# Versatile Graphene-Based Fibrous Systems for Military Applications

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## *ABSTRACT*

*Due to the increased concern about environmental sustainability, the use of biobased composites in automotive, construction, packaging and medical applications is in full growth. In order to improve the overall properties of these green composites, the addition of carbon-based materials as reinforcement is attracting attention. The use of graphene nanoplatelets (GNPs) due to their high electrical, thermal and mechanical properties could be the key to enlarge the application of composites in demanding areas such as military or aerospace. In this work, it was studied the effect of using GNPs as reinforcing agents of poly (lactic acid) (PLA)/jute composites. For this purpose, first, the fabrication of PLA films by solvent casting was optimized. After this, for the PLA/GNPs films production several polymeric formulations were optimized including different percentages of nanoplatelets (0.5, 1, 3, 5, 10, 15 and 30% (w/w)) and the use of polyethylene glycol (PEG) as dispersive agent. With the polymeric films optimized, the jute/PLA sandwich composites were produced by compress molding technique using these films with and without GNPs. All the developed samples were characterized by Raman Spectroscopy, Thermogravimetric analysis (TGA) and FESEM (Field emission scanning electron microscopy). All the techniques showed that the GNPs were successfully incorporated onto the composites. After characterization, several properties were analyzed including electrical conductivity, mechanical tests, electromagnetic interference (EMI) shielding and antibacterial behavior. A strong correlation was observed between the increased percentage of nanoplatelets with the enhancement of composite's properties. The composites with different percentages of GNPs exhibited very good values of electrical conductivity ranging from 2×10-9 to 39.6 S/m. It was also observed an increase on Young's modulus values. Comparing the values obtained without nanoplatelets with the ones with 3%(w/w), the increase is almost double. The highest increase observed was for the composite with 30% of GNPs. Antibacterial assays demonstrated that GNPs presents an antibacterial behavior by contact, preventing the growth of Gram-positive and Gram-negative bacteria. All the composites revealed EMI shielding effect reaching efficiency values of 39 dB in frequency of 3GHz. Overall, this work demonstrates that the jute/PLA composites with GNPs presents some potential to be used in several military areas including automotive and personal protective equipment.*

## 1.0 INTRODUCTION

Nowadays, graphene is one of the most studied materials and is highly attractive for military applications in the land, air, sea and maritime domains. Their extraordinary physical properties include lightness, flexibility, thermal conductivity, excellent mechanical and electrical properties [1,2]. However, pure graphene is not yet produced in large scale and the price is still very high. In contrast, graphene nanoplatelets are already produced in large-scale with lower manufacturing costs exhibiting exciting properties when compared with pure graphene [3].

GNPs, have been used in the composites area, as polymer filler/reinforcement replacing several carbon allotropes (ex: carbon nanotubes and carbon black), metallic nanoparticles and clays mainly due to their high surface area which improves the interaction between the graphene sheets and polymeric matrix. The addition of graphene to polymers results in a significant improvement of polymers' overall properties and can also

introduce new properties, leading to new applications. For example, these 2D carbon-based fillers are very attractive for the development of next generation sports equipment, cementitious materials for construction, anti-corrosion coatings, structural elements in aerospace, wind turbine systems, automotive lightweight components, EMI shielding materials, military protective equipment, among others [4,5].

Recently, with the environmental consciousness growing, the interest and research for sustainable materials are acquiring more and more importance. In this way, the use of bio-based polymers and natural fibres for composites development is preferable over the synthetic ones [6]. Regarding bio-based polymers, PLA, extracted from renewable sources, exhibit several advantages, the most important one is their biodegradability [7]. Likewise, natural fibres, including cotton, jute, sisal, kenaf, flax, are very promising materials due to its biodegradability, low-cost and lightweight [8,9]. Therefore, these green materials can be used as a valuable alternative to overcome the problems of non-biodegradable synthetic polymers and fibres, leading to the development of environmental-friendly composites. However, the bio-based polymers like PLA normally exhibit low mechanical, thermal and electrical properties. Thus, the incorporation of nano-sized carbon based reinforcements as the GNPs, is of particular importance in order to improve the composites performance for several military applications, including military cloths or tents, vehicle parts, protective coatings, multi layered personal protection systems and EMI shielding [10]. In this context, graphene-based materials are being studied for personal ballistic protection. According with Lee *et al*, graphene exhibited superior performance when compared with the commonly used steel plates [11]. Nine *et al* reported the application of graphene in coatings for anti-scratch, corrosion resistance, flame retardant, anti-gas, antiseptic and electromagnetic shielding applications [12]. Due to their excellent electrical properties, graphene based materials are commonly used in monitoring and sensing military applications including bombs/explosives detection [13] and monitorization of military personnel stress level [14]. In addition, the development of capacitors using graphene can be used for example to recharge military electronic devices [15]. Overall, the use of graphene-based materials as reinforcement of jute/PLA composites could provide an enormous range of solutions for the military field whether in the area of personal protection, mobility or infrastructures.

