation of the projectile in the material. Mechanism of cone formation on the back face of the target, failure by tensile of the primary fibers, secondary fibers deformation, cutting and friction of the fibers with the projectile, delamination, and matrix breaking, when applicable, are most relevant [20–23].

In general, when a projectile hits a textile (fabric) target, it stretches the fibers toward the back face of the compound, propagating transverse and longitudinal/radial waves that promote a conical deformation in the material. The fibers directly impacted by the projectile (primary fibers) are responsible for the penetration resistance, being subjected to higher tensions until reaching the failure by tensile rupture [20,23,24]. The other fibers, not directly affected by the projectile (secondary fibers), suffer a conical deformation Fig. 1, contributing to the dissipation of energy in the material. Since the impact effects are localized, the area of the secondary fibers is restricted to a radius $r_c$ equal to the distance traveled by the deformation waves generated from the impact [20].

During projectile penetration, the fabric intersections can promote lateral displacement of the fibers without breaking, but reducing the potential for energy dissipation and generating a perforation smaller than the original diameter of the projectile [25,26,18]. The friction interactions at the intersections of the fibers under ballistic impact are improved when different contour conditions (for example, the addition of lubricants) are applied under a smooth surface fabric [25,27–30]. Oliveira [31] reported that aramid plates, whose fibers were treated with shear thickening fluid (STF) based on colloidal nano-silica, impacted by 9 mm ammunition, showed an improvement of about 25% in the absorbed energy, demonstrating an efficient interaction of a non-Newtonian fluid with aramid fibers in ballistic protection.

With the emergence of graphene as a high strength and rigid material [32–34], researchers have been working to show that combining this material with aramid can significantly improve the mechanical and ballistic performance of the fiber. Recent results revealed that the application of graphene nanoplates on the surface of these fabrics improves tensile strength, Young’s modulus and tenacity of the nanocomposites [35,36]. Other studies [37,38] suggest that the oxide graphene (GO), consisting of regions interspersed with sp2-hybridized carbons containing carboxyl groups and sp3-hybridized carbons with hydroxyl and epoxy functional groups in their basal planes, improves the interaction of polymeric fiber surfaces. This improvement is attributed to the better mechanical fit at the nano-charge-matrix interface and its two-dimensional geometry. It was suggested that GO may be responsible for the higher stiffness obtained in the nanocomposite, resulting from the hexagonal and 2D arrangement of the atoms of covalently bound carbon in a honeycomb structure [20,33,38].

In this view, the present work evaluates the ballistic response of a did phase material composed of aramid fabric coated with GO, before and after deposition, through the energy dissipated by the impact of the 9 mm projectile and against the target as well as by the type of failure suffered by the material.

2. Materials and methods

2.1. Synthesis of graphene oxide

The graphene oxide (GO) was fabricated from the graphite flakes, number 332461, supplied by Sigma-Aldrich, using the modified Hummers method [39–41]. In short, from flakes of graphite the following steps were performed: (i) intercalation, by the addition of sulfuric acid and sodium nitrate; (ii) oxidation, by the addition of potassium permanganate, with stirring for 7 days; (iii) exfoliation, by means of additions of dilute solutions of sulfuric acid and hydrogen peroxide, follows by washing and centrifugation cycles [42,43]. Fig. 2 illustrates these steps performed for the production of graphene oxide.

Graphene oxide flakes suspended in the aqueous medium were produced at a concentration of 2 mg/ml.

2.2. Preparation of aramid fabrics coated with graphene oxide flake

Aramid fabric circular plies having a diameter of 15 cm were cut from a Twaron® textile, with T750 weave and 460 g/m² grammage, supplied by Teijin Aramid, with a linear density of
3360 Dtex - 2000 filaments. These aramid plies were heated to 100 °C to remove adsorbed moisture on the fibers. The filtration in this method was applied either once or twice, characterizing two different GO-coated aramid fabric pieces, with first and second filtration, respectively. The GO flakes suspended in the aqueous medium with a concentration of 2 mg/ml, were deposited on both surfaces of the aramid fabric pieces by the vacuum filtration method. The GO-modified pieces were then vacuum dried in a desiccator. After drying, the pieces were again heated to a temperature of 120 °C for 30 min in an oven. This treatment promotes an increase in the adhesion of the GO to the fiber, related to the formation of the functional groups (–COOH) on the surface of the fiber and the greater interaction of these with the oxygenated groups in the GO [42]. Each ballistic sample was composed of 5 piece layers as further described.

