# PROCESSING AND CHARACTERIZATION OF POLYETHYLENE TEREPHTALATE GLYCOL-MODIFIED/EPOXY CARBON NANOTUBES-GLASS FIBERS COMPOSITES

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#### ABSTRACT

Glass fibers are materials commonly employed for the reinforcement of several polymers. Aircraft parts, rocket motor cases and automobiles, are examples of several structural composites where glass fibers have been used. It is well known that increasing the efficiency of stress transfer from the polymeric material to the fiber may lead to enhanced mechanical performance and, as with any composite materials, the interface between both materials play a critical role in the final mechanical properties. The presence of carbon nanotubes on the fibers surface may improve the adhesion between fibres and matrix since they may interlock with the polymer chains and thus creating a physically strong adhesion between the two phases.

In this work, carbon nanotubes were synthesized on the surface of carbon and glass fibers, by chemical vapour deposition of ethylene, under different experimental conditions. The resulting fibers-carbon nanotubes hybrids were further characterized by energy dispersive X-ray analyses, scanning electron microscopy, Raman spectroscopy and thermogravimetric analyses. The selected glass fibers-carbon nanotubes synthesized were embedded in polyethylene terephtalate glycol (PETG) and epoxy resin and the effect of the quality and amount of carbon nanotubes within the different samples on the fiber/matrix interfacial strength of PETG and epoxy fiber composites was evaluated by single fiber fragmentation tests (SFFT), microscopy and photoelasticity analyses. The results were compared with the sized treated fibers.

In relation to the PETG fiber composites, the results show that the sized treated fibers have a better fiber/matrix adhesion, when compared to fibers with CNTs grown on their surfaces. No significant difference in the fiber/matrix interfacial strength was found between the PETG composites using glass fibers containing carbon nanotubes on their surfaces.

On the other hand, the presence of carbon nanotubes on the fibers surface seems to enhance the interfacial bonding between fiber and epoxy. These observations are however only based on microscopy and photoelasticity analyses.

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## INTRODUCTION

In order to overcome the low stiffness and strength of polymeric materials, inorganic particles have been added to polymer matrices. By combining the advantages of the constituent phases, the resulting polymer composites may reveal significant improved mechanical and thermal properties allowing them to be used in many applications in different sectors. Fiber reinforced polymer composites are a class of composite materials which consist of reinforcing fibers embedded in a polymer matrix used in a wide range of applications including aircrafts, submarines, satellites, automobiles, among many others. However, one of the main issues in traditional fiber reinforced polymer composites is an insufficient bonding at the fiber/matrix interface which causes inefficient energy transfer compromising their final properties. The growth of carbon nanotubes on the surfaces of the glass fibers may represent a promising approach to enhance the interfacial interactions between fiber-carbon nanotubes (CNTs) and the resin matrix, when compared to the typical commercial fiber sizing, contributing to an improvement of final mechanical and thermal properties.

This work is mainly devoted to the synthesis of multiwall carbon nanotubes on the surfaces of E-glass fibers under different experimental conditions and evaluation of their effect on the matrix-filler interfacial properties.

The main objectives of this thesis include:

- Synthesis of carbon nanotubes by chemical vapour deposition of ethylene on the E-glass fibers, varying the temperature, time of deposition and hydrogen environment.
- Characterization of the synthesized hybrids of glass fibers and carbon nanotubes by energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), Raman Spectroscopy and termogravimetric analyses (TGA).
- Embedment of single fibers synthesized into epoxy resin and PETG, and evaluation of fiber-matrix interfacial properties by single fiber fragmentation tests and photoelasticity analyses.

In addition, an attempt to grow carbon nanotubes on carbon fibers was made and the preliminary results are presented and discussed.

#### **1. FIBER REINFORCED COMPOSITES**

The structural material obtained from combining two or more components in order to achieve a combination of properties that are not available in any individual constituent, is termed composite. In polymer engineering, the introduction of inorganic materials at different scales (from nano to macro) into polymer matrices, as reinforcing materials, is termed polymer (nano)composite and they typically exhibit improved properties when compared to pure polymers.

Polymer composites with micro-sized particles include for example the use of sand, concrete, silica flour, cemented carbide or fibers dispersed throughout the polymer matrix. Fiber reinforced polymer composites, as the name indicates, consists of reinforcing fibers embedded in polymer matrices. The matrices include a wide range of thermoplastic and thermoset polymers, such as polyamide, polyether, epoxy and polyester resins [1]. Glass fibers or carbon fibers are usually the reinforcements of choice since they may lead to significant improvements on the structural properties of the resulting composite material, such as increased stiffness, strength and resistance to high temperatures. Carbon fibers are stiffer and lighter than glass fibers, although one of the major limiting factors for their use is the cost. Therefore, glass fiber reinforced polymer composites are the most widely used in several engineering applications.

