Integrated Master in Chemical Engineering

# *Development of epoxy-based nanocomposites for multifunctional applications*

## A Master's Dissertation

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*Não tenhas pressa. Mas não percas tempo*

*José Saramago*

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# Resumo

Neste trabalho, o principal objetivo foi desenvolver nanocompósitos à base de resina epóxida contendo nanotubos de carbono (MWCNT) e/ou grafite exfoliada (GnP) de modo a conseguir ter efeitos sinérgicos obtendo simultaneamente boas propriedades mecânicas e elétricas para produzir compósitos para aplicações multifuncionais. Os nanocompósitos foram preparados através de uma máquina de rolos de modo a assegurar uma boa dispersão. As propriedades elétricas e mecânicas dos nanocompósitos foram avaliadas com o objetivo de estudar o efeito destas cargas nas propriedades do polímero, bem como o efeito sinérgico proveniente da sua combinação. A dispersão obtida durante a mistura foi analisada por microscopia ótica e por TEM, e a processabilidade dos materiais foi avaliada por reologia, através de varrimentos de taxas de corte entre 0,01 e 100 $s^{-1}$. Adicionalmente, investigou-se a relação entre o nível de dispersão alcançado e a melhoria nas propriedades elétricas e mecânicas.

A incorporação de MWCNT na resina epóxi induziu um aumento significativo na condutividade elétrica. Para 0,250% (m/m) de MWCNT/epóxi, a condutividade elétrica é $10^{-3}$ $S.m^{-1}$, correspondendo a um material semicondutor na gama de proteção de interferência eletromagnética. Nanocompósitos de epóxi/GnP, não apresentaram melhorias significativas na condutividade elétrica, apresentando um ligeiro aumento em comparação com a de epóxi. Com 5% (m/m) de GnP, observou-se um aumento de apenas 4 ordens de grandeza (de $10^{-11}$ $S.m^{-1}$ a $10^{-7}$ $S.m^{-1}$), não se tendo verificado formação de uma rede condutora. Quanto às propriedades mecânicas, obtiveram-se os melhores resultados para 0,06% (m/m) de MWCNT, mostrando um aumento de 18% no módulo, 36% na resistência à rutura e 38% no alongamento à rutura. Para valores superiores de incorporação de MWCNT, os resultados começam a degradar-se devido a problemas de processamento. Por outro lado, a adição de GnP tornou o material menos resistente e mais frágil. A diferença nestes resultados deve-se à geometria das cargas (1D no caso de MWCNTs e 2D no caso de GnPs) que leva a diferentes níveis de dispersão. Os nanocompósitos de epóxi/MWCNT exibem maiores níveis de dispersão que os nanocompósitos epóxi/GnP, tendo o primeiro menor numero de aglomerados visíveis. O processamento de nanocompósitos com MWCNT apresenta algumas limitações devido à viscosidade destes. No entanto com a combinação de MWCNT com GnP na resina epóxi, a viscosidade da suspensão diminuiu, sem existir perda de propriedades. Nos nanocompósitos híbridos epóxi/MWCNT/GnP/, a rede condutora foi formada a uma concentração inferior do que a dos nanocompósitos de somente MWCNT e GnP. Com apenas 0,094% (m/m) de MWCNT combinado com 0,031% (m/m) de GnP, a condutividade elétrica é de $10^{-4}$ $S.m^{-1}$ enquanto que com 0,125% (m/m) de MWCNT a condutividade elétrica é de $10^{-5}$ $S.m^{-1}$. No entanto, relativamente às propriedades mecânicas, para a concentração estudada (0,250% (m/m)), nenhum benefício na combinação das cargas foi observado.

**Palavras Chave:** Nanotubos de carbono, grafite exfoliada, nanocompósitos, dispersão, propriedades elétricas, propriedades mecânicas, efeitos sinergéticos

# Abstract

In this work, the main objective was to develop nanocomposites based on epoxy resin containing carbon nanotubes (MWCNT) and/or exfoliated graphite (GnP) in order to achieve synergistic effects while obtaining good mechanical and electrical properties to produce nanocomposites for multifunctional applications. The nanocomposites were prepared a three-roll machine to improve dispersion. The electrical and mechanical properties of the manufactured nanocomposites were assessed to see the effect of the addition of these fillers in the properties of the polymer, as well as the synergetic effect from their combination. The dispersion was analyzed by optical microscopy and TEM, and the processability of the system was evaluated by rheology. In addition, was investigated the relation between the level of dispersion attained and the enhancement in the electrical and mechanical properties.

The incorporation of MWCNT to the epoxy resin induced a significant increase in electrical conductivity. For 0.250 wt.% MWCNT/epoxy, the electrical conductivity is $10^{-3}$ S.m$^{-1}$, corresponding to a semiconductor material in the EMI shielding range. Epoxy/GnP nanocomposites did not show significant improvements in the electrical conductivity, showing a slight increase in comparison with epoxy. With 5 wt.% of GnP, an increase of only 4 orders of magnitude (from $10^{-11}$ S.m$^{-1}$ to $10^{-7}$ S.m$^{-1}$) was observed, and no conducting network was formed. As for the mechanical properties, the best results were obtained for 0.06 wt.% MWCNT, showing an increase of 18% in the modulus, 36% in the tensile strength and 38% in the elongation at break. For higher values of incorporation of MWCNT, the results begin to degrade due to processing problems. On the other hand, the addition of GnP made the material less resistance and more brittle. The difference in these results is due to the geometry of the fillers (1D in the case of MWCNTs and 2D in the case of GnPs) that leads to different levels of dispersion. MWCNT/epoxy nanocomposites exhibit higher dispersion levels than GnP/epoxy nanocomposites, having the first one an inferior number of agglomerates. The processability of nanocomposites with MWCNT presents some limitations due to their high viscosity, however with the combination of MWCNT with GnP in the epoxy resin, the viscosity of the suspension decreased without loss of properties. In the MWCNT/GnP/epoxy hybrid nanocomposites, the conductive network was formed at a lower concentration than the nanocomposites of only MWCNT and GnP. With only 0.094 wt.% MWCNT combined with 0.031 wt.% GnP the electrical conductivity is $10^{-4}$ S.m$^{-1}$ whereas with only 0.125 wt.% MWCNT the electrical conductivity is $10^{-5}$ S.m$^{-1}$. However, regarding the mechanical properties, for the studied concentration (0.250 wt.%), no benefit in the combination of the nanofillers was observed.

**Keywords:** Carbon nanotubes, exfoliated graphite, nanocomposites, dispersion, electrical properties, mechanical properties, synergistic effects.

# Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.

Porto, July 2017

Magda Dias da Silva

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# Notation and Glossary

| | | |
|---|---|---|
| $A$ | Area | $m^2$ |
| $d$ | Diameter | m |
| $E$ | Young modulus | MPa |
| $I$ | Current | A |
| $K$ | Thermal conductivity | $W.m^{-1}.K^{-1}$ |
| $L$ | Length | m |
| $R$ | Resistance | Ω |
| $TS$ | Tensile strength | MPa |
| $V$ | Voltage | V |

## *Greek letters*

| | | |
|---|---|---|
| $\sigma$' | Electrical conductivity | $S.m^{-1}$ |
| $\rho$' | Electrical threshold | wt.% |
| $\rho$ | Resistivity | Ω·m |
| $\dot{\gamma}$ | Shear rate | $s^{-1}$ |
| $\sigma$ | Tensile stress | MPa |
| $\eta$ | Viscosity | Pa.s |

## *List of acronyms*

| | |
|---|---|
| CB | Carbon black |
| CF | Carbon fibers |
| CFRP | Carbon fibers reinforced polymers |
| CNT | Carbon nanotube |
| DGEBA | Diglycidyl ether of bisphenol-A |
| E/CF | Epoxy/carbon fibers |
| GnP | Graphene nanoplate |
| GO | Graphene oxide |
| MWCNTs | Multi-wall carbon nanotubes |
| OM | Optical microscopy |
| SWCNTs | Single-wall carbon nanotubes |
| TEM | Transmission electron microscope |
| TRM | Three roll milling |

# 1 Introduction

In the last few decades, there has been an increasing interest in science and technology at the nanometer scale, and now these fields are getting more relevant in aerospace and space applications [1, 2]. Nanomaterials, defined as materials with at least one dimension smaller than 100 nm, are widely used in novel technological applications due to their remarkable properties in comparison with coarser fillers [3, 4]. Polymeric nanocomposites result from combination of two or more materials to form a single one with distinct phases at the nanometric scale.

The incorporation of nanofillers into polymers is a common practice that allows the design and development of new materials with tailored properties [2, 5]. At first, nanocomposites based on materials available on the nature were developed, but these presented poor electrical, mechanical and thermal conductivity. Therefore, carbon-based nanofillers, such as carbon black (CB), carbon nanotubes (CNT), graphene nanoplates (GnP) and graphene were introduced [2]. GnP and CNTs are promising materials since they present high aspect ratio due to their nanometric size, leading to better structural and functional properties [4].

However, from a practical point of view, the incorporation of carbon nanofillers into polymer matrices with a homogeneous dispersion and a good interfacial interaction is a challenge due to the strong van der walls forces and lack of chemical functionalities at the surface [6]. To obtain a homogeneous dispersion of carbon nanoparticles into polymer matrix, a variety of strategies has been applied. Nevertheless, it is still an important subject to study once the final properties of the developed nanocomposites are strongly dependent with the dispersion level and interface attained.  It is known that depending on the type of the carbon nanofiller, different dispersion and performance levels can be obtained, thus the potential of the combination of GnP and MWCNT, is being investigated.

## 1.1 Presentation of the work

The main goal of this work is to develop epoxy-based nanocomposites containing CNTs and/or GnPs for multifunctional applications.

To successful achieve the objectives of this work it was necessary to elaborate a strategic plan that include the following steps:

- Assessment of the dispersion level attained during mixing at different length scales by either optical microscopy (OM) and transmission electron microscope (TEM);
- Characterization of nanocomposites regarding their DC electrical properties;

- Mechanical characterization of the nanocomposites through the performance of tensile tests.

## 1.2 Presentation of the company

INEGI was founded in 1986 in the Mechanical Engineering and Industrial Engineering Department in FEUP. Nowadays, it has its own building, located in Porto and has a total of 250 collaborators. Is an institute of new technologies that aims to contribute to industrial development and economy, through innovation based on scientific and technologic knowledge. This institute has more than 25 years of experience in projects with national and international companies.

UMEC is INEGI's Composite Materials and Structures Research Group, in which this project was developed. It performs Research & Development as well as Technology Transfer in all fields related to Composites, including materials development and modelling, process modelling and optimization to prototyping and pre-series production. UMEC has been involved in R&D projects commissioned by private and state-owned companies, public services and European programs. in fact, the European Aerospace Industry is the main client and partner of INEGI's R&D projects.

A significant part of INEGI-UMEC activities has been focused in the development of the basic materials to be used in the development of high performance composite structures, the development of associated manufacturing processes, and the testing and validation of such materials, processes and structures.

## 1.3 Contributions of the work

The development of carbon -fiber reinforced polymer composites with increased functionality (mechanical, thermal and electrical properties) is desired. Thus, one of the approaches is to incorporate carbon nanofillers into polymeric matrix. This project enabled to assess the possibility of combining MWCNTs with GnPs to try to take advantage of their individual properties, reducing the limitations in the processing.

## 1.4 Outline

This dissertation is divided in five chapters. In the first chapter, the main objectives and the strategy used to develop this work will be introduced. The second chapter is dedicated to the state of the art of polymer-based nanocomposites, with special focus on the influence of conductive carbon fillers on the thermal, electrical and mechanical properties of the polymer. In chapter three, the materials selected for the preparation of nanocomposites are described, as well as a brief explication of the operation system of each equipment and the experimental procedure. In chapter four, the most important results are presented and discussed. The conclusion of the dissertation, and proposed future work are presented in chapter five.

# 2 Context and State of Art

## 2.1 Nanocomposites

Polymer nanocomposites have caught the attention of industrial and scientific communities due to their huge potential for developing novel, smart and high-performance materials. Ever since the discovery of fullerenes ($C_{60}$), an interest in the properties and applications of carbon allotropes as fillers in polymeric composites has emerged. These exhibit a high surface-volume ratio, unusual mechanical, thermal, and electrical properties [4, 7].

## 2.2 Carbon nanoparticles for multifunctional composites

Carbon is a very interesting element in the Periodic Table and forms many allotropes, such as diamond (3D), graphite (3D), graphene (2D), CNTs (1D), and buckyballs (0D). The representation of these carbon allotropes is presented in Figure 1.

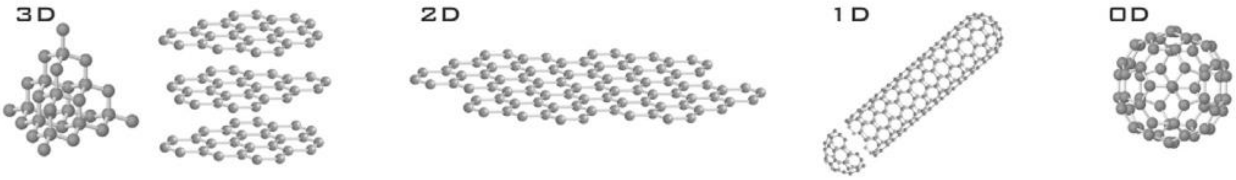


*Figure 1 - Crystal structures of the different allotropes of carbon. (Left to right) Three-dimensional diamond and graphite (3D); two-dimensional graphene (2D); one-dimensional nanotubes (1D); and zero-dimensional buckyballs (0D)[8].*

### 2.2.1 Carbon nanotubes (CNTs)

CNTs are constituted by cylindric layers of graphene, separated by only 0.34 nm due to the Van der Waal forces. CNTs exhibit high Young's modulus (1 TPa), high tensile strength (20–100 GPa), extremely low electrical resistivity ($10^{-5}$ Ω.cm), and high thermal conductivity between 650 and 10000 $W.m^{-1}k^{-1}$ [1, 2, 9-11].

There are two main types of CNTs, single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). These differ in the arrangement of the graphene, i.e. whereas SWCNTs is constituted by only one layer of graphene, MWCNTs can have several layers, as shown in Figure 2. The SWCNTs are stronger and their diameters are few nanometers. The MWCNTs diameters are 10–200 nanometers.

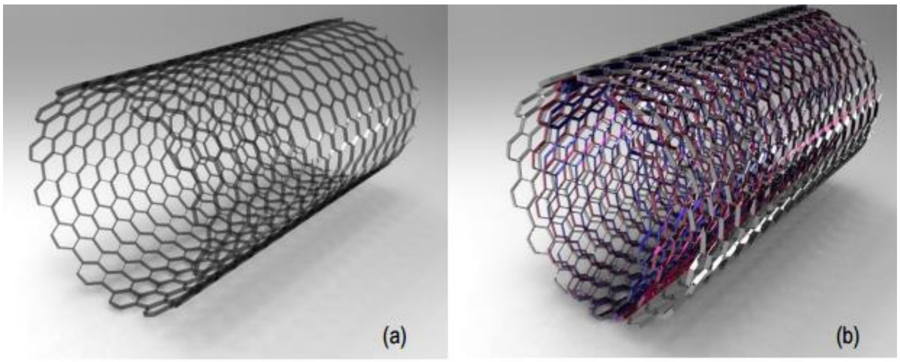


*Figure 2 -Structural forms of CNTs: a) SWNTs and b) MWNTs [12].*

The extremely high cost of CNTs is a major limitation, and for this reason other carbon nanofillers have been replacing them in many applications, like GnPs and graphene which have comparable properties with a more accessible cost [4, 13, 14].

