Development of high-performance epoxy-graphitic carbon nitride nanocomposites
(versão final após defesa)

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Liane Raquel Neves Moura

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Resumo

A introdução de nanopartículas em resinas epóxi é uma das várias maneiras de reforçar polímeros. Assim, esta dissertação explora a síntese, caracterização e otimização do desempenho de nanocompósitos de epóxi-nitreto de carbono grafítico (GCN), com foco na melhoria das propriedades mecânicas e térmicas. A pesquisa envolve a preparação de nanocompósitos à base de epóxi através da incorporação de diferentes concentrações de nanopartículas de GCN na resina epóxi, utilizando técnicas de manufaturas comuns, e a subsequente análise das suas características estruturais e propriedades. Além disso, este trabalho visa entender a influência da carga de GCN e das partículas de Silsesquioxano Oligomérico Poliédrico (POSS) na resistência mecânica e estabilidade térmica do nanocompósito, visando aplicações aeronáuticas e aeroespaciais.

Os resultados experimentais indicam que as propriedades mecânicas com melhorias mais acentuadas foram observadas para o nanocompósito reforçado com uma concentração de 0.25 wt.% de GCN. Consequentemente, esta concentração foi a selecionada para os laminados de fibra de carbono, concluindo que a adição de GCN resultou em melhorias de até 81% na resistência à flexão (de 369.8 para 670 MPa) e até 135% no módulo de flexão (de 25.2 para 59.3 GPa), dependendo das velocidades de teste. Além disso, foram observados aumentos de 25% na resistência à tração (de 408.3 para 509.6 MPa) e 39% no módulo elástico (de 20.3 para 28.1 GPa).

Como mencionado, o documento apresenta a influência da adição de partículas de POSS aos laminados de fibra de carbono reforçados com GCN. Comparando as propriedades obtidas para a amostra de controlo com as obtidas para as amostras reforçadas, é possível concluir que a incorporação de ambos os nano reforços permite melhorias de até 111% na resistência à flexão (de 369.8 para 781.2 MPa) e até 117% no módulo de flexão (de 25.2 para 54.7 GPa), para diferentes velocidades de teste. Em termos de resistência à tração e módulo elástico, os aumentos foram de 30% (de 408.3 para 529.9 MPa) e 12% (de 20.3 para 22.7 GPa), respectivamente.

As propriedades térmicas dos laminados também foram examinadas, através de análise termogravimétrica (TGA) e calorimetria diferencial de varredura (DSC). Verificou-se que a adição de nano reforços não resultou em melhorias nas temperaturas de transição vítrea e decomposição, embora uma melhoria na massa residual tenha sido observada nos laminados reforçados apenas com GCN.

Finalmente, as propriedades hidrofóbicas das duas composições e da amostra de controlo foram avaliadas, recorrendo à análise do ângulo de contato com a água (WCA). Concluiu-se que a presença dos reforços impacta positivamente estas propriedades, com uma melhoria mais pronunciada na amostra reforçada apenas com GCN (de 73.6 para 82.5°).

Palavras-chave

Nanocompósitos de alta performance; Nitreto de Carbono Grafitico; Aplicações aeronáuticas; Silsesquioxano Oligomérico Poliédrico; Époxi; Fibra de carbono.

Abstract

The introduction of nanofillers into epoxy resins is one of the numerous ways of reinforcing polymers. In accordance, this dissertation explores the synthesis, characterization, and performance optimization of epoxy-graphitic carbon nitride (GCN) nanocomposites, focusing on enhancing their mechanical and thermal properties. So, the research involves the preparation of epoxy-based nanocomposites through the incorporation of different concentrations of GCN nanoparticles into the epoxy resin, using common processing techniques, and subsequent analysis of their structural characteristics and properties. Besides that, this work aims to understand the influence of GCN loading and Polyhedral Oligomeric Silsesquioxane (POSS) particles on the nanocomposite's mechanical strength and thermal stability, aiming at aeronautical and aerospatial applications.

The experimental results indicate that the most enhanced mechanical properties were observed for the nanocomposite reinforced with a concentration of 0.25 wt.% GCN. Consequently, this concentration was selected for the carbon fibre laminates, concluding that the addition of GCN resulted in an improvement of up to 81% in flexural strength (from 369.8 to 670 MPa) and up to 135% in flexural modulus (from 25.2 to 59.3 GPa), depending on the testing speeds. Increases of 25% in tensile strength (from 408.3 to 509.6 MPa) and 39% in elastic modulus (from 20.3 to 28.1 GPa) were also observed.

As mentioned, the document also examines the influence of adding POSS particles to the carbon fibre laminates reinforced with GCN. Comparing the properties attained for the control sample with the ones obtained for the reinforced samples, it is possible to conclude that the incorporation of both nano reinforcements allows for improvements between up to 111% in flexural strength (from 369.8 to 781.2 MPa) and up to 117% in flexural modulus (from 25.2 to 54.7 GPa), for different testing speeds. In terms of tensile strength and elastic modulus, the increases were 30% (from 408.3 to 529.9 MPa) and 12% (from 20.3 to 22.7 GPa), respectively.

The thermal properties of the laminates were also examined, through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was found that the addition of nano reinforcements did not result in significant improvements in the glass transition and decomposition temperatures, although an improvement in the residual mass was observed in the laminates reinforced only with GCN.

Finally, the hydrophobic properties of the two compositions and the control sample were evaluated, using water contact angle analysis (WCA). It was concluded that the presence of the reinforcements positively impacts these properties, with a more pronounced improvement in the sample reinforced only with GCN (from 73.6 to 82.5°).

Keywords

High-performance nanocomposites; Graphitic Carbon Nitride; Aeronautical Applications; Polyhedral Oligomeric Silsesquioxane; Epoxy; Carbon Fibre.

Contents

List of Figures

List of Tables

Acronyms

CB	Carbon Black
CF	Carbon Fibre
CNF	Carbon Nanofibre
CNT	Carbon Nanotubes
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry Analysis
FTIR	Fourier Transform Infrared Spectroscopy
GCN	Graphitic Carbon Nitride
GNP	Graphene Nanoplatelets
GO	Graphene Oxide
IFSS	Interfacial Shear Strength
ILSS	Interlaminar Shear Strength
ND	Nanodiamond
NG	Nano graphite
PHRR	Peak Heat Release Rate
PMC	Polymer Matrix Composite
PNC	Polymer Nanocomposites
POSS	Polyhedral oligomeric silsesquioxanes
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
THRR	Total Heat Release Rate
WCA	Water Contact Angle

List of Symbols

ε_f	-	Flexural Strain
ε_t	-	Tensile Strain
σ_f	MPa	Flexural Strength
σ_t	MPa	Tensile Strength
b	mm	Width
E_f	GPa	Flexural Modulus
E_t	GPa	Elastic Modulus
F	N	Applied Force
h	mm	Thickness
L	mm	Span
s	mm	Deflection
Td	^oC	Decomposition Temperature
Tg	^oC	Glass Transition Temperature
Tm	^oC	Melting temperature

Chapter 1

Introduction

This chapter is an overview of the increasing applications of composite materials in the aeronautical and aerospace industries. With the demands for high-performance materials in these fields, composite materials appear as a good match for the requirements imposed by sustainability and security policies, such as good specific strength and excellent fatigue behaviour. This study focuses on the investigation of the application of epoxy nanocomposites reinforced with Graphitic Carbon Nitride (GCN) in those fields.

The following sections describe the motivation, the research objectives and the thesis outline.

1.1 Motivation

The Aerospace and aeronautical industries present a high demand for lightweight high-performing materials. Besides the safety matters that led to the demand for high-performance materials, the desire to reduce greenhouse gas emissions and meet the targets set to achieve the Sustainable Development Goals adopted by the United Nations State Members [1] also requires the optimization of the materials used in these fields, as the aviation industry is accountable for 2.6% of global carbon emissions according to Delbecq et al. [2]. With these concerns in mind, manufacturers have increased the integration of composite materials in their product designs besides their application in smaller quantities even since the first flight of the Wright Brothers in 1903 [3].

The most commonly used reinforcements applied in composite materials are glass and carbon fibres. However, these fibres have already provided everything they are capable of [4]. To achieve better mechanical and thermal qualities, nano-reinforcing materials including carbon nanotubes, graphene sheets and graphitic carbon products are under research. Moreover, epoxy resins are the thermoset polymers that are applied the most in the Aeronautical and Aerospace industries, given their low cost, good specific strength and chemical stability. However, their low fracture toughness and low glass transition temperature can limit their performance in demanding applications.

Epoxy-based nanocomposites have emerged as a promising class of materials due to their exceptional mechanical, thermal, and electrical properties. Amongst the various nanofillers, graphitic carbon nitride (GCN) nano reinforcements stand out for their unique two-dimensional structure, excellent chemical stability, and tunable electronic properties, besides the lower costs of production, ease of optimal dispersion and fewer environmental impacts, when compared with commonly used reinforcements.

With the work already developed in mind, this document aims to investigate the development of high-performance epoxy composites reinforced with GCN.

1.2 Research Objectives

This research aspires to study the performance improvement acquired with the introduction of GCN nanoparticles into carbon fibre/epoxy laminates, specifically in the mechanical, thermal and hydrophobic properties of this material. Moreover, it aims to tailor these nanocomposites for structural components in the aeronautical and aerospace industries. Besides that, this document aims at the understanding of the interactions between the epoxy matrix and nanofillers and to provide insights into the design and optimization of high-performance nanocomposite materials. In addition, the study dwells on the influence of POSS nanoreinforcements on the properties of the GCN nanocomposites.

To achieve that, an extensive contextualization of the state-of-the-art regarding the improvements accomplished through the addition of different types of carbon-based nanofillers and POSS nanoparticles was carried out. Later, a dispersion optimization process was also performed to obtain the appropriate dispersion. The research proceeded with the study on the influence of GCN loading on the mechanical properties of the epoxy resin, followed by the mechanical and thermal characterization of those improvements on the carbon fibre laminates. Subsequently, the impact of POSS on the same properties of the laminates was evaluated. Then, an ample comparison between the results obtained was performed, followed by the assessment of the study limitations and future works.

1.3 Thesis Outline

This work is organized into five different chapters:

- The first chapter, Introduction, gives an overview of composite materials in aeronautical and aerospace industries, the project's motivation, its objectives, and the thesis outline.
- Chapter 2, State-of-the-Art, reviews the existing research on high-performance composites, focusing on carbon-based macro and nano reinforcements and POSS nanoparticles.

- Chapter 3, Materials and Experimental Procedure, provides a description of the materials used, the manufacturing procedures, and testing methods.
- Chapter 4, Results and Discussion, analyses the dispersion, the mechanical properties (flexural and tensile), the thermal properties, and the water contact angle, reporting the influence of the introduction of GCN and POSS nanoreinforcements into the carbon fibre/epoxy laminates.
- Chapter 5, Conclusion, summarises the findings, and the limitations and gives suggestions for future work.

Chapter 2

State-of-the-Art

This second chapter overviews the research already made on the topic of high-performance composites and their application in the aeronautical and aerospace fields to increase the theoretical knowledge in those topics. As a consequence, this chapter will be divided into two parts: the first one relies on carbon-based elements as macro-reinforcements and the second one will be focused on carbon-based nano-reinforcements.

2.1 Composite Materials

Many materials are effectively composite materials. Even Nature produces these materials which are materials made up of at least two non-mixable constituents which, when joined, lead to better properties than the ones of the primary materials [5]. Commonly known Natural Composite materials are wood, bones and teeth. These materials usually have a problem of anisotropy- i.e. their properties vary with direction changes- given its fibrous reinforcement and so natural materials need to be explored around such anisotropy.

In contrast, artificial composite materials can be meticulously crafted to leverage the unique strengths of each component while mitigating their weaknesses, resulting in a final product that outperforms traditional materials.

Polymer matrix composites (PMCs) are a class of advanced materials composed of a polymer resin matrix reinforced with high-strength fibres or particles. These composites harness the unique properties of both the polymer matrix and the reinforcing materials to create structures with enhanced mechanical, thermal, and chemical characteristics.

2.2 Polymer Matrix

The polymer matrix serves as the primary binding material, providing cohesion and transferring loads between the reinforcing fibres or particles and sheltering those from the atmospherical agents and chemical attacks. Common polymer matrices used in PMCs include epoxy, polyester, vinyl ester, and phenolic resins, each offering distinct properties suitable for specific applications [6]. Each of these resins has its advantages and disadvantages which are resumed in Table 1.

Table 1. Advantages and disadvantages of various thermoset resins [6]

Type of Resin	Advantages	Disadvantages
Epoxy	• High mechanical and thermal properties • High water resistance • Long working times available • High-temperature resistance • Low cure shrinkage • High dimensional stability • Low electrical conductivity	• More expensive than vinyl esters • Component mixing is critical
Polyester	• Easy to use • Low cost compared to epoxy and vinyl ester	• Limited mechanical properties • High styrene emissions • Limited range of handling times • High cure shrinkage
Vinyl ester	• High chemical resistance • Higher mechanical properties than polyesters	• Post-cure treatments required for higher properties • High styrene content • More expensive than polyester • High cure shrinkage
Phenolic	• Good mechanical properties • Heat and impact resistance • High chemical and moisture resistance • Low cost • Low smoke emission	• Very low toughness • Brittle behaviour • Its resistance is badly affected by moisture
Polyurethane foam	• Low cost • High thermal insulation • Quick and easy application • High adhesive properties • Extremely lightweight • Doesn't release harmful gases or dust	• The spray foam insulation method is expensive

2.2.1 Epoxy resins

Epoxy resins are prized in aerospace and aeronautical industries for their exceptional strength, lightweight nature, and superior adhesive properties, allowing them to withstand the extreme conditions of space and high-altitude flighting. Given their high strength-to-weight ratio, epoxy resins contribute to fuel efficiency and enable aircraft to achieve greater speeds and altitudes. In addition, their good adhesion to various substrates provides a reliable chemical bond between different materials used in aircraft construction, such as metals, composites, and fibres, enhancing structural integrity and durability, crucial aspects for withstanding the rigorous demands of flight while ensuring safety. Additionally, their excellent resistance to corrosion, fatigue, and temperature fluctuations further bolsters their suitability for aerospace applications where reliability and performance are paramount [7].

Green epoxies, also known as environmentally friendly epoxies, are gaining traction in the aerospace and aeronautical industries due to their reduced environmental impact and health hazards compared to traditional epoxy resins. These eco-friendly formulations often use bio-based or renewable raw materials, reducing dependence on fossil fuels and decreasing carbon and volatile compound emissions during manufacturing and application, contributing to better air quality and manufacturing safety. Despite their eco-conscious composition, green epoxies maintain similar performance characteristics to their conventional counterparts, offering the same high-standard properties. As sustainability becomes an increasingly important focus across industries, the adoption of green epoxies in aerospace and aeronautical applications aligns with the sectors' commitment to reducing their carbon footprint while maintaining the stringent performance standards required for safe and efficient flight and space operations [8].

2.3 Reinforcement

The reinforcing phase of PMCs typically consists of fibres or particles made from materials such as carbon, glass, aramid (e.g., Kevlar), or natural fibres like bamboo or hemp. These reinforcing materials impart strength, stiffness, and other desirable properties to the composite structure. Carbon fibres, renowned for their exceptional strength-to-weight ratio and stiffness, are often used in high-performance applications where lightweight and high strength are critical, such as aerospace components but their development has reached their maximum performance and nano reinforcements have been getting attention in the last 20 years [9].

2.3.1 Carbon Fibre

Carbon Fibre (CF) is the most common reinforcement applied to PMCs in aeronautical and aerospace structural elements to date, given its improved mechanical properties, allowing them to replace the more conventional materials, like aluminium and titanium alloys, for primary structures [10]. Carbon fibres are composed of small crystallites of graphite and given their bonding types, this type of reinforcement is highly anisotropic, just like natural composite materials. Besides that, imperfections in alignment can result in points of weakness leading to the wane of the mechanical properties of the product.

According to Rahmani et al. [10], carbon fibre has a tensile strength of 2550 MPa, an elastic modulus of 135 GPa and an elongation at break of 2.1%. Their work covered the impact of the addition of 3 and 5 layers of CF with different orientations to 3 types of epoxy resin with a reinforcement percentage of 40 wt.%. This work concludes that fibre orientation is the parameter that controls the mechanical properties of the final product.

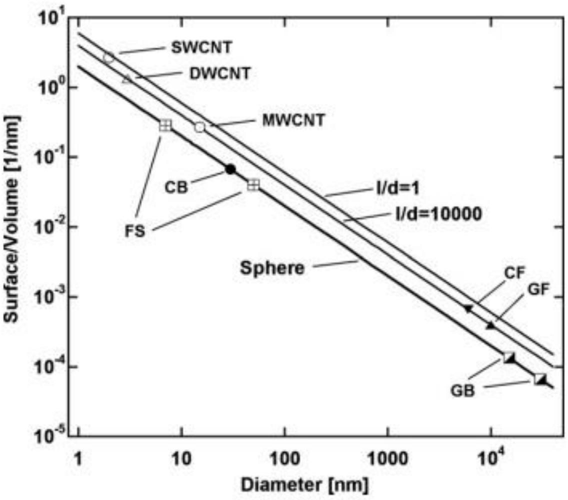
The achievement of maximum improvement in the mechanical properties of composite materials reinforced with CF is highly dependent on the interfacial bonding between the fibres and the matrix and so, a lot of work has been done to enhance interfacial adhesion strength resorting to surface treatments. According to J.-S. Lee et al. [11], air oxidation treatment generates micropores which increase the surface area and functional groups on the fibre's surface. They also discovered that the heat treatment of the CF increases the surface area and transforms micropores into macropores with resin-accessible size. So, to achieve the best adhesion between the fibres and the matrix, it is necessary to perform a preliminary treatment of the fibres.