When inorganic particles reach the nanometer dimensions, they usually possess unique mechanical and chemical properties and together with their large surface area and high aspect ratio nanoparticles may impart to polymer nanocomposites extraordinary properties. Therefore, the reinforcement of polymers by addition of nanoparticles has been an area of intense research in the last years because of the potential applications they can be used. Carbon nanotubes, silicate layered clays and spherical silica and aluminium particles are examples of common nanoparticles added to polymers and the subject of numerous investigations [2-10]. Despite the potential future of polymer nanocomposites, there are several issues related to their synthesis which must be overcome such as nanoparticles aggregation and their compatibility with polymer matrices. Moreover, the high costs associated with the production of nanoparticles such as CNTs, hinder the mass commercialization of polymer nanocomposite materials.

Among other factors, the mechanical properties of polymer composites depend strongly on the particle–matrix interface [11, 12]. The interface can be described as the boundary between the fiber and the polymer matrix where interactions between the fiber and the matrix occurs, creating an interphase region which consists of a certain volume of material affected by the interactions at the interface [13], schematically represented in Figure 1A). These interactions may occur through different mechanisms such as mechanical interlocking of the two different materials, chemical bonding, and physical bonding such as electrostatic interactions [14]. A good interfacial bonding ensures the load transfer from matrix to the reinforcement particles, therefore enhancing the fiber reinforced composite performance.

The objective of growing carbon nanotubes on glass fibers is to improve the bonding between the polymer matrix and the fiber. It is imagined that the carbon nanotubes attached to the surfaces of the fibers interlock the polymer chains creating a physically strong adhesion between the two phases. A schematic representation can be seen in Figure 1 B), where the interphase comprises the interlayer formed by the grown carbon nanotubes and the portion of the matrix affected by the presence of the carbon nanotubes.



Figure 1: Schematic representation of the composite interphase (A) and interphase between the glass fiber and polymer matrix in the presence of carbon nanotubes on the surface of the fiber (B).

Since hybrids of fiber and carbon nanotubes were synthesized in this work, in the following sections a brief introduction concerning glass and carbon fibers, carbon nanotubes and hybrids of fibers-CNTs will be presented.

#### 2. GLASS AND CARBON FIBERS

Glass fibers are composed primarily of silica (SiO<sub>2</sub>) covalent bonded on a tetrahedral arrangement with four oxygen atoms surrounding the silicon atom in the center of the structure. The tetrahedral share of the oxygens composes the tridimensional network, Figure 2, which contributes to the high strength and modulus of the material. The presence or addition of elements such as sodium, boron, iron, aluminum and calcium modify the network by establishing ionic bonds with the oxygen increasing fibers formability.



Figure 2: SiO<sub>2</sub> tetrahedral structure.

Glass fibers are usually produced by melt spinning, where raw materials are melted and the molten glass is mechanically drawn downwards trough small holes continuously. The fine filaments are cooled down and wrapped onto high speed drums. The diameter of the fibers can be controlled not only by the size of the holes but through the viscosity of the glass by varying the temperature and composition. Fibers, when bundled, tend to damage themselves by fiber-fiber abrasion effect creating surface defects and reducing their individual mechanical strength. To minimize this damage, fibers are treated with a sizing by spraying an emulsified polymer mix with water creating a thin protective layer on the surface of the fibers increasing also anti-static properties. Moreover, the sizing material has coupling agents to improve the bonding between the fibers and polymer matrices.

Glass-fibers are generally characterized by their high stiffness and relatively low density. The three most popular types of fibers include C-glass, S-glass and E-glass fibers, which are distinguished by its composition and properties, Table 1, and therefore they are used in different applications. C-glass fibers are used in corrosion resistance applications including for example chemical filters and battery plate wrappers, and S-glass fibers are known for their use on special applications due to their high tensile strength and Young's modulus and superior temperature resistance. E-glass fibers are commonly used in electrical applications, and its high tensile strength and stiffness allied to their low cost, makes these fibers as preferred potential materials for polymer matrix reinforcement.

Composition(%)	E-Glass	C-Glass	S-Glass
SiO <sub>2</sub>	52.4	64.4	64.4
$Al_2O_3 + Fe_2O_3$	14.4	4.1	25.0
CaO	17.2	13.4	_
MgO	4.6	3.3	10.3
$Na_2O + K_2O$	0.8	9.6	0.3
$B_2O_3$	10.6	4.7	_
BaO	_	0.9	_
Properties			
ρ (Mg m <sup>-3</sup> )	2.60	2.49	2.48
$K(W m^{-1} K^{-1})$	13	13	13
$\alpha (10^{-6}  \mathrm{K}^{-1})$	4.9	7.2	5.6
σ(GPa)	3.45	3.30	4.60
E (GPa)	76.0	69.0	85.5
T <sub>max</sub> (°C)	550	600	650

Table 1: Composition and physical properties of the E-, C- and S-glassfibers. Adopted from [15].