### 2.2.2 Graphene nanoplates (GnP)

GnP consists in few layers of graphene stacked and connected by Van der Wall forces usually with 1-15 nm thickness (Figure 3). It is an anisotropic material, that due to the nature of its chemical bonds and to its small spacing between layers - 3,35 Å - doesn't have affinity with hydrophilic and hydrophobic polymers [15].

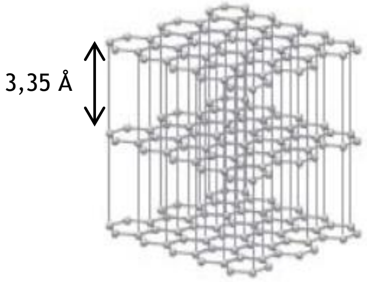


*Figure 3 – GnP [1].*

In comparison with other nanoparticles, GnP is a promising alternative for improving the properties of composites and decreasing the cost associated with other nanofillers. GnP based materials may offer certain property improvements that CNTs cannot provide when dispersed in a polymer composite, such as improving gas permeation resistance and thermal conductivity of the composite, due to its two-dimensional platelet geometry [15]. GnPs have already shown promising results in the formation of thermal interface materials and electrically conducting polymers [16].

Fabrication of epoxy/GnP composites typically involves a multi-step process starting from the production of GnP suspensions in various solvents followed by mixing with polymers and solvents evaporation.

Both CNT and GnP have demonstrated remarkable mechanical, electrical, and thermal properties and have enormous potential as nanofillers. However, they tend to entangle and agglomerate during processing of nanocomposites which is a problem. The properties of CNT and GnP are compared in Table 1.

*Table 1 – Comparison of graphene, CNT and GnP properties [2, 17].*

| Material | Tensile strength (MPa) | Thermal conductivity ($W.m^{-1}k^{-1}$) at room temperature | Electrical conductivity ($S.m^{-1}$) |
|---|---|---|---|
| CNT | $60 \times 10^3$ – $150 \times 10^3$ | $3.50 \times 10^3$ | $3.00 \times 10^3$– $4.00 \times 10^3$ |
| GnP | $10 \times 10^3$ – $20 \times 10^3$ | $3.00 \times 10^3$ | $3.00 \times 10^3$ |

### 2.2.3 Hybrid nanocomposites based on CNTs and GnP

Hybrid nanocomposites have been widely developed where two or more nanofillers are used for improving composite properties by combining the advantages of each filler [18-22].

Hybrid nanocomposites containing simultaneously CNTs and GnP can improve performance of polymer nanocomposites. GnPs are expected to increase thermal conductivity by providing 2D path for phonon transmission, while CNTs are expected to increase electrical conductivity of the polymer material [23]. Moreover, significant improvements in the mechanical properties of CNTs/GnPs hybrid nanocomposites have been recently reported by Ashad, *et al.* [20] in pure magnesium. These nanocomposites exhibited improvement in elastic modulus (E) (+17%), and yield strength ($\boldsymbol{\sigma}$) (+15%).

The mechanism of the synergetic effect is not totally understood, Liu *et al.* [23] stated that the synergetic effect in the thermal conductivity of epoxy composites with a hybrid of CNTs and GnPs has its origins in bridging the planar nanoplatelets by the flexible CNT rods, resulting in a 3D network.

Moreover, this strategy can also reduce the limitation associated with manufacture process of CNTs nanocomposites. When GnP is combined with CNTs, less concentration of CNTs is required and, thus the viscosity of the system will be lower than the viscosity of the nanocomposite with only CNTs (at same filler content), leading to a better processability.

## 2.3 Dispersion in nanocomposites

One of the challenges in processing carbon nanofillers suspensions is achieving good quality dispersion into the polymeric matrix, due to interparticular Van der Walls interactions and lack of chemical functionalities at the surface [23]. For GnP additional interplanar π-π interactions make it even more challenging to disperse these nanofillers in the matrices [24]. When a nanocomposite is produced, one essential goal is to get a good dispersion of the nanofiller, because the properties of the composites are largely influenced by the level of dispersion attained. Without an appropriate dispersion, fillers act as defect points, limiting the mechanical performance of the nanocomposite.

Several approaches are used to overcome limitations associated with dispersion known as mechanical methods, as ultrasonication and three-roll mill. These involve the separation of nanofillers from each other, however higher frequencies/shear mixing can fragment them, and decreasing their aspect ratio [25].

To improve the interface, non-covalent and covalent strategies are applied, for example, the addition of surfactants, and functionalization of graphene and CNTs [26-29]. The different ways that exist of functionalization have a big impact in the properties of the nanocomposite. In the last few years, the non-covalent surface treatment by surfactants has been widely used. In a covalent functionalization, there is a structural change that involves a hybridization of carbon atoms from $sp^2$ to $sp^3$, leading to a loss of the electrical properties, whereas in a non-covalent functionalization there is no structural change, being particularly attractive since it has the possibility of adsorbing various groups on the nanofillers surface without disturbing the π system of the graphene sheets [6, 10, 30].

There are several studies about the influence of dispersion of nanofillers on mechanical, thermal and electrical properties in epoxy nanocomposites [6, 31-33]. Kumar *et al.* [6] applied simultaneously ultrasonic waves and shear force generated by axial flow impeller and achieved cluster free uniform dispersion of MWCNTs in epoxy matrix, which lead to enhanced tensile strength by 35%, toughness by 53% and storage modulus by 35% on loading of 0.75 wt.% of MWCNTs in epoxy. Lachman *et al.*[33] studied the relationship between CNT/epoxy interfacial molecular structures and found that its toughness increases with the interfacial adhesion. Guadagno *et al.*[32] reported different experimental procedures (mechanical mixing, high energy ball milling and ultrasonication) for incorporation of MWCNTs in epoxy resin where best results were obtained by using sonication for 20 min [15].

The dispersion assessment of carbon nanoparticles at different length scales is an important task and cannot be done by naked eye, it is necessary to use optical microscopy (OM) in transmittance mode or transmission electron microscope (TEM).

### 2.3.1 Functionalization of carbon nanoparticles

Functionalization of carbon nanoparticles is a prerequisite to take advantage of most of the properties enabling facile fabrication of novel nanomaterials. Most of the functionalization approaches developed can be categorized into two categories: covalent and non-covalent functionalization [34].

### Covalent functionalization

Covalent functionalization can be held resourcing to oxidant agents, by halogenation (mostly with Cl or Br), or by adding radicals to GnPs and CNTs. In the case of SWCNTs as they only have a carbon layer, surface modifications have a strong impact on their properties. In the case of MWCNTs, the modification does not affect the inner layers, which remain intact.

Recently, there has been a big progress in the chemical functionalization of CNTs for various applications. Several functional groups have been successfully attached to the nanotubes, making them very promising for different applications in high-performance composites. The chemical functionalization of nanotubes has been performed by attaching chemical groups to the nanotube through chemical covalent bonding. Among the various groups used for functionalizing nanotubes, the carboxylic acid group (-COOH) is considered the best chemical group for such purpose, because the carbon atom is covalently bonded to the tube and the –OH group can be exchanged by other groups using standard chemical reactions allowing one to attach more complex molecules such as amino acids [35].

### Non-covalent functionalization

Non-covalent functionalization is an alternative method for tuning the interfacial properties of nanoparticles. Besides polymers, surfactants have also been employed to functionalize CNTs or graphene. Several studies have contributed to studying the effects of surfactant on dispersibility in the polymer. The surfactants studied previously include polyoxyethylene, Tergitol NP-7, Triton X-100 among others. The physical adsorption of surfactant on the CNT surface lowered the surface tension of CNT, preventing effectively the formation of aggregates. The efficiency of this method depends strongly on the properties of surfactants, and polymer matrix [28, 34].This modification method can maximally preserve graphene’s natural structure, however, the interactions between functionalities and graphene surface are relatively weak.

Surfactants are amphiphilic organic compounds, which means that they have a hydrophobic (polar) group and a (nonpolar) hydrophilic group. Due to this feature, they are ideal for interfacing hydrophilic and hydrophobic structures. Several studies have shown that this non-destructive method normally involves simple procedures, improves stability and allows the dispersion of CNT in different aqueous or organic solvents depending on the concentration and nature of the surfactant. The disadvantage is that large concentrations are required to promote good dispersion, which will influence the electrical properties negatively.

In Table 2 a comparison of various techniques for carbon nanofillers dispersion in polymer composites is presented.

*Table 2 - Comparison of various techniques for carbon nanofillers dispersion and improving interfase in polymer composites [34].*

| Techniques | Factor | | | | | | |
|---|---|---|---|---|---|---|---|
| | Damage to the fillers | Suitable polymer matrix | Governing factors | Availability | Easy to use | Interaction with polymer matrix | Re-agglomerations of fillers in matrix |
| Ultrasonication | Yes | Soluble polymers, low viscosity polymer | Sonication time | Commonly use in lab, easy to operate and clean | - | - | - |
| Three roll mill | No | Liquid polymer | Rotation speed, distance between rolls | Hard to clean after use | - | - | - |
| Covalent functionalization | Yes | - | - | - | No | Strong | Yes |
| Non-covalent functionalization | No | - | - | - | Yes | Weak | No |

The mechanisms of dispersion of polymeric nanocomposites with CNTs and GnP is well documented and understood in the literature.

### 2.3.2 Dispersion of CNT

The dispersion process of MWCNT agglomerates can occur by two different mechanisms: through rupture and/or through erosion (Figure 4). In rupture mechanisms, agglomerates are successively broken down into smaller aggregates, resulting in undesired breakage of tubes (mainly on defect locations) reducing their aspect ratio. This process results from a balance between hydrodynamic stresses and agglomerate cohesion. In erosion mechanism, the size of agglomerates is reduced in comparatively longer time and dispersion is driven mainly by melt infiltration. This mechanism leads to well infiltrated agglomerates and is not expected to cause damage to the tubes [36].

Both mechanisms of dispersion should exist during any melt mixing operation and all agglomerates are subjected to simultaneous dispersion by erosion and rupture. Nevertheless, depending on compounding conditions, one mechanism could dominate the other.

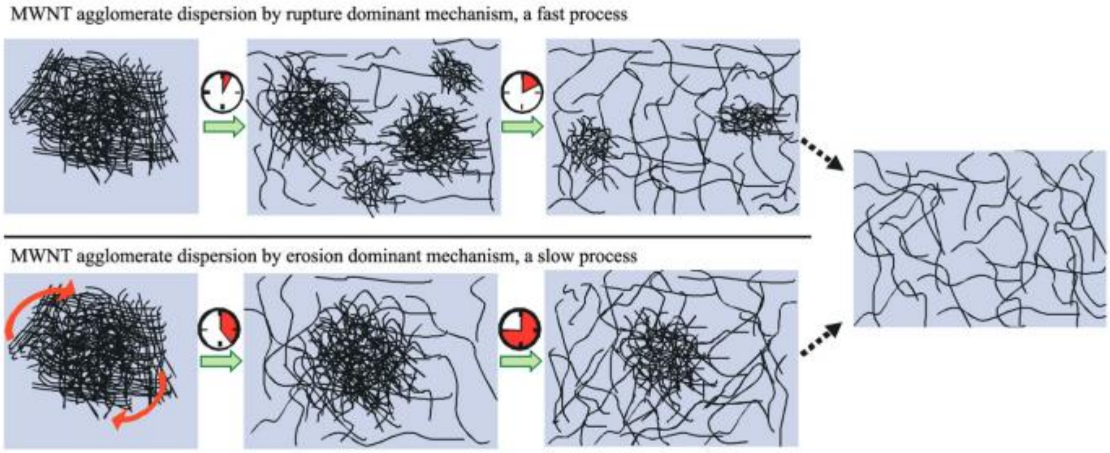


*Figure 4 - Schematic descriptions of MWNT agglomerate dispersion mechanisms [36].*

Dispersion contributes significantly to the final properties of the material and is also difficult to control. For dispersion to occur, the hydrodynamic forces must be greater than the cohesive forces between the agglomerates [37].

### 2.3.3 Dispersion of GnP

The challenge in the dispersion of GnP in different polymer systems led to the development of new forms of preparation and processing nanocomposites with GnP. These can be divided into two groups, those that use solvents, for instance *in situ* polymerization, where the graphite is added to a solution of monomers, occurring polymerization by the action of temperature and those that use physical means in their dispersion for example melt blending. It is generally found that nanocomposites made by *in situ* polymerization methods have better mechanical properties compared to the melt blending processes as they develop a better dispersion, prevention of agglomeration and stronger interactions between the reinforcement and the polymer, but requires the use of hazardous organic solvents for the dissolution of most synthetic polymers [38, 39]. On the other hand, melt blending is compatible with existing industrial procedures, providing the hydrodynamic stresses and residence times necessary to exfoliate and disperse GNP.

Graphite has three general states of platelet dispersion, as shown in Figure 5, (a) phase separated, (b) intercalated, (c) exfoliated. The latter is the most desired because it results in particles with higher area/volume ratio [15].

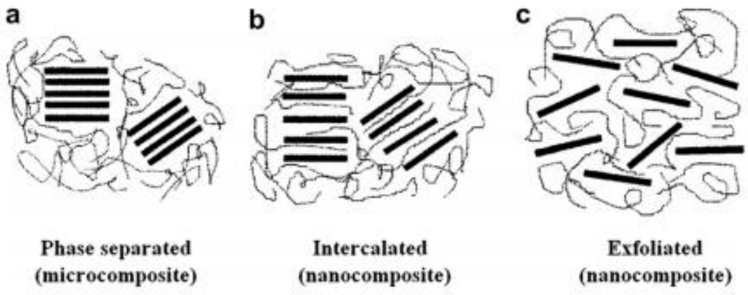


*Figure 5 - Three general states of platelet dispersion [15] .*

Furthermore, it seems that the addition of CNTs significantly influences GnPs dispersion in the matrix. The fracture surface of epoxy/CNTs/GnPs hybrid nanocomposites indicates that the CNTs with GnPs form 3D hybrid structure which inhibits face to face aggregation of GnPs. This will increase the contact surface area between CNTs/GnPs structures and the epoxy matrix, which is beneficial for their mechanical properties [40]. Figure 6 shows a schematic representation of the reinforcement dispersion in the epoxy composites.