2.3.2 Carbon-based Nanocomposites

Polymeric nanocomposites (PNCs) can be defined as the combination of two or more materials, which have a polymer as the matrix and with the dispersed phase having one dimension less than at least 100 nm [12].

Usually, the addition of carbon-based nano reinforcements aims to achieve multifunctionality and to be able to fully customize the mechanical, electrical and thermal properties of a material [13] and to solve the drawbacks encountered with the utilization of conventional reinforcements. In the common carbon fibre-reinforced composites, there is the need for higher loadings for the sake of obtaining increments in the properties of the final material, augmenting the weight of the structure whilst, with nano reinforcements, increments up to 25% can be achieved with concentrations of less than 2 wt% [14].

In contrast to conventional composites that are controlled by the properties of the fibre, matrix and their interface, nanocomposites bring some challenges to the table given the complexity of interactions that have to be clarified due to the control that the particle, the matrix and the manufacturing process has on the properties of the final product [15]. Figure 1 shows the ratio between the surface and the volume of different aspect ratios CNTs.



Caption:
SWCNT: Single wall CNT
DWCNT: Double wall CNT
MWCNT: Multi wall CNT
FS: fumed silica
CB: carbon black
GB: glass balls
GF: glass fibre
CF: carbon fibre

Figure 1. The ratio of particle surface and volume for spherical and fibrous particles as a function of the particle diameter [15]

It is possible to see that the addition of a small content of nano-particles provides huge surface areas that can enhance the cross-linking density in thermo-set polymers, resulting in increased mechanical properties by changing the polymer morphology. For instance, the surface area of SWCNT is 1000 times higher than the one of CF [15].

2.3.3 Carbon Nanotubes

To date, Carbon Nanotubes (CNTs) are the nano-materials that have gained the most attention and the ones that are researched the most. They are made of graphene sheets that roll up, forming a tube shape.

CNTs exhibit a high aspect ratio with low density and high strength and stiffness, properties that make them a good candidate for the reinforcement of polymeric matrices with the prospect of improving their mechanical, physical and electrical properties [15]. According to Fiedler et al. [15], the issues that need to be solved to enhance the matrix's properties when reinforcing them with CNTs are the interfacial bonding and the proper dispersion in the matrix.

According to Kim et al. [16], the addition of 0.3 wt % of CNTs to epoxy/woven CF composite panels had little influence on the tensile properties of the panel given their relation with the fibre domain whilst it positively impacted the flexural properties which are based on the matrix, increasing the flexural modulus by 1%, the flexural strength by 18% and the fracture strain by 11%. So, CNTs can be used as a reinforcement of the matrix's properties but, even at a small loading of CNTs, Scanning Electron Microscopy (SEM) analysis showed ineffective load transferability due to weak bonding at the interfaces between the matrix/ fibre and the CNTs, suggesting the necessity for an improvement in the fabrication process and the requisite for surface treatments of CNTs.

In the mechanical properties of CNT-reinforced epoxy composites, Karapapas et al. [17] studied the influence of this reinforcement in mode I and mode II fracture behaviours on epoxy/ CF composites and concluded that contents of 1 wt.% of CNTs led to an increase of 60% in the fracture toughness of the laminates in mode I. For mode II, the addition of 0.5% and 1% of CNTs was examined and resulted in the augment of 45% and 75% of the fracture toughness, respectively. These increments in fracture toughness are related to the surface adhesion between the matrix and the reinforcement that improves the load transferability between those phases, which is key to improved mechanical properties of epoxy matrices. Besides these results, they also concluded that the addition of 0.1% CNTs decreased the fracture properties given the presence of agglomerations.

Kim et al. [18]studied the effects of surface modification on the flexural and wear behaviours of CNT/epoxy composites and discovered that the flexural properties of the composite were improved by the addition of surface-modified CNTs, that the silane-treated CNTs gave an increase of 34% and 20% bigger in the flexural modulus and flexural strength, respectively, when compared with acid-treated CNTs. Besides that, they also discovered that the wear behaviour had identical conclusions as the flexural properties, associating these phenomenons to the improved dispersibility and interfacial bonding between the silane-modified CNTs and the epoxy.

Thus, it is possible to affirm that the addition of CNTs to epoxy-based composites enhances the mechanical properties of the final product when surface treatments are performed on the CNTs.

To study the influence of the addition of CNTs to epoxy matrices on the thermal properties, Neto et al. [19] investigated how different percentages of CNTs and different sonication power outputs affected those properties. Their work described that the degradation temperature of the composite increased, such that the highest sonication power output studied, 75 W for 40 minutes using a 4 mm probe, was the most effective in the dispersion of the CNTs corresponding to the highest glass transition temperature (T_g).

2.3.4 Graphene

Graphene has been studied as a potential filler given its exceptional electrical and thermal properties aligned with high strength and modulus discovered to be set between 300 GPa and 900 GPa [14] and it is incorporated into epoxy resins via GNP or GO. According to Zaghloul et al. [14], graphene also is incorporated into epoxy resins to act as a flame retardant agent of the resin, reducing the risk of combustion of the material and the emission of pollutant gases.

Rehman et al. [20] studied the behaviour of epoxy composites reinforced with 0.3, 0.5, 0.7 and 1% of graphene nanoplatelets (GNPs) and discovered that the addition of the graphene particles raised the Elastic modulus and that this increase peaked at 0.5% wt. with an increment of 37%. In the case of the Ultimate Tensile Strength, a was observed a decrease that was attributed to the dependence on the sample conditions, like the particle's dispersion and the solvent used, besides the poor interfacial bonding between the constituents. This work also performed a Thermogravimetric analysis (TGA) in which was discovered that for a concentration of 1.5% wt of graphene, the initial decomposition temperature, which corresponds to 5% weight loss, decreased from 339° C to 330 ° C. The authors state that this phenomenon can occur due to the decomposition of the interfacial epoxy chains.

Shen et al. [21] also studied the influence of graphene nanoplatelets on the mechanical properties of epoxy resins. They discovered that loading of 0.25 wt.% of GNPs led to an increase in tensile strength of 20%, the flexural strength of 9% and flexural modulus of 12% and Wang et al. [22] discovered that adding 5 wt.% of GNPs increased the Elastic modulus by 48.8% and the flexural modulus by 25.7%. Besides them, many other researchers [23] focused their studies on the influence of this type of reinforcement and had results similar to the ones described prior and ascribe the stated phenomenons to the strength of the nanofillers, and the robust interfacial adhesion between the nanofillers and matrix.

Wan et al. [24] reclined their studies on the graphene oxide (GO) positive influence on the epoxy matrix's mechanical and thermal properties, comparing the functionalized version of the reinforcement with the as-produced one. They describe that the functionalized version of GO improved the dispersion of the filler in the matrix leading to increased thermal stability, the initial decomposition temperature increased by 14 °C, and tensile strength and fracture toughness which increased by 79% with the loading of 0.1 wt.% and 41% for the loading of 0.25 wt.%, respectively. The same behaviour was observed for the as-produced GO, but the maximum values are lower than the ones verified for the functionalized version of the filler. They also noted that the fracture toughness dropped when the loading of filler was higher than 0.5 wt.%. This occurrence was described as happening due to the nonuniform dispersion of the filler and the weak interfacial bonding between GO and the matrix.

Zhao et al. [25] also studied the mechanical behaviour of epoxy nanocomposites reinforced with graphene oxide and discovered that silane-functionalized GO increased the epoxy's hardness by 3.3% for the loading of 0.3%, the value from which the hardness decreased. The authors associate this phenomenon with the difficulty of homogenous dispersion and the infiltration of the filler in the epoxy matrix for those values of loading. The same behaviour was observed for the flexural properties, the flexural strength increased until the 0.3 wt.% of filler loading and then decreased, being that the loading of 0.3 wt.% increased this property by 14.7%. Besides the mechanical properties, GO also increased the glass transition temperature from 91.7° C, for the pure epoxy, to 99.6° C for loading of 0.3 wt.% of functionalized GO.

2.3.5 Carbon Nanofibers

Carbon nanofibers (CNFs) find diverse applications in the aeronautical and aerospace industries due to their unique combination of properties, including high strength, lightweight, electrical conductivity, and thermal and chemical stability [26], so they have been used for structural composites, electromagnetic interference shields, thermal management systems and lightning strike protection devices.

Bortz et al. [27] studied the enhancement that the addition of carbon nanofibers to structural epoxy elements could have. The authors discovered that increasing CNF concentrations led to higher fracture toughness (K_{IC}), being that the concentration of 1 wt.% of CNF increased this parameter by 78%. They also analysed the fatigue life of the same composites and determined that for loadings of 0.5 wt.% and 1 wt.%, it increased by 180% and 365% respectively for a strength amplitude of 20 MPa. For a strength amplitude of 40 MPa, the fatigue life of the sample with 0.5 wt.% loading decreased whilst the one with 1 wt.% concentration increased by 10%. This phenomenon occurs due to the weak surface bonding between CNFs and matrix.

Chen et al. [28] studied the incorporation of different concentrations of differently functionalized CNfs into epoxy matrices. They discovered that all three types of functionalized CNF - electrospun carbon nanofibers, vapour growth carbon nanofibers and graphite carbon nanofibers - improved the impact absorption and tensile strength of the neat epoxy resin. They studied the concentrations of 0.1 wt.%, 0.3 wt.% and 0.5 wt.% and discovered that the highest concentration led to the highest increment on those properties for all the samples. Besides the properties referenced previously, the authors also analysed the flexural properties of the samples and the same behaviour was verified being that the maximum flexural strength and elastic modulus were recorded for the sample with 0.5 wt.% of functionalized CNFs. For higher concentrations, the mechanical properties dropped given the formation of filler agglomerates and the inhomogeneous dispersion of the CNF particles.

Aziz et al. [29] compared the behaviour of pristine CNFs and functionalized CNFs and discovered that the storage modulus slightly decreased for concentrations up to 2 wt.% for the amine-functionalized CNFs in the glassy state and loadings up to 0.5 wt.% for the pristine CNFs. Nevertheless, it increased for higher loadings for both samples. Subsequently, the authors proceeded to perform a tensile test to determine the tensile strength and modulus of the two additivated epoxies. The results for the tensile strength show an increase of 22% for the loading of 2 wt.% of the functionalized form of CNFs and a rise of 11.8% for the loading of 5 wt.% of the pristine CNF. For the same loadings, the elastic modulus increased by 27% and 7.3% for the functionalized and pristine forms, respectively. For higher loadings, both tensile strength and modulus decrease and the authors associate this aspect with a poor interface and incomplete wetting of the nanofibers. In conclusion, the dispersion was improved by the functionalization of CNF, leading to a better load transfer and, consequently, higher mechanical properties. Besides the mechanical tests, the authors performed thermal stability, dielectric and electrical conductivity tests and discovered that the glass transition temperature had a higher increase for the functionalized CNF when compared to the pristine form. The same behaviour was registered for the dielectric properties and the electrical conductivity.

Through the work developed by Santos et al. [30], it is possible to conclude that CNFs are good epoxy reinforcements when the dispersion and processing techniques are adequate and that increasing the CNF content in epoxy matrices leads to a significant improvement in mechanical properties. In the case of the flexural strength, there were recorded improvements between 10 and 416.8% for concentrations within 0.25 and 1 wt.%. For the flexural modulus, the increments were between 0.5 and 143.6% and for the tensile strength and modulus, there was an augmentation between 3 and 64.9% and 1.2 and 98.3%, respectively. For low-velocity impact strength, the gains recorded were between 8.3 and 25% for the damaged area reduction and 1.7 and 88.6% for the absorbed energy. The authors also studied the Glass-ionomer cement (G_{IC} and G_{IIC}) and recorded improvements between 4.7% and 1650% for the G_{IC}, while for G_{IIC}, the improvements were between 21.7% and 208.6%.

2.3.6 Carbon Black

Carbon black (CB) has emerged as a promising reinforcement material for epoxy resins, offering enhanced mechanical and barrier properties and high electrical conductivity [31].

Öner [32] studied the effects on the mechanical and thermal properties of the reinforcement of epoxy resins with carbon black nanoparticles obtained from waste tyres. The author discovered that the degradation temperature increased with the addition of CB and the mass loss decreased with the same parameter. In terms of the glass transition temperature (T_g), was observed an increase with the addition of the nano-reinforcement and the maximum value was registered for a concentration of 0.6 wt.% of CB, the value from which T_g decreased. In addition, the author tested the flexural strength of the samples and obtained an increase for all doped samples when compared with the neat epoxy and the maximum increase was registered for the sample with 1 wt.% of CB with the value of 11.6%. These increments are associated with the large surface area of the CB particles which enhances the bonding between the nanofiller and the epoxy matrix.

Dungani et al. [33] also studied the influence of the addition of CB on the mechanical properties of epoxy resins and discovered that the highest increase in Vicker's hardness and fracture toughness was registered for the loading of 5 wt.% of CB for the three types of CB under study, with increases as high as 537% for the Vicker's Hardness and 1045% for the Fracture toughness. The decreasing trend registered for loadings higher than 5% was attributed to the formation of agglomerations. When the fracture surface was analysed, the authors noticed that the addition of higher concentrations (>5%) increased the number and the elongation of cracks, leading the samples to become brittle, increasing the absorption of fracture toughness by the CB particles, which was made by crack deflection and fracture of the particles.

Alo et al. [34] investigated the effects of the addition of graphite synthetic powder and CB to a matrix of a blend of polypropylene and epoxy on the electrical and mechanical properties of the matrix. The results obtained suggest an increase in flexural strength and modulus between the filler content of 50 wt.% (49% Graphite + 1% CB) and 60 wt.% (57% Graphite + 3% CB). Higher loadings led to a decrease in that property. The authors suggest that this phenomenon could happen due to the good interaction between the filler and the matrix and the higher content of the rigid graphite filler for lower loadings. The further increase in filler content leads to agglomerations and worse strength transmission. In terms of electrical conductivity, the results indicate that the augment of filler content leads to the increase of that property up to 83% for the in-plane direction and 24% for the through-plane direction. The authors also compared this electrical property between samples just with graphite filler and the ones with the two fillers and discovered that the best electrical conductivity was obtained for the later condition.

2.3.7 Nanodiamond

In recent years, nanodiamonds (ND) have come into view as promising reinforcement agents for epoxy resins, offering a unique combination of mechanical and tribological properties [31]. This reinforcement consists of graphene sheets arranged in a diamond shape.

Neitzel et al. [35] studied the tribological properties of nanodiamond additive epoxy composites and discovered that for samples containing 7.5 and 12.5 vol.% the bulk wear resistance was improved but for concentrations of 25 vol.% the wear marks and agglomerates of filler became noticeable by light microscopy. In terms of the friction coefficient, it was clear that the addition of ND reduced the friction coefficient between 16.3 and 87.5%. This property started to decrease with the addition of ND, reaching the lowest values for the sample with a concentration of 7.5 vol.%, and then increasing again, which can be due to the agglomeration of ND particles sticking out of the matrix in the higher filler contents.

Zhai et al. [36] researched the improvement of the reinforcement of epoxy resins with nanodiamond powder and revealed that the Vicker's hardness and the Elastic modulus increase when the filler content is below 0.3 wt.%, the value for which reaches the maximum increase of 24.7% and 54.2%, respectively. For higher concentration values, both properties decrease, a phenomenon attributed to the conglomeration of the nanoparticles. Then, the authors performed an SEM analysis and compared the fracture surfaces of the pristine epoxy, which showed almost parallel crack propagation, and the sample with 0.3 wt.% ND which presented a rougher surface, an indicator of the distortion of the crack propagation and an increase in the energy necessary for that propagation by the ND particles.

According to Neitzel [37], the lower concentrations, the ND nanoparticles agglomerate and form clusters that make the load's transmission difficult. This affirmation is based on the TEM images that show agglomerates for the sample with 2 vol.% of ND and an interconnected network for the one with 25 vol.%. For the loading of 25 vol.% of ND, Meyers hardness, Vicker's hardness and elastic modulus improved by 300, 270% and 350%, respectively. Moreover, the creep decreased by 44% for the same loading. Besides the mechanical properties, the thermal conductivity was also studied and it was concluded that, for the same loading, the thermal conductivity increased by 25%. The authors also refer that for small concentrations of ND, there is no significant change in the mechanical and thermal properties of the composite but that changes for loadings higher than 12 vol.%, a value that suggests that the nanoparticles start to be in direct contact creating a network of their own.

Farooq et al. [38] studied the ablative properties of nanodiamond-reinforced epoxy composites and concluded that the maximal thermal conductivity was higher for a concentration of 0.4 wt.%, an increase of 47%. Furthermore, the addition of the same concentration of ND led to and reduction of 12.6% in the erosion rate of the composite.

2.3.8 Fullerene (C60)

Fullerene is another graphene-based material used as an epoxy reinforcement due to its positive influence on the mechanical and tribological properties of epoxy composites.

Liu et al. [39] compared the tribological and corrosion resistance properties of epoxy composites reinforced with fullerene (C60) and graphene and discovered that the addition of the functionalized version of the two nanofillers limited the penetration depth for loading lower than 0.5 wt.%. For higher loadings, it was observed an aggregation of the fillers and cracks started to appear. Besides that, the authors noted that the penetration depth in the composites reinforced with C60 was lower than the one observed for the graphene ones. Furthermore, it was noticed that the friction coefficient decreased for low concentrations (<0.5 wt.%) and increased when the loading passed that value, being lower for the graphene composites than the C60 ones, for dry sliding. The opposite happened for seawater lubrification. Concerning the corrosion resistance properties, it was concluded that the protection efficiency of the reinforced composites was higher compared to the neat epoxy. Besides that, it was possible to conclude that the optimal content of filler was 0.5 wt.% and that the C60 reinforced materials had lower protection compared to the other ones.