In this work, composites were developed based on jute fabric and PLA films by compress moulding technique. Firstly, the polymeric films production was optimized and performed by solvent casting methodology. Furthermore, the GNPs reinforcement was performed onto the polymeric films in order to improve the platelets dispersion and the final composites homogeneity. Several GNPs percentages onto the PLA formulations were tested and PEG was used as dispersive agent. All the samples were characterized by SEM, ATR-FTIR, Raman and TGA. Additionally, several tests were perf\ormed in order to evaluate the potential of these fibrous systems for applications in the military field. The samples exhibited high values of electrical conductivity and EMI shielding effect which is very important for their use in smart fibrous systems (monitoring and sensing applications) and in the signature management field. Along with the electrical properties, the mechanical properties were also analysed considering their use in the personal protection area. Finally, the antibacterial capability was analysed having in the horizon their application in the CBRNe area as protective systems against chemical and biological warfare agents.

## 2.0 MATERIALS AND METHODS

### 2.1 Materials

PLA was purchased from Resinex (Portugal). The jute fabric was supplied by RCS (Braga Portugal) with an areal density mass of 430g /$m^2$. The GNPs were purchased from Graphenest® (Portugal) with number of layers: 8 – 30, thickness: 3 - 10 nanometers, Lateral dimensions: 0.5 - 2.0 micrometers and 150 $m^2$/g of surface area. Dichloromethane was supplied by Sigma Aldrich, PEG 4000 was provided by Acofarma and Sodium hydroxide (NaOH) 99+% was provided by Normax Chem (Portugal).

### 2.2 Polymeric films production

PLA films were produced by solvent casting technique, using dichloromethane as solvent. For the PLA films without GNPs, 3% of PLA (v/w) was added to dichloromethane and kept under stirring for 2 hours until the polymer was fully dissolved. After this, the liquid was poured into petri dishes and left at room temperature for 24 hours, until total solvent evaporation. For the films reinforced with GNPs, several percentages of nanoplatelets were tested including: 0.5, 1, 3, 5, 10, 15 and 30% (w/w), relative to the polymer initial weight. The formulations containing PLA and GNPs were subjected to an extra hour of mechanical stirring after GNPs addition, followed by one hour of ultrasonic bath. The use of PEG as dispersive agent onto the PLA formulation was also tested using a final ratio of 80%PLA/20% PEG.

### 2.3 Fabrics treatment and Composites development

As described in several works [16] the fibres' pretreatment could enhance the fibres adhesion to the polymeric matrix. In this way, the composites were produced using alkali treated jute fabrics. The alkali surface pretreatment was applied using an aqueous solution of NaOH (1M). The fabrics were added to the solution under stirring at room temperature for 30 minutes. Afterwards, the fabrics were removed from the solution rinsed with water and left to dry at 80 °C for 1h.

The alkali treated fabric was used for the jute/PLA sandwich composites development. In this case, one piece of jute fabric was used with PLA films (with and without GNPs and PEG) on the top and bottom surfaces to fabricate sandwich composites by compress moulding. The processing temperature was 180°C, with a pressure of 4 tons under 10 minutes.

### 2.4 Characterization Tests and Properties evaluation

#### 2.4.1 Raman Spectroscopy

Raman spectroscopy was used to analyse the nanoparticles structure and quality, the quantity of stacked platelets and the GNPs dispersion onto the composites. The spectra were obtained on a Horiba LabRAM HR Evolution confocal microscope (Horiba Scientific, Longjumeau, France) using a laser excitation of 532 nm (2.33 eV). A 100x objective lens was used to focus the laser onto the sample.

#### 2.4.2. Thermogravimetric analysis (TGA)

TGA analysis was performed using a STA 700 from SCANSCI to evaluate the influence of jute fibre and GNPs incorporation on the composite degradation temperature. The TGA trace was obtained in the range of 25–600 °C, under nitrogen atmosphere, with a constant heating rate of 20 °C/min.

#### 2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

The morphological analysis of the developed samples was performed in an Ultra-high-resolution Field Emission Scanning Electron Microscopy (FESEM), NOVA 200 Nano SEM, FEI Company (Hillsboro, OR, USA). Before the analysis, the samples were covered with a very thin film (20 nm) of Au-Pd (80–20 weight %), using a high-resolution sputter coater, 208 HR Cressington Company (Watford, UK), coupled to a MTM-20 Cressington High Resolution Thickness Controller.

### 2.4.4 Mechanical Properties Evaluation

All the composites were subjected to tensile tests according to an adaptation of the standard ASTM D5035. These tests were made using a Hounsfield tensile tester Tinius Olsen model H100KPS with load cell of 100KN traction device, with the following settings: sample width = 40 mm; sample length ≥ 150 mm; distance between grips = 50 mm; testing speed = 100 mm $min^{-1}$. After testing, the modulus of elasticity was calculated through the stress-strain curves obtained during the test.

### 2.4.5 Electrical conductivity

The electrical resistivity of films and composites was measured by the 2-wire method, where the voltage was applied from -0,8V to 0,8V, step of 0,1, and the current measured by a Keithley 6487 picometer/voltage source. The tests were performed at room temperature and in direct current (DC) mode. The electrical resistivity (ρ) was calculated by:

$$\rho = R\,\frac{A}{L} \tag{1}$$

where R is the electrical resistance, A is the area of the electrode (6 x 1 $mm^2$) and L is the distance between the electrodes (2mm). The electrical conductivity is given by the inverse of electrical resistance ($\sigma = 1/\rho$). Three different points in each sample were analyzed in order to confirm the samples homogeneity.