Carbon fibers may be defined as materials with mainly carbon within its composition, and with a filament morphology consisting of  $sp^2$  bonded carbon aligned parallel to the long axis of the fiber [16]. Carbon fibers have diameters approximately between 5 and 10  $\mu$ m and its structure is comparable to that of graphite, with the graphene layers arranged in a regular pattern.

Carbon fibers can be manufactured from decomposition of hydrocarbon gases or controlled pyrolysis of appropriate fibers. The most common precursors include polyacrylonitrile (PAN), rayon and pitch. Therefore, carbon fibers can be classified according to their precursor materials, to the heat treatment during manufacturing process, and according to their mechanical properties, Table 2. The structure of the fibers depends on the precursor and manufacturing processes which in turn affect their final properties.

<b>Fiber Properties</b>	<b>Precursor Materials</b>	<b>Final Heat Treatment</b>
<ul> <li>Type UHM: Ultra-high-modulus, &gt;450 GPa;</li> <li>Type HM: High-modulus, between 350-450 GPa;</li> <li>Type IM: Intermediate-modulus between 200-350 GPa;</li> <li>Type HT: Low modulus and hightensile, modulus &lt; 100 GPa and tensile strength &gt; 3.0 Gpa;</li> </ul>	<ul> <li>PAN-based carbon fibers;</li> <li>Pitch-based carbon fibers;</li> <li>Rayon-based carbon fibers;</li> <li>Gas-phase-grown carbon fibers.</li> </ul>	<ul> <li>HTT, High-heat-treatment carbon fibers, final heat treatment &gt; 2000 C;</li> <li>IHT, Intermediate-heat-treatment carbon fibers, final heat treatment &gt; 1500 C;</li> <li>Low-heat-treatment carbon fibers, final heat treatment &gt; 1000 C.</li> </ul>

Table 2: Classification of carbon fibers. Adapted from [14].

#### 3. CARBON NANOTUBES

Carbon has six electrons which occupy the atomic orbitals  $1s^2$ ,  $2s^2$  and  $2p^2$  and it can hybridize in sp<sup>3</sup>, sp<sup>2</sup> and sp forms. In materials such as graphene, carbon nanotubes and fullerenes, three outer-shell electrons of the carbon occupy the sp<sup>2</sup> orbital forming three in plane sigma bonds and one electron occupies the orbital 2p forming the out of plane  $\pi$  bond, Figure 3.

In a carbon nanotube, which can be imagined as a hollow cylinder formed by rolling a graphene sheet, the circular curvature of the graphene sheet will cause rehybridization of sigma and  $\pi$  bonds, in which the three sigma bonds are slightly out of plane and for compensation the  $\pi$  bond will be more delocalized outside the tube.

Carbon nanotubes may be broadly classified in single wall (SWCNT) or multiwall carbon nanotube (MWCNT), depending on the number of graphene cylinders that constitute the carbon nanotube, Figure 4. SWCNTs typically present diameters ranging from 0.4 nm to 3 nm and MWCNTs have diameters approximately between 1.4 nm and 100 nm, with lengths up to few centimetres [17].



Figure 3: Schematic representation of sp<sup>2</sup> hybrid orbital in graphene [18].



Figure 4: Representation of A) SWCNT and B) MWCNT [17].

Multiwall carbon nanotubes were first reported by Iijima [19] in 1991, and described as a finite graphitic carbon needles comprising coaxial tubes of graphitic sheets ranging from 2 to approximately 50. The carbon nanotubes had diameters ranging from 2.3 nm to a few tens of nm and lengths up to 1  $\mu$ m, Figure 5. They were produced by arc-discharge evaporation of carbon in a vessel filled with inert gas.

Single wall carbon nanotubes are reported a couple of years later by Iijima et al. [20] and Bethune [21], Figure 6. Iijima et al.[20] synthesized single wall carbon nanotubes with diameters of approximately 1nm, by an arc-discharge process. The carbon arc reactor was operated with a gas mixture of argon, methane and iron, and the single shell tubes grew in the gas phase. The authors suggested that the iron particles in the vapour phase may have assisted the formation of the SWCNTs and also verified that no tubes were formed in the absence of any of the three gases. Bethune et al. [21] reported the synthesis of single wall carbon nanotubes also by an arc-discharge process, and with diameters of nearly 1.2nm. The electrodes were filled with different powdered metals (Fe, Ni and Co) and vaporized resulting in the formation of single wall carbon nanotubes when cobalt was used.