On the other hand, Pikhurov et al. [40] studied the effect of low contents of fullerene on the dielectric properties of epoxy resins and concluded that elastic modulus and tensile strength increased, for concentrations as little as 0.1 wt.% the increment was 10%. For loading of 0.08 wt.% of C60, the impact strength increased by 71%. The results of this work describe that the addition of fullerene particles leads to an increase in dielectric permittivity, indicating the loss of molecular mobility in the glassy stage and, consequently, the hardening of the matrices' chains.

Zuev [41], in the work up to the previous study, examined the effect of the same nanofiller on the toughening of epoxy composites and reported that the addition of concentrations of C60 between 0.01 wt.% and 0.12 wt.% did not affect the glass transition temperature, concluding that the introduction of this filler does not affect the thermal properties of the matrix. Regarding the mechanical properties, the inclusion of C60 nanofillers in concentrations between 0.01-0.12 wt.% into the matrix led to increments of 10-15% in elastic modulus and strength. Moreover, it was possible to observe an increase in impact strength linear with the augment in filler content, reaching 300% for the highest concentration studied. These results were achieved given the lack of agglomerations of nanofiller and the good interface adherence between the filler and the matrix.

Jiang et al. [42] obtained similar results to the ones described previously for the standard transverse tension test, reaching an increment in elastic modulus, tensile strength and elongation of just 6%, besides testing samples with higher contents of C60 (1-3 wt.%). As was observed in the previous work, this study also concluded that the addition of fullerene particles improved the toughness of the matrix, seeing as the fracture toughness was increased by 31% with the addition of 3 wt.% of fullerene to unidirectional CFRP laminates. In contrast, the transverse fibre bundle tension approach performed by the authors led to very different results as the maximum strength by 42% with a loading of 3 wt.% of fullerene. In the SEM images, it became clear that the addition of this nanofiller led to a better fibre/matrix adhesion, despite the occurrence of cracks on the fracture surface, leading to improvements in the mechanical properties of the composite.

2.3.9 Nano graphite

Nano graphite (NG) is another carbon-based nanomaterial, composed of graphene layers, that has emerged as a promising reinforcement agent for epoxy resins due to its exceptional mechanical, electrical, and thermal properties.

Joshi et al. [43] studied how the mechanical, electrical and wear characteristics of epoxy composites vary with the addition of nano graphite. They identified that the electrical conductivity increases with the addition of NG, reaching an increased value of 21% by the weight fraction of 20 mg/dL and 427% for 100 mg/dL of NG. For the mechanical properties, the authors discovered that the addition of NG led to an increase in tensile, compressive and impact strengths, achieving increments as high as 44%, 5.3% and 32%, respectively, for a weight fraction of 300 mg/dL. The hardness also increased reaching an augment of 25% for the same weight fraction. The elongation and the wear loss were affected by the concentration of NG as well, decreasing by 44% and 8-10% (for pressures of 2 and 4 bar), respectively for the loading cited before. The results obtained were associated with the brittle behaviour of the graphite-epoxy composites.

Huan et al. [44] discovered that the thermal conductivity increased with increasing nano-graphite content, reaching an increment of 38.2% for a loading of 2.05 wt.% of NG. In the case of the mechanical properties, the tensile strength observed decreased with the NG content and the elongation at break was maintained. Such results were expected by the authors given the fact that higher conductivity is expected with decreasing tensile strength for values above the critical loading of 0.75 wt.%. The authors ascribe this behaviour to the interconnection network created by the filler's particles.

According to Maheshwari et al. [45], the presence of different nanofillers enhances the mechanical properties of epoxy nanocomposites. Specifically, NG almost doubled the tensile strength for the concentration studied of 3 wt.%. The same occurred for the compressive strength. In terms of Rockwell hardness, the addition of NG led to an increase of 24%. In addition, the compressive modulus improved by 54%, the roughness by 458% and the Elastic modulus by 62%, reaching the highest improvement of the 3 nanofillers in comparison, due to the high qualitative content of oxygen-bearing functionalities of the NG particles.

2.3.10 Graphitic Carbon Nitride as a Reinforcing Agent

In the recent past, graphitic carbon nitride (GCN) has attracted attention from researchers given its low cost and good chemical stability, owning to its graphite-like structure, as shown in Figure 2. Being the most stable allotrope of carbon nitrides, GCN exhibits high thermal stability and can reinforce the mechanical properties of epoxy resins [46].

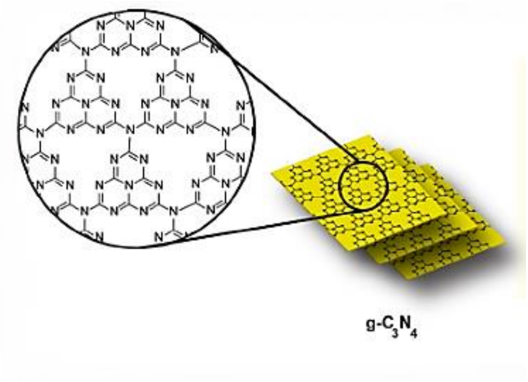


Figure 2. Graphite-like structure of GCN nanofillers [47]

Baghdadi et al. [46] studied the mechanical and thermal properties of GCN-based epoxy composites and discovered that GCN has a decomposition temperature of about 640ºC, a massive improvement compared to the product that is used to synthesize that nanofiller which has a decomposition temperature of 305.15ºC, but in the case of the polymeric matrix, the improvement was 8.9% leading the decomposition temperature to reach a maximum of 371.79ºC for the loading of 0.125 wt.% of GCN. In terms of the glass transition temperature, the authors noticed that the maximum improvement (6.8%) was reached when the loading of GCN was 0.25 wt.%, which is no notable improvement as per the authors. The Dynamic Mechanical Analysis (DMA) analysis also proved an improvement in the storage modulus in both the glassy and rubbery stages, which indicates a good interaction between the matrix and the reinforcement. In the case of the mechanical properties, the improvements were also noticed where the content of 0.5 wt.% led to improvements of 21.5%, 8.1% and 77.3% in tensile strength, elastic modulus and fracture toughness, respectively. Those results are related to the improvement of the interfacial adhesion between the filler and the matrix.

Wang et al. [48] studied how the mechanical properties varied with the addition of GCN. The authors discovered that the maximum increase in Elastic modulus was registered for a concentration of 4 wt.% of GCN, an increment of 31.8%, while the maximum flexural modulus was registered for the highest concentration studied (5 wt.%), an augment of 28.3%. Moreover, the tensile and flexural strengths also increased until the loading of 1 wt.%, the value from which the results showed a decreasing trend. The improvements in those properties were 16% and 12.7%, respectively. This enhancement in the mechanical properties is attributed to the good surface bonding between the filler and the matrix, the curly structure of the particles and the large surface area of the nanosheets. The fracture surface morphology was also studied and the authors noted that the smooth surface of pristine epoxy was altered with the addition of GCN, with the fracture surface exhibiting a rougher morphology. In terms of the thermal properties, it was an increase in glass transition temperature increased 8ºC. Besides that, the authors also noted that for loadings higher than 3 wt.% of GCN, agglomerations occurred, reducing crack deviation efficiency.

Naidu et al. [49] examined the erosion behaviour of GCN-reinforced epoxy composites and discovered that, given the maximum erosion angle interval of 45º to 60º, GCN-reinforced epoxy has a semi-ductile nature. They also observed that the erosion rate decreases for filler percentages up to 3 wt.%, gradually increasing onwards. This increment is attributed to the weak bond between the filler and the epoxy matrix.

According to Wang et al. [50], the thermal conductivity augments with the ascending filler content. The authors observed that the 3D nanosheets had a higher impact on thermal conductivity when compared to randomly dispersed GCN, leading to an increment of 353% compared to the 300% for the loading of 17 wt.% of those types of filler. It was also noted that the electrical resistivity and the shore hardness decreased with increasing filler concentrations, but still maintained high electrical insulation and hardness values in the 3D filler. Benefiting from the continuous heat conduction pathways existing in the 3D nanosheets and the improved interfacial interactions between GCN and epoxy resin, 17.0 wt % of the 3D filler obtained a superior thermal conductivity with an elevation of 535% on neat epoxy.

Xavier et al. [51] studied the flame retardant properties and anticorrosion behaviour of epoxy composites with GCN modified with an inorganic nanofiller (3-trimethoxysilylpropyl diethylenetriamine hafnium(IV) oxide (HfO2)). They observed that weight losses for increased temperatures were significantly reduced with the addition of 0.6 wt.% GCN. Besides that, the addition of that concentration of filler led to a decrease in heat and smoke releases, revealing that the addition of GCN to epoxy resin can positively impact the flame retardant properties of this polymer, reducing those properties by 73% and 57%, respectively. In terms of anticorrosion properties, the authors discovered that the addition of 0.6 wt.% of the filler to the coating of a steel bar offered optimal barrier protection and anti-corrosion performance. Furthermore, the mechanical properties of the composites also were improved reaching an increase of 236%, 386% and 249% in tensile strength, hardness and adhesion strength, respectively, characteristics obtained given the high surface area of the GCN particles and the strong surface bonding they create with the epoxy resin.

Chen et al. [52] affirm that GCN is recognized as a flame retardant ascribed to its nitrogen richness and thermal stability. To reduce gas release during combustion, the author included metal elements in the GCN nanofiller and discovered that the char yield, characterized by thermogravimetric analysis (TGA) of the filler at 800ºC is 28.4%. Moreover, the authors observed that 10 wt.% of the GCN-modified filler improved the limiting oxygen index by 31.5% and reduced the peak heat release, total heat release, peak smoke production, total smoke production peak CO production, and peak CO2 production by 47.9%, 37.5%, 20%, 44.5%, 30.9%, and 42.5%, respectively. Those improvements were related to the thermal stability of GCN nanoparticles, ensuring that this filler is a feasible solution for the epoxy's flame retardant problem in an economical way. The results obtained were attributed to the high thermal stability of the nanoparticles and the formation of an intact carbon layer at the sample´s surface.

2.3.11 Polyhedral oligomeric silsesquioxane

Polyhedral Oligomeric Silsesquioxane (POSS) is a class of nanomaterials that have gained significant attention across various scientific disciplines and industrial applications. Its ability to integrate seamlessly with various composites opens up a myriad of possibilities for enhancing the structural integrity, thermal stability, and mechanical properties of aerospace composite materials. Figure 3 presents a representation of the POSS' chemical structure, the characteristic responsible for the enhancements experienced in the works described in the following paragraphs.

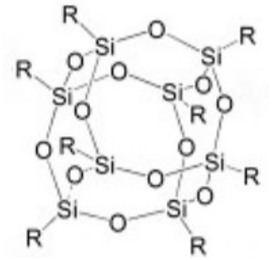


Figure 3. Molecular structure of POSS [53]

According to Liu et al. [54], the addition of 2 wt.% of GO grafted with POSS leads to an improvement in initial thermal decomposition temperature of 3.5% and 363% for the storage dynamic modulus and for the concentration of 5 wt.%, it was noticed an increment of 7.8% in glass transition temperature. In terms of the mechanical properties, the first loading mentioned was the one with the highest increments in impact strength, tensile strength and elastic modulus, 146%, 25% and 15 %, respectively. The highest improvement in flexural strength, 59%, was registered for the loading of 3 wt.%. These improvements were related to the thermal stability and the strong bonding between the matrix and the reinforcement.

Heid et al. [55] studied the influence of the addition of glycidyl-POSS to an epoxy resin and discovered that there were no significant improvements in the glass transition temperature. But in the case of the erosion properties, improvements up to 722% were registered for the concentration of 20 wt.% and 206% for concentrations as little as 1 wt.%. The thermal conductivity was also improved, reaching an increment of 120% for the same concentration.

Following Wu et al. [56], flame-retardant properties of epoxy resins are enhanced by the incorporation of POSS nanoparticles, being that the peak heat release rate (PHRR) decreased by 33% but the total heat release rate (THRR) did not show any variation for a loading of 10 wt.%.

2.4 Final Remarks

Given the works stated previously, it is clear that all nanofillers are able to improve the epoxy's properties either mechanical, thermal or flame-retardant ones. For instance, a concentration of 3 wt.% of fullerene can lead to an improvement in maximum strength of 42% [42], due to good adhesion between the nano reinforcement particles and the polymeric matrix. Owing to their high surface areas, CNTs can increase the fracture toughness in mode I fracture testing by 60% with a concentration of as little as 1 wt.% [16]. However, the optimal incorporation of these reinforcements and, thus, supreme improvement of the epoxy's properties are dependent on surface modifications of CNTs. This can elevate production costs, environmental hazards and toxicity concerns and limit the possibility of scaling up the composite's production, topics that are imperative in today's aeronautical and aerospace applications.

Likewise, when incorporated into epoxy resins, GCN nanofillers significantly enhance the material's mechanical performance, improving its resistance to strain, formation of cracks, and fracture, as stated by Baghdadi et al. [46]. The authors noted an increment of 77.3% in fracture toughness for the loading of 0.5 wt.% of GCN into epoxy. Furthermore, GCN exhibits excellent thermal stability, maintaining its structural integrity at high temperatures, which translates flame retardant properties and anticorrosion behaviour for the epoxy composite as shown by Xavier et al. [51] who discovered that, with the addition of 0.6 wt.% GCN to the polymer, the heat and smoke release can be reduced by 73 and 57%. Additionally, its chemical inertness ensures compatibility with epoxy matrices and provides long-term stability against chemical degradation, making it an ideal choice for applications in harsh environments such as aerospace and aeronautical industries.

Alongside the exceptional mechanical, thermal, and chemical properties, the potential to obtain GCN particles in a cost-effective and environmentally friendly manner, makes it the optimal nanofiller for reinforcing epoxy resins, offering unparalleled performance and durability in high-performance composite materials. Hand in hand with this filler, POSS emerges as a capable flame-retardant filler that, in combination with GCN, is expected to increase the mechanical and thermal properties of the matrix.

Chapter 3

Materials and Experimental Procedure

3.1 Materials

As discussed in Chapter 2, combining an epoxy resin with graphitic carbon nitride offers a compelling solution to enhance the overall performance and functionality of epoxy materials. The incorporation of GCN nanoparticles into epoxy matrices can lead to improvements in mechanical strength, thermal conductivity, flame retardancy, and UV stability.

Accordingly, and aspiring the optimal dispersion of the nanocomponents, the polymeric matrix chosen was the low-viscosity epoxy resin AH150 and IP 430 hardener sourced from Ebalta [57], whose properties, as per the manufacturer, can be seen in Table 2.

Table 2. Epoxy resin Ebalta AH 150: processing data and physical properties as per the manufacturer [57]

Product		**Epoxy Resin AH 150**	**Hardener IP 430**	**Mixture AH 150/IP 430**
Colour	-	opaque	transparent	Opaque
Mixing ratio	-	100	30	
Density at 20°C	g/cm^3	1.16	0.93	1.13
Viscosity at 25°C	mPa.S	800	20	250
Pot life - 200g at 20°C	minutes	-	-	300-430
Curing time at room temperature	hours	-	-	36-48
Post-curing	hours	-	-	3-5 at 80°C

In addition to the low viscosity, this mixture presents good mechanical properties, as shown in Table 3, and high chemical stability, convenient characteristics for a high-performance nanocomposite developed for aeronautical components.

Table 3. Physical properties of the epoxy resin AH 150, as per the manufacturer [57]

Property		**Mixture AH 150/IP 430**
Flexural Strength	MPa	125 ± 1.2
Flexural Modulus	GPa	3.4 ± 0.3
Flexural elongation at break	%	5.9 ± 0.1
Charpy Impact Resistance	KJ/m^2	60 ± 6
Compressive Strength (0.75% proof stress)	MPa	95 ± 5
Service Limiting Temperature	°C	79 ± 3
Shore Hardness	Shore D	85 ± 3

The Graphitic Carbon Nitride (GCN) nanoparticles were synthesized via the thermal pyrolysis of melamine. The primary constituent, melamine, underwent thermal decomposition in a furnace at a temperature of 550°C for a duration of 4 hours. This process was conducted in an alumina crucible with a controlled heating rate of 10°C per minute. After the thermal decomposition, the resulting GCN powder was subjected to a fine grinding process and sieved through a 38 micrometres (µm) sieve to ensure similar dimensions for all the particles. The finely ground GCN powder was then incorporated into the epoxy resin.

When producing the laminates, 12 layers of woven High Strength 3K Carbon Fibre Fabric, whose properties can be seen in Table 4, were laminated with the GCN-reinforced epoxy resin.

Table 4. Physical properties of the carbon fabric, as per the manufacturer [58]

Property		**HS 3K Carbon Fibre**
Mass per area	g/m^2	196 (± 4 %)
Weight – warp and weft	g/m^2	98 (± 4 %)
Thickness	mm	0.25 (± 15 %)
Thread/ cm – warp and weft	-	4.9
Weave	-	Twill 2/2
Tensile Strength	MPa	3530
Tensile Module	GPa	230
Stretching	%	1.5
Poisson's Rate	-	0.25
Density (g/cm^3)	g/cm^3	1.73

Finally, intending to evaluate the effect of POSS nanofillers in the GCN-reinforced laminates, EP0409 – Glycidyl POSS which was sourced from Hybrid Plastics was also introduced. The properties of this material, as described by the manufacturer, are shown in Table 5.