### 2.4.6 Electromagnetic shielding (EMI)

The electromagnetic shielding was measured using the standard ASTM D4935-99. The samples were placed between two coaxial flanges which act both as sample holders and TEM waveguide. The tests fixture is connected to a Vector Network Analyzer (Rohde & Schwarz ZNB8) with the assistance of two coaxial cables and two 10 dB 50Ω attenuators. EMI shielding can then be measured by the decay of the transmitted signal between the coaxial ports and referred by the VNA as S21 or S12 scattering parameter (voltage from port1 to port2 or v.v.).

### 2.4.7 Antibacterial tests

The antibacterial activity of the samples was assessed, following the standard Halo method (JIS L 1902:2008), against Gram-negative (Escherichia coli) and Gram-positive (Staphylococcus aureus) bacteria. Before adding the samples on the bacterial environment, they were sterilized under UV radiation. Regarding the Halo method, nutrient agar (NA) was prepared, autoclaved and applied onto petri dishes until agar solidification. After agar solidification, square composites' samples of 1cm x 1cm were placed over the agar dishes and incubated for 24 hours at 37 ºC. The antibacterial activity of the samples was evaluated by the inhibition zone appearance, which indicates the absence of bacteria growth (Three replicates of each condition).

## 3.0 RESULTS AND DISCUSSION

### 3.1 Films and composites development

As previously mentioned, the principal goal of this work was to develop a composite of PLA and jute fabric reinforced with graphene nanoplatelets. For that purpose, several PLA/GNPs formulations using

different nanoplatelets percentage (between 0.1% and 30% (w/w)) were optimized for the film's development by solvent casting. The dispersion and distribution of carbon-based nanoparticles onto polymeric matrices is crucial in order to obtain an effective reinforcement and is directly related to their final mechanical, thermal and electrical properties. Thus, an homogeneous dispersion and distribution of the nanoparticles in the PLA films could be responsible from forming the nanoplatelets binding network, transferring its high properties to the final composites [17]. Therefore, it is of extreme importance to analyze the dispersion/distribution of the nanoparticles in the matrix and its direct influence on the final composite's properties. In the case of carbon nanoparticles, due to its high Van der Waals interaction, which makes difficult the dispersion and stabilization in the matrix, it is necessary to apply different techniques to achieve a better stabilization [18]. In this way, the introduction of PEG as dispersive agent was tested. After the film's formation, they were used for the sandwich jute composite's fabrication by compress moulding. For simplify the reading the films were named by: PLA, PLA/PEG, PLA+x%GNPs or PLA/PEG+x%GNPs and the composites based on the developed films and jute by: Jute/PLA/PEG+xGNPs%. Figure 1 shows as example the alkali treated jute fabric used in this work (A), the jute/PLA composite (B) and the jute/PLA/PEG composite reinforced with GNPs (C).

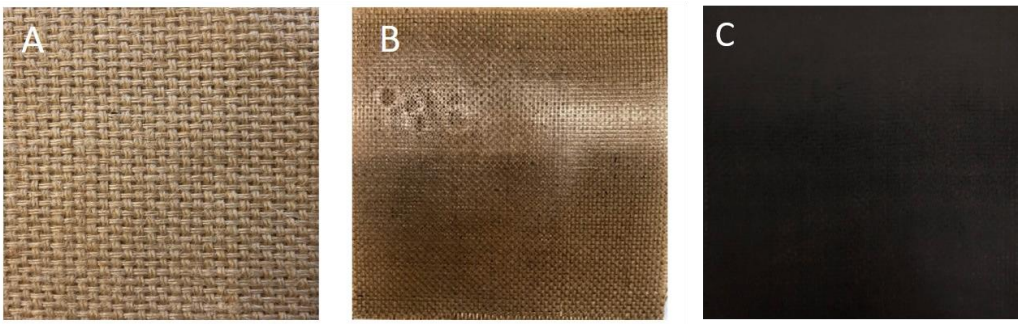


**Figure 1: Treated jute (A), Jute/PLA/PEG composite (B) composite with GNPs (C).**

### 3.2 Characterization of polymeric films and composites

#### 3.2.1 Raman Spectroscopy

Raman spectroscopy is a valuable technique for the structural characterization of graphitic materials, providing important information about materials' defects and number of staking graphene layers. The Raman spectra of graphite/graphene present three characteristic peaks, namely D, G and 2D. The D band of graphene nanoplatelets at around 1350 $cm^{-1}$ is due to out of plane breathing mode of $sp^2$ atoms and indicates the presence of defects or edges. The G ($E_{2g}$ phonon) and 2D (major fingerprint of graphene) peaks are always observed approximately at 1580 $cm^{-1}$ and 2700 $cm^{-1}$ respectively [19]. The shape, position and intensity of the 2D band relatively to the G band depend on graphene number of layers [20]. Figure 2 shows the spectrum of GNPs powder used in this work for comparison purposes with the final developed composites. As it can be observed, all the characteristic peaks of GNPs are present including the D band which even with low intensity indicates the presence of some structural defects. The 2D band shape, the relation between this band and the G band and the value of I2D/IG ratio (~0.5) is characteristic of few/multilayer graphene [21]. In addition, Figure 2 exhibits as example, the spectra of three different surface points in the jute/PLA/PEG+15% GNPs sample. Although some differences in the peaks shape of the three different points (possibly related with some heterogeneity due to the presence of natural fibres), in all points it is visible the fingerprint peaks of GNPs indicating that the nanoplatelets are distributed all over the composite.