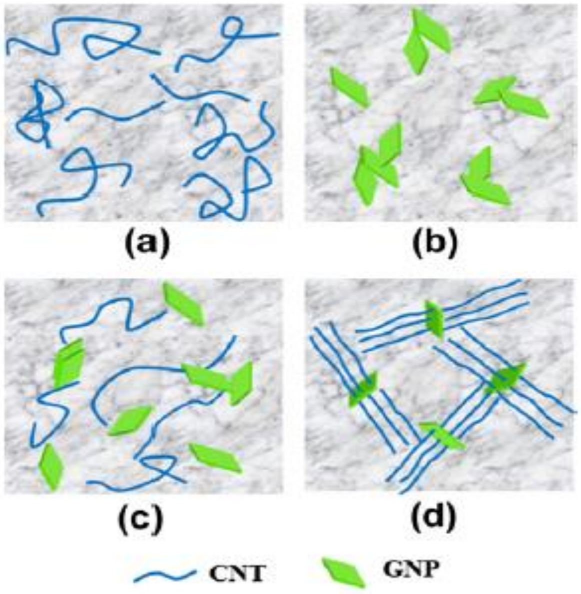


*Figure 6 - Schematic images of the reinforcement dispersion in the epoxy composites (a) CNTs; (b) GNPs, (c) CNT + GNP mixture, (d) CNT/GNP hybrids [41].*

## 2.4 Effects of carbon nanofillers on nanocomposite properties

There are several studies about the enhancements of the mechanical, thermal and electrical properties of composites after the addition of graphene, GnP, CNTs or combinations of them.

### 2.4.1 Thermal Properties

Tao *et al.* [42] presented that graphene was the best material to enhance the thermal performance due to its lamellar structure. A study was made evaluating the differences between the utilization of graphene and the utilization of exfoliated graphite in paraffin/graphene composites and looking at the results it is possible to conclude that there is no significance difference between the materials used [43]. The results are shown in Table 3.

*Table 3 – Thermal conductivity of graphene and GnP in paraffin based composites adapted from [43].*

| wt. % | 0.2 | 0.5 | 1 | 1.5 | 2 |
|---|---|---|---|---|---|
| Graphene | 0.33 W.m$^{-1}$K$^{-1}$ | 0.35 W.m$^{-1}$K$^{-1}$ | 0.37 W.m$^{-1}$K$^{-1}$ | 0.41 W.m$^{-1}$K$^{-1}$ | 0.46 W.m$^{-1}$K$^{-1}$ |
| Exfoliated graphite | 0.31 W.m$^{-1}$K$^{-1}$ | 0.32 W.m$^{-1}$K$^{-1}$ | 0.34 W.m$^{-1}$K$^{-1}$ | 0.38 W.m$^{-1}$K$^{-1}$ | 0.41 W.m$^{-1}$K$^{-1}$ |

Recently, Liu *et al.* [43] reached the conclusion that when GnP is used, the thermal conductivity and the flexural modulus are enhanced, and the greater the amount of GnP, the better these properties are.

One of the advantageous of using GnP is the possibility to use higher concentrations because it does not add problems in the viscosity of the nanocomposites, so researchers analyzed wide ranges of concentration, between 0.1 and 20 wt.% GnP. It was obtained by Li *et al.* [44] a nanocomposite with thermal conductivity of 16.75 W.m$^{-1}$K$^{-1}$, that increased to 35 W.m$^{-1}$K$^{-1}$ at 90°C by exploiting vertically stacked multilayer graphene in epoxy resins with a content of 11.8 wt.% GnP. Debelak *et al.* [14] observed that polymers filled with 20 wt.% GnP in epoxy have seen a significant improvement in the thermal conductivity, increasing from 0.2 to 5 W.m$^{-1}$K$^{-1}$.

With a lower content, 2 wt.% GnP, Chandrasekaran *et al.* [16] obtained a thermal conductivity value of 0.210 W.m$^{-1}$K$^{-1}$ at room temperature. It is important to use low filler content, because it allows to keep the glass transition temperature, the viscosity and the curing parameters almost unchanged [45].

The thermal properties tend to increase with increasing size of the particle, increasing GnP load content and temperature [43, 46].

### 2.4.2 Electrical Properties

The electrical properties of CNTs and GnP can make an insulating material into an electrical conductive material due to the formation of a continuous conducting network [1]. For that, it is necessary to add a critical percentage of filler to the matrix, known as threshold. Above this value, there is a conductor path in the matrix and below this amount there is no percolation.

The electric conductivity depends strongly on the processing and dispersion of the filler in the matrix. Pegel *et al.* [47] concluded that the agglomeration of CNTs can be advantageous to the electrical property although other authors [48, 49] state that a good dispersion leads to better electrical conductivity. Different studies show that for the same material, the threshold can change according to its dispersion or functionalization of the filler [15].

Nanocomposites containing CNTs exhibit higher electrical conductivity at lower concentrations than GnP. In Table 4 it is compared the results of GnP and CNT, the first one had an increase of 7 orders of magnitude relatively to neat epoxy and the second one had an increase of 9 orders of magnitude, showing that both are excellent conductive fillers for epoxy, although the latest has better results [18, 50].

*Table 4 – Electrical Properties of GnP and CNT [50].*

| Carbon nanoparticle | Preparation method | Electrical Property |
|---|---|---|
| GnP | Sonication in acetone | $\rho_{\sigma}$=1.0 wt.%<br>$\sigma$=$10^{-5}$ S.cm$^{-1}$ |
| CNTs | | $\rho_{\sigma}$=0.25–0.3 wt.%<br>$\sigma$ =$10^{-3}$ S.cm$^{-1}$ |

In 2007, Debelak *et al.* [14] analyzed the size of the particle and the load levels from 0.1wt.% to 2 wt.% of GnP using Epon 862 as resin. The electric resistivity decreased with the increase of concentration of GnP and the size of the particle. This is explained because larger flakes of GnP have a better ability to form a conducting material due to their higher aspect ratios.

Recent publications [14] that have studied GnP filled polymers made by *in situ* polymerization, reported percolation thresholds of electrical conductivities from 0.75 to 2 wt.% and maximum electrical conductivities between $10^{-4}$ S.cm$^{-1}$ and 0.5 S.cm$^{-1}$. In the case of using TRM technology to produce GnP/epoxy resins it was obtained a relatively low percolation threshold (0.52 wt.%) combined with an electrical conductivity of $10^{-2}$ S.m$^{-1}$ at 3 wt.% GnP [49].

### 2.4.3 Mechanical Properties

Mechanical properties depend on the interface interaction between the nanofiller and the polymeric matrix, therefore a good interaction is required. In the literature, the best results in mechanical properties were obtained using GO in epoxy matrixes.

According to Diu [51], graphene and GO are effective fillers for epoxy-based composites, and have found successful usage in epoxy/carbon fibers (E/CF) composites to enhance the interfacial and/or in-plane mechanical properties. Wan et *al.* [52, 53] performed studies about epoxy composites filled with both GO and diglycidyl ether of bisphenol-A functionalized GO (DGEBA–f–GO) with different filler loading levels to investigate the correlations between surface modification, morphology, dispersion/exfoliation and interfacial interaction of sheets and the corresponding mechanical properties of the composites. Covalent functionalization of GO by grafting DGEBA chains was carried out and the DGEBA–f–GO sheets exhibit well exfoliated and highly dispersed states on the surface. They could see that the surface functionalization of DGEBA layer effectively improve the compatibility and dispersion of GO sheets in epoxy matrix. Furthermore, the tensile test indicated that the DGEBA–f–GO/epoxy composites have higher tensile modulus and strength than either the neat epoxy or the GO/epoxy composites. These results are present in Table 5.

*Table 5 – Mechanical Properties of GO and DGEBA-f-GO.*

| Carbon nanoparticle | Resin System | Preparation method | Curing parameters | Mechanical Properties | Ref. |
|---|---|---|---|---|---|
| **GO (0,10 – 0,50 wt.%)** | DGEBA<br>4 - methylhexahydrophtalic anhyfride + N,N – Benzyldimethylamide | Sonication in acetone + Ball mill | 90 °C, 30 min. + 120°C, 1h + 140 °C, 30 min. + 160°C, 2h | E ↑ 7% (0,5 wt.%)<br>Tensile strength ↑ 35% (0,1 wt.%)<br>$\varepsilon_b$ ↑ 12% (0,1 wt. %)<br>$k_{Ic}$ ↑ 26% (0,25 wt.%)<br>Tg ↑ 2°C (0,25 - 0,50 wt.%) | [52, 53] |
| **DGEBA – f-GO**<br>**(0,10 -0,50 wt.%)** | | | | **E ↑ 13% (0,25 wt.%)**<br>**Tensile strength ↑ 79% (0,1 wt.%)**<br>**$\varepsilon_b$ ↑ 72% (0,1 wt. %)**<br>**$k_{Ic}$ ↑ 41% (0,25 wt.%)**<br>**Tg ↑ 4°C (0,50 wt.%)** | |

On the other hand, the addition of GnP in fiber reinforced composites attracted some interest especially in terms of mechanical and thermal properties. A study performed by Yasmin, A. *et al*. [54] in 2004, using DGEBA as a resin system and GnP between 2,5 wt% and 5 wt% shown increase in tensile strength (↑21%) , elastic modulus (↑25%), storage modulus and Tg, and the CTE decreased to almost half of its original value with the increased of GnP.

To understand the role of CNTs in mechanical properties of carbon fibers composites, tests were carried on by Zhau *et al*. [55] in 2017 where CNTs were introduced in the matrix .The modulus of virgin CFs (without surface treatment), CFs and CF-CNTs are 281.5 GPa, 273.9 GPa and 264.6 GPa respectively. In this investigation, it was possible to obtain 10.22 and 15.14% increases in flexural strength and flexural modulus, respectively, over the E/CF, with the addition of CNTs to the epoxy matrix. Moreover, the tensile strength of composites containing CNTs was higher than that of E/CF, indicating a similar enhancement trend to the flexural properties, and the tensile strength increased by 24.42% for E/CF-CNTs.

It was observed by Wang *et al.* [56] that from a certain value of CNT, the mechanical properties started to decrease, this is caused possibly because of a failure in dispersion.

### 2.4.4 Synergetic effects

There are studies performed about the synergy effects of GnP with CNTs and with CB with positive results in electrical, mechanical and thermal properties [19, 21]. These results are presented in Table 6.

*Table 6 – Synergetic effects of GnP +CB + MWCNT.*

| Carbon nanoparticle | Resin System | Preparation method | Curing parameter | Electrical Properties | Mechanical Properties | Thermal Properties | Ref |
|---|---|---|---|---|---|---|---|
| **GnP (2 wt.%)** | E 44<br>Dicyandiamide | Sonication in acetone | 120 °C, 1h +185 °C, 3h | $\rho_\sigma$ = 1,0 wt.%<br>$\boldsymbol{\sigma}$ = $10^{-8}$ S.cm$^{-1}$ | | | [19] |
| **GnP + CB (9:1, 1 wt.%)** | | | | $\rho_{\sigma}$=0,5 wt.%<br>$\boldsymbol{\sigma}$ = 1,6 x$10^{-6}$ S.cm$^{-1}$ | | | |
| **GnP + CB + MWCNT** | | | | $\rho_\sigma$ = 0,2 wt.%<br>**$\boldsymbol{\sigma}$ = 2,18 x$10^{-3}$ S.cm$^{-1}$** | | | |
| **GnP (1wt.%)** | EPON 128 | Ultrasonication | | | Tensile modulus ↑23%<br>Tensile strength ↑0.9% | ↑24% | [21] |
| **MWCNT (1 wt%)** | | | | | Tensile modulus 4↑<br>Tensile strengh<br>12.5% | ↑62% | |
| **MWVNT + GnP 1:9**<br>**(1 wt.%)** | | | | | Tensile modulus<br>23%↑<br>Tensile strengh<br>15%↑ | ↑47% | |

In a different study dedicated to study the synergetic effect on conductivity of CNT and GnP, the conductive network was formed at a lower overall filler concentration (0.62 wt.%) than for the single CNT (0.84 wt.%) and GnP (0.88 wt.%) filled systems. This can be explained by the formation of conductive pathways more efficiently when combining 1D CNTs with 2D GnP. This happened when the ratio CNT: GnP was 8:2 [18].

It has been shown in the literature that a combination of two or more carbon fillers can improve the electrical performance and other properties because of the synergetic effect.

# 3 Materials and Methods

In the elaboration of this work, the materials used were:

- Epoxy resin: Araldite LY 556 from Hunstman Corporation (Europe), with a viscosity of 10-12 x $10^3$ mPa.s and a density of 1.15 – 1.20 g.cm$^{-3}$.
- Hardeners: A mixture of aradur 1571 (23: 100) and accelerator 1573 (5:100) was prepared using a mechanical stirrer at 1000 rpm and then added hardener XB 3903 (12:100).
- Carbon nanotubes, NC 7000 produced by catalytic carbon vapor deposition (CCVD) purchased by Nanocyl S.A. (Belgium).
- Graphene nanoplates: Grade M, with average particle size 15 μm, supplied from XG Sciences (xGnP) (USA).

In Table 7, Table 8, and Table 9 is shown the properties of these materials.

*Table 7 – Properties of the hardeners.*

| Properties of the hardeners | | | |
|---|---|---|---|
| Commercial name | Aradur® 1575 | Accelerator 1573 | Hardener XB 3403 |
| Aspect | White viscous paste | White viscous paste | Clear liquid |
| Viscosity at 25°C (mPa.s) | 28 - 40 x$10^3$ | 60 -90 x$10^3$ | 5 -20 |
| Density at 25°C (g.cm$^{-3}$) | 1.2 | 1.08 | 1.0 |
| Storage temperature (°C) | < 8 | < 8 | 2 – 40 |

*Table 8 – Properties of CNTs.*

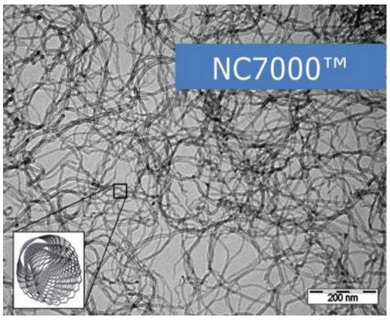
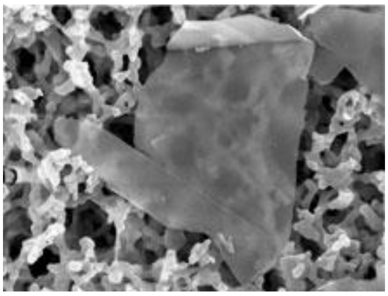
| Properties of carbon nanotubes | | |
|---|---|---|
| Commercial name | NC700 |  |
| Carbon purity | >90% | |
| Diameter (nm) | 9.5 | |
| Density (g.cm$^{-3}$) | 0.066 | |
| Surface area (m$^2$.g$^{-1}$) | 250-300 | |
| Aspect | Black powder | |
| Average length (μm) | 1.5 | |

*Table 9 -Properties of GnP.*

| Properties of graphite nanoplates | | |
|---|---|---|
| Commercial name | xGnP -Grade M |  |
| Carbon purity | >99.5% | |
| Diameter ($\mu$m) | 15 | |
| Density (g.cm$^{-3}$) | 0.03 – 0.10 | |
| Surface area (m$^2$.g$^{-1}$) | 120-150 | |
| Aspect | Black powder | |

## 3.1 Preparation of the nanocomposites

In this experimental work, nanocomposites containing MWCNT and GnP were prepared. The composites were manufactured with different loads, between 0.06 wt.% and 1 wt.% for CNTs and between 1 wt.% and 5 wt.% for GnP. The maximum load in epoxy/MWCNT nanocomposites was stablish at 1 wt.% because above this value, the suspensions present significant limitations in processing. It was also produced hybrids nanocomposites with different loads of MWCNT and GnP.