Table 5. Properties of the POSS nanofiller, as described by the manufacturer [59]

Property		**EP0409 – Glycidyl POSS**
Apperance	-	Clear viscous liquid
Refractive Index at 20.5ºC	-	1.4813
Viscosity at 25 °C	Pa.S	4 – 6
Thermal Stability (5% wt loss)	ºC	365

3.2 Manufacturing Procedure

3.2.1 Control Sample

The samples of neat epoxy resin also referred to as control samples throughout the document were prepared in strict accordance with the manufacturer's guidelines [57] and taking into account the work developed by Santos et al. [60]. Initially, 135 g of epoxy resin was measured and, then, 40.5 g of hardener was added to the epoxy to fulfil the dimensions needed. These components were then homogenized manually mixing using a stirrer. This was succeeded by a degassing procedure conducted in a vacuum vessel for a duration of 10 minutes, the purpose of which was to eliminate any entrapped air bubbles caused by the mixing process. The sample was then subjected to a curing process, which was carried out in a 200 x 200 x 3 mm^3 cardboard mould for a period of 48 hours at room temperature. Following this, a post-curing process was implemented at a temperature of 80ºC for a dwell of 5 hours in a Carbolite NR200-F fan convection oven.

3.2.2 Reinforced Nanocomposites

A similar process to the one stated previously was used for the reinforced samples. The manufacturing procedure started with the measurement of the bulk GCN powder necessary for the different loadings (0.25, 0.5, 0.75, 1 and 2 wt.%). In order to attain an optimal dispersion within the reinforced specimens, the Graphitic Carbon Nitride (GCN) powder in its bulk form was introduced into 10 mL of ethanol. This mixture was subjected to an evaporation process at a temperature of 90ºC while concurrently being stirred at a velocity of 620 rpm with the aid of a magnetic hot plate Ibx Instruments H03D.

Subsequently, the GCN particles were incorporated into the epoxy resin and subjected to a dispersion process with a duration of one hour, utilizing a digital overhead stirrer LBX OS20 series vertical rotation stirrer at 1100 rpm and a sonication bath using an Ultrasonic Cleaner AU-65 which operated at a frequency of 40 Hz. Midway through this process, the GCN/epoxy mixture was exposed to an ultrasonication process for a total duration of one minute divided into two parts, facilitated by a Qsonica Q125 Sonicator ultrasonic processor with an ultrasonic probe, to further enhance the dispersion of the nano reinforcements [61].

Upon completion of this process, the hardener was introduced into the preceding mixture and subjected to the identical curing process as that of the neat epoxy samples, preceded by the same degassing process.

The manufacturing process implemented for the nanocomposites can be seen in Figure 4.

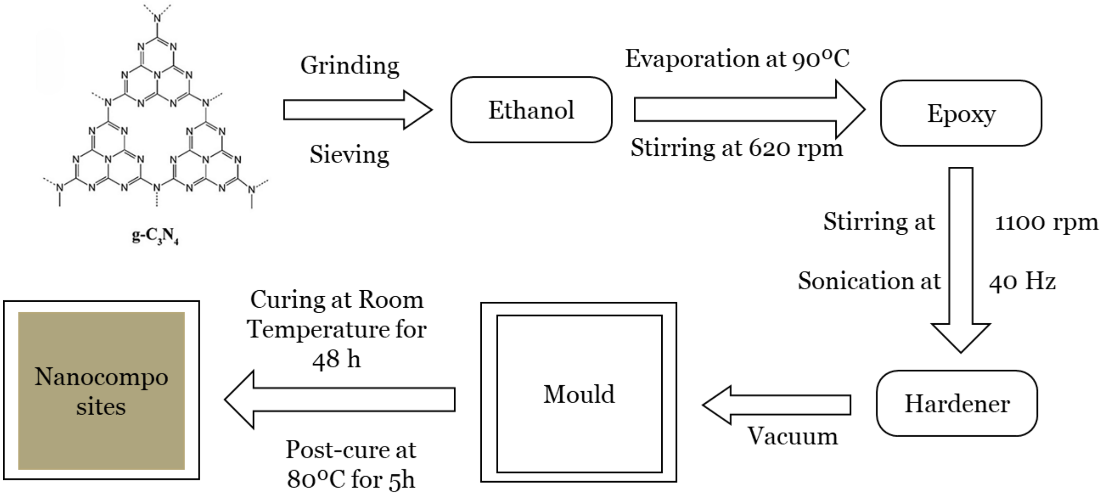


Figure 4. Nanocomposites' manufacturing process

3.2.3 Laminates

Following the methodology delineated prior, and adjusting the quantities necessary to fulfil the dimensions wanted, the GCN-reinforced and GCN+POSS-reinforced epoxy resins were prepared and, then, twelve meticulously hand-trimmed strata of 300 x 300 mm^2 carbon fibre tissue were methodically arranged and unified in a unidirectional sequence, adhering to the established hand lay-up technique. Subsequently, upon the completion of the layering process, the composite was sandwiched between dual sheets of release paper, ensconced within an absorbent textile, and subsequently ensheathed within a vacuum bag. This assembly was then affixed to a vacuum pump for a duration of thirty minutes. Thereafter, the ensemble was subjected to a regulated force of 2.5

kilonewtons (kN) throughout the entirety of the resin's curing period (48 hours) before the post-curing process at 80ºC for 5 hours as stated by the manufacturer.

Per the same procedure, the Polyhedral Oligomeric Silsesquioxane (POSS) nanoparticles were introduced into the epoxy matrix before the agitation and sonication steps, guaranteeing the nanoparticles' optimal dispersion.

Figure 5 represents a schematic view of the manufacturing process used to fabricate the carbon fibre laminates.

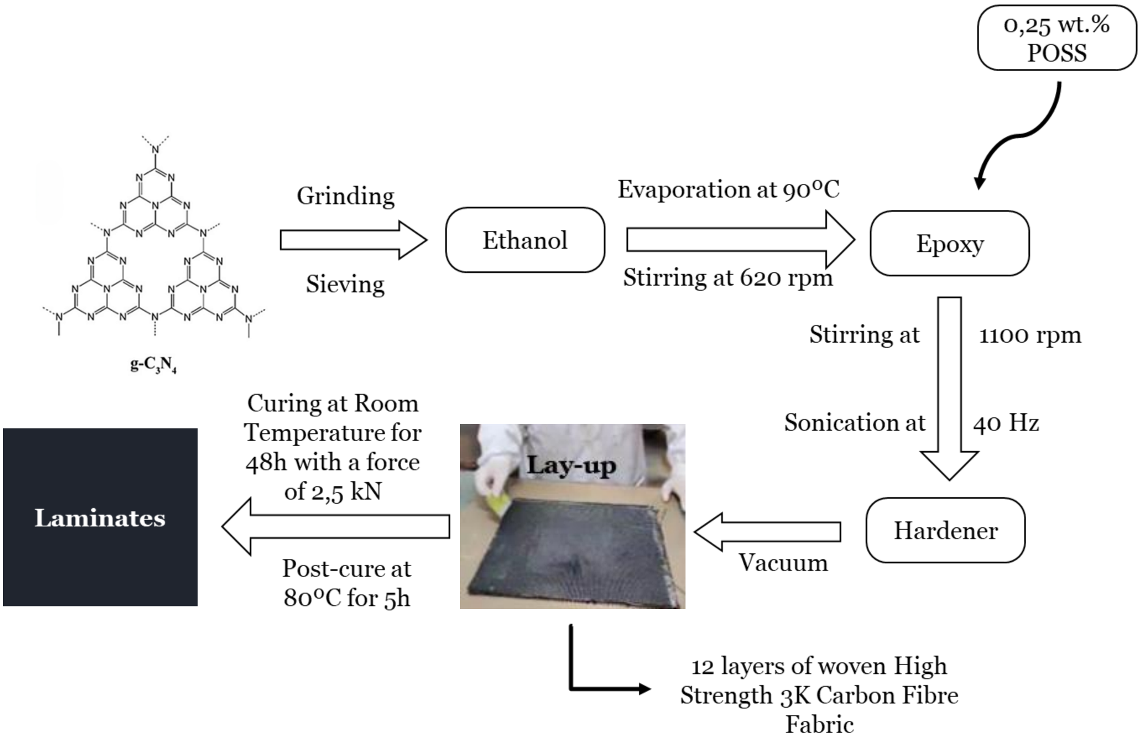


Figure 5. Laminates' manufacturing process

3.3 Testing Procedure

3.3.1 Flexural Properties Tests

Taking into account the applications aspired for this material, the flexural properties of the samples were ascertained through the application of a three-point bending test. This test involves the exertion of a load at a constant velocity at the midpoint of the specimen's span. The execution of these tests was facilitated by a Shimadzu Autograph AGS-X universal testing machine, operating at a displacement rate of 2 mm/min and utilizing a loading cell of 10 kN, conducted in strict adherence to the EN ISO 178:2003 standard testing methodology, using a span length of 50 mm. The data obtained from the flexural tests was then processed using the *Trapezium v 1.5* software.

Moreover, to generate a chart representing viscoelastic behaviour, the examinations were also executed at velocities of 20 and 200 mm/min for the fibre-reinforced specimens, following the same procedure.

So to obtain the maximum flexural strength and the flexural strain at break, Equations 1 and 2 were used, respectively:

$$\sigma_f = \frac{3\,FL}{2\,bh^2} \tag{1}$$

$$\varepsilon_f = \frac{6\,sh}{L^2} \tag{2}$$

where

- σ_f is the flexural strength [MPa];
- ε_f is the flexural strain;
- F is the applied force in Newtons [N];
- L is the span in millimetres [mm];
- b is the width of the specimen in millimetres [mm];
- h is the thickness of the specimen in millimetres [mm];
- s is the deflection in millimetres [mm].

With the strength-strain curves plotted, the flexural modulus, E_f [GPa], can be calculated from the slope and considering the initial linear elastic region, according to Equation 3:

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \tag{3}$$

where

- $\varepsilon_{f1} = 0.0005$;
- $\varepsilon_{f2} = 0.0025$;
- σ_{fi} is the corresponding flexural strength for the deflections given by Equation 4

$$s_i = \frac{\varepsilon_{fi}\,L^2}{6h} \tag{4}$$

Moreover, it was possible to calculate the storage energy by integrating the characteristic strength-strain curve. So, the properties that are compared in the results chapter are the maximum flexural strength, the flexural modulus, the flexural strain and the storage energy.

In accordance with the specified standard, five specimens from each sample were cut from the mould, each measuring 80 x 10 x 3 mm^3, using a Struers Accutom-2 cutting machine, equipped with an IsoMet Diamond Disc 15LC. Examples of specimens cut from the nanocomposite and the laminated slabs are presented in Figures 6 and 7, respectively.

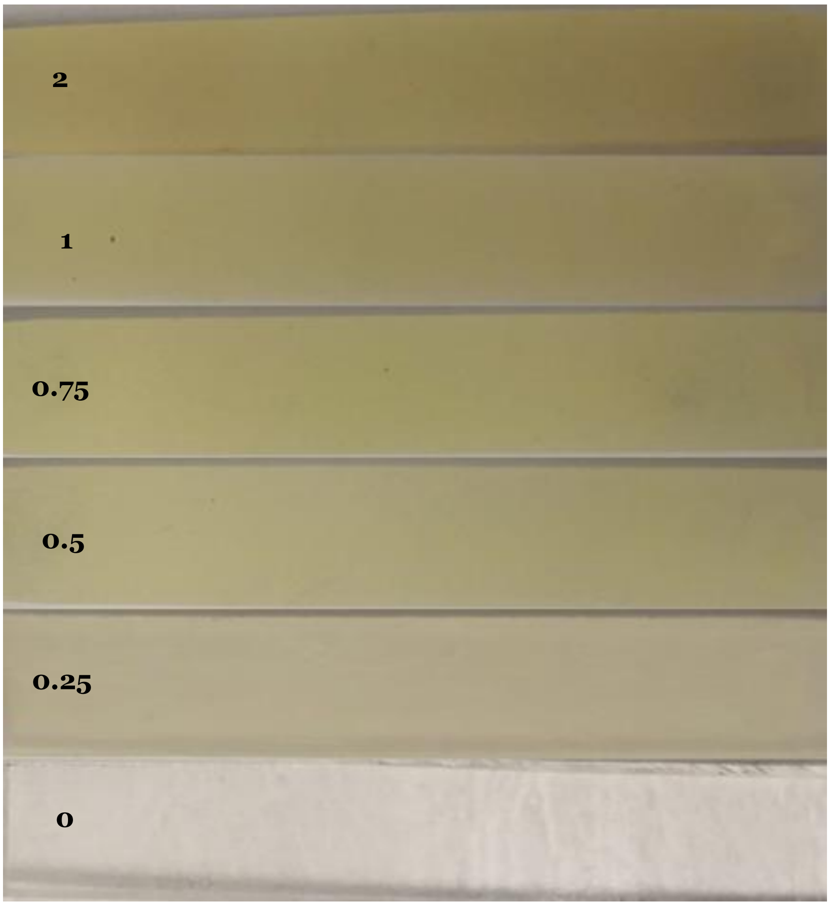


Figure 6. Epoxy and GCN nanocomposite flexural test specimens

Figure 7. Epoxy and carbon fibre laminated flexural test specimens

3.3.2 Tensile Properties Tests

The tensile properties were evaluated following the ASTM D2990 and D638 standard methods, to understand how the material behaves whilst it is being stretched. These tests were conducted with a Shimadzu Autograph AGS-X universal testing machine, operating at a displacement rate of 2 mm/min, utilizing a 50 kN loading cell and wedge type of self-aligning grips. Subsequently, the data obtained from the tensile tests was processed using *Trapezium v 1.5* software.

In order to measure the strain values accurately, the Software ZEISS Inspect Correlate was used as well as the high-resolution camera ARAMIS Adjustable 2D Digital Image Correlation (DIC) system to obtain the images for the software.

Subsequently, to acquire the tensile strength and elastic modulus, Equations 5 and 6 were used:

$$\sigma_t = \frac{F}{bh} \tag{5}$$

$$E_t = \frac{\sigma_{t2} - \sigma_{t1}}{\varepsilon_{t2} - \varepsilon_{t1}} \tag{6}$$

where

- σ_t is the tensile strength [MPa];

- ε_t is the tensile strain;
- F is the applied force in Newtons [N];
- b is the width of the specimen in millimetres [mm];
- h is the thickness of the specimen in millimetres [mm];

To prepare the experimental characterization, following the standards, 5 specimens with a *dog bone* structure were cut from the moulds with the dimensions shown in Figure 8, resorting to a water jet cutting machine.

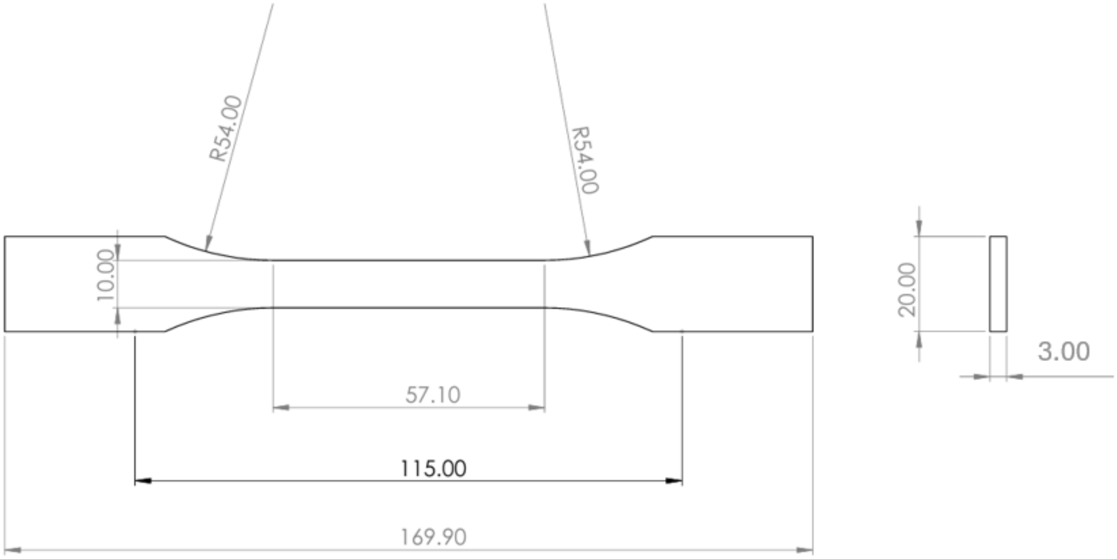


Figure 8. Dimensions of the tensile test specimen

In Figures 9 and 10, it is possible to observe the nanocomposites and the laminated specimens cut through that method.