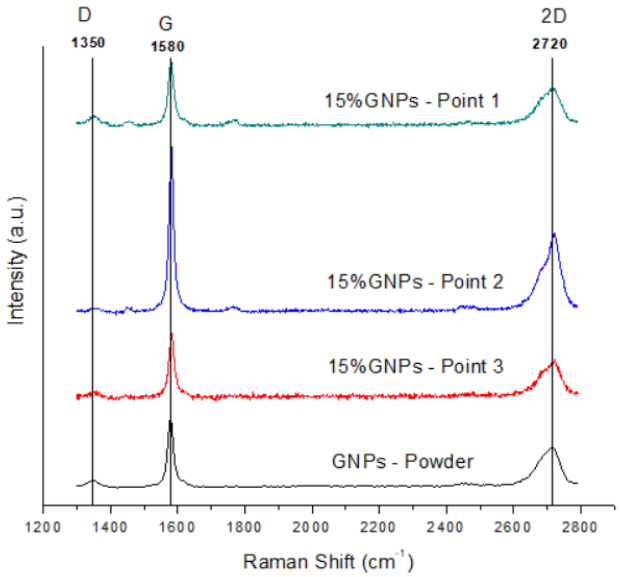


**Figure 2: Raman spectra of GNPs powder and three points on the composite jute/PLA/PEG +15% GNPs.**

### 3.2.2 Thermogravimetric analysis (TGA)

With TGA analysis of films and composites (Figure 3) it was possible to infer about the thermal stability of the developed composites, the maximum degradation temperature of each constituent and the influence of GNPs addition. The samples were heated to 600°C at a rate of 20°C/min and the weight loss was measured. It was observed that PLA degradation starts at 305°C until 409°C. For PEG starts at 325°C and ends at 425°C. For the treated fabric it starts at 204°C and ends at 330°C. Finally, for GNPs, there is no degradation up to 600°C. For both cases (films and composites) the addition of GNPs increased the quantity of residues in the samples (after 400ºC). The residues quantity is directly related with the percentage of nanoplatelets under use in each sample.

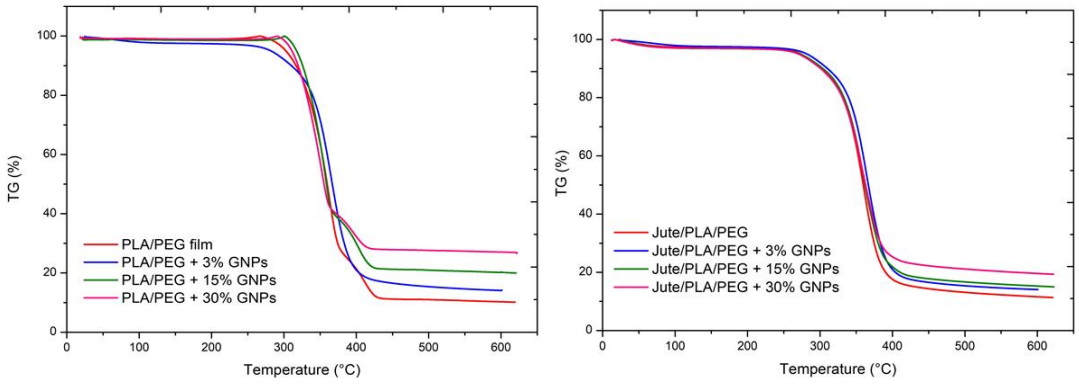


**Figure 3: TGA of films in relation of addition of GNPs and TGA of composites jute/PLA/PEG + GNPs.**

### 3.2.3. Field Emission Scanning Electron Microscopy (FESEM)

Figure 4 exhibit the FESEM images of the composite Jute/PLA/PEG with addition of 3% GNPs (B and D) and 30% of GNPs (A and C). Figure 4 (A) shows the composite surface where is visible the jute fibres homogeneously coated with PLA. In the Figure (B) and (C) the nanoplatelets are distributed all over the fabric with the presence of some aggregates. Finally, in Figure (D) one multi-layer nanoplatelet can be observed between the jute fibre and the polymeric coating.