Three test groups were prepared for the study: Received Aramid (uncoated and dried at 100 °C), Aramid + GO (1) (samples coated with GO on a first filtration, thermally treated at 120 °C) and Aramid + GO (2) (GO-coated samples in a second filtration, thermally treated at 120 °C). Because it was an experimental study, a small amount of GO (1 l) was used to coat the aramid fabric. Thus, the vacuum filtration methodology was performed either one or two times using the same chemical solution.

The morphology of the samples was determined by atomic force microscopy (AFM), scanning electron microscopy (SEM) and optical microscopy (OM). AFM was performed on a Park System XE7 equipment in intermittent mode with a silicon tip, operating under the resonance frequency of 13 kHz and force of 0.18 N/m. SEM observation was conducted on a Quanta FEG 250 FEI microscope with secondary electrons operating under 10 and 30 kV at low vacuum.

As the samples were not coated with a polymer resin to prevent removal of the GO impregnated into the aramid fabric, a sample of the GO-coated fabric was removed for manual manipulation for about 1 min. This was intended to check the possible loss of tissue due to surface coating. SEM micrographs, Fig. 3, show a partial break of the GO sheets on the fiber surface. Since a significant amount of GO remained in the fiber, it was assumed that the adhesion of the GO into the fiber was efficient and that the manipulation of the samples during the ballistic test would not significantly affect the results of this work.

2.3. Preparation of ballistic samples

For the ballistic test, Fig. 4 shows both aramid fabric samples (Twaron®0 without GO coating and samples for each condition of GO-coated aramid fabric with one or two filtrations. These samples were prepared with the aid of an industrial sewing machine, in which for each ballistic sample, five pieces layers were sewn from each evaluation group.

For fixing the samples to the test apparatus, a system displaying an aperture in the center with a diameter of 5 cm, was prepared with two aluminum plates. The samples were fixed between these plates with the id of screws, as illustrated in Fig. 5.

The ballistic tests were carried out according to the NNI Standard 0106.01 [44] level II, using 9 mm ammunition fired from a weapon (gun barrel) on targets 5 m away, at an incident angle of 0°. Fig. 6 illustrates schematically the ballistic test setup located at the Brazilian Army shooting range facility (CAEx), Rio de Janeiro, Brazil.

The ballistic performance of the nanocomposite was evaluated considering the energy absorbed, calculated by Eqs. (1) and (2), using the residual (Vr) and impact (Vi) velocity obtained by Doppler radar model Weibel SL-520P, after complete perforation. Where Ei is the absorbed energy, Ei the impact of energy and ER the residual energy.

\[
E = \frac{1}{2}m \cdot (V^2)
\]  

\[
E_r = E_i - E_R = \frac{1}{2}m \cdot (V_r^2 - V_i^2)
\]
Fig. 3 – SEM of the manually manipulated sample (magnification of 1000 and 3000×).

Fig. 4 – Ballistic samples made from aramid fabrics reinforced with graphene oxide. (a) Aramid, (b) aramid + GO (1), (c) aramid + GO (2).

Fig. 5 – The system produced for fixing ballistic samples in the test apparatus.

Fig. 6 – (a) Ballistic test scheme [32,33] and (b) photograph the apparatus used by CAEx.
Analysis of variance ANOVA was performed to statistically validate the absorbed energy values, Eq. (2), by the different groups of samples: Received Aramid; Aramid + GO (1) and Aramid + GO (2) investigated.

The damage produced by the projectile impact, in terms of the occurrence of stretching or cutting of the threads, was analyzed by visual inspection. The topography of the fracture surfaces of GO-coated and as-received aramid fabric was analyzed by SEM.