The samples were first mixed in a mechanical stirrer. Then a three-roll mill machine was used to promote a better dispersion of the nanofillers in the matrix. After the processing of the suspensions, the rheological measurements were performed. The final step consisted in the addition of hardeners to the nanocomposites, and after a passage on the three-roll mill to remove air bubbles, the nanocomposites were cured at 120 °C for 2h. The manufactured samples are presented in Table 10.

*Table 10 – Composition of the prepared samples.*

| MWCNT loading (wt%) | GnP loading (wt%) | MWCNT/GnP loading (wt%) |
|---|---|---|
| 0.015 | - | - |
| 0.03 | - | - |
| 0.06 | - | - |
| 0.125 | - | - |
| 0.250 | - | - |
| 0.500 | - | - |
| 0.750 | - | - |
| 1.00 | - | - |
| - | 0.500 | - |
| - | 1.00 | - |
| - | 2.00 | - |
| - | 3.00 | - |
| - | 4.00 | - |
| - | 5.00 | - |
| 0.03 | 0.03 | 0.06 (50:50) |
| 0.045 | 0.015 | 0.06 (75:25) |
| 0.06 | 0.06 | 0.125 (50:50) |
| 0.09 | 0.035 | 0.125 (75:25) |
| 0.0625 | 0.1875 | 0.250 (25:75) |
| 0.125 | 0.125 | 0.250 (50:50) |
| 0.1875 | 0.0625 | 0.250 (75:25) |
| 0.250 | 0.250 | 0.500 (50:50) |
| 0.375 | 0.125 | 0.500 (75:25) |
| 0.375 | 0.375 | 0.750 (50:50) |
| 0.5625 | 0.1875 | 0.750 (75:25) |
| 0.500 | 0.500 | 1.00 (50:50) |
| 0.750 | 0.250 | 1.00 (75:25) |

### 3.1.1 Mechanical Stirrer

The equipment used for the pre-mixing of the samples was the Overhead Laboratory Stirrer CAT R100C (Figure 7), placed in the *hotte* of the laboratory. The propeller employed for this task was a dispersing homogenizer blade, with a diameter of 35 mm. The agitation was done at 1000 rpm during 15 minutes. The mechanical stirrer and the propeller are illustrated in Figure 7.

*Figure 7 - Overhead Laboratory Stirrer CAT R100C.*

However, the mixture provide by this equipment is not perfect, mainly near the recipient walls.

### 3.1.2 Three roll milling

A three roll mill is an intensive mixer that uses shear force created by three horizontally positioned rolls, rotating in opposite directions at different speed relative to each other, to mix, disperse or homogenize materials fed into it [57]. Among the shear mixing techniques, three-roll milling is one of the best methods as it is solvent free, scalable, uniformly shears the entire volume of the material, and can easily handle high loadings of carbon nanofillers [29]. The suspensions are fed between the feed and central rollers and the milling cycle can be repeated several times to maximize dispersion. This equipment and a scheme of its operation are shown in Figure 8.

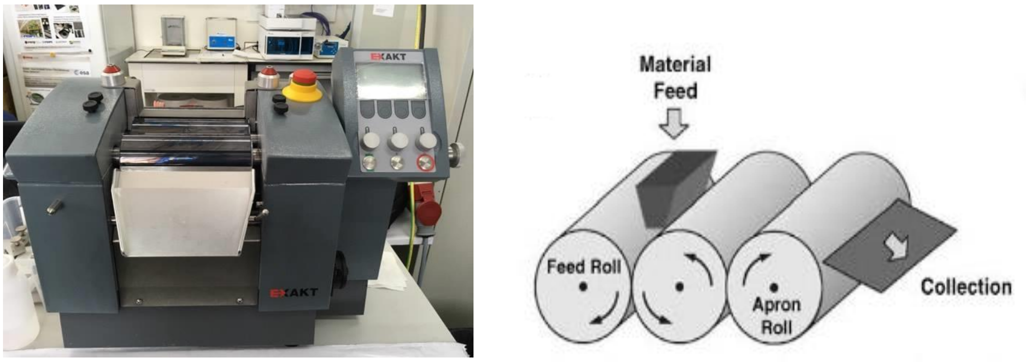


*Figure 8 – Three-roll milling.*

In this work, the equipment used was EXAKT 80® from EXAKT Technologies, Inc. at room temperature. The procedure consists in 5 cycles in which the whole suspension was milled 5 times per cycle to achieve a uniform dispersion at 200 rpm. The gap between the feed roll and the apron roll was varied from 120 µm to 5 µm, leading to an increasing nominal shear rate, as shown in Table 11. With this technique, it is possible to obtain shear rates comparable to extrusion and injection molding in the two last cycles [58].

*Table 11 – Nominal shear rate; **δ1** – gap between the middle and the apron roll; **δ2** – gap between the feed roll and the middle.*

| | **δ1 (μm)** | **δ2 (μm)** | **Nominal shear rate ($s^{-1}$)** |
|---|---|---|---|
| 1st cycle | 120 | 40 | 28.000 |
| 2nd cycle | 90 | 30 | 37.000 |
| 3rd cycle | 60 | 20 | 56.000 |
| 4th cycle | 30 | 10 | 110.000 |
| 5th cycle | 15 | 5 | 220.000 |

## 3.2 Characterization of the nanocomposites

### 3.2.1 Optical microscopy

The influence of different loadings of carbon nanoparticles on the dispersion level of epoxy-based nanocomposites was evaluated by OM. This characterization technique is used to evaluate the morphology of the nanocomposites after processing. This technique allows to quantify the number and size of particles and agglomerates.

For optical observations, thin sections of approximately 5 μm were cut using a microtome Leitz fitted with a glass knife at 45° at room temperature. Optical micrographs were taken using a Leica DFC 280 digital camera coupled to a BH2 Olympus microscope in transmission mode, using a 1.6x ocular magnification and 20x or 40x objective. Quantitative particle analysis was performed by the digital image processing software ImageJ. At least 15 images were considered for the statistical analysis.

The number of agglomerates and area ratio, used as dispersions indicators, are normalized by equation 1 and equation 2.

$$Number\ of\ agglomerates = \frac{Average\ number\ of\ agglomerates}{observation\ area} \times 10^6 \qquad Equation\ 1$$

$$area\ ratio = \frac{Average\ area\ of\ \ agglomerates}{observation\ area} \times 100 \qquad Equation\ 2$$

In the dispersion analysis of the epoxy/MWCNT and epoxy/GnP nanocomposites the observation area was 3.48 x $10^5$ μ$m^2$ and 8.62 x $10^4$ μ$m^2$ respectively.

### 3.2.2 TEM

Transmission electron microscopy (TEM) was conducted using JEOL JEM-1400 Transmission Electron Microscope at 80 kV.

### 3.2.3 Rheology – Steady shear experience

A Discovery hybrid rheometer, DHR-1 from TA Instruments (Figure 9), was used to study the processability of the materials. The rheological measurements were conducted before the curing process. All measurements were held in steady mode with a 25 mm parallel plate geometry. The lower plate was held stationary, while the upper plate rotates. The viscosity of all the epoxy/MWCNT and epoxy/GnP and epoxy/MWCNT/GnP suspensions were measured at 25 °C, varying shear rates between 0.01 and 100 $s^{-1}$. In addition, temperature sweeps was performed to evaluate the processability of the material at different temperatures [59].

*Figure 9 - Rheometer DHR-1.*

### 3.2.4 Electrical Properties

Electrical property of nanocomposites was measured to verify if the addition of nanofillers led to a conducting material.

Electrical resistance (*R*) of the nanocomposites was calculated from the slope of *I–V* curves measured with an automated Keithley 487 picoammeter/voltage source. *I–V* data points were collected between Au/Pd contacts deposited on both sides of the composites with a Polaron SC502 sputter coater. Four measurements were made for each composition, and the average value calculated.

Resistivity was measured with circular contacts of $\phi$ = 5 mm diameter with an applied voltage ranging between −10 V and +10 V. The resistivity of the composites ($\rho$) was calculated according to equation 3 [60].

$$R = \frac{\rho l}{A} \qquad Equation\ 3$$

Where R is the electrical resistance, ρ is the resistivity, l is the length of the material and A is the cross-sectional area through which the current is flowing.

The resistivity of a material is independent of its geometry making it a useful quantity to compare different materials.

The conductivity was calculated using equation 4.

$$\sigma' = \frac{1}{\rho} \qquad Equation\ 4$$

Where $\sigma'$ is the electric conductivity.

The theoretical electrical percolation threshold, $\rho'_c$, for CNT, is estimated by equation 5 [18].

$$\rho'_c = \frac{0.5}{\eta} \qquad Equation\ 5$$

where $\boldsymbol{\eta}$ = $l/d$ is the aspect ratio of the CNTs, and $l$ and $d$ are the average length and diameter of the nanotubes, respectively.

### 3.2.5 Mechanical Properties

Quasi static mechanical measurement was conducted to determine the Young modulus (*E*), tensile strength (*TS*) and the elongation at break ($\varepsilon_b$). In this measurement, a constant deformation is applied to the material and the force necessary to produce this deformation is measured.

In the mechanical experience was used the machine INSTRON 4208 with a load of 100 kN. The tensile test was conducted following the designation ISO 527-2 [61] with a steady speed of 1.0 mm/min. Were conducted 6 measurements for composition, and the tensile properties were average from the results obtained from four selected specimens.

Specimens of neat epoxy, epoxy/MWCNT, epoxy/GnP and finally specimens of hybrids nanocomposites were produced with the type dog-bone, (Figure 10).

*Figure 10 - Specimen with the dog-bone geometry.*

With this test, it is obtained the stress/strain curve of the nanocomposites. In Figure 11 is presented a typical stress/strain curve of composite materials.

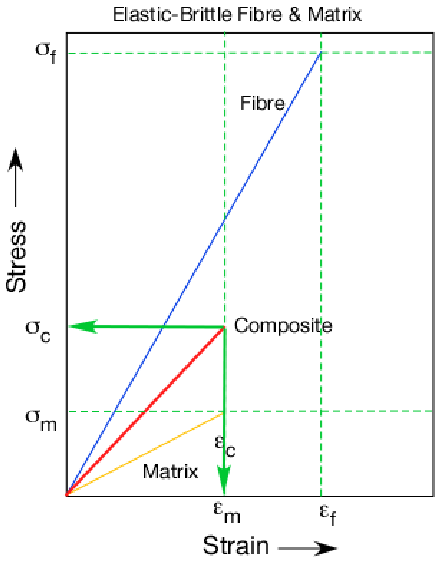


*Figure 11 - Typical stress-strain behavior of composites [62].*

The Young modulus ($E$) is calculated from the slope of $\sigma/\varepsilon_b$ curves, according to equation 6 that follows ISO 527-2.

$$E = \frac{\sigma_{0.25} - \sigma_{0.05}}{\varepsilon_{0.25} - \varepsilon_{0.05}} \qquad Equation\ 6$$

Where $\varepsilon_{0.25}$ and $\varepsilon_{0.05}$ correspond to the deformation of 0.25% and 0.05%, and respective values of tension.

Also, the tensile strength ($TS$) can be calculated through equation 7.

$$TS = \frac{F}{A} \qquad Equation\ 7$$

Where, $TS$ is the tensile strength, $F$ is the force applied, and $A$ is the area.

The elongation at break ($\varepsilon_b$) is obtained through equation 8. It expresses the capability of a material to resist changes of shape without crack formation.

$$\varepsilon_b = \frac{\Delta l}{l_0} \qquad Equation\ 8$$

Where $\varepsilon_b$ is the elongation at break that the material suffers, $\Delta l$ is the elongation and $l_0$ is the initial distance between moorings (50 mm).

# 4 Results and Discussion

## 4.1 Electrical Properties

Epoxy resin is an insulating material and, therefore the incorporation of conductive carbon nanofillers, such as CNTs and GnP, aims to increase the electrical conductivity of the polymeric material. The load, the shape and the dispersion degree of nanofillers incorporated strongly influence the electrical conductivity of the nanocomposites [14]. Therefore, the influence of the nanofillers content in the electrical conductivity was study and the results are shown in Figure 12.

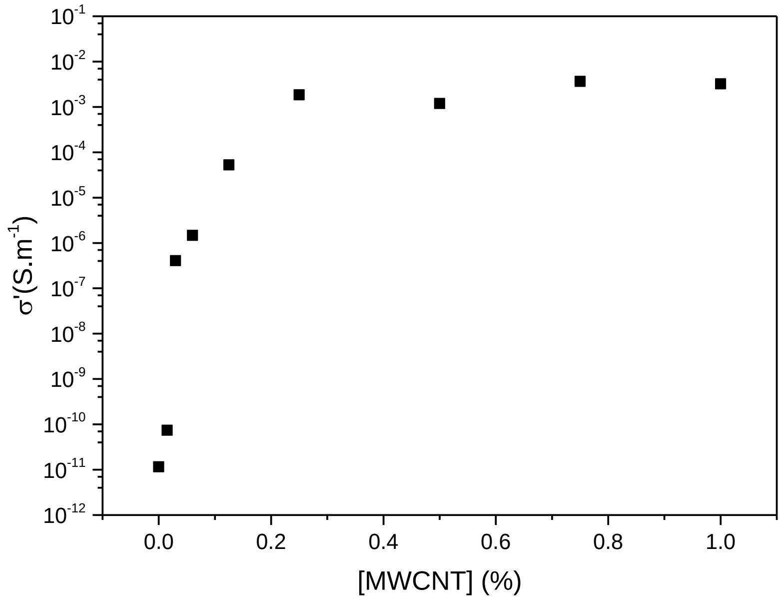


*Figure 12 – Electrical conductivity of MWCNT/epoxy nanocomposites.*

The epoxy resin LY 556 is an insulating material, showing an electrical resistivity of 1.16 x10$^{-11}$ S.m$^{-1}$. As it is possible to see from Figure 12, increasing MWCNT content leads to an improved electrical conductivity.

After incorporation of only 0.06 wt. % of MWCNT, the electrical conductivity increases 6 orders of magnitude (from 10$^{-11}$ to 10$^{-5}$ S.m$^{-1}$). At 0.250 wt.% MWCNT a plateau is attained, suggesting that regardless of the quantity of MWCNT that is added, it is not possible to increase the electrical conductivity, reaching a maximum of 10$^{-3}$ S.m$^{-1}$, which corresponds to a semi-conductive material in the range of EMI shielding [63].

The conductivity of filled conductive polymeric systems derives from the formation of a conductive network by the fillers in the matrix [31]. The theoretical percolation threshold obtained by equation 5 is 0.32 vol.% MWCNT, considering $l$ = 1.5 μm and $d$ = 9.5 nm. This corresponds to a weight fraction of 0.055 wt.% since the skeleton density of MWCNTs is 2.1 g.cm$^{-3}$ [64] and the density of epoxy is 1.21 g.cm$^{-3}$. Experimentally, in Figure 12 is possible to see that the percolation threshold happens between 0.03 wt.% and 0.06 wt.%.