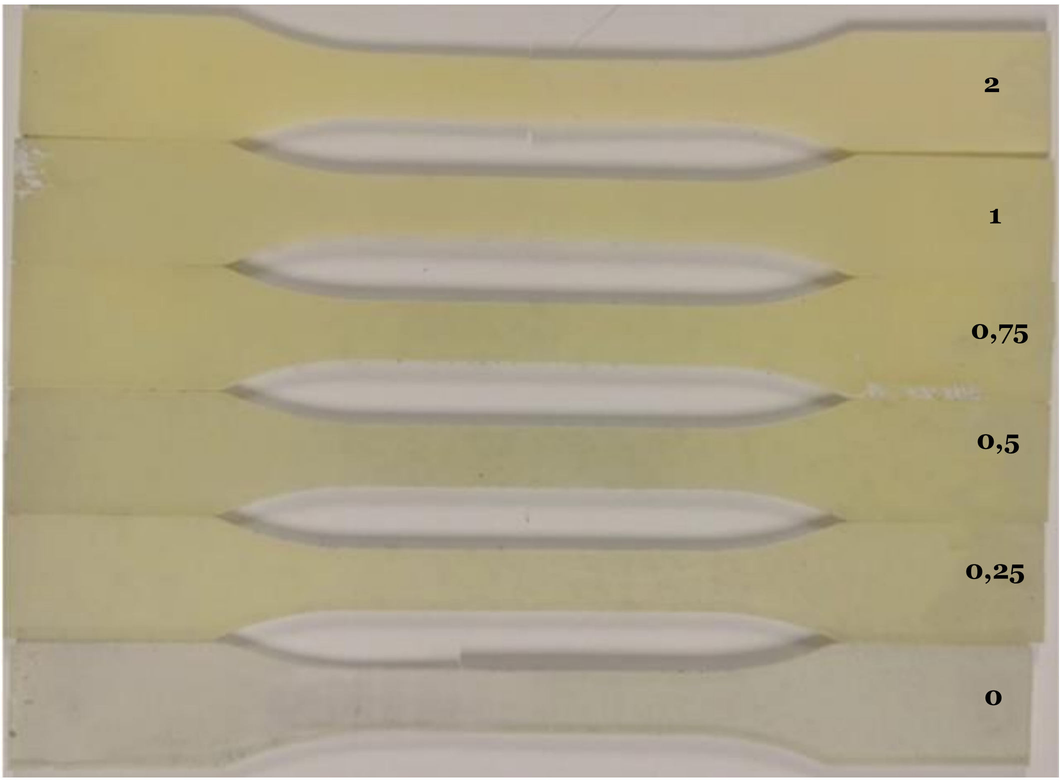


Figure 9. Epoxy and GCN nanocomposite tensile test specimens

Figure 10. Epoxy and carbon fibre laminated tensile test specimens

3.3.3 Thermogravimetric Analysis

A Thermogravimetric Analysis (TGA) is another valuable thermal analysis technique. In TGA, a sample's mass is continuously measured while it is heated, typically in an inert gas atmosphere. As the sample undergoes reactions (such as thermal decomposition), any gaseous byproducts are removed, and the remaining mass changes are recorded. TGA provides insights into phenomena like phase transitions, chemisorption, and solid-gas reactions. It's especially useful for studying polymeric materials, including thermoplastics, elastomers, and composites.

The TGA test was performed under nitrogen at a rate of 10 ºC/min from room temperature until 800 ºC, according to the procedure described by Baghdadi et al. [46], resorting to Universal V4.2E TA Instruments equipment.

3.3.4 Differential Scanning Calorimetry Analysis

Differential Scanning Calorimetry (DSC) is a thermoanalytical technique that measures the difference in heat required to increase the temperature of a sample and a reference material. Both the sample and reference are kept at nearly the same temperature throughout the experiment. Essentially, DSC allows us to study how a material's heat capacity changes with temperature. As a sample is heated, any changes in its heat capacity are tracked by monitoring the heat flow, enabling the determination of the Glass transition temperature (Tg) and Melting temperature (Tm), based on the endothermic peaks the DSC curve experiences.

The DSC analysis was conducted following the procedure described by Galy et al. [62], using a heating rate of 10 ºC/min until a maximum temperature of 350 ºC, resorting to a Netzsch DSC 204 cell and Netzsch TASC 414/3 A controller.

3.3.5 Water Contact Angle Analysis

Water Contact Angle Analysis is a valuable technique used to assess the wettability of solid surfaces. The contact angle is the angle formed between a liquid droplet and a solid surface where they meet. Specifically, it's the angle between the surface tangent on the liquid-vapor interface and the tangent on the solid-liquid interface at their intersection. A surface is considered hydrophilic if the water droplet spreads across it, i.e. the contact angle is lower than 90°. Conversely, a surface is hydrophobic if the contact angle is greater than 90°.

Various methods exist for measuring contact angles. In this study, the Sessile-drop method, which captures the angle of a liquid droplet on a solid surface, was used.

Chapter 4

Results and Discussion

This chapter aims to characterize the properties of nanocomposites and laminates resulting from the incorporation of graphitic carbon nitride (GCN) and polyhedral oligomeric silsesquioxane (POSS) particles into the epoxy matrix, acting as a nano reinforcement. The main goal of this investigation is to understand how these nanofillers influence the mechanical, thermal, and other properties of the composite materials as they will experience various types of loading throughout their operational lifespan when used in aeronautical and aerospace.

4.1 Dispersion

The characteristics of nanocomposite materials are profoundly influenced by the distribution of nano-scale reinforcements within the matrix. Graphitic Carbon Nitride (GCN) nanoparticles exhibit superior properties over other nanomaterials owing to the presence of surface functional groups. These groups facilitate enhanced adhesion to the epoxy matrix, thereby optimizing the composite's overall performance [48].

Figure 11 shows the optical microscopic images of the reinforced specimens. It is observable that the larger agglomerations manifest at a concentration of 0.75 wt.%. This occurrence may be attributed to the chemical interactions inherent within the GCN particulates or to the higher surface roughness of the GCN nanoparticles. The regions characterized by GCN agglomerations function as imperfections within the system, thereby initiating the formation of additional fissures. The existence of these agglomerations creates zones of elevated stress concentration, which serve as the starting points for cracks and lead to premature failure of the specimen under examination [46].

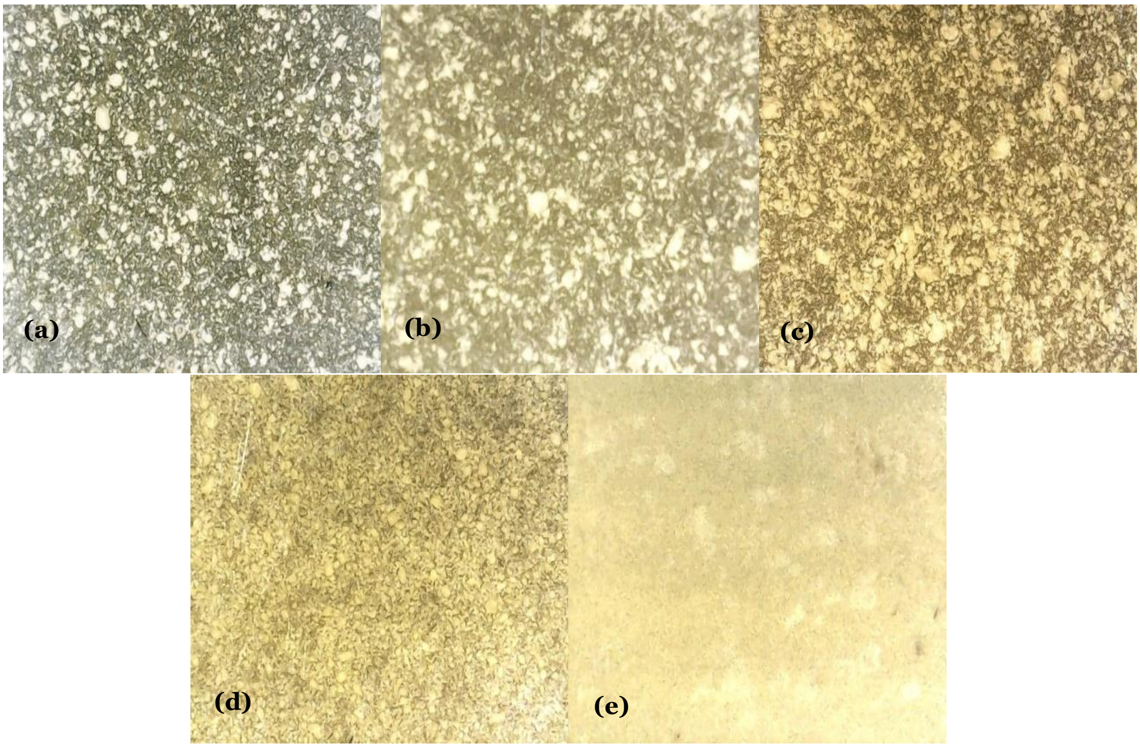


Figure 11. Optical microscope images of epoxy nanocomposites with different loadings of GCN: (a) 0,25 wt.%; (b) 0,5 wt.%; (c) 0,75 wt.%; (d) 1 wt.%; (e) 2 wt.%

The optimal microscope images indicate that the dispersion of GCN within the epoxy matrix was considered within acceptable parameters, notwithstanding the presence of conspicuous agglomerations at the lower extremity of the moulds. These agglomerations had a measurable impact on the material's characteristics, as a variation in the flexural properties was observed upon inverting the samples, i.e. using the lower surface of the mould as the upper testing surface, suggesting that the material exhibited superior performance under compressive forces as opposed to tensile ones.

Additionally, the 2 wt.% reinforced sample exhibits the least amount of agglomerations, likely owing to the different particle sizes of the GCN powder used. During the production of the reinforcement, the product was sieved through a smaller sieve, leading to a better dispersion of particles within the epoxy matrix. Although this difference did not influence the mechanical results of the sample, it highlighted the importance of the sieving process in achieving the least amount of agglomerations, which could lead to better results for other concentrations.

4.2 Nanocomposites

4.2.1 Flexural Properties

Static flexural tests were performed on neat epoxy, also referred to as the control sample, and on the samples reinforced with the different GCN concentrations, following the procedure stated previously, in section 3.3.1. These tests allowed for the collection of flexural properties, enabling a comparison between the reinforced samples and the neat epoxy. Table 6 encapsulates the data derived from the flexural tests conducted on all specimens. Concurrently, Figure 12 presents the outcomes on flexural strength, flexural modulus, strain, and storage energy, respectively.

Table 6. Summary of the flexural properties of the fabricated epoxy and GCN nanocomposites

Filler content [wt.%]	**Flexural Strength [MPa]**	**Flexural Modulus [GPa]**	**Flexural Strain [%]**	**Storage Energy [mJ/mm^3]**
0	116.5 ± 8.9	3.3 ± 0.26	6.94 ± 0.26	552.7
0.25	124.4 ± 2.3	3.3 ± 0.26	6.88 ± 0.42	601.4
0.5	120.8 ± 7.3	3.2 ± 0.11	6.39 ± 0.27	510.2
0.75	114.0 ± 7.6	3.3 ± 0.13	5.76 ± 0.49	441.6
1	105.6 ± 8.2	3.2 ± 0.27	5.70 ± 0.09	425.0
2	91.7 ± 1.8	2.9 ± 0.09	4.71 ± 0.51	273.8

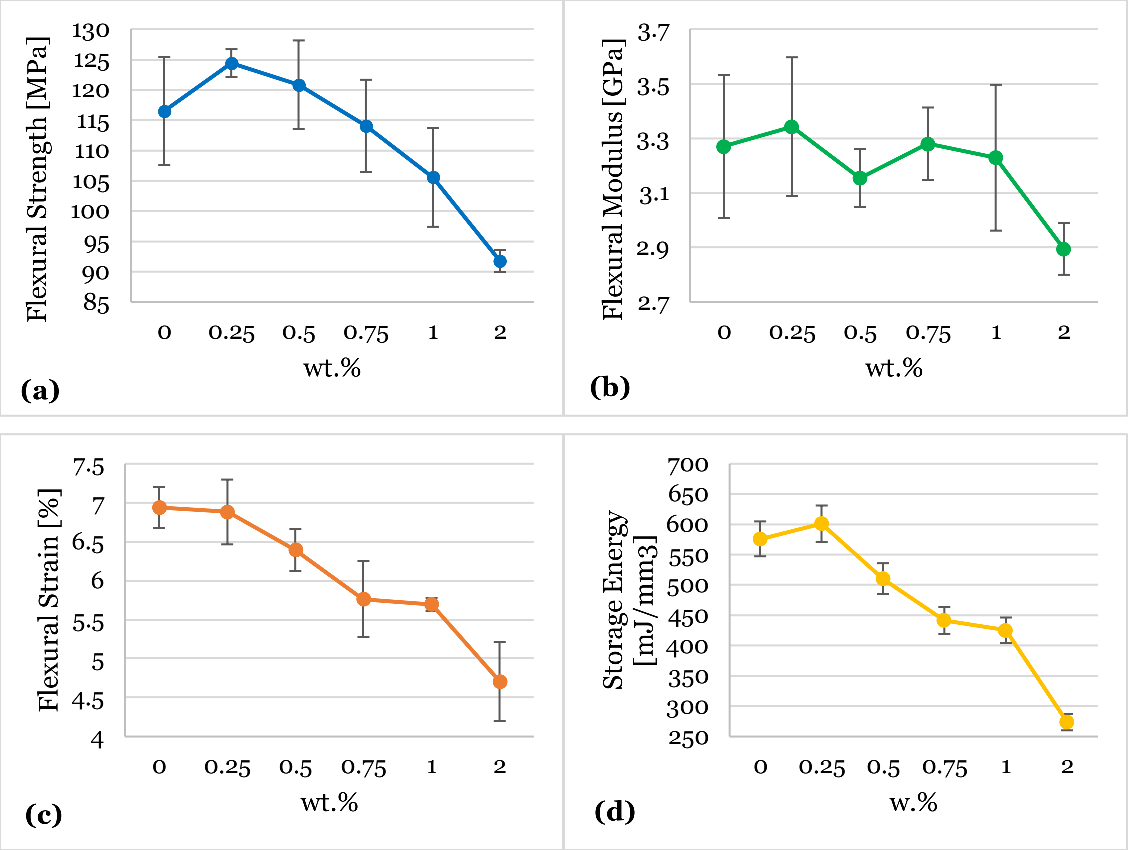


Figure 12. Flexural properties evolution of the epoxy and GCN reinforced nanocomposites with increasing GCN loading: (a) flexural strength, (b) flexural modulus, (c) flexural strain, (d) storage energy

The data indicates an enhancement in the peak flexural strength at a nano reinforcement concentration of 0.25 wt.%, succeeded by a decrease for concentrations exceeding this value. This trend is consistently observed across the flexural modulus and storage energy metrics. While a slight increase in flexural modulus was observed for the concentrations of 0.75 wt.% and 1 wt.% of GCN, the best overall values were achieved with a loading of 0,25 wt.%. Moreover, the flexural strain decreases with the increasing nanofiller load.

Following the improvements noted, Figure 13 illustrates the comparison between the characteristic strength-strain curves for the epoxy composite with a 0.25 wt.% concentration of GCN and the neat epoxy. It is observed a 7% increase in flexural strength (from 116.5 to 124.4 MPa) compared to the neat epoxy, a slight increase of 2% in flexural modulus (from 3.27 to 3.34 GPa), and a reduction of 0.8% in flexural strain. These improvements demonstrate the positive impact of incorporating GCN nanoparticles on the flexural properties of the epoxy matrix.

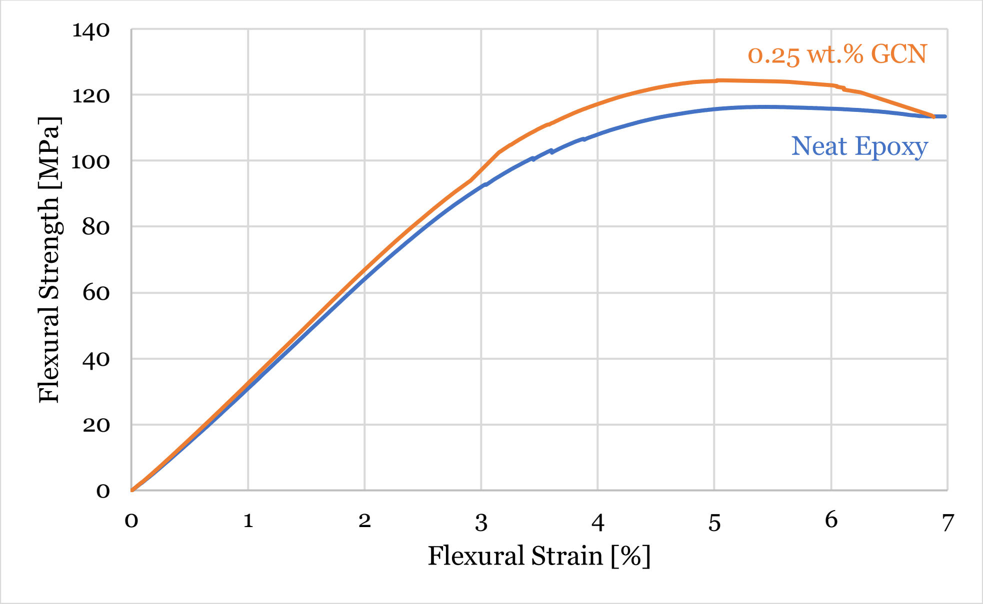


Figure 13. Comparison between the characteristic flexural strength versus flexural strain curves for the neat epoxy and the 0.25 wt.% GCN-reinforced samples

4.2.2 Tensile Properties

The tensile properties were tested for the 5 concentrations of GCN as well as the control sample, following the procedure described previously in Section 3.3.2, enabling the comparison of the results. The tensile data for the nanocomposites is summarized in Table 7 and Figure 14.