2.4. Physico-chemical characterizations

Physical-chemical analyses were performed to evaluate the impregnation of GO onto the surface of aramid fabric and compared to untreated fabric and as-produced GO.

Raman spectroscopy was performed in a NT-MDT NTEGRA spectrometer, with laser wavelength (λ) 473 nm and radiation time of 100 s [43]. Fourier Infrared spectroscopy (FTIR) analysis was performed using a Frontier FT-IR/FIR spectrometer, in the region between 400 cm$^{-1}$ and 650 cm$^{-1}$, applying the attenuated total reflectance (ATR) technique. This analysis was used to verify the existence of changes in the structure of the samples, serving as a tool to identify possible variations in the wavelength and characteristic absorptions of the samples. The spectra were normalized based on the band at 821 cm$^{-1}$, attributed to stretching vibrations of the C–H bonds of the aromatic ring present in the backbone of the aramid fiber. This band does not present significant variations of intensity when the fiber is subjected to thermochemical treatment [45].

3. Results and discussion

3.1. FTIR and Raman spectroscopy

Fig. 7 shows the spectra obtained by FTIR and Raman, characterizing the graphene oxide (GO) produced by the modified Hummers method similar to what was reported in other works [46–50].

The FTIR spectrum of GO in Fig. 7(a) shows the main characteristic absorption bands of the material. The large band in the spectral region of 3000–3700 cm$^{-1}$ is attributed to stretching and vibrations of hydroxyl groups (O–H) of water molecules adsorbed onto GO. This indicates that the sample produced has a high hydrophilic character [46,48]. The characteristic bands observed in the 2110 and 1633 cm$^{-1}$ regions can be attributed, respectively, to epoxidized groups in the basal planes and to carbonyl groups (C=O) and carboxylic groups (–COOH) [49].

The Raman spectrum in Fig. 7(b) shows a large and intense D-band at 1356 cm$^{-1}$ resulting from sp3 carbon stretching and a visible G-band at 1590 cm$^{-1}$ due to the stretching of sp2 carbons [51]. The acute aspect of the D band, in this case, implies the occurrence of sp3-type structural disturbance generated from the modification of the original carbon atoms of the sp2-type graphene [46,48,49]. In the spectral region of 2924 cm$^{-1}$, there is another band characteristic of defects in the material, called 2D, which can be associated with the number of layers. When the 2D band exhibits an enlargement as seen in Fig. 7(b), it is an indicative that possibly graphene has four or more layers [52,53]. Thus, the sample reveals all the main characteristics of the GO.

3.2. AFM, SEM and OM

SEM and AFM micrographs show that the GO synthesized by the Hummers method has a two-dimensional sheet-like structure [41]. The thickness profile extracted by AFM, Fig. 8(a), shows that the graphene flakes are approximately 3.05 nm. According to Lima et al. [43] and Chen et al. [53], a mono-layer of GO has a thickness of approximately 0.8 nm. This indicates that the material produced has sheets of ~4 layers. The application of these GO nanoplates onto the surface of aramid fabrics may show a significant improvement in the fracture toughness of the material, attributed to the best mechanical fit between the nano load-matrix interface and its two-dimensional geometry [38].

Fig. 9 shows images by OM and SEM of the three distinct samples. Both OM, Fig. 9(a), and SEM, Fig. 9(b), micrographs of Aramid Received sample display smooth surfaces suggesting, respectively, well-cleaned aramid fabric and related fibers. The OM Fig. 9(c), and SEM, Fig. 9(d), micrographs of Aramid + GO (1) show surfaces partially covered with relatively large GO flakes from a first filtration. Surfaces covered with GO from a second filtration are shown by OM, Fig. 9(e), and SEM, Fig. 9(f), micrographs for the Aramid + GO (2) sample. In particular, the aramid fiber shown by SEM in Fig. 9(f) reveals a surface almost completely covered with small GO flakes forming a veil-flake film, first mentioned by Lee et al. [34]. As further discussed, this more uniform GO coating might be responsible for the superior ballistic performance of the Aramid + GO (2) sample.