Better results were obtained in this work in comparison with the ones obtained in the literature. Yue *et al.* [18] reached a maximum of 10$^{-4}$ S.m$^{-1}$ with 1 wt.% MWCNT whereas in this work with only 0.250 wt.% MWCNT the electrical conductivity was 1.85 x 10$^{-3}$ S.m$^{-1}$.

The ability of a filler material to form a percolated network is determined by the filler state of dispersion and geometry. Thus, these impressive electrical conductivity values can be attributed to the characteristics of the MWCNTs used, namely its low bulk density which is expected to lead to a good dispersion. Nanofillers with lower density allow a greater infiltration of the polymer molecules inside, making the dispersion faster. On the other hand, denser fillers require hydrodynamic forces and longer residence times to attained similar levels of dispersion [36]. In addition, MWCNTs of lower density occupy more volume and therefore have more opportunities to interconnect than compact MWCNTs [65].

The electrical conductivity of GnP/epoxy nanocomposites was also measured, being shown in Figure 13. With 5 wt.% of GnP an increase of only 4 orders of magnitude is observed (from 10$^{11}$ S.m$^{-1}$ to 10$^{-7}$ S.m$^{-1}$) and no plateau is reached. Thus, it can be concluded that no electrical percolation threshold was obtained.

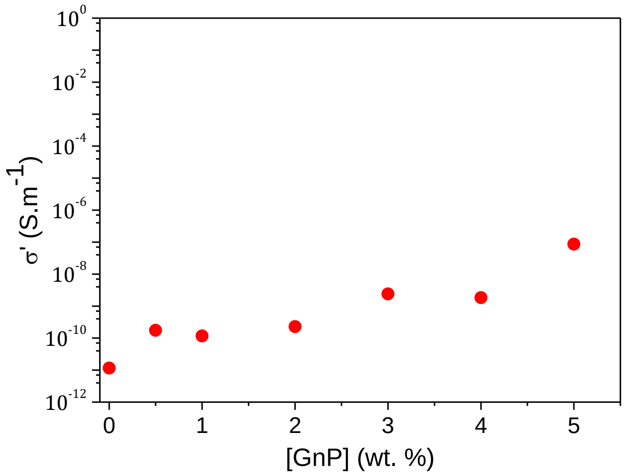


*Figure 13 - Electrical conductivity of GnP epoxy based nanocomposites.*

The experimental values of electrical conductivity of GnP/epoxy nanocomposites are lower to the ones found in the literature. Yue *et al.* [18] achieved with 4 wt.% epoxy/GnP nanocomposites with an electrical conductivity of 2.1 x 10$^{-5}$ S/m. The lower electrical conductivity obtained in this work can be attributed to the size of the platelets, since these were about 3 times bigger than in the literature, which made them more suitable to improve thermal properties.

Comparing both nanofillers, nanocomposites with GnP not only percolate at higher filler contents, but also their conductivity is several orders of magnitude lower than MWCNT composites. These results meet the ones found in the literature, where the percolation thresholds amount to 0.25–0.3 wt.% in MWCNTs corresponding to an electrical conductivity of $10^{-7}$ S.m$^{-1}$ and 1.0 wt.% to GnP corresponding to an electrical conductivity of $10^{-9}$ S.m$^{-1}$, confirming a much higher efficiency of MWCNTs in forming the electrical conducting network [50].

This difference in electrical conductivity values is due to the geometry of the fillers (1D in case of MWCNTs and 2D in case of GnPs) [16]. The hollow nature of MWCNTs and a high electrical conductivity along tube axis, reduces the percolation threshold of this nanofiller [50].

According to some authors a good dispersion of carbon nanotubes within the polymeric matrix is desirable to enhance the nanocomposite electrical conductivity [48, 49], others believe that the presence of a network of dispersed particles and agglomerates may form a conductive network structure [13, 47]. Thus, in this work, optical microscopy was used to study the dispersion of MWCNT and GnP in the epoxy matrix.

Dispersion is related to the degree of individual separation of fillers, and it is ideal that a sample presents a good dispersion of nanofillers in polymeric matrix, i.e., fillers must be individually separated and well distributed in the epoxy resin, but sufficiently close to each other to stablish interactions to form the network.

With the results from optical microscopy of epoxy/MWCNT nanocomposites is possible to conclude that a good dispersion was attained, since few agglomerates are visible (black spots) and the area ratio is low. These results are shown in Figure 14 and Table 12. The histograms in Figure 15 shows more detail information.

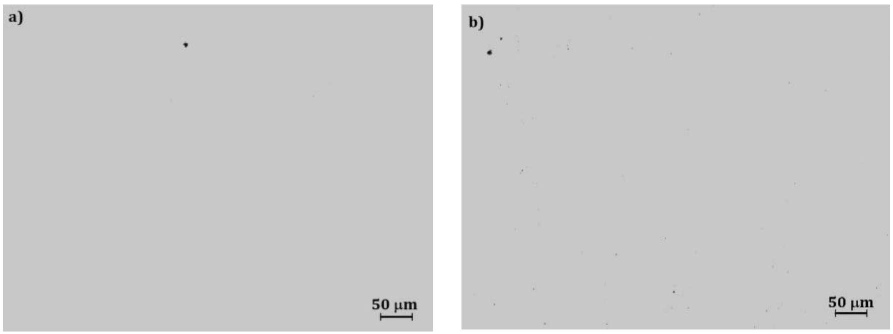


*Figure 14 - Optical micrographs of epoxy-based nanocomposites containing a) 0.5 wt.% and b) 1.0 wt. % of MWCNTs prepared at 200 rpm using a three-roll mill.*

*Table 12 - Assessment of dispersion of the epoxy-based nanocomposites containing 0.5 wt.% and 1.0 wt. % of MWCNTs prepared at 200 rpm using a three-roll mill.*

| | **0.5 wt. % MWCNT** | **1.0 wt. % MWCNT** |
|---|---|---|
| Area ratio (%) | 0.018 ± 0.008 | 0.048 ± 0.012 |
| Number of agglomerates ($mm^{-2}$) | 20.0 ± 19.0 | 106 ± 39 |

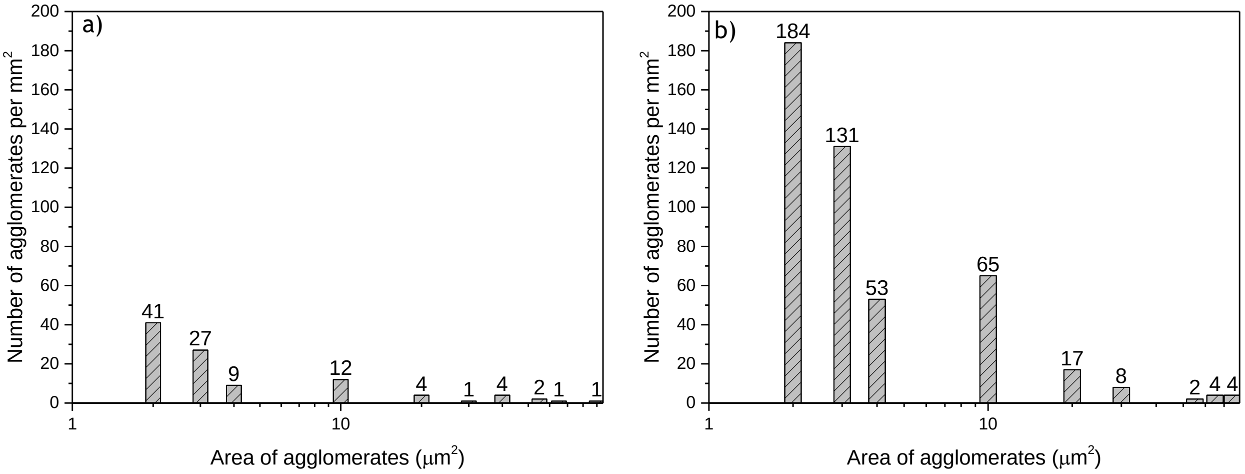


*Figure 15 - Distribution of the sizes of the agglomerates for a) 0.5 wt.% epoxy/MWCNT nanocomposite and b) 1.0 wt.% epoxy/MWCNT nanocomposite*

The analyses from optical microscopy (Figure 14 and Table 12) shows an increase in the number and size of agglomerates as the carbon nanofillers concentration increases.

The specimen with 1 wt.% MWCNT reveal to be the one with the higher amount of aggregates per observation area. This phenomenon is explained in the literature by the increase in viscosity caused by the increase in concentrations [36]. This is going to be shown in section 4.2.

It is possible to visualize in Figure 15 that the majority of MWCNT agglomerates have areas between 1 and 3 $\mu m^2$ and few agglomerates have areas superior to 10 $\mu m^{2.}$

This analysis allowed to conclude that the increase of MWCNT concentration leads to the formation of more agglomerates with higher area, which may indicate a worse dispersion of the nanofiller with the increase of concentration.

The dispersion of epoxy/GnP nanocomposites was also assessed. For this analysis, was considered that particles with an area inferior to 225 $\mu m^2$ are not agglomerates, due to the dimensions of the GnP particles used ($A \approx 225$ $\mu m^2$). The results are presented In Figure 16, Table 13 and in the histograms in Figure 17.

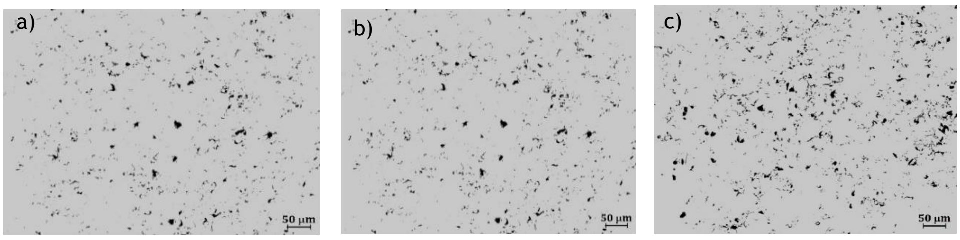


Figure 16 - *Optical micrographs of epoxy-based nanocomposites containing different loadings, a) 0.5 wt.% GnP, b) 1 wt.% GnP, c) 2 wt.% GnP, prepared at 200 rpm using a three-roll mill.*

*Table 13 – Assessment of dispersion of the epoxy-based nanocomposites containing different loadings of GnPs prepared at 200 rpm using a three-roll mill.*

| | 0.5 wt.% GnP | 1 wt.% GnP | 2 wt.% GnP |
|---|---|---|---|
| Area ratio (%) | 36.73 ± 4.66 | 21.20 ± 4.20 | 11.88 ± 13.54 |
| Number of agglomerates ($mm^{-2}$) | 553.14 ± 50.14 | 544.35 ± 86.48 | 1082.10 ± 249.93 |

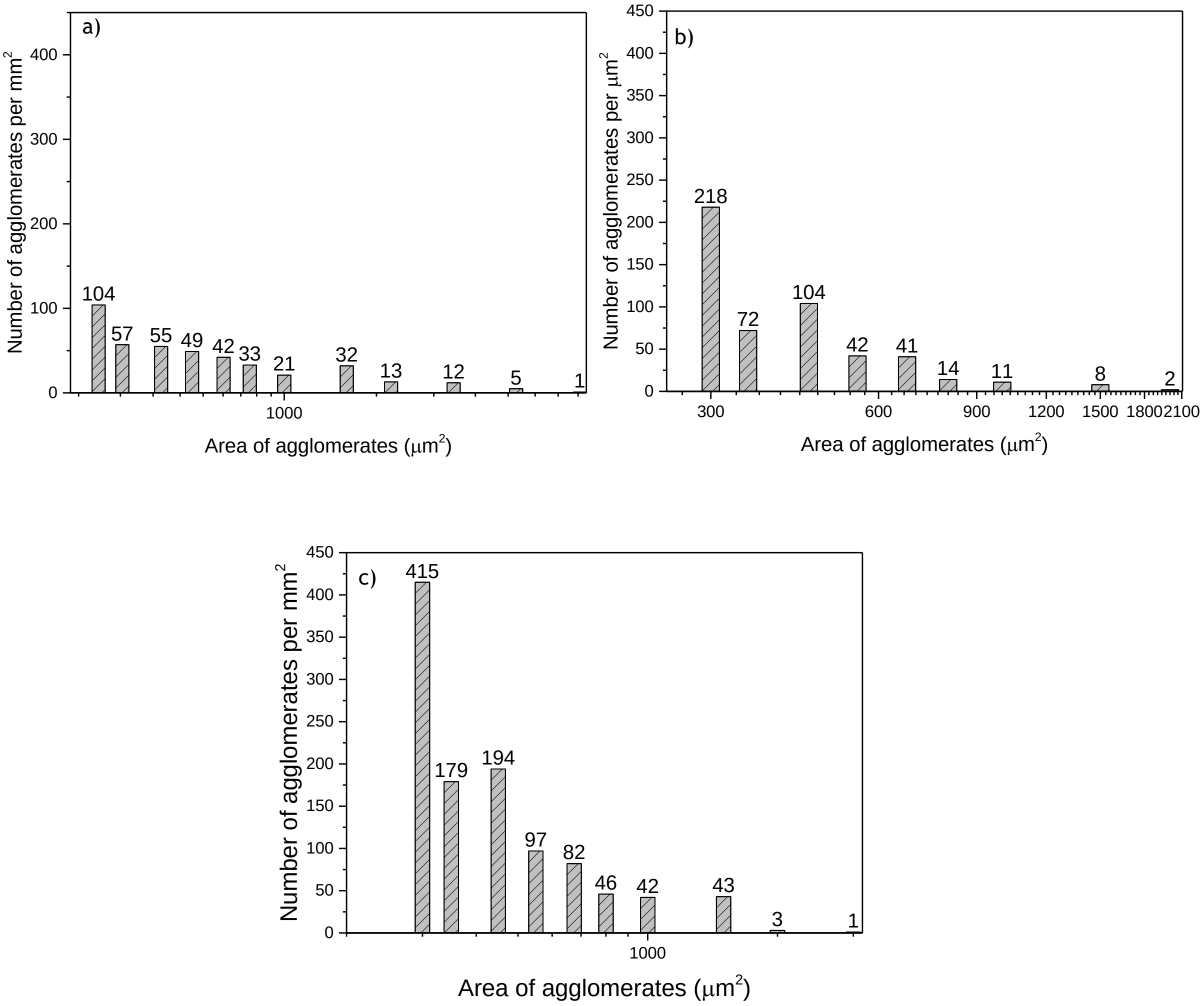


*Figure 17 – Distribution of the sizes of the agglomerates for a) 0.5 wt.% epoxy/GnP nanocomposite, b) 1.0 wt.% epoxy/GnP nanocomposite and c) 2.0 wt.% epoxy/GnP nanocomposite*

In the OM images (Figure 16) the individualized particles of GnP can be seen, unlike those of MWCNTs.

These results show the tendency of GnPs to form agglomerates. This happens mainly due to the $\pi$ -$\pi$ interaction between individual sheet.