Table 7. Summary of the tensile properties of the fabricated epoxy and GCN nanocomposites

Filler content [wt.%]	**Tensile Strength [MPa]**	**Elastic Modulus [GPa]**	**Tensile Strain [%]**
0	46.5 ± 4.3	2.4 ± 0.16	2.07 ± 0.17
0.25	48.5 ± 4.3	3.0 ± 0.15	1.96 ± 0.33
0.5	48.6 ± 5.9	2.3 ± 0.14	2.43 ± 0.29
0.75	47.6 ± 2.2	2.4 ±0.03	2.28 ± 0.13
1	44.4 ± 4.0	2.6 ± 0.08	2.09 ±0.47
2	45.6 ± 5.7	1.9 ± 0.17	3.52 ± 0.39

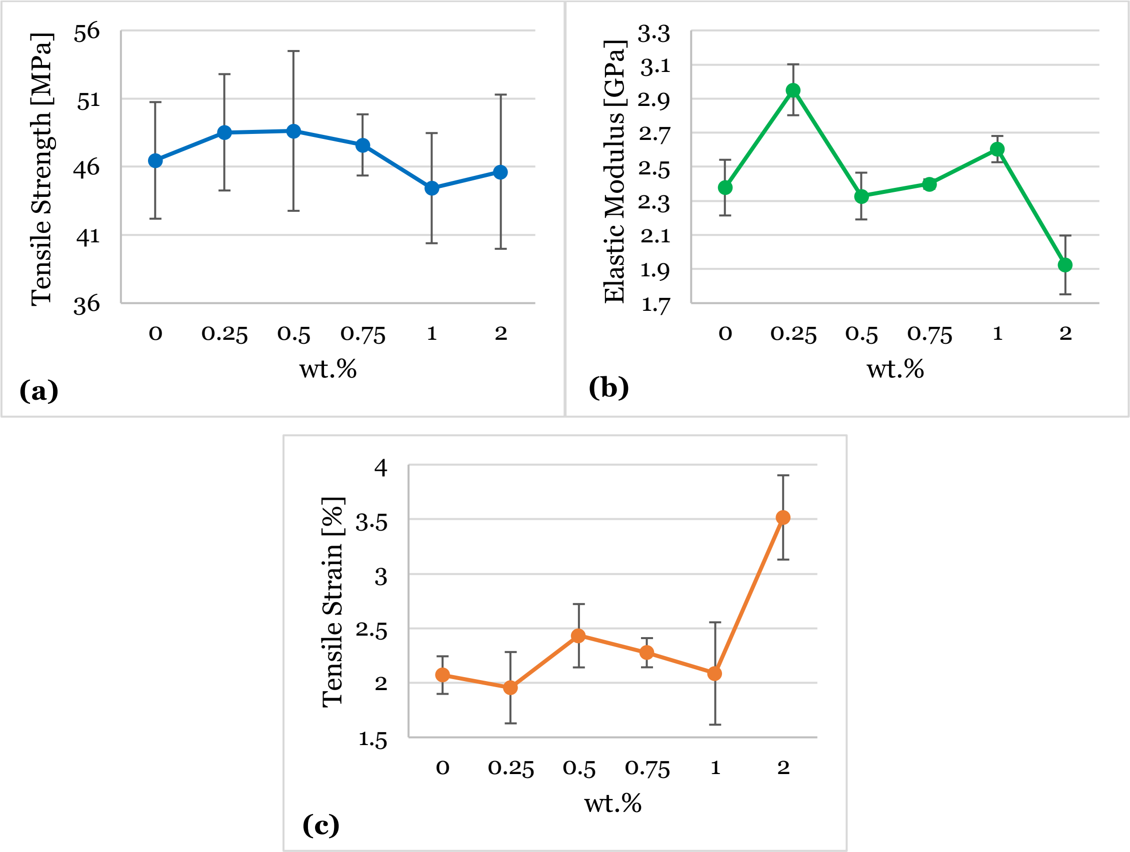


Figure 14. Evolution of the tensile properties of the epoxy and GCN nanocomposites with increasing GCN loading: (a) tensile strength, (b) elastic modulus, (c) tensile strain

The tensile test data reveals a modest increase in tensile strength for samples reinforced with concentrations below 1 wt.%. The most notable enhancements were observed at concentrations of 0.25 wt.% and 0.5 wt.%, with increases of 4% (from 46.5 to 48.5 MPa) and 5% (from 46.5 to 48.6 MPa) in tensile strength, respectively. While a slight improvement of 2% (from 46.5 to 47.6 MPa) was observed at 0.75 wt.%, higher concentrations did not demonstrate significant enhancements in tensile strength. Regarding the elastic modulus, the greatest improvement was recorded for the 0.25 wt.% concentration, which exhibited an elastic modulus 24% higher (from 2.4 to 3 GPa) than the control sample. Smaller improvements were noted for the concentrations of 0.75 wt.% and 1 wt.%, with increases of 1% and 10% (from 2.4 to 2.6 GPa), respectively. In terms of tensile strain, the only concentration that showed a reduction was 0.25 wt.%. These findings highlight the positive impact of GCN nanoparticles on the tensile properties of the epoxy matrix, with the optimal concentration for enhanced mechanical properties being 0.25 wt.%.

4.3 Carbon Fibre-Reinforced Laminates

Following the previous results, which demonstrated the optimal flexural and tensile characteristics at a loading of 0.25 wt.% GCN, further characterization was conducted on carbon fibre-reinforced laminates incorporating GCN and POSS at this concentration. The laminates were fabricated following the procedure outlined in section 3.2.3.

4.3.1 Flexural Properties

As stated in the previous chapter (in section 3.3.1), the flexural properties were tested for 3 different strain rates: 2, 20 and 200 mm/min, aiming to examine the viscoelastic behaviour of the laminates. Accordingly, the results obtained for the velocity of 2 mm/min are encapsulated in Table 8, and which characteristic strength-strain curves are presented in Figure 15.

Table 8. Summary of the flexural properties of the fabricated carbon fibre-reinforced laminates at the testing velocity of 2 mm/min

Filler content [wt.%]	**Flexural Strength [MPa]**	**Flexural Modulus [GPa]**	**Flexural Strain [%]**
0	362.6 ± 22.0	25.2 ± 6.64	2.45 ± 0.90
0.25 GCN	729.1 ± 59.0	59.3 ± 3.80	1.52 ± 0.05
0.25 GCN + 0.25 POSS	749.4 ± 75.9	54.7 ± 7.38	1.76 ± 0.10

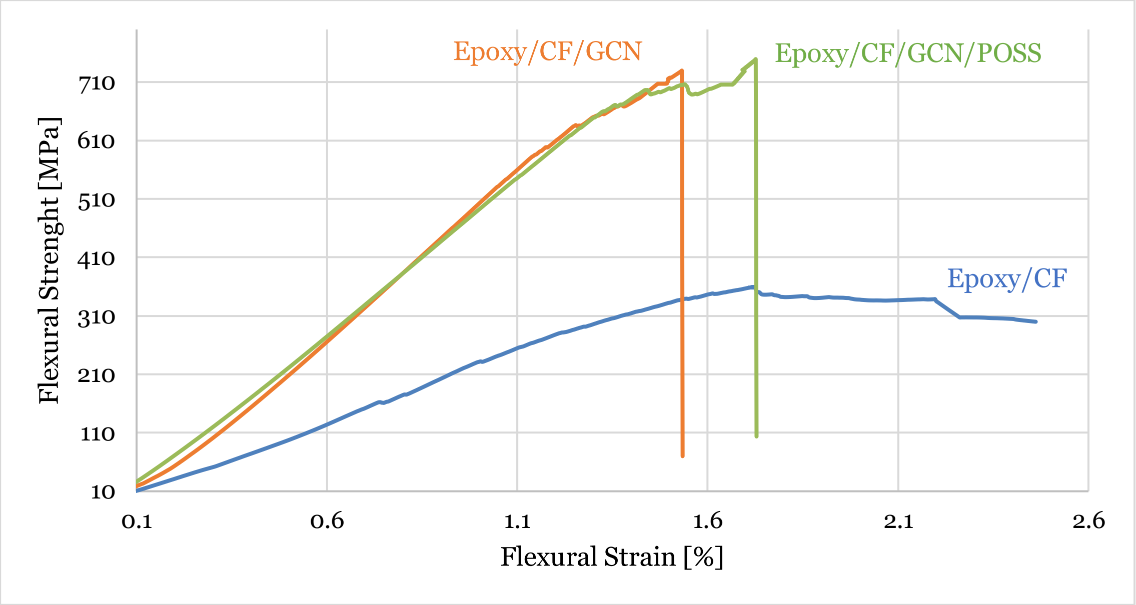


Figure 15. The flexural strength-strain characteristic curve for the laminates at a strain rate of 2 mm/min

The findings show a 101% increase in flexural strength (from 362.6 to 729.1 MPa) and a 135% increase in flexural modulus (from 25.2 to 59.3 GPa) for samples reinforced with GCN, Epoxy/CF/GCN. For specimens incorporating POSS (Epoxy/CF/GCN/POSS), the increase in flexural strength was slightly higher at 107% (from 362.6 to 749.4 MPa), but the improvement in flexural modulus was less significant at 117% (from 25.2 to 54.7 GPa), even though this was not apparent in the graphical representation. Despite the higher values, the standard deviation in flexural strength remains within acceptable limits, validating the results.

As stated previously, the laminated samples were tested for another two strain rates, 20 and 200 mm/min, allowing for the evaluation of the viscoelastic behaviour of the epoxy matrix and the laminates. The results obtained from these tests are presented in Tables 9 and 10, respectively. Moreover, Figures 16 and 17 present the comparison between the strength versus strain curves of the 3 materials for the 20 and 200 mm/min strain rates, respectively.

Table 9. Summary of the flexural properties of the fabricated carbon fibre-reinforced laminates at the testing velocity of 20 mm/min

Filler content [wt.%]	Flexural Strength [MPa]	Flexural Modulus [GPa]	Flexural Strain [%]
0	441.2 ± 51.4	38.2 ± 3.02	1.98 ± 0.04
0.25 GCN	774.8 ± 73.8	60.2 ± 0.87	1.55 ± 0.06
0.25 GCN + 0.25 POSS	757.1 ± 78.5	54.9 ± 4.11	1.64 ± 0.14

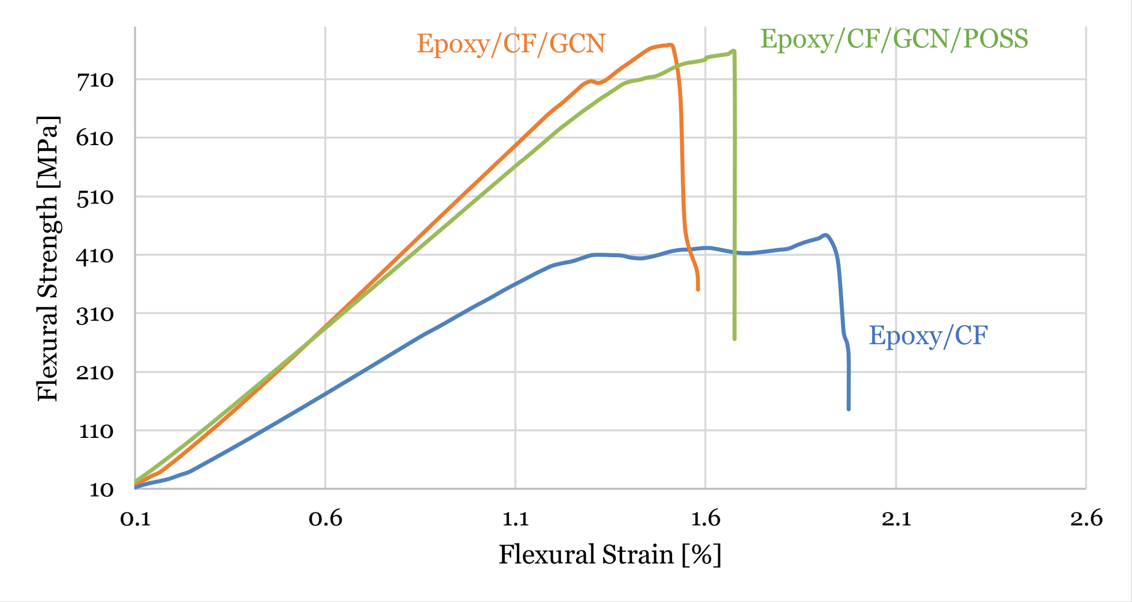


Figure 16. The flexural strength-strain characteristic curve for the laminates at a strain rate of 20 mm/min

Based on the data presented in Table 8 and Figure 16, we can draw the following conclusions for the displacement rate of 20 mm/min, comparing the neat epoxy and the reinforced samples: for the Epoxy/CF/GCN samples, there is a remarkable improvement of 76% in flexural strength (from 441.2 to 774.8 MPa) and the flexural modulus also shows a significant increase of 57% (from 38.2 to 60.2 GPa). For the Epoxy/CF/GCN/POSS specimens, the flexural strength improves by 72% (from 441.2 to 757.1 MPa) and the flexural modulus experiences a 44% enhancement (from 38.2 to 54.9 GPa). Additionally, the simply reinforced sample exhibits the least strain, followed by the one with POSS reinforcement.

Table 10. Summary of the flexural properties of the fabricated carbon fibre-reinforced laminates at the testing velocity of 200 mm/min

Filler content [wt.%]	**Flexural Strength [MPa]**	**Flexural Modulus [GPa]**	**Flexural Strain [%]**
0	369.8 ± 10.4	34.8 ± 4.34	2.14 ± 0.14
0.25 GCN	670.0 ± 59.2	54.3 ± 4.06	1.98 ± 0.13
0.25 GCN + 0.25 POSS	781.2 ± 57.5	56.6 ± 10.54	2.06 ± 0.23

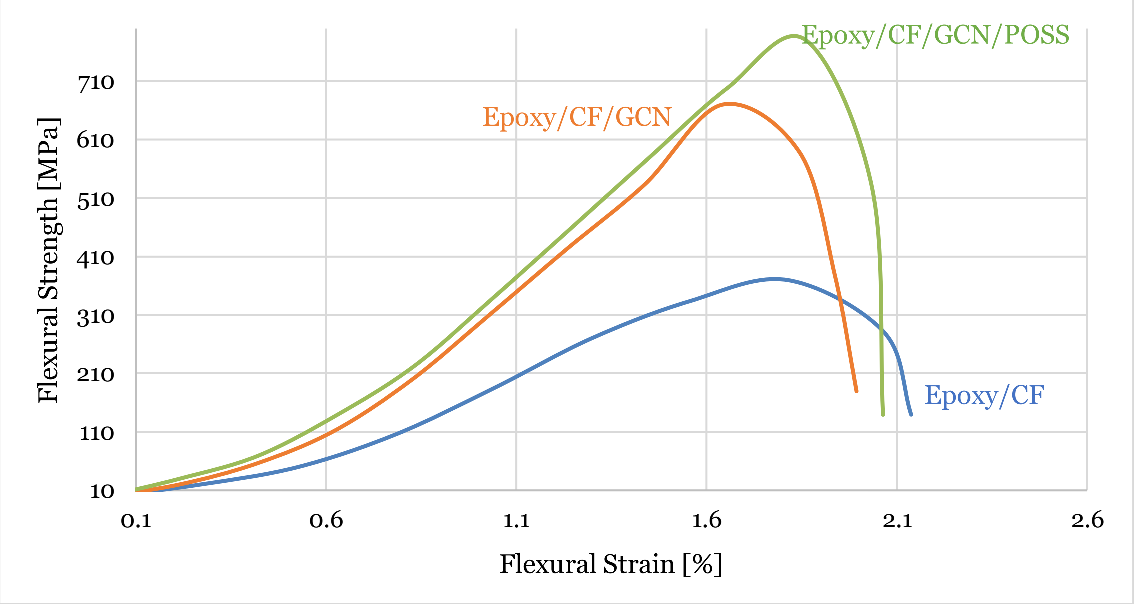


Figure 17. The flexural strength-strain characteristic curve for the laminates at a strain rate of 200 mm/min

The experimental results demonstrate a substantial enhancement in both flexural strength and modulus for Epoxy/CF/GCN samples when compared with the neat epoxy ones when tested at the strain rate of 200 mm/min. Specifically, there was an 81% increase in flexural strength (from 369.8 to 670 MPa) and a 56% rise in flexural modulus (from 34.8 to 54.3 GPa). Also, in comparison with the neat epoxy samples, specimens incorporating POSS (Epoxy/CF/GCN/POSS) exhibited an even greater improvement (111%) in flexural strength (from 369.8 to 781.2 MPa) and the increase in flexural modulus was more pronounced, from 34.8 to 56.6 GPa (63%). Additionally, the Epoxy/CF/GCN material exhibits the lowest strain, followed by Epoxy/CF/GCN/POSS.

Moreover, when crosschecking the results for the different strain rates, it is possible to conclude that the maximum flexural strength and the flexural modulus that the samples withstand tend to increment between the strain rates of 2 and 20 and diminish between 20 and 200 for the Epoxy/CF and Epoxy/CF/GCN samples. However, for the Epoxy/CF/GCN/POSS specimen, the maximum flexural strength and flexural modulus increased with the increment in testing velocity. When it came to the flexural strain, the control samples saw a decrease in that property for increasing strain rates, with the lower values registered for the strain rate of 20 mm/min. The opposite occurred for the Epoxy/CF/GCN sample, with increased flexural strain for higher strain rates. Lastly, the Epoxy/CF/GCN/POSS specimen experienced a decrease in flexural strain between the strain rates of 2 and 20 mm/min followed by a higher increment between 20 and 200 mm/min. Figure 18 presents the results of the viscoelastic behaviour of the laminates.