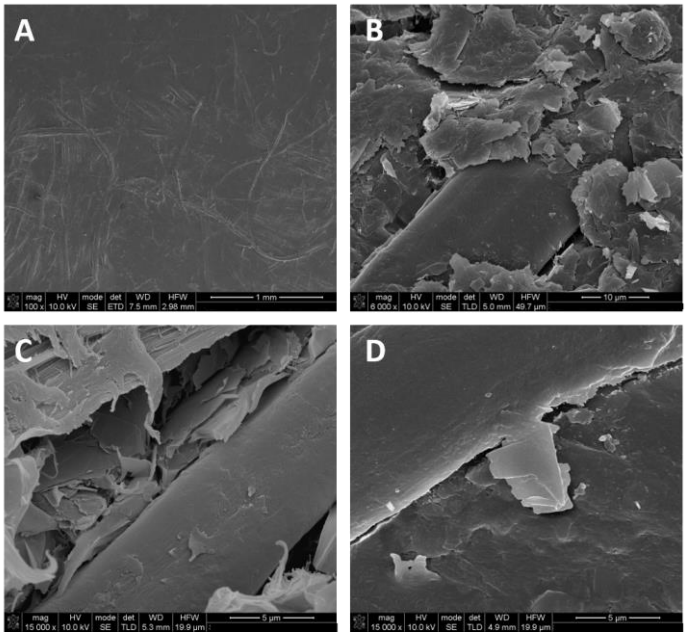


**Figure 4: FESEM images of composite jute/PLA/PEG+15%GNPs in different sites and using different magnifications.**

### 3.3. Mechanical Properties evaluation

The tensile tests were performed to infer about the influence of GNPs addition in the PLA/PEG/jute fibre composite. Figure 5 shows the relation between the Young's modulus as a function of GNPs percentage. There was an increase in the modulus related to the increase of GNPs percentage. For the addition of 3% GNPs, the modulus increased from 0,63GPa, Jute/PLA/PEG, to 1,04 GPa, a total of 65% of increase. Additionally, for the composite with 15% of GNPs, the Young's modulus increases to 1,18 GPa, about 87% of increase comparing with composite without GNPs. Lastly, for the composite with 30% GNPs, the Youngs' modulus value measured was 1,5 GPa, about 139% more than the composite without GNPs. Thus, the addition of GNPs turns the composite more rigid, increasing the elastic modulus.

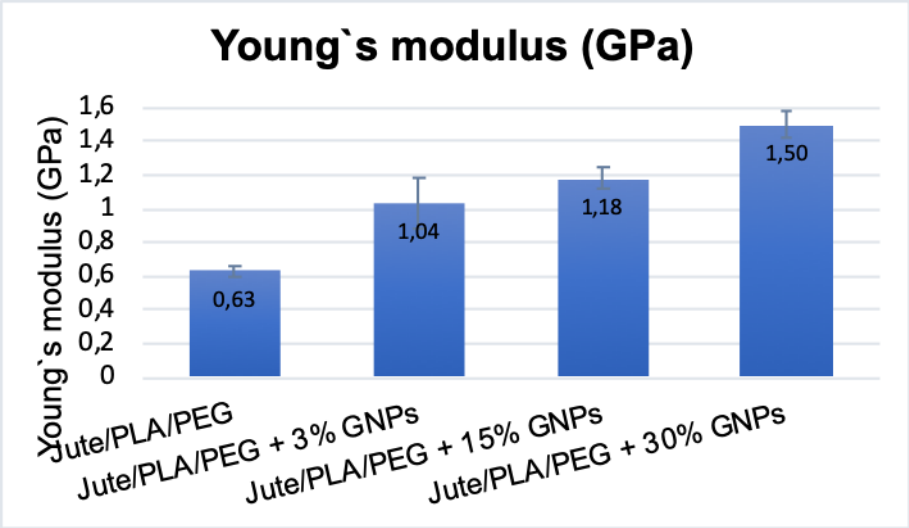


**Figure 5: Young modulus of the composites with addition of GNPs.**

### 3.4 Electrical conductivity

The composites´ electrical properties reinforced with GNPs are directly related with the dispersion and distribution of the nanoparticles in the matrix, the quantity of nanoparticles added in the matrix, the manufacturing process and the interaction nanoparticles/matrix. Thus, the control of these factors can increase the possibility to create a binding network between the nanoparticles, conducting electric current, increasing the final values of electrical conductivity [18-20]. Table 1 presents the values of electrical conductivity for the GNPs/PLA films and the influence of PEG addition. Thus, it is possible to observe an increase of electrical conductivity related with the increase of GNPs percentage. Also, the addition of PEG increased the electrical conductivity when compared to the same quantity of GNPs without PEG. With this, it is possible to conclude that the addition of PEG increases the dispersion and homogeneous distribution of the nanoplatelets onto the PLA.

**Table 1: Electrical conductivity of films related with addition of GNPs and PEG.**

| Samples | Electrical conductivity - without PEG (S/m) | Electrical conductivity - with PEG (S/m) |
|---|---|---|
| PLA | - | - |
| PLA + 0,5% GNPs | - | - |
| PLA + 1,0% GNPs | $2,0 \times 10^{-9}$ | $3,0 \times 10^{-6}$ |
| PLA + 3% GNPs | $1,8 \times 10^{-2}$ | $4,4 \times 10^{-1}$ |
| PLA + 5% GNPs | $2,2 \times 10^{-1}$ | $2,1 \times 10^{-1}$ |
| PLA + 10% GNPs | $2,0 \times 10^{-1}$ | 3,3 |
| PLA + 15% GNPs | 8,1 | 39,6 |
| PLA + 30% GNPs | 15,5 | 19,0 |

Table 2 shows the conductivity values of the composites produced with the previous presented films. These composites were produced by compression using two films on each side of the jute fabric. The use of four films, two above and two below, during the sandwich formulation, increased the electrical conductivity. This behavior occurs due to the sum of dispersions of GNPs in each film, which when overlapped, increase the percolation network, and consequently the electrical conductivity. Also, the addition of jute fabric (with high values of electrical resistivity) did not significantly influence the

electrical conductivity.