The specimen with 2.0 wt.% GnP demonstrates a higher number of agglomerates per observation area, however with less dimension in comparison with the aggregates formed in the samples with inferior concentrations.

To further investigate filler dispersion into epoxy nanocomposites at the nanoscale, TEM analyses was performed. The images obtained for 0.5 wt.%, epoxy/MWCNT, 1 wt.% epoxy/MWCNT and 1 wt.% epoxy/GnP are presented in Figure 18.

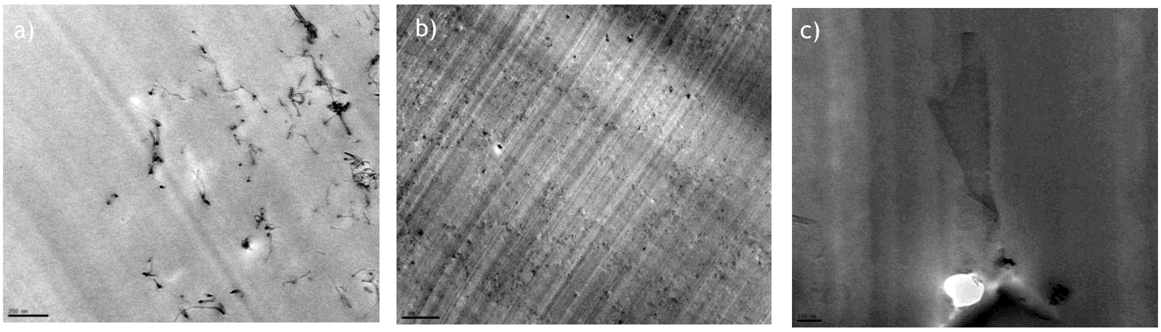


*Figure 18 – Pictures obtained by TEM for a) 0.5 wt.% epoxy/MWCNT b) 1 wt.% epoxy/MWCNT and c) 1 wt.% epoxy/GnP.*

Figure 18 a) shows a good dispersion of the filler, although with some agglomerates visible. In Figure 18 c) is possible to see a nanoplates of graphene.

According to these results, is more challenging to disperse GnPs compared to MWCNTs, probably because the Van der Waals' force between adjacent GnP may be stronger than those between MWCNT, due to the two-dimension geometry of GnP.

The results shown in this work seem to support the hypothesis, defended by Siddiqui and Li *et al.* [48, 49] i.e. that the presence of a good dispersion leads to the formation of an effective conductive path.

## 4.2 Steady shear experiments: rheological percolation and processability

The formation of filler networks in nanocomposites can be evaluated by the rheological response of the system.

Figure 19 displays the obtained results and is possible to observe that the addition of carbon nanofillers changes the behavior of the epoxy resin.

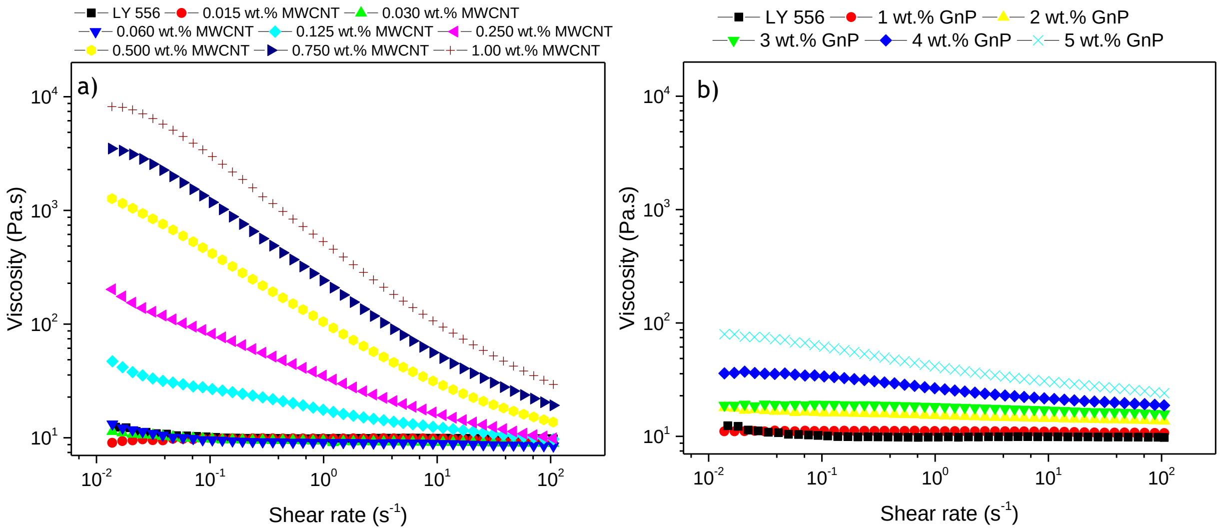


*Figure 19 – Viscosity of a) epoxy/MWCNTs suspensions, b) epoxy/GnP suspension as a function of shear rate.*

Epoxy resin and its nanocomposites containing MWCNTs up to 0.06 wt.% exhibit a Newtonian behavior due to its low molecular weight. As the nanofiller content increases (Figure 19 a), the viscosity is dramatically increased, making processing of the mixture much more difficult.

At low MWCNT concentration (from 0.125 wt.%), a strong shear thinning effect is observed suggesting that rheological percolation threshold was achieved. Shear thinning behavior suggests that a conductive network is formed. The interactions between MWCNTs are the main contribute to the formation of the network [66]

Regarding the rheological results for the GnP suspensions (Figure 19 b), it is possible to observe that epoxy-based nanocomposites containing GnP have lower viscosity than those containing MWCNT. This occurs because interfacial bonding between GnP and epoxy resin is weaker. With 1 wt.% GnP the viscosity is about $10^1$ Pa.s whereas for 1 wt.% MWCNT the viscosity is about $10^4$ Pa.s.

Slight shear thinning is observed only at concentrations higher than 4.0 wt.% of GnP.These results are in agreement with reported rheological percolation thresholds for GnP and CNT suspensions in which CNTs exhibit much lower rheological percolation threshold than GnPs [18]. However, there are studies where GnP percolates at lower concentrations than in this work, Khanam [67] obtained percolation at 1 wt.% GnP.

Figure 20 a) shows that the increase of MWCNT content, increases the viscosity of the suspension (especially at low shear rates) as predicted by Fan *et al.* and Carreua *et al.* [68, 69]. This is due to the higher number of interactions between the MWCNTs as concentrations increases. In Figure 20 b), the same behavior is shown for GnP/epoxy suspensions.

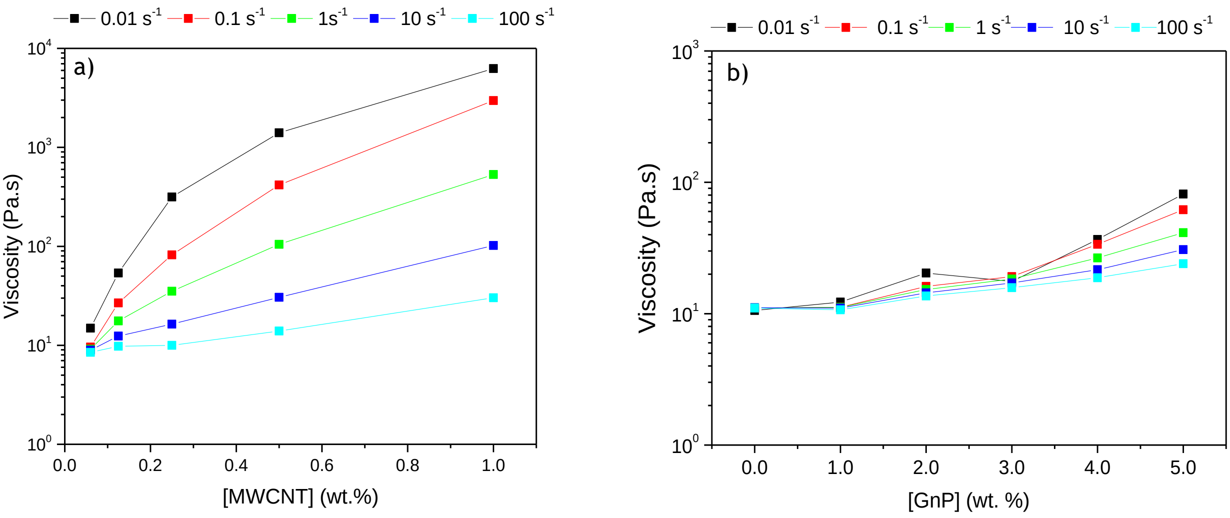


*Figure 20 – a) Viscosity as a function of MWCNT loading at different shear rates, b) Viscosity as a function of GnP loading at different shear rates.*

For the epoxy/MWCNT nanocomposites, the electrical threshold happened before the rheological one. The electrical percolation threshold is reached when there is a conductive path since the end of the nanocomposite to the other end, while the rheological one is not reached until a rigid physical MWCNT network is formed. However, when the electrical threshold is reached the amount of filler is not yet high enough to significantly affect the elasticity/rigidity of the polymer matrix. More MWCNT are needed to form a network inside the polymer matrix that significantly solidifies the latter [70].

On the other hand, the rheological percolation for epoxy/GnP nanocomposites was smaller than the electrical one, implying that when the rheological percolation threshold is reached, the GnP are not in direct contact with each other yet [70]. The rheological percolation is reached when the distance between MWCNT reaches a critical threshold. This distance between entanglements depends on the type of the polymer and is of the order of tens of nanometers.

The use of MWCNTs increases the viscosity of nanocomposites, as demonstrated, inducing some drawbacks in the processability. Since viscosity can be affected by temperature, Figure 21 shows the temperature dependence of the viscosity of the nanocomposites with loadings of 0.125 wt.% and 1.00 wt.% MWCNT/epoxy nanocomposites. As expected, the viscosity decreases as the temperature increases, because during heating the intermolecular distances increase which reduces the attractive forces between the molecules, decreasing the viscosity [71]. The viscosity starts to increase from 80ºC due to the reticulation of MWCNT.

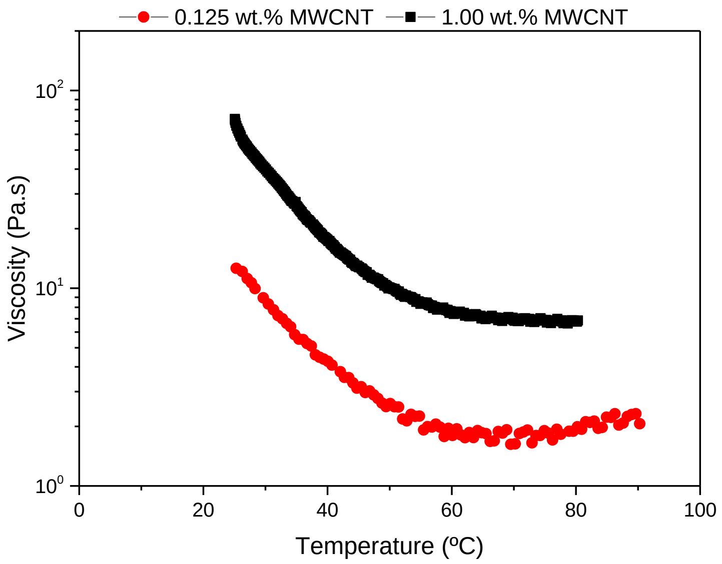


*Figure 21 - Viscosity of MWCNT/epoxy nanocomposites as function of temperature.*

## 4.3 Mechanical Properties

Tensile tests were carried out to investigate the effects of adding GnP and MWCNT on epoxy nanocomposites on mechanical properties.

In Figure 22, the stress/strain curves of epoxy/MWCNT nanocomposites is plotted. Introducing small amount of this nanofiller, between 0.03 wt.% and 0.250 wt.%, did not affect the material nature, remaining a brittle material. However, there were noticeable enhancements on the modulus, tensile strength and elongation at break (Figure 23).

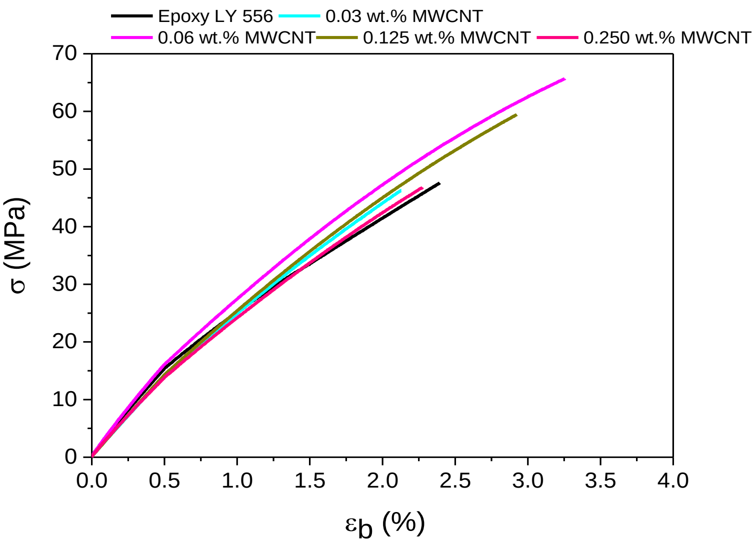


*Figure 22 – Stress/strain curves of epoxy/MWCNT nanocomposites.*

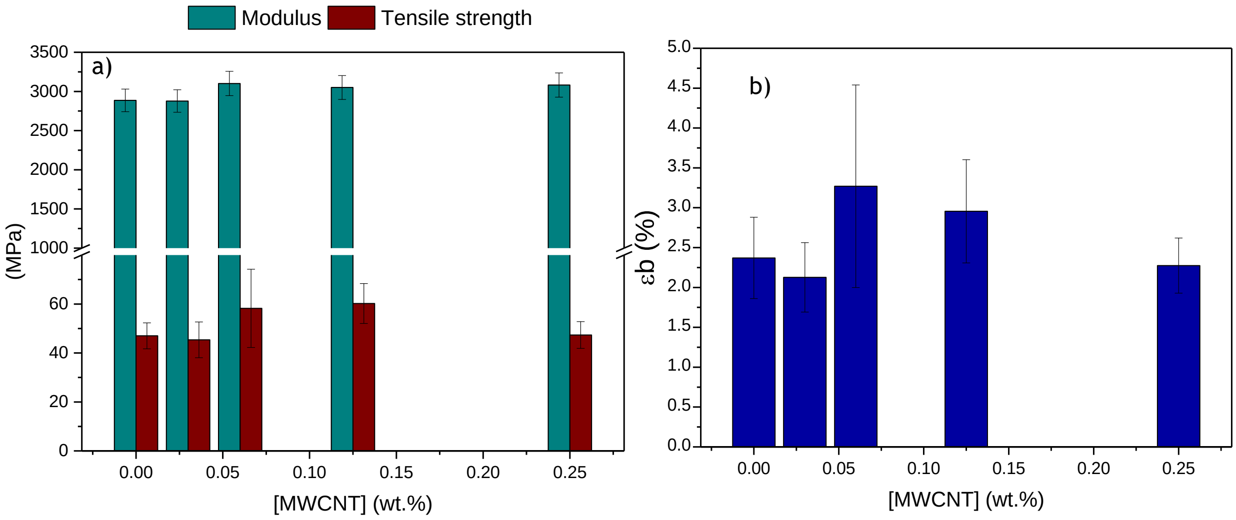


*Figure 23 – a) Modulus and tensile strength of epoxy/MWCNT nanocomposites b) Elongation at break of epoxy/MWCNT nanocomposites.*

With only 0.03 wt.% MWCNT there was no significant effects in the mechanical properties of the nanocomposite. From 0.06 wt.% of MWCNT, the modulus increases relative to the neat epoxy resin, increasing the stiffness of the nanocomposite. For concentrations of 0.06 wt.% MWCNT and 0.125 wt.% of MWCNT, the ultimate tensile strength and elongation at break increase 24%, 38% and 43%, 24% respectively. With 0.250 wt.% these values decreases, probably because problems in processing, that led to defects, namely air bubbles.