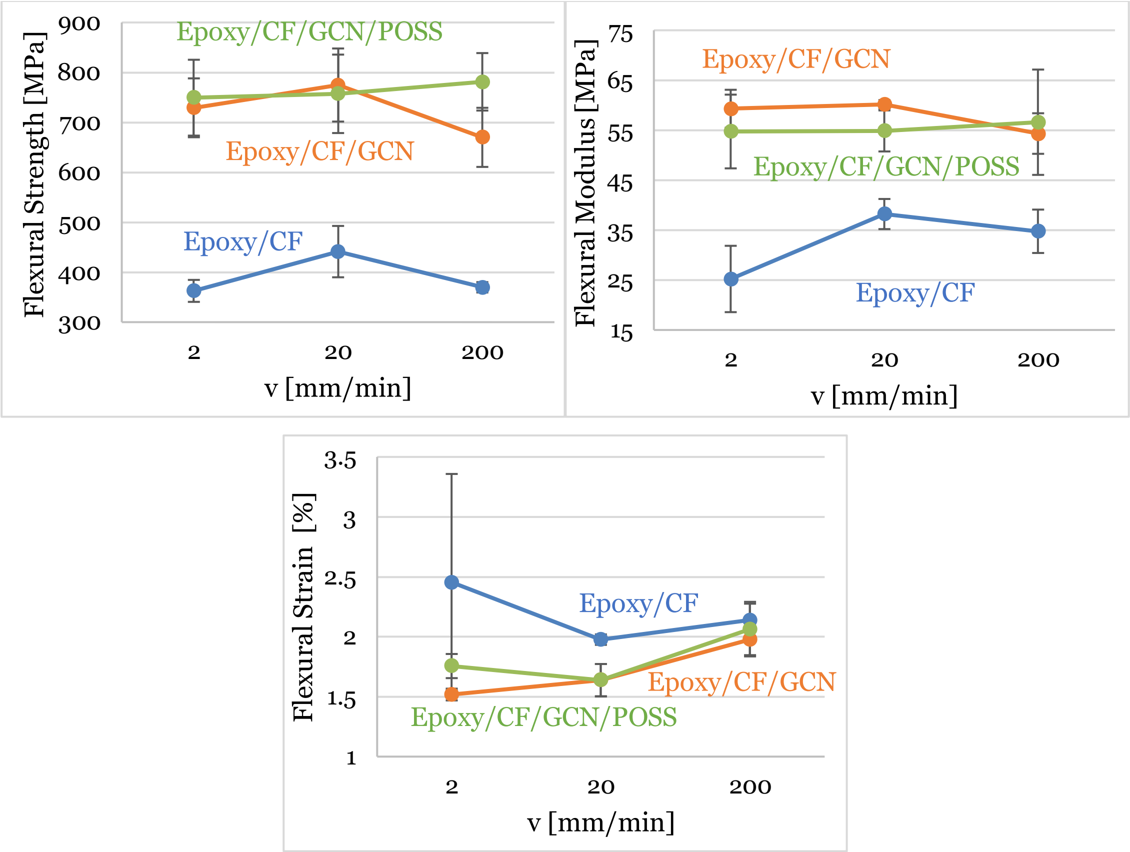


Figure 18. Viscoelastic behaviour of the laminates in terms of: (a) flexural strength, (b) flexural modulus, (c) flexural strain

In the study conducted by Song et al. [63], the flexural properties of epoxy composites reinforced with carbon fibres, whose surface was modified via in-situ with GCN nanofiller, exhibited an increase of 11% (from 719.5 to 795.1 MPa) in flexural strength and 10% in flexural modulus (from 47.1 to 51.8 GPa). The improvements observed in this document indicate a significantly greater enhancement in these properties at lower GCN concentrations, underscoring the potential for further optimization and application in advanced composite materials.

4.3.2 Tensile Properties

Considering the results detailed previously, the laminates were fabricated with a concentration of 0.25 wt.% of GCN and an equivalent amount of POSS. The obtained results of the tensile properties of the laminates are presented in Table 11 and Figure 19.

Table 11. Summary of the tensile properties of the fabricated carbon fibre-reinforced laminates

Filler content [wt.%]	**Tensile Strength [MPa]**	**Elastic Modulus [GPa]**	**Tensile Strain [%]**
0	408.3 ± 6.9	20.3 ± 2.77	3.39 ± 0.13
0.25 GCN	509.6 ± 31.1	28.1 ± 0.88	2.93 ± 0.21
0.25 GCN + 0.25 POSS	529.9 ± 21.4	22.7 ± 3.07	3.74 ± 0.25

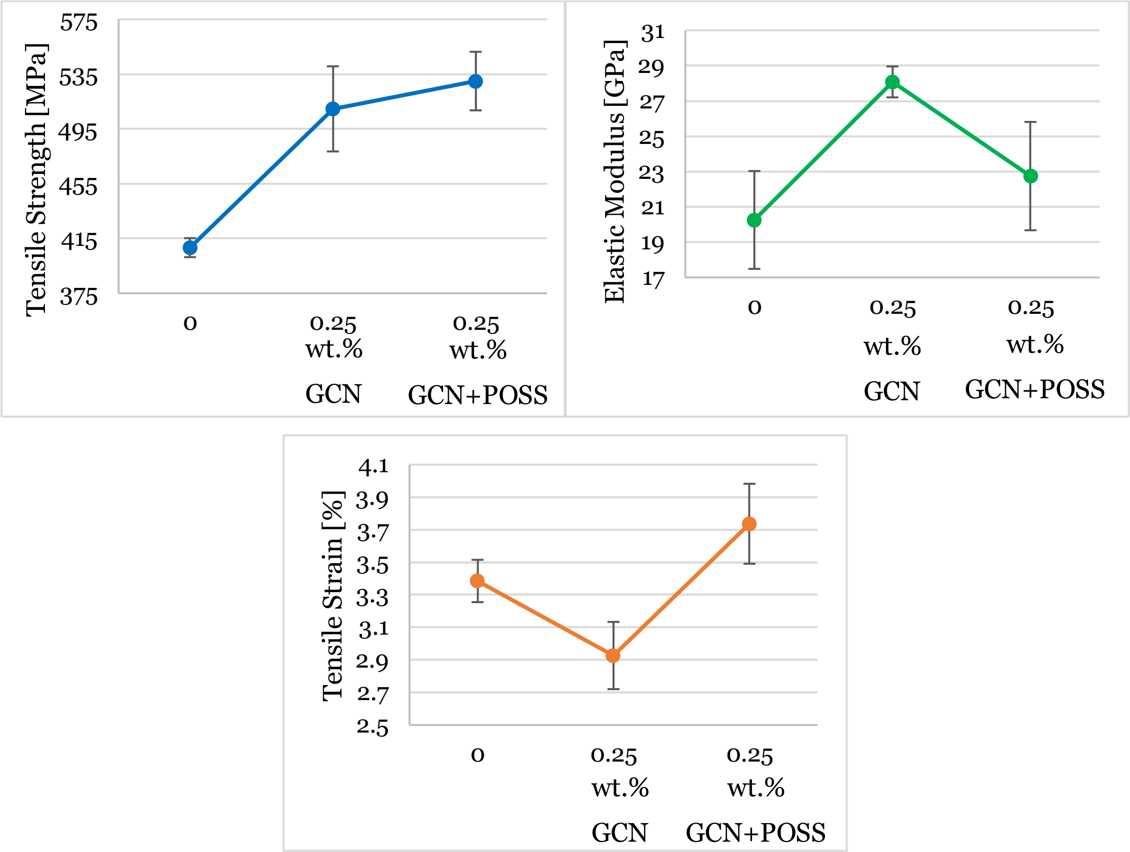


Figure 19. Evolution of the tensile properties of the laminates: (a) tensile strength: (b) elastic modulus; (c) tensile strain

The tensile strength of the GCN-reinforced laminates increased by 25% (from 408.3 to 509.6 MPa), while the POSS-reinforced laminates exhibited a 30% increase (from 408.3 to 529.9 MPa). Regarding the elastic modulus, the most significant improvement was observed in the Epoxy/CF/GCN samples, which exhibited a 39% (from 20.3 to 28.1 GPa) increase compared to the 12% (from 20.3 to 22.7 GPa) improvement in Epoxy/CF/GCN/POSS samples. In terms of tensile strain, the GCN-reinforced laminates showed a reduction of 14% (from 3.39 to 2.93%), while the POSS-reinforced laminates exhibited a slight increase of 10% (from 3.39 to 3.74%).

In the study published by Naidu *et al.* [64], improvements of 24.8% in tensile strength were reported for glass fibre/epoxy laminates reinforced with 1.5 wt.% of GCN nanoparticles. Song *et al.* [63, 65] also registered increments in tensile strength and elastic modulus of 20% (from 564.9 to 675.3 MPa) and 16% (from 50.1 to 58.3 GPa), respectively, for epoxy composites reinforced with carbon fibres whose surface was modified with GCN nanofiller. However, in the current work, comparable results were achieved with a loading of 0.25 wt.%, revealing the potential for significant enhancements in tensile strength at lower nanoparticle concentrations. This finding underscores the efficiency and effectiveness of GCN nanofillers in reinforcing composite materials, paving the way for further research and potential applications in advanced material engineering.

4.3.3 Thermogravimetric Analysis

The TGA analysis allows for the identification of material components, prediction of behaviour under thermal stress, and assessment of the material's suitability for specific applications. The obtained results, in terms of the decomposition temperature (T_d) and residual mass, are shown in Table 12 and Figures 20 and 21 present the remaining weight percentage and the derivative of the remaining weight under the temperature, respectively.

Table 12. Results of the TGA analysis of the fabricated carbon fibre-reinforced laminates

Filler content [wt.%]	**T_d [°C]**	**Residual Mass [%]**
0	372.58	58.5
0.25 GCN	346.57	61.4
0.25 GCN + 0.25 POSS	348.49	57.0

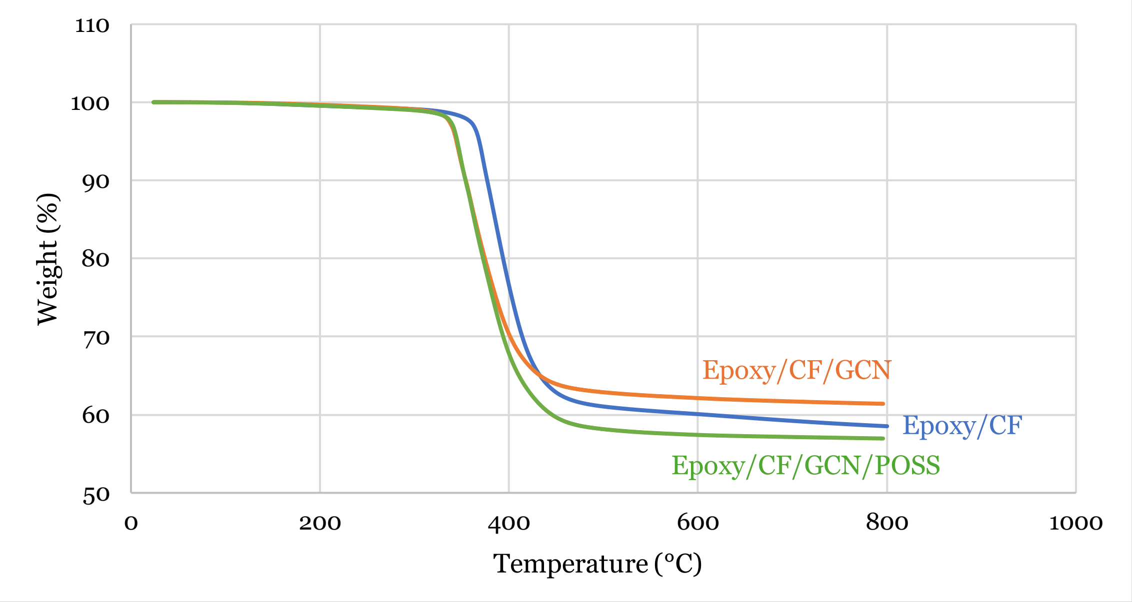


Figure 20. TGA curve for the laminates: remaining weight percentage as a function of the temperature

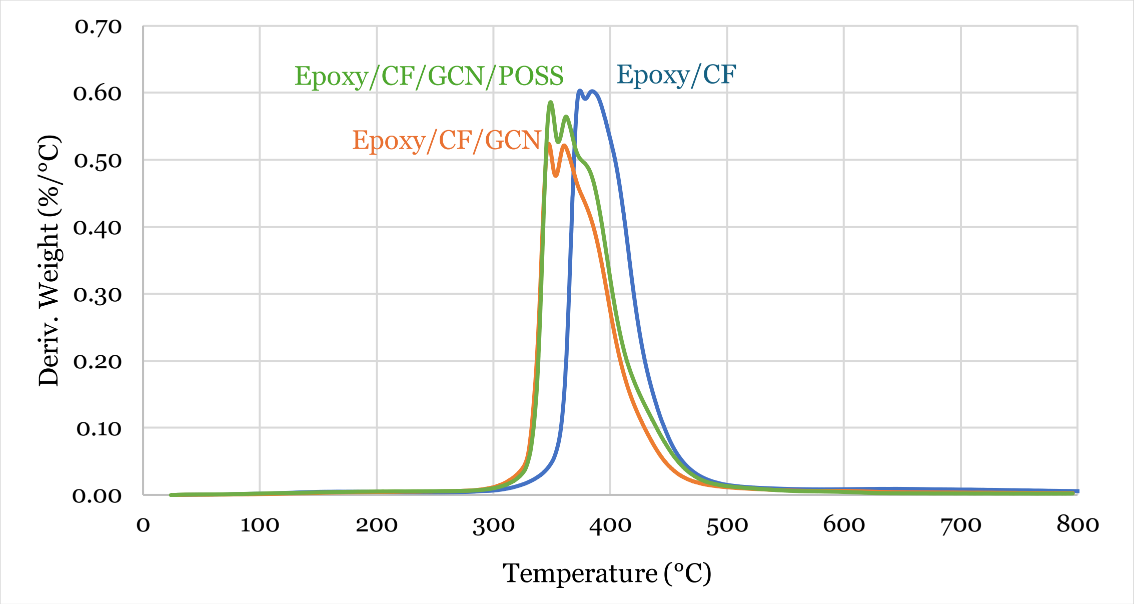


Figure 21. TGA curve for the laminates: evolution of the derivative of the remaining weight percentage as a function of the temperature

The TGA analysis reveals that the samples suffer significant thermal decomposition, with major mass losses occurring at a temperature of around 372ºC for the control sample, 346ºC for the Epoxy/CF/GCN sample and 348ºC for the Epoxy/CF/GCN/POSS specimen. In terms of residual mass after thermal degradation, as shown in Figure 20, the GCN-reinforced laminates present a slightly higher value when compared to the neat epoxy, suggesting improved char yield.

This analysis suggests that the reinforcement of epoxy with GCN and POSS (Epoxy/CF/GCN/POSS) results in the most significant thermal decomposition. This finding contrasts with the results presented by Qi *et al.* [66], where the introduction of GCN particles into the laminates did not lead to an increment in degradation temperature. However, the conclusions in terms of residual mass are similar. Both studies indicate that the incorporation of GCN nanoparticles can improve the char yield of epoxy-based composites. This suggests that the thermal degradation mechanisms may be influenced by the specific formulation and processing conditions of the materials.

These results are crucial to understanding the thermal behaviour and stability of the samples, which can impact further material processing and application decisions. So as the definition of T_d is the temperature at which the sample goes through chemical changes, separating into simpler compounds [67], the laminates should not be used in applications that involve temperatures exceeding their Td. By analysing the thermal properties of the laminates, we can identify suitable operating conditions and potential limitations for their use in various applications.

4.3.4 Differential Scanning Calorimetry Analysis

DSC analysis provides valuable insights into the thermal behaviour of a material, which can be crucial for understanding its stability, purity, and suitability for aerospace and aeronautical applications, for example. The results of this analysis are presented in Table 13 and Figures 22 and 23.