Figure 5: Transmission electron microscopy image of the MWCNTs reported by Ijima, 1991[19].



Figure 6: Transmission electron microscopy image of a SWCNT reported by Bethune, 1993[21].

Since then significant research has been made in both synthesis and characterization and their potential use in several engineering applications. Carbon nanotubes possess remarkable mechanical properties with reported Young's modulus values over 1 TPa and tensile strength over 100 GPa [22], Table 3. Simultaneously with their low density, high aspect ratio and high surface area, carbon nanotubes are used as reinforcing fillers in the production of polymer nanocomposites [23, 24]. Other applications include thin films, energy storage, field emission displays, electronic circuits and biomedical supports.

	Young's Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm <sup>3</sup> )
MWCNTs	1200	~150	2.6
SWCNTs	1054	75	1.3
SWCNTs bundle	563	~150	1.3
Graphite	350	2.5	2.6
Steel	208	0.4	7.8

Table 3: Mechanical properties of the carbon nanotubes. Adopted from [22].

#### 3.1 CARBON NANOTUBES: SYNTHESIS

Carbon nanotubes can be synthesized by several processes, but the most known methods are chemical vapour deposition, laser ablation and arc-discharge[25]. In spite of the high graphitization of the carbon nanotubes produced by laser ablation and arc-discharge methods, they normally are accompanied by by-products such as amorphous carbon and fullerenes and further purification methods are necessary. Moreover, the costs associated with carbon nanotubes production by arc-discharge and laser ablation processes are very high.

Chemical vapour deposition (CVD) of carbon represents an economic and simple technique to synthesize carbon nanotubes and which allows the patterning of CNTs, morphology control and the possibility of growing carbon nanotubes on a wide range of substrates. The schematic representation of the CVD system is represented in Figure 7, and is mainly composed of a furnace and a gas flow system.

In a typical procedure, the substrate material with metal catalysts is placed inside the tube reactor and a hydrocarbon gas is allowed to flow through the tube at elevated temperatures. The metal nanoparticles catalyze the dissociation of the hydrocarbon gas and at the same time the carbon diffuses through metal nanoparticles. When the metal nanoparticles become saturated the carbon precipitates on their surface in an energetically stable tubular form.

MWCNTs have been reported to grow by CVD between reaction temperatures of 550-750°C [26-28] and SWCNTs are typically produced using temperatures ranging from 850-1500°C [29-31]. The most commonly hydrocarbon gases used include methane, ethylene, and acetylene.



Figure 7: General setup of the catalytic chemical vapour deposition process. Adopted from [32].

The typical catalytic particles used include transition metals such as iron, cobalt and nickel due to their electronic structure. These metals have non-filled d-orbitals and therefore are able to interact with hydrocarbon molecules and promote its dissociation. Moreover, the carbon solubility on these metals allows the diffusion of carbon and formation of metastable carbides which may assist the carbon nanotubes growth [33]. Mixture of metals are also often used for the production of carbon nanotubes and normally yield better results in terms of the quality of CNTs [33].

On the other hand, carbon nanotubes have also been reported to grow directly on several substrates without the use of catalyst particles by a CVD process. Liu et al. [34], in 2009, reported the growth of SWCNTs by a CVD process on a deposited silica oxide film without the use of metal catalysts. The SiO<sub>2</sub> film was sputtering deposited onto a silicon wafer and put inside the tube furnace. The chemical vapour deposition of methane was made at 900 °C, during 20 min, under an atmosphere of hydrogen. The results showed the presence of dense and uniform SWCNTs on the surface of the substrate and since nanoparticles were formed after hydrogen treatment, the authors speculated they acted as active sites for the growth of carbon nanotubes. In the same study, the authors also reported the successful growth of SWCNTs scratching a clean silica wafer with a sharp tip and further subjected it to a CVD process. SWCNTs were only found in the scratched area and the authors suggested that the scratching of the silica wafers make the SiO<sub>2</sub> layer crack creating active sites, similar to the SiO<sub>2</sub> film deposition, that further facilitate the carbon nanotubes growth. In 2010, Liu et al [35] reported the growth of SWCNTs on a SiO<sub>2</sub> substrate by CVD of ethanol at 850 °C during 30 min, under Ar/H<sub>2</sub> atmosphere. The silica substrates were annealed under hydrogen conditions before the chemical vapour deposition process which was found to be crucial for the growth of SWCNTs. Chen et al., in 2011, reported the growth of SWCNTs from SiO<sub>2</sub> nanoparticles synthesized by thermal oxidation of 3aminopropyltriethoxysilane (APTES). The authors suggested the carbon atoms collide with the silica nanoparticles and diffuse along their surfaces, leading to the formation of the carbon nanotube structure.

#### 3.2 CARBON NANOTUBES: GROWTH MECHANISM