**Table 2: Electrical conductivity of composites with 3, 15 and 30 % of GNPs.**

| Samples | Electrical conductivity without PEG (S/m) | Electrical conductivity with PEG (S/m) |
|---|---|---|
| Jute/PLA | - | - |
| Jute/PLA + 3% GNPs | $1{,}2 \times 10^{-5}$ | $1{,}0 \times 10^{-3}$ |
| Jute/PLA + 15% GNPs | 20,0 | 55,2 |
| Jute/PLA + 30% GNPs | 109,0 | 73,4 |

### 3.5 Electromagnetic shielding

Several studies conclude that the EM radiation in contact with electronic equipment can interfere on the signal or damage it. At the same time, constant exposure of EM radiation, in the human body, interferes in the growth of the cells and can cause the formation of cancerous cells [21,22]. Therefore, due the growing use of electronic equipment, it was noted the need to create materials that prevent the passage of EM radiation, namely EMI shield. Thus, the efficiency in the shielding of electromagnetic waves is dependent to the frequency of incident radiation, the environment in which the wave propagates, and the characteristics of the material used as shield. In this way, materials with high electrical conductivity presents better shielding responses by reflection, related with electric field of the EMI wave [23,24]. In this work, the efficiency of the EMI shielding was measured in the frequency range between 0 and 3GHz. It was observed a relation between the addition of GNPs, with the efficiency increase of the shield, as can be observed in Figure 6. For frequencies below 500 MHz, the highest efficiency was 76 dB, for the composite with 30% of GNPs. Additionally, for 3GHz, the highest efficiency was 39 dB, also for the composite with 30% GNPs. This behavior is associated with the electrical conductivity of the material, as was observed before, the increase of GNPs on the composites, increases the electrical conductivity of material [23-25].

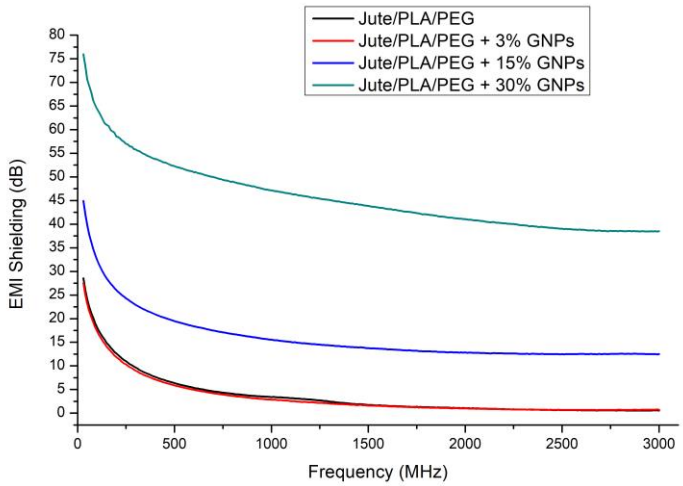


**Figure 6: EMI shielding of composites with different amounts of GNPs.**

### 3.6 Antibacterial tests

Several studies report an antibacterial activity adding GNPs in different polymerics matrix [26-28]. To explain the antibacterial response of GNPs, three mainstream mechanisms are proposed, namely nanoknives, explained by the action of sharp edges that in contact with the bacterial result in a loss membrane integrity and leakage of ribonucleic acid (RNA). Oxidative stress, that can interfere in a bacterial metabolism, disrupting essential cellular functions, causing the cell death. And lastly, wrapping of bacterial membranes, related from the flexible thin film structure of GNPs that can isolate the bacterial from their surrounding environment [29-32]. In the present study, antibacterial tests using the halo method were performed in order to analyze the antibacterial effect of GNPs. The tests were performed using Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) bacteria cultures. Jute fabric was used as control and the jute/PLA/PEG+15%GNPs composite was tested as example. The samples were in contact with the bacteria cultures for 24 hours. After this time, the samples were removed and the antibacterial activity by contact was analyzed.

Figure 7 presents the obtained results for the jute fabric in contact with S. aureus (A) and E. coli (B); bacteria growth after jute removal (B and F); composite in contact with both cultures (C and G) and bacteria cultures after composite removal (D and H). After jute removal (B and F) it is possible to observe that the culture was intact, the bacteria continued to growth. However, when the composite with GNPs was removed (D and H), no bacteria was observed in the sample site exhibiting the antibacterial behavior by contact of the composite with GNPs.

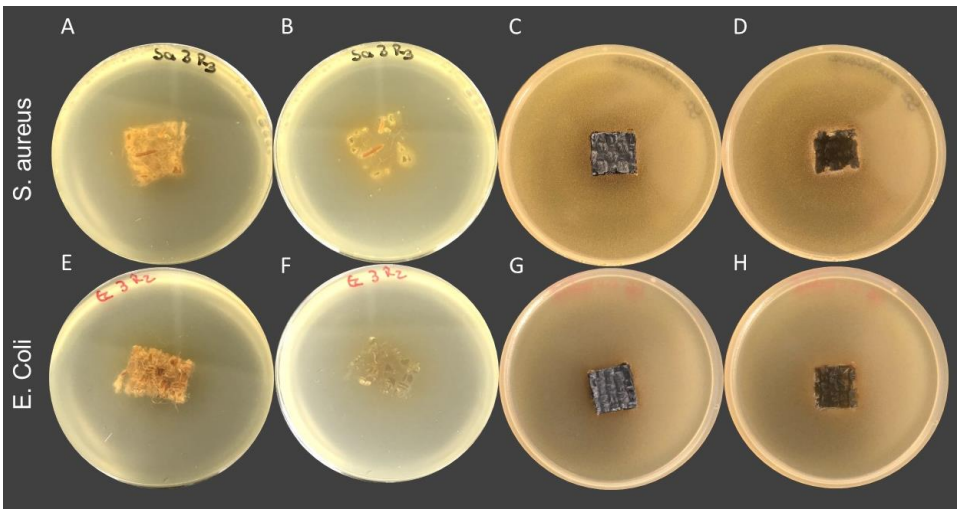


**Figure 7: Antibacterial tests: (A) S. aureus with jute; (B) after jute removal; (C) with Jute/PLA PEG+15% GNPs and (D) after composite removal. From E to H: the same samples under study but using E. coli.**