Fig. 10 shows by AFM nanometric details on the surface of the three distinct samples. Aramid Received, Fig. 10(a), display a comparatively more smoother surface with a maximum roughness around 2 nm. The GO flakes covering the surface of the Aramid + GO (1) sample, Fig. 10(b), contribute to a sensibly rougher surface with thickness oscillation above 4 nm. By contrast, the more uniform graphene oxide veil-coated Aramid + GO (2) sample, Fig. 10(c), has a thickness that reaches about 7 nm.

3.3. Ballistic absorbed energy

Table 1 shows the calculated values from Eq. (2) of the absorbed energy (E$_b$) by the studied materials in ballistic tests. Since the Doppler radar did not capture the impact velocity ($V_i$) on the samples, it was assumed that the projectile velocity at the exit of the gun barrel to be ($V_j$) [6,54,55].

The results showed that the ballistic resistance of the aramid fabric increases with the deposition of GO by values up to 50% higher than those for the as-received fabric. It is noted in Table 1 that the resistance varied significantly as a

<table>
<thead>
<tr>
<th>Evaluation group</th>
<th>$\rho A$ (Kg/m$^2$)</th>
<th>Energies absorbed (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aramid Received</td>
<td>2,34</td>
<td>106,4</td>
</tr>
<tr>
<td>Aramid + GO (1)</td>
<td>2,27</td>
<td>116,6</td>
</tr>
<tr>
<td>Aramid + GO (2)</td>
<td>2,22</td>
<td>159,6</td>
</tr>
</tbody>
</table>
function of the areal density of the samples. In the case of the Aramid + GO (2) sample, the second filtration may have contributed to the GO flakes entering more into the fabrics, increasing the friction between them and the projectile. Consequently, the ballistic energy absorption of the material is significantly increased.

These results, associated with those found by Gago et al. [56], Wetzel et al. [57] and Bizao et al. [32] support the feasibility of the development of new nanocomposites for ballistic applications.

Fig. 7 shows the variation of the ballistic absorbed energy with the sample areal density, from the date in Table 1. In this figure is noteworthy the marked increase in absorbed energy for the second filtration Aramid + GO (2) sample with relatively smaller areal density. It is then suggested that the GO coating process might interfere with the space between yarns of the aramid fabric, reducing slightly its areal density. At the same time, a better GO coating significantly increases the absorbed energy owing to further discussed fracture mechanisms.

The results show in Table 1 and Fig. 11 were validated by ANOVA. Table 2 presents the values of the ANOVA parameters F, F critical (Fc) and P. In this table, considering that 5% (0.05) is the level of significance, then those with F > Fc are associated with 95% of confidence for their difference. Moreover, if P < 0.05, a significant distinction might exist between values.

As presented in Table 2, based on the ANOVA, the surface deposition of GO onto aramid fabric causes a statistically significant increase in the ballistic absorbed energy. In other words, the hypothesis that the values are the same can be rejected with 95% of confidence.

### 3.4 Damage in fracture analysis

Figs. 12 and 13 show the macroscopic damage imposed to the ballistically tested samples. It can be seen in Fig. 12 that all tested samples were completely perforated, indicating that the initial energy of the projectile was greater than the kinetic
Fig. 9 - Microscopic images of the light field type with the magnification of 200 μm and SEM (16,000×), of the Aramid Received (a) and (b), coated with of GO: Aramid + GO (1) (c) and (d), Aramid + GO (2) (e) and (f).
energy that the target could absorb. The cone formed in the back face of the aramid fabric during the ballistic event is attributed to the propagation of transverse waves in the fibers [58], pulling all the yarns towards the point of impact [20]. In this case, the resistive force of the aramid fabric during the ballistic impact was attributed to the yarns and their fibers (primary fibers) directly affected by the projectile and responsible for the greater absorption of kinetic energy during the event. The deformation of the other fabric yarns within the conic region (secondary fibers) added to this energy absorption.