Table 13. Results of the DSC analysis of the fabricated carbon fibre-reinforced laminates

Filler content [wt.%]	**T_g [°C]**	**T_m [°C]**
0	62	339
0.25 GCN	57	335
0.25 GCN + 0.25 POSS	58	338

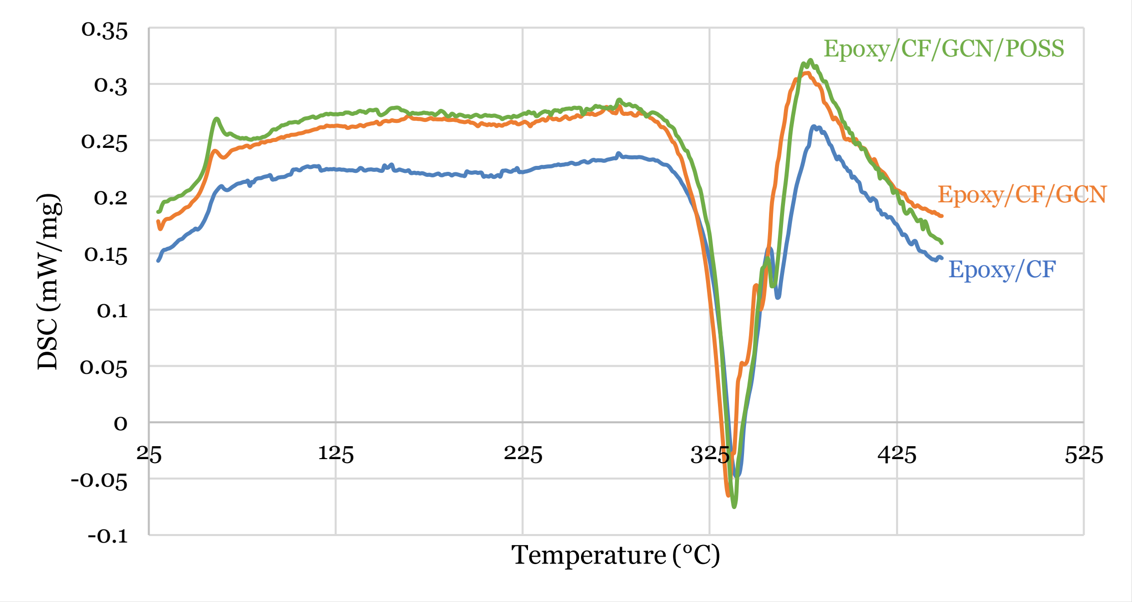


Figure 22. DSC thermograms of the carbon fibre-reinforced laminates

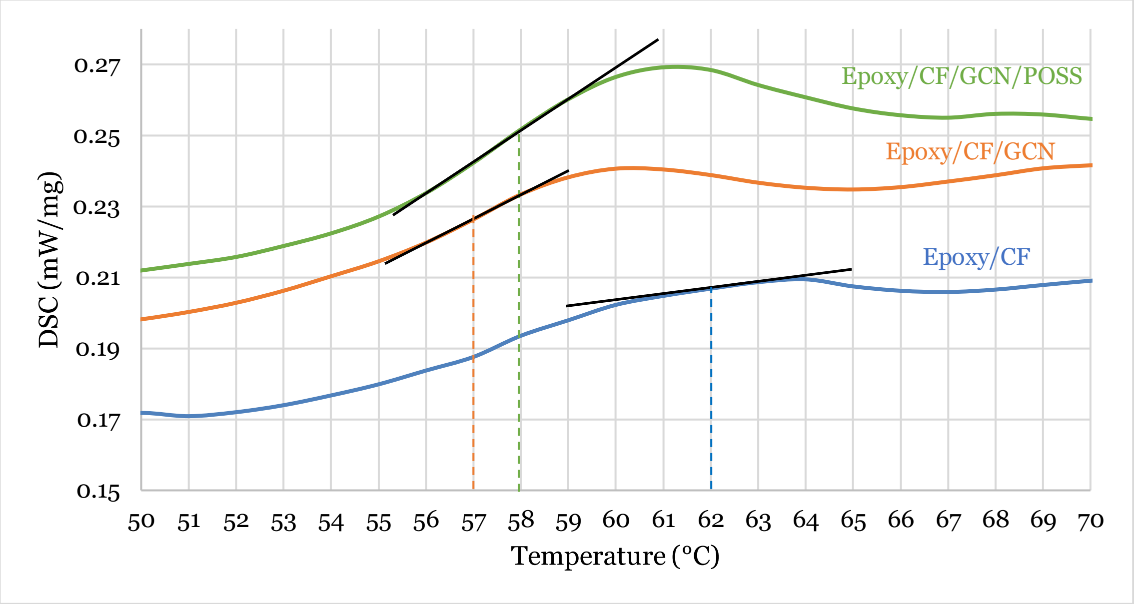


Figure 23. Zoom of the DSC thermograms of the laminates into the Tg zone

The DSC analysis indicates that the incorporation of GCN and POSS nanoparticles has a limited impact on the thermal properties of the laminates. While both nanofillers can slightly influence Tg and Tm, the changes are relatively small and may not significantly affect the overall performance of the materials. Both GCN-reinforced and GCN/POSS-reinforced laminates exhibited a slight decrease in Tg (from 62 to 57 ºC) compared to the neat epoxy laminate. A similar trend was observed for Tm, with both reinforced laminates showing a slight decrease (from 339 to 335 ºC) compared to the neat epoxy. The addition of POSS appeared to slightly mitigate the reduction in Tg (from 62 to 58 ºC) and Tm (from 339 to 338 ºC) observed with GCN reinforcement.

The incorporation of carbon fibre fabric into the epoxy led to a decrease in the limit service temperature from 79°C (as per the datasheet of epoxy) to 62°C. This phenomenon can be attributed to constraints in the molecular chains' mobility, resulting in a decrease in Tg, as discussed by Nakka [68]. This finding highlights the importance of considering the interaction between the epoxy matrix and the reinforcing fillers when designing composite materials for high-temperature applications.

4.3.5 Water Contact Angle Analysis

The water contact angle test measures the angle formed between a water droplet and the surface of the material, providing insight into the surface wettability of the laminates. The results of the WCA analysis performed are shown in Table 14 and Figure 24.

Table 14. Results of the WCA analysis for the different carbon fibre-reinforced laminates

Filler content [wt.%]	**WCA [º]**
0	73.6 ± 5.9
0.25 GCN	82.5 ± 2.2
0.25 GCN + 0.25 POSS	79.0 ± 2.1

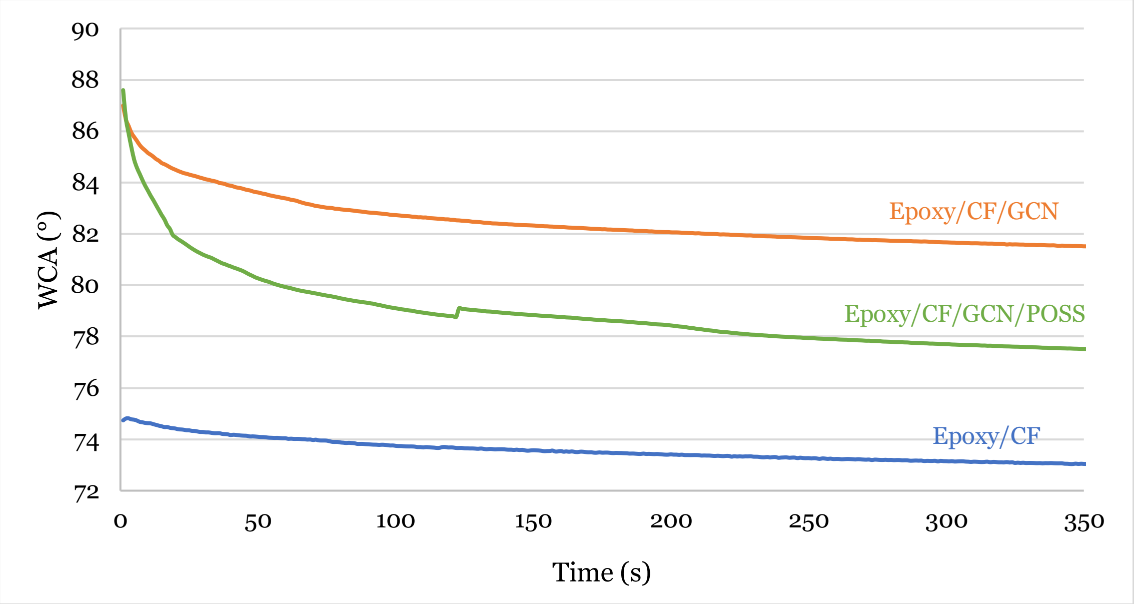


Figure 24. Characteristic curve for the water contact angle measurements for the different laminates

The WCA measurements show that the incorporation of GCN and POSS nanoparticles into the epoxy/carbon fibre laminates significantly enhanced their hydrophobicity, as evidenced by the increased water contact angles. The Epoxy/CF/GCN samples exhibited a slightly higher increase in WCA (from 73.6º to 82.5º) compared to the Epoxy/CF/GCN/POSS samples (from 73.6º to 79.0º), suggesting that GCN may have a slightly stronger hydrophobic effect. The reinforced samples reached equilibrium contact angles relatively quickly, with a substantial drop in WCA observed within the first two minutes of the test suggesting an increased convergence time. The hydrophobicity of the laminates was found to be relatively isotropic, with no significant variation in WCA observed when testing in different directions.

The Epoxy/CF/GCN samples demonstrated a particularly significant increase in hydrophobicity, likely due to the unique surface properties of GCN that contribute to a more substantial reduction in surface energy, as discussed by Xavier et al. [51]. On the other hand, the combination of GCN and POSS, while still enhancing the hydrophobicity, showed a less pronounced effect compared to GCN alone. This could be attributed to interactions between GCN and POSS, which might alter the overall surface characteristics. Furthermore, the water contact angle analysis demonstrates the positive impact of GCN and POSS nanoparticles on the hydrophobicity of the epoxy/carbon fibre laminates. This property can be beneficial in applications where moisture resistance is crucial, such as outdoor exposure.

4.4 Wrapping Thoughts

The previously discussed results and improvements can be attributed to the increased surface area of the GCN-reinforced nanocomposite. Additionally, the enhancement of these properties occurs due to the improved interfacial bonding between the GCN nanoparticles and the epoxy matrix. These factors contribute to a better mechanical interlocking effect of the reinforcement within the matrix, thereby enhancing the mechanical properties [48]. Furthermore, the GCN particles act as barriers to crack propagation, diverting cracks and creating a physical barrier, which leads to the ability to withstand higher forces and an increase in strain energy consumption [66].

Moreover, the incorporation of POSS into the structure results in improved flexural properties and altered fracture behaviour, consistent with the findings of Rashid *et al.* [69]. The cage structure of POSS molecules may induce the formation of a cross-linking network between the POSS particles and the epoxy molecules, providing strengthening and toughening effects.

The combination of both, GCN and POSS, reinforcements led to significant improvements in the mechanical properties of the laminates, surpassing the enhancements experienced by the solely GCN-reinforced samples for some of the properties, notably the flexural and tensile strengths. However, in most cases, the flexural and elastic modulus were slightly diminished.

In the flexural tests, the inherent characteristics of the nanocomposite lead to matrix failure under compression, which is accompanied by fibre delamination and debonding from the matrix. Additionally, a reduction in the area of the linear elastic region occurs, resulting in premature plastic strain, as documented by Liu *et al.* [70]. In terms of the viscoelastic behaviour, Santos *et al.* [30] state that with increasing strain rate, the strength and modulus have tendencies to improve whilst the strain usually decreases. However, this behaviour was not consistently registered throughout this study, leading to the conclusion that the addition of GCN and POSS altered the composite's sensitivity to strain rate, whilst still improving the overall mechanical properties [30].

In the tensile tests, the observed damage is characterized by broken fibres and longitudinal cracks, attributable to the brittle nature of the matrix. Additionally, fibre pullout occurs, along with the phenomena described for the flexural tests. These observations are consistent with the findings reported by Lei *et al.* and Zimmermann [71, 72].

In terms of the thermal properties, the TGA and DSC analysis suggest that the concentration of nano reinforcements introduced (0.25 wt.%) did not lead to significant improvements, contrasting with what is revealed in the literature. Regarding the hydrophobic properties, the WCA analysis performed concluded that the addition of GCN and POSS improved the hydrophobicity of the laminates, most likely due to the chemical structure they support [51].

In brief, the incorporation of GCN and POSS nanoparticles into epoxy/carbon fiber laminates has led to significant improvements in mechanical properties, particularly flexural strength and modulus. However, the thermal properties of the nanocomposites were not significantly affected by the addition of these nanofillers at the studied concentration of 0.25 wt.%.

Chapter 5

Conclusion

This chapter provides a comprehensive overview of the research findings presented in earlier sections, such as a summary of key findings and highlighting the most significant results obtained and their implications.

5.1 Conclusions of the Research Work

In this dissertation, epoxy-based nanocomposite using graphitic carbon nitride (GCN), and POSS nanofillers with different loadings have successfully been prepared and characterized. The results indicate that the static and dynamic mechanical properties of Epoxy/CF/GCN nanocomposites have been significantly improved at a low loading of GCN (0.25 wt.%), where the maximum values of tensile and flexural strengths were achieved. Posteriorly, the laminates were prepared with an epoxy matrix and 12 layers of carbon fibre woven fabric which served as a control sample. To the reinforced samples, the loading of 0.25 wt.% GCN was introduced into the epoxy matrix, showing excellent improvements in mechanical properties. When compared to neat epoxy laminates, the addition of GCN resulted in an increment of 101% in flexural strength (from 362.6 to 729.1 MPa) and 135% in flexural modulus (from 25.2 to 59.3 GPa). Additionally, the incorporation of 0.25 wt.% POSS into these laminates, Epoxy/CF/GCN/POSS, increased the flexural strength at 107% (from 362.6 to 749.4 MPa) to the control sample, this increment is slightly higher compared to the solely GCN-reinforced sample. However, the increment in flexural modulus is less significant compared to GCN-reinforced laminates, which increased at 117% (from 25.2 to 54.7 GPa).

The samples were tested at different strain rates, such as 2 mm/min., 20 mm/min., and 200 mm/min. When crosschecking the results for different strain rates, the following observations can be made: For the control (epoxy/CF) and GCN-reinforced samples (epoxy/CF/GCN), the maximum flexural strength and flexural modulus tend to increase between strain rates of 2 and 20 mm/min but decrease between 20 and 200 mm/min. For the combined nanofiller samples (epoxy/CF/GCN/POSS), both the maximum flexural strength and flexural modulus increase with increasing testing velocity. The control samples exhibit a decrease in flexural strain for increased strain rates, with the lowest values observed at 20 mm/min. The GCN-reinforced samples show an opposite trend, with increased flexural strain for higher strain rates. Finally, the combined nano-reinforcement samples experience a decrease in flexural strain between 2 and 20 mm/min followed by a higher increment between 20 and 200 mm/min. These findings highlight the significant influence of strain rate on the mechanical properties of the nanocomposite materials, showing that the incorporation of nanofillers, particularly the combined nano-reinforcement (GCN+POSS), demonstrates enhanced flexural behaviour, especially at higher strain rates. Moreover, the research findings obtained in this work indicate a significantly greater enhancement in these properties at lower GCN concentrations compared to reported values in the literature [63].

The tensile strength of the laminated samples increases at 25% (from 408.3 to 509.6 MPa) for epoxy/CF/GCN and 30% (from 408.3 to 529.9 MPa) for epoxy/CF/GCN/POSS specimen. However, the most significant improvement in the elastic modulus was observed for the epoxy/CF/GCN sample, which exhibited a 39% increase (from 20.3 to 28.1 GPa) for epoxy/CF/GCN compared to the 12% improvement (from 20.3 to 22.7 GPa) for epoxy/CF/GCN/POSS samples. In terms of tensile strain, there is a reduction of 14% (from 3.39 to 2.93 %) for the GCN-reinforced specimen and an increment of 10% (from 3.39 to 3.74 %) for the POSS-reinforced laminates. These findings, presented in this dissertation, are comparable to literature values obtained with 1.5 wt% of GCN loadings [64], despite the usage of only 0.25 wt% of GCN in our study. This strongly suggests that the incorporation of GCN as a nanofiller in epoxy composites can significantly enhance their mechanical properties, even at relatively low concentrations.

The water contact angle of the laminate surfaces resulted in a slight hydrophobia (82.5° for GCN, and 79° for GCN/POSS-reinforced samples) compared to the control sample surface (73.6°). Thermal analysis of the laminates reveals that the samples undergo significant thermal decomposition, with major mass losses occurring at 372°C for the control sample, 346°C for the solely GCN-reinforced sample and 348°C for the specimen reinforced with both nanoparticles. The DSC analysis also showed that the T_g values are slightly reduced for the Epoxy/CF/GCN (57°C) and Epoxy/CF/GCN/POSS (58°C) reinforced laminates compared to the control sample (62°C). This could be attributed to the plasticising effect of nanofillers and their structural characteristics, limiting molecular movements.

The results obtained in this research indicate that the structural characteristics of graphitic carbon nitride, such as its multi-scale 2D lamination structure, large specific surface area, and naturally terminated amino groups, have demonstrated significant potential in promoting the dispersion of nanoparticles and strengthening the epoxy matrix through adequate chemical interactions. The incorporation of GCN as a nanofiller for fabricating epoxy nanocomposites has proven to be highly effective. The strategies developed in this research work offer a promising avenue for the fabrication of high-performance composites for aeronautical and aerospace applications and the research presented in this thesis has contributed to the advancement of knowledge in the field of nanocomposites. Future research efforts can build upon these findings by focusing on investigating the impact of GCN on the interfacial properties of the epoxy matrix and studying the relationship between hydrogen bond energy dissipation in the interlayers. By exploring these aspects, we can further optimize the properties of epoxy-based nanocomposites and expand their potential applications in aeronautical and aerospace engineering.

However, the above research findings demonstrate that the incorporation of GCN and POSS into carbon fibre/epoxy laminates results in significantly improved mechanical properties, with flexural strength reaching 780 MPa and tensile strength reaching 530 MPa. These enhanced properties make these composites promising candidates to replace aluminium alloys in critical aircraft structural elements, such as longerons, beams and other critical structural elements. Additionally, the enhanced hydrophobicity of these nanocomposites suggests that they may be particularly well-suited for applications where exposure to moisture is a concern, such as components exposed to harsh environmental conditions or those operating in high-humidity environments.

5.2 Future Work

Given the findings presented in this dissertation, several avenues for future research can be identified to further explore the potential of epoxy-based nanocomposites reinforced with graphitic carbon nitride (GCN), such as:

- Optimizing the concentration and dispersion of GCN nanoparticles to enhance mechanical and thermal properties, investigating the improvements achieved with lower concentrations of GCN.
- Exploring the chemical modification of GCN nanoparticles with different chemical groups or treatments to further enhance their dispersion in the epoxy matrix.
- Assessing the long-term durability and performance of the developed nanocomposites under various environmental conditions, including exposure to extreme temperatures, humidity, and mechanical stress.
- Studying the flame-retardant properties of the material could unveil new applications in safety-critical areas.
- Exploring the incorporation of self-healing agents in the epoxy matrix to improve the longevity and reliability of the materials.
- Investigating the electrical conductivity and dielectric properties of the nanocomposites to explore potential applications in electronics and electromagnetic interference (EMI) shielding.
- Studying the interfacial bonding and shear strength to enhance the mechanical performance and durability of the composites.
- Evaluating the damage mechanisms responsible for the failure of the material when subjected to different types of loads.

- Conducting numerical simulations of the micromechanical behaviour of the nanofillers in the fibre’s interface would also open other insights into the material's performance under different conditions.
- Investigating the potential use of these nanocomposites in other fields where their unique properties could offer significant advantages to enhance efficiency and lifespan, as in biomedical devices, sensors, prosthetics, wind turbine blades, solar panel structures, and the automotive industry.

By pursuing these research directions, we can further optimize the properties of epoxy-GCN nanocomposites and expand their potential applications in various fields.

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