## 4.0 CONCLUSIONS

In this work, PLA/jute composites reinforced with GNPs were produced. For this purpose, several polymeric formulations were optimized in order to develop PLA films with different amounts of GNPs. These films were used for the jute composites development by compress moulding. Regarding the films, the addition of PEG improved the GNPs dispersion in the matrix, and as consequence was observe an increase on electrical properties. Also, it was observed that with increased percentage of GNPs the conductivity value also increased and values between $2\times10^{-9}$ and 39.6 S/m were achieved. The composites produced were characterized by Raman spectroscopy, TGA and FESEM. FESEM demonstrated that compressing moulding technique was efficient for the polymer impregnation in the jute fabric and the presence of GNPs was also visible. Additionally, the Raman spectroscopy exhibited a homogeneous dispersion and distribution of GNPs

onto the composites by the measurement of different points in the same sample.

Several properties of the composites were studied, namely: mechanical and electrical, EMI shielding and antibacterial. In all the cases, the GNPs addition in different percentages promoted the properties enhancement. For example, when 30% of GNPs was added, there was an increase in the elasticity modulus of 139% when compared to the composite with nanoplatelets. At the same time, the composite reached very high values of electrical conductivity (109 S/m) and electromagnetic shielding efficiency of 39 dB at 3GHz. Regarding the antibacterial behavior, the addition of GNPs inhibited the Staphylococcus aureus and Escherichia coli growth by contact.

Considering the application of the developed systems in the military field, they are very promising solutions for personal protective equipment. However, they could be great solutions for interior parts of military vehicles. Their sustainability, lightness (natural fibres), smart properties (electrical conductivity), EMI shielding effect and antibacterial properties could be the solution for the increasing demands of the automotive area about sustainability, lightweight and active materials.

## REFERENCES


[1] P. Bazylewski and G. Fanchini, "1.13 - Graphene: Properties and Applications," D. L. Andrews, R. H. Lipson, and T. B. T.-C. N. and N. (Second E. Nann, Eds. Oxford: Academic Press, 2019, pp. 287–304.

[2] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat. Publ. Gr.*, pp. 183–191, 2007.

[3] P. Cataldi, A. Athanassiou, and S. I. Bayer, "Graphene Nanoplatelets-Based Advanced Materials and Recent Progress in Sustainable Applications," *Applied Sciences* , vol. 8, no. 9. 2018.

[4] I. Zaman, B. Manshoor, and A. Khalid, "From clay to graphene for polymer nanocomposites — a survey," *J. Polym. Res.*, pp. 1–11, 2014.

[5] A. Elmarakbi and W. L. Azoti, "Novel composite materials for automotive applications: Concepts and challenges for energy-efficient and safe vehicles," in *10th International Conference on Composite Science and Technology*, 2015, no. September, pp. 1–10.

[6] J. F. Pereira *et al.*, "Mechanical Performance of Thermoplastic Ole fi n Composites Reinforced with Coir and Sisal Natural Fibers : In fl uence of Surface Pretreatment," *Polym. Compos.*, pp. 1–10, 2019.

[7] R. Siakeng, M. Jawaid, H. Ariffin, S. M. Sapuan, M. Asim, and N. Saba, "Natural Fiber Reinforced Polylactic Acid Composites : A Review," *Wiley Online Libr.*, pp. 1–18, 2019.

[8] A. K. Yetisen, H. Qu, A. Manbachi, H. Butt, and M. R. Dokmeci, "Nanotechnology in Textiles," *ACS Nano*, pp. 3042–3068, 2016.

[9] S. Mahmud, M. Sultana, M. Pervez, M. Habib, and H.-H. Liu, "Surface Functionalization of 'Rajshahi Silk' Using Green Silver Nanoparticles," *Fibers*, vol. 5, no. 3, p. 35, 2017.

[10] F. Sarker, N. Karim, S. Afroj, V. Koncherry, K. S. Novoselov, and P. Potluri, "High-Performance Graphene-Based Natural Fiber Composites," *ACS Appl. Mater. Interfaces*, vol. 10, pp. 34502–34512, 2018.

[11] J. Lee, P. E. Loya, L. Jun, and E. L. Thimas, "Dynamic mechanical behavior of multilayer graphene via supersonic projectile penetration," *Mater. Sci.*, vol. 346, pp. 1092–1096, 2014.

[12] J. Nine, M. A. Cole, D. N. H. Tran, and D. Losic, "Graphene : a multipurpose material for protective coatings," *J. Mater. Chem. A Mater. energy Sustain.*, vol. 3, pp. 12580–12602, 2015.