The best results were obtained for 0.06 wt.% MWCNT/epoxy nanocomposites, having a modulus of 3.10 x $10^3$ MPa ± 3.16 x$10^2$ MPa, tensile strength of 58.2 MPa ± 16.0 MPa and elongation at break of 3.27% ±1.27%.

Figure 24 shows the tensile stress/strain curve of epoxy/GnP nanocomposites at different filler loadings.

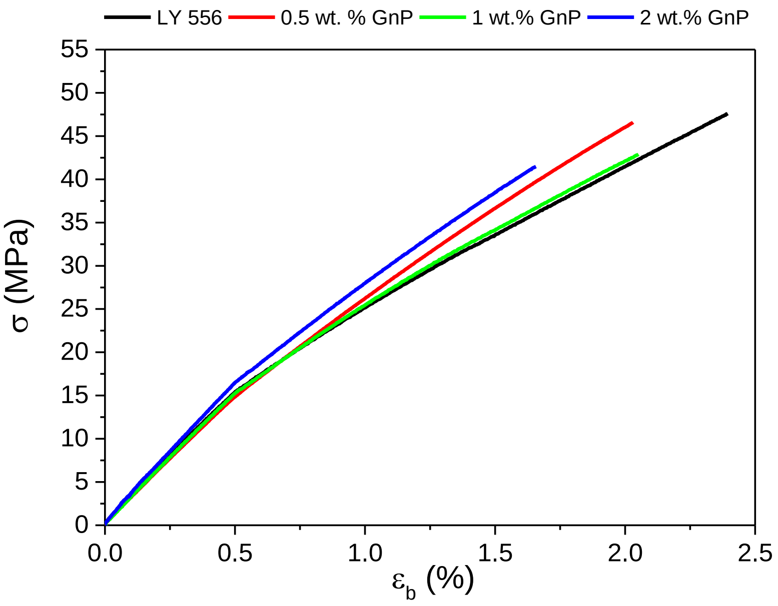


*Figure 24 - Stress/strain curve of GnP/epoxy nanocomposites.*

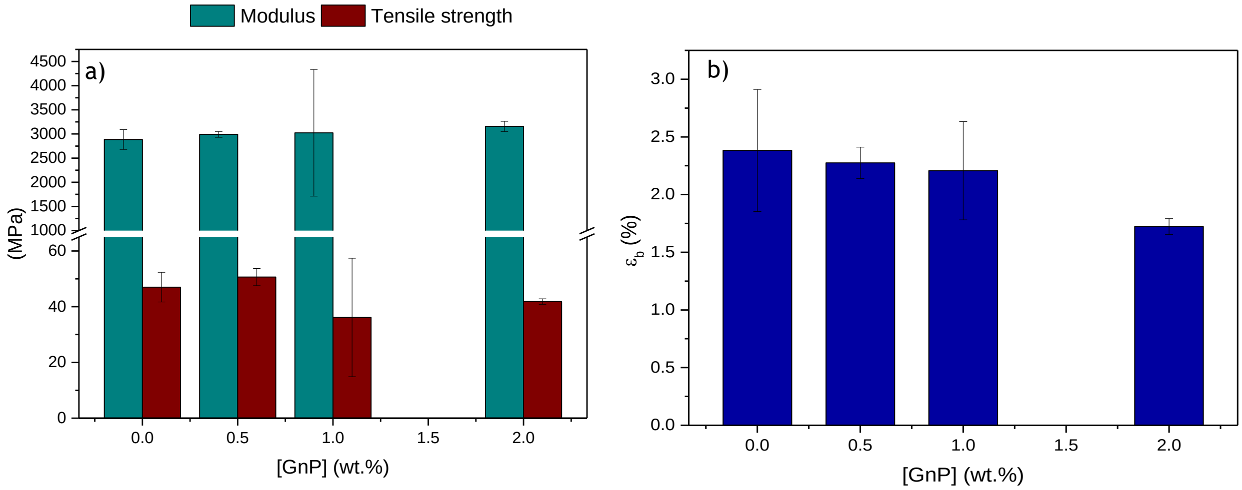


*Figure 25 - a) Modulus and tensile strength of epoxy/GnP nanocomposites b) Elongation at break of epoxy/GnP nanocomposites.*

Epoxy resin shows a brittle behavior and with the addition of carbon nanoparticles, the material becomes even more brittle, resulting in a decrease in the elongation at break (Figure 25 b). On the other hand, the modulus increases slightly with the addition of GnP, making the material stiffer (Figure 25 a). The highest modulus was achieved by 2 wt.% GnP/epoxy with an increment of up to 3.16 x $10^3$ MPa ± 1.05 x$10^2$ MPa, which correspond to a 9% increment compared to the neat epoxy (E= 2.89 x$10^3$ MPa ± 2.06 x$10^2$ MPa).

Meanwhile, epoxy/GnP nanocomposites present a lower tensile strength than neat epoxy, showing that the addition of GnP makes the material less resistant. A similar behavior has been reported in previous works. Ghaleb *et al.* [26] obtained a decrease of 48% and 28% with 0.05 vol.% and 0.1 vol.% loading of GnP in the tensile strength of nanocomposite, respectively.

The addition of GnPs did not bring benefits to the mechanical and electrical performance of nanocomposites. These results are in agreement with Yang *et al.* [21] that states that this lower improvements can be attributed to the formation of agglomerates with relatively low surface area that restrict polymers to flow into the agglomerates, resulting in the formation of holes and voids between GnPs and epoxy.

Analyzing the results, it can be concluded that MWCNT presents better mechanical properties than GnP, also shown in literature by Zakaria *et al.* [72] who obtained enhancements of 13% for modulus, 2% for tensile strength, and a decrease of 15% in elongation using 0.5wt.% GnP in epoxy, whereas using 0.5 wt.% MWCNT obtained 13% enhancement in modulus, 8% enhancement in tensile strength and a decrease of 12% in elongation. These results are attributed to the fact that two-dimensional GnP is more easily aggregated than MWCNT due to its larger surface areas and plane-to-plane contact areas, making the MWCNT easier to disperse than the GnP in the epoxy matrix. The dispersion assessment showing the dispersion in both nanofillers was shown in section 7.1.

Mechanical properties are highly dependent on the good interface surface obtained between the nanofiller and the resin, therefore it can be concluded that a better interface surface was obtained by the MWCNTs/epoxy nanocomposites.

## 4.4 Hybrid nanocomposites

Combination of GnP and MWCNT to take advantage of the properties of each nanofiller was performed and analyzed in this work.

Looking at the results, although epoxy/MWCNT nanocomposites show best results regarding electrical and mechanical properties, these nanocomposites, present high viscosity, making their processing very difficult [73]. Therefore, since GnP has a significant lower viscosity than MWCNT, their combination can also be beneficial for this problem.

The rheological experiments for the hybrid nanocomposites (Figure 26 a)) demonstrate a decrease in the viscosity of the system relatively to the nanocomposite with only MWCNT, as expected since the amount of MWCNT incorporate is reduced. In Figure 26 b) for the same MWCNT content (0.250 wt.%), due to the addition of GnP, the suspension of the hybrid nanocomposite has a lower viscosity. These results show that the substitution of MWCNT with GnP can help to improve the limited processability of these nanocomposites, if the performance can achieve the same level as the one using a greater content of MWCNT without additional GnP.

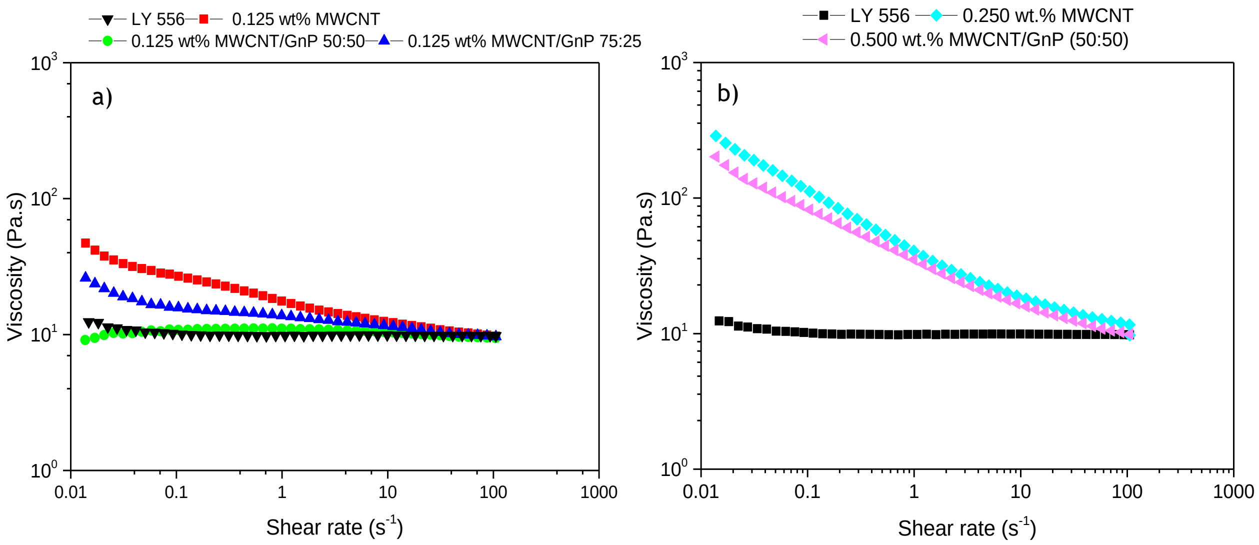


Figure 26 – a) Viscosity of MWCNT/GnP epoxy suspension as function of the shear rate for suspension with same carbon nanoparticle content; b) Viscosity of MWCNT/GnP epoxy suspension as function of the shear rate for suspensions with same MWCNT content.

The electrical conductivity of the hybrid nanocomposite containing 1 wt.% carbon nanoparticles, (MWCNT: GnP 75:25) reaches a remarkable 3.9 × $10^{-3}$ S/m, which is more than 4 orders of magnitude higher than that of the nanocomposite with 5 wt.% GnP alone, and slightly superior to the corresponding value for the nanocomposite with 1 wt.% MWCNTs alone.

In Figure 27 a) the combination 0.125 wt.% carbon nanoparticles (MWCNT: GnP, 75:25), i.e. with only 0.094 wt.% MWCNT, presents an electrical conductivity of $10^{-4}$ $S.m^{-1}$ whereas with 0.125 wt.% MWCNT the electrical conductivity is $10^{-5}$ $S.m^{-1}$, showing the benefits of the hybrid system and emerging as an economically viable solution since GnP is more economical than MWCNT.

In the literature, the maximum electrical conductivity obtained was $10^{-6}$ $S.m^{-1}$ for 0.62 wt.% MWCNT/GnP, 80:20 [18]. With this work with only 0.06 MWCNT/GnP (75:25) this value is achieved and at 0.125 wt.% MWCNT/GnP (75:25) the electrical conductivity is 1.80 x $10^{-4}$ $S.m^{-1}$.

In the MWCNT/GnP hybrid system, in the combination 75:25, the conductive network was formed at a lower overall filler concentration than for the single MWCNT and GnP filled systems.

This can be explained by the formation of conductive pathways more efficiently when combining 1D MWCNTs with 2D GnPs.

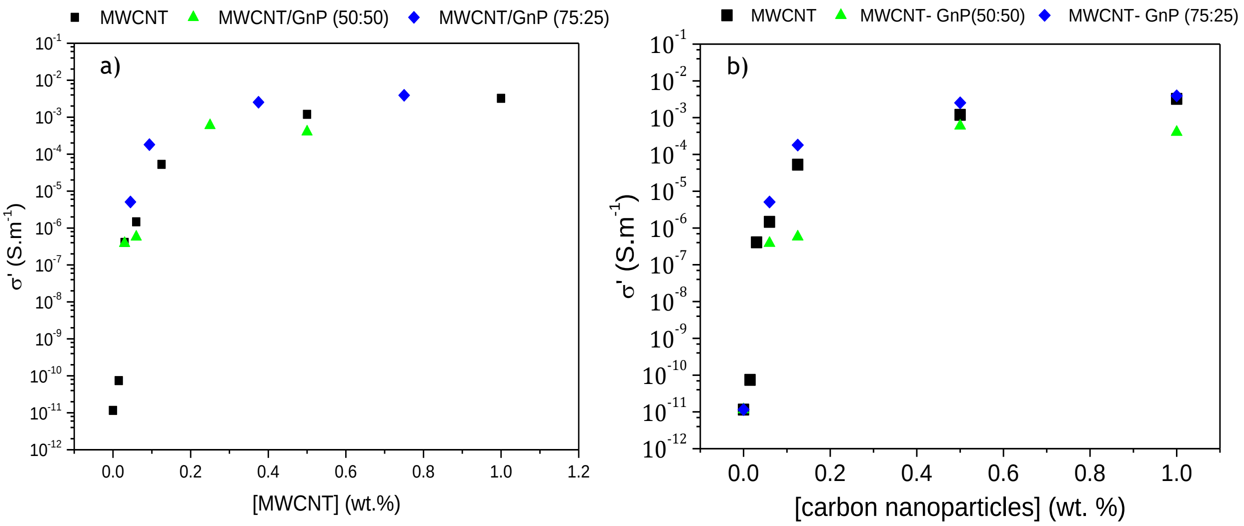


*Figure 27* – Electrical conductivity of MWCNT/GnP epoxy based nanocomposites.

The results obtained for the hybrid nanocomposites suggest that synergistic effects between MWCNTs and GnPs was achieved in the electrical properties.

Regarding the mechanical properties, the stress/strain curves of hybrid epoxy based nanocomposites are shown in Figure 28. The modulus, tensile strength and elongation at break are shown in Figure 29 and Figure 30.