Fig. 13 shows SEM micrographs of the fracture surface of the distinct samples after the ballistic test. Fig. 13(a) reveals that there was a displacement towards the side of the fibers in the
Aramid Received sample. This is probably due to the lower friction between the projectile and the target [26]. As a result, the portion of fibers struck by the projectile was smaller and, consequently, there was lower energy absorption by the material. In Fig. 13(b) it is noted that there was fibrillation along the diameter of the aramid fibers due to the existence of a gradient of properties inherent to the manufacturing process. This mechanism promoted by the stretching of fibers is known as “peeling” [59,60].

On the other hand, Fig. 13(c) shows that the aramid fabric coated with GO presented a greater amount of fibers ruptured after the ballistic test. Microscopically, there was a marked pull-out effect of the fibers, accompanied by fractures in a typical tensile morphology [60], Fig. 13(d), contributing significantly to the greater energy absorption of the material when compared to the as-received aramid fabric. It is proposed that GO coated on the surface of the aramid fabric promotes a higher interfacial resistance in the fibers, which causes a greater resistance to friction between projectile and target. In this case, the improvement of this resistive force associated with the GO coating friction promotes an amount of microfibrillation in the fracture of the fibers during the ballistic impact, contributing to the greater absorption of energy, shown in Fig. 13(d).

Another point worth discussing is the nanometric scale of the GO, especially in the second filtration Aramid + GO (2). As indicated by Zeng et al. [38], the GO-coated aramid fibers might be considered a nanocomposite in which the nano-sized flakes of GO form a surface coating that reinforces the fibers. Indeed, the results in Table 1 and Fig. 11 revealed a ballistic reinforcement of GO-coated in comparison with non-coated as-received aramid fabric. Although the reinforcement effect of both graphene and GO on aramid fabric/KevlarTM has already been known [33,36,38], the present work is for the first time presenting a ballistic reinforcement caused by nanometric GO coating on aramid fabric.

4. Conclusions

The results of the ballistic test on graphene oxide (GO) coating aramid fabric demonstrated that this GO-coated nanocomposite enables the development of novel materials for personal and vehicular ballistic protection.

- The GO sheets, with up to 2 nm in thickness, produced by the modified Hummers method was found to have besides their main characteristics, a high hydrophilic character revealed by FTIR and Raman spectroscopy.
- The thermal treatment at 120 °C improved the adhesion of the GO sheets to the aramid fibers, disclosed by AFM and SEM, which could be attributed to the formation of functional groups on the surface of the fiber with the oxygenated groups in the graphene oxide.
- The ballistic test on GO-coated aramid fabric showed a significant improvement in absorbed energy of up to 50% when compared to the uncoated aramid fabric, possibly due to higher friction between the fibers. ANOVA statistically validated these results.
- The main mechanisms of damage observed were microfibrillation failure and primary fiber tensile rupture as well as secondary fiber deformation, friction between fiber and projectile due to cone formation in the back face of the nanocomposite.

![Fig. 11 – Ballistic absorbed energy of the distinct aramid fabric samples as a function of the fabric areal density.](image)

![Fig. 12 – Photographs of the samples ballistically tested with 9 mm ammunition. (a) Aramid Received, (b) Aramid + GO (1) and (c) Aramid + GO (2).](image)
Fig. 13 – SEM fractures of tested ballistically samples with 9 mm ammunition. (a) The cone fracture surface of the Aramid Received sample, (b) “peeling” of the aramid fibers coated (4000×), (c) cone fracture surface in the Aramid + GO (2) and (d) microfibrillation of aramid fibers with GO after the ballistic test (8000×).

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The authors of this paper thank the Brazilian support agency CAPES for funding; to the Protective and Nanostructured Materials Coating Laboratory (PUC-RJ) for the contribution to the analyses, and to the Brazilian Army Evaluation Center (CAEx) for conducting ballistic tests.

REFERENCES


[18] Abrate S, Ahmadi M. Dynamic deformation, damage and fracture in composite materials and structures. Woodhead Publishing; 2016. Copyright® Elsevier Ltd. All rights reserved.