[13] Y. T. Yew, A. Ambrosi, and M. Pumera, "Nitroaromatic explosives detection using electrochemically exfoliated graphene," *Nat. Publ. Gr.*, no. April, pp. 1–11, 2016.

[14] A. Omar *et al.*, "Development of Cortisol Immunosensor Based Reduced Graphene Oxide ( rGO ) for Future Application in Monitoring Stress Levels Among Military Personnel," in *Defence S&T Technical Bulletin*, 2017, no. April 2018, pp. 142–149.

[15] M. H. Ervin, L. T. Le, and W. Y. Lee, "Inkjet-Printed Flexible Graphene-Based Supercapacitor," *Electrochim. Acta*, vol. 147, pp. 610–616, 2014.

[16] D. P. Ferreira, J. Cruz, and R. Fangueiro, "Chapter 1 - Surface modification of natural fibers in polymer composites," in *Woodhead Publishing Series in Composites Science and Engineering*, G. Koronis and A. B. T.-G. C. for A. A. Silva, Eds. Woodhead Publishing, 2019, pp. 3–41.

[17] V. Singh, D. Joung, L. Zhai, and S. Das, "Progress in Materials Science Graphene based materials : Past , present and future," *Prog. Mater. Sci.*, vol. 56, no. 8, pp. 1178–1271, 2011.

[18] D. G. Papageorgiou, I. A. Kinloch, and R. J. Young, "Mechanical properties of graphene and graphene-based nanocomposites," *Prog. Mater. Sci.*, vol. 90, pp. 75–127, 2017.

[19] A. B. and Y. K. G. Iftikhar Ahmad, Joseph E. McCarthy, "Development of Graphene Nano-Platelet Based Counter Electrodes for Solar Cells," *Materials (Basel).*, vol. 8, pp. 5953–5973, 2015.

[20] M. Rashad, F. Pan, Z. Yu, M. Asif, H. Lin, and R. Pan, "Investigation on microstructural, mechanical and electrochemical properties of aluminum composites reinforced with graphene nanoplatelets," *Prog. Nat. Sci. Mater. Int.*, vol. 25, no. 5, pp. 460–470, 2015.

[21] M. S. and P. C. Todor Batakliev, Ivanka Petrova-Doycheva, Verislav Angelov, Vladimir Georgiev, Evgeni Ivanov, Rumiana Kotsilkova, Marcello Casa, Claudia Cirillo, Renata Adami, "Effects of Graphene Nanoplatelets and Multiwall Carbon Nanotubes on the Structure and Mechanical Properties of Poly(lactic acid) Composites: A Comparative Study," *Appl. Sci.*, vol. 9, p. 469, 2019.

[22] W. Bauhofer and J. Z. Kovacs, “A review and analysis of electrical percolation in carbon nanotube polymer composites,” *Compos. Sci. Technol.*, vol. 69, no. 10, pp. 1486–1498, 2009.
[23] H. Haris Perlman, “United States Patent,” vol. 2, no. 12, pp. 3–5, 1993.
[24] D. Micheli *et al.*, “Electromagnetic characterization and shielding effectiveness of concrete composite reinforced with carbon nanotubes in the mobile phones frequency band,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 188, pp. 119–129, 2014.
[25] X. Colin Tong, *Advanced materials and design for electromagnetic interference shielding*, 1st ed. New York: CRC Press, 2009.
[26] M. C. Ribadeneura, “EMI shielding composites based on magnetic nanoparticles and nanocarbons,” Universidad Carlos III de Madrid, 2014.
[27] M. C. Ribadeneyra, “EMI shielding composites based on magnetic nanoparticles and nanocarbons,” p. 223, 2014.
[28] S. Sankaran, K. Deshmukh, M. B. Ahamed, and S. K. K. Pasha, “Recent advances in electromagnetic interference shielding properties of metal and carbon fi ller reinforced fl exible polymer composites : A review,” *Composites*, vol. 114, no. April, pp. 49–71, 2018.
[29] R. Scaffaro, L. Botta, A. Maio, M. C. Mistretta, F. Paolo, and L. Mantia, “Effect of Graphene Nanoplatelets on the Physical and Antimicrobial Properties of,” 2016.
[30] A. Fonseca, S. Nejati, M. Elimelech, E. Engineering, N. Haven, and U. States, “Antimicrobial Properties of Graphene Oxide Nanosheets : Why Size Matters,” no. 7, pp. 7226–7236, 2015.
[31] L. Feng and Z. Liu, “Graphene in biomedicine : opportunities and challenges S pecial R eport,” vol. 6, pp. 317–324, 2011.
[32] X. Zou, L. Zhang, Z. Wang, and Y. Luo, “Mechanisms of the Antimicrobial Activities of Graphene Materials,” 2016.
[33] O. Akhavan and E. Ghaderi, “Toxicity of Graphene and Graphene Oxide Nanowalls Against Bacteria,” vol. 4, no. 10, pp. 5731–5736, 2010.
[34] S. C. Smith and D. F. Rodrigues, “Carbon-based nanomaterials for removal of chemical and biological contaminants from water : A review of mechanisms and applications,” vol. 1, 2015.
[35] I. E. Mej, C. M. Santos, and D. F. Rodrigues, “Nanoscale Toxicity of a polymer – graphene oxide composite against bacterial planktonic,” pp. 4746–4756, 2012.