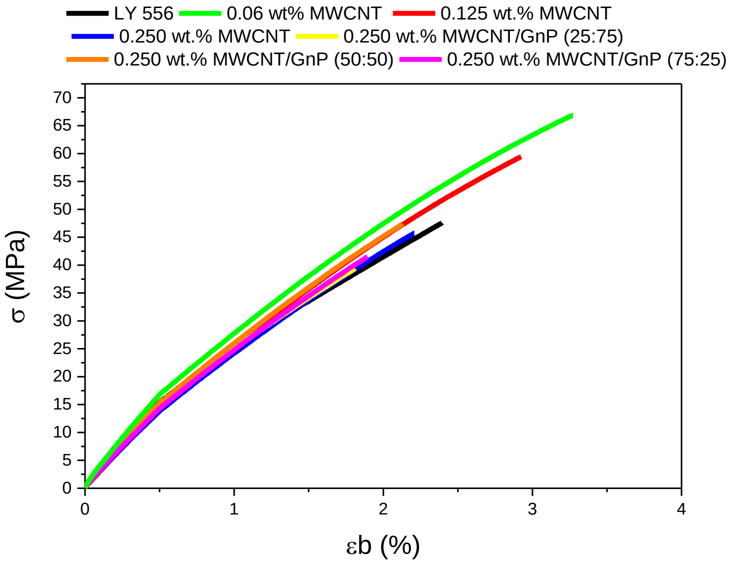


*Figure 28 – Curve stress/strain of epoxy/MWCNT/GnP nanocomposites.*

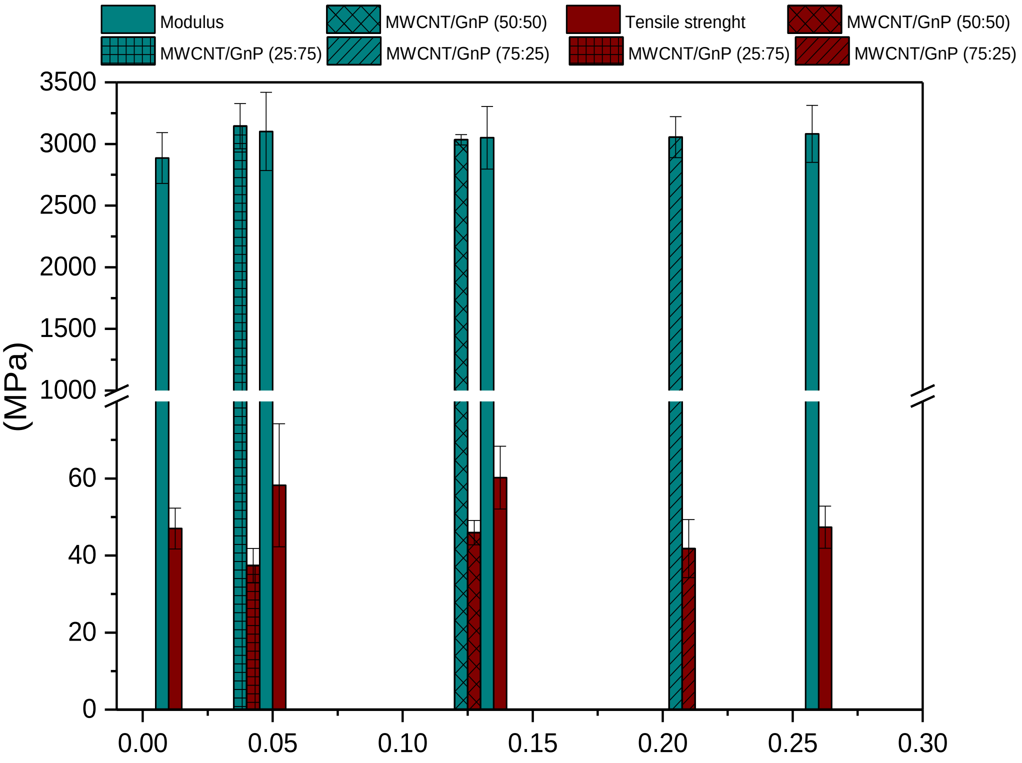


*Figure 29 - Modulus and Tensile strength of epoxy/MWCNT/GnP nanocomposites.*

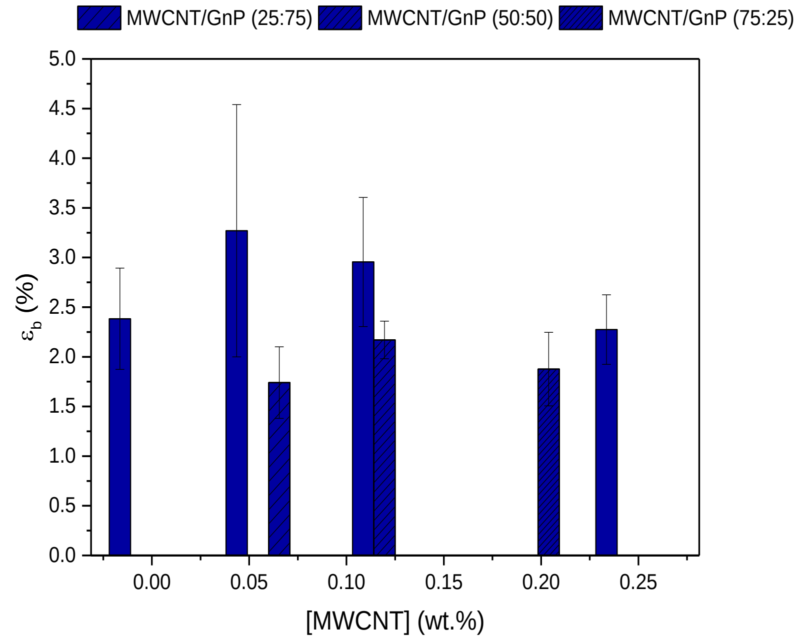


*Figure 30 - Elongation at break for epoxy/MWCNT/GnP nanocomposites.*

The combination of MWCNTs with GnP was not beneficial for the final properties of the nanocomposite. At same MWCNTs loading (0.06 wt.%), the nanocomposite with only MWCNTs has a higher tensile strength than the one combined with 0.1875 wt.% GnP, that had a result even inferior to the tensile strength of neat epoxy, showing that the addition of GnP is prejudicial. A similar behavior happened to the nanocomposites with 0.125 wt.% MWCNT, where the hybrid nanocomposite presented a smaller tensile strength than neat epoxy.

Regarding the modulus, all the nanocomposites show slightly enhanced compared to the neat epoxy however there is no synergetic effect observed. Hybrid nanocomposites made the material less resistance, not showing improvements in the elongation at break.

These results are contradictory with literature [41], where the combination of these nanofillers leads to improved mechanical properties. Li *et al.* studied the mechanical properties of epoxy and their composites with the same content (0.5 wt.%) of CNTs, GnPs and CNT/GnP hybrids. They found that the best result was for the tensile strength of the hybrid nanocomposite with an enhancement of 36%.

As it was mentioned before, the level of dispersion and morphology of the agglomerates affects the final properties of the nanocomposite [38]. If the dispersion is better, the network is likely to be formed easily making the threshold lower, ( verified in section 4.1) and also translate in high mechanical properties of the corresponding epoxy nanocomposites [18, 49].

The OM for the hybrid nanocomposites is present in Figure 31 and Table 14 and shows positive results regarding the effect of the combination of both fillers in the dispersion of the nanocomposite.

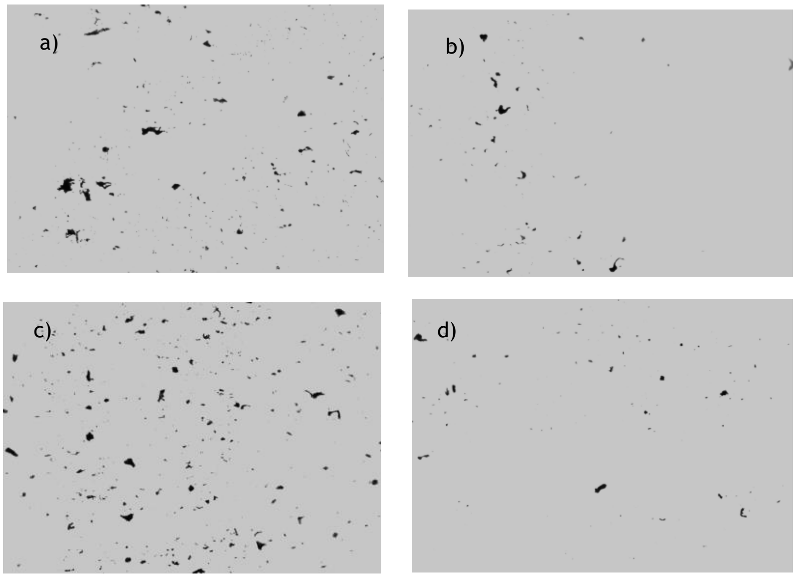


*Figure 31* - Optical micrographs of epoxy-based nanocomposites containing different loadings of MWCNT/GnPs, a) 0.5 wt% MWCNT/GnP (50:50); b) 0.5 wt.% MWCNT/GnP (75:25); c) 1 wt.% MWCNT/GnP (50:50); d) 1 wt.%MWCNT/GnP (75:25) prepared at 200 rpm using a three-roll mill.

*Table 14* - Assessment of dispersion of the epoxy-based nanocomposites containing different loadings of MWCNTs/GnPs prepared at 200 rpm using a three-roll mill.

| | 0.5 wt.%MWCNT/GnP (50:50) | 0.5 wt.%MWCNT/GnP (75:25) | 1wt.%MWCNT/GnP (50:50) | 1wt.%MWCNT/GnP (75:25) |
|---|---|---|---|---|
| Area ratio (%) | 5.30 ± 1.64 | 3.36 ± 1.19 | 17.57 ± 3.78 | 14.08 ± 1.63 |
| Number of agglomerates ($mm^{-2}$) | 107.53 ± 41.18 | 544.35 ± 86.47 | 355.09 ± 61.37 | 244.98 ± 45.91 |

Observing the results, it is possible to compare the dispersion of the nanocomposites with 0.5 wt.% GnP and 1wt% (50:50) MWCNT/GnP. It is well noticed that the combination of MWCNTs with GnP allows a better dispersion of the latter, since the area ratio and the number of agglomerates is much lower than the ones obtained for the epoxy/GnP nanocomposites (see Table 13). Accordingly, with Yue *et al.* [18], this improvement is due to the creation of a three-dimensional network, which inhibits face to face aggregation of GnPs.

In addition, and as expected, nanocomposites with 1 wt.% MWCNT GnP/epoxy present larger values of area ratio and number of agglomerates since higher incorporations tend to form larger and more agglomerates.

From Table 14 is possible to observe that combinations of 75:25 MWCNT/GNP induce a better dispersion, resulting in fewer number of agglomerates and inferior area ratio comparing with the combination 50:50 MWCNT/GnP. It is relevant to notice that this was also the combination with a better electrical conductivity. Once again this proves the role of dispersion in the properties of the nanocomposites, and that a better dispersion leads to enhanced properties.

# 5 Conclusion

The main goal of this work was to develop epoxy-based nanocomposites containing MWCNT and/or GnP to obtain synergistic effects to achieve both good mechanical and electrical properties to produce nanocomposites for multifunctional applications.

High electrical conductivity was obtained at low loading of MWCNT. After incorporation of only 0.06 wt. % of MWCNT, the electrical conductivity increased 6 orders of magnitude (from $10^{-11}$ to $10^{-5}$ $S.m^{-1}$). For 0.250 wt.% MWCNT is reached the maximum value of $10^{-3}$ $S.m^{-1}$, which corresponds to a semi-conductive material in the range of EMI shielding. Nanocomposites reinforced with GnP show dramatically lower electrical conductivity even at high concentrations. With 5% wt.% of GnP, an increase of only 4 orders of magnitude in comparison with epoxy is observed (from $10^{-11}$ $S.m^{-1}$ to $10^{-7}$ $S.m^{-1}$), indicating that there is no electrical conducting path. Thus, MWCNTs induce better results in the electrical conductivity of the nanocomposites in comparison with GnP due to the differences in the fillers geometry.

The formation of a physical network was assessed by rheology. The introduction of MWCNTs in epoxy matrix, led to a significant increase of viscosity. In the nanocomposites epoxy/MWCNTs a shear thinning behavior was observed at and above 0.125 wt.% loading, indicating that from this value a network is formed. Regarding the rheological results for the GnP suspensions, it was possible to observe that epoxy-based nanocomposites containing GnP have lower viscosity than those containing MWCNT because interfacial bonding between GnP and epoxy resin is weaker. With 1 wt.% GnP the viscosity is about $10^1$ Pa.s whereas for 1 wt.% MWCNT the viscosity is 4 orders of magnitude superior ($10^4$ Pa.s).

For the epoxy/MWCNT nanocomposites the electrical threshold happened before the rheological one, indicating that when the electrical threshold was reached the amount of filler was not yet high enough to significantly affect the rigidity of the polymer matrix. On the other hand, the rheological percolation for epoxy/GnP nanocomposites was smaller than the electrical one, implying that when the rheological percolation threshold was reached, the GnP were not in direct contact with each other yet.

The mechanical properties were improved with the addition of small amounts of MWCNTs. With only 0.06 wt.% MWCNT the material got stiffer and more resistant, with enhances of 18% in modulus, 36% in tensile strength and 38% in elongation at break. From 0.125 wt.% the mechanical properties started to deteriorate, due to problem in processing and defects. Adding GnP did not bring benefits to the nanocomposite regarding the mechanical properties making it less resistant.

The difference in the final properties either electrical and mechanical, obtained by MWCNTs and GnP are attributed to the level of dispersion of the filler into epoxy attained. This first filler had fewer agglomerates with small areas than GnP, indicating that better dispersion was achieved in MWCNT. Therefore, is possible to conclude that if the dispersion is better, the network is likely to be formed easily, making the threshold lower and also translate in high mechanical properties of the corresponding epoxy nanocomposites.

The dispersion assessment also enables to conclude that the processing of the nanocomposites in the three-roll machine was an effective method to promote the dispersion.

It was verified that when MWCNTs are combined with GnP, less concentration of MWCNTs was required thus, the viscosity of the system decreased compared with the viscosity of the nanocomposite with only CNTs (at same filler content). This strategy leads to a better processability. In addition, the electrical properties of the nanocomposites were not loss.

In the MWCNT/GnP hybrid nanocomposites, the conductive network is formed at a lower filler concentration than for the single MWCNT and GnP filled systems. With only 0.094 wt.% MWCNT combined with 0.031 wt.% GnP the electrical conductivity was $10^{-4}$ $S.m^{-1}$ whereas with 0.125 wt.% MWCNT the electrical conductivity was $10^{-5}$ $S.m^{-1}$.

On the other hand, the MWCNT/GnP hybrid nanocomposite did not improve the mechanical properties of the nanocomposite for the studied concentration.

However, it was proved that the addition of MWCNT to GnP improves the dispersion of the former nanofiller due to the formation of a three-dimensional network that inhibits the agglomeration of GnP.

Although it was not performed in this work, knowing the thermal properties of GnP it is expected that their incorporation on the nanocomposites leads to improvements in these properties.

## 5.1 Future Work

To continue this work, the following ideas are presented for future work.

- Characterization of the thermal properties of the epoxy based nanocomposites containing MWCNTS and/or GnP using Thermal Gravimetric Analysis (TGA);
- Process nanocomposites with incorporation levels of MWCNT/GnP inferior to 0.125 wt.% to observe if synergetic effects are obtained with this composition in the mechanical properties;
- Production of prepreg carbon fiber reinforced polymers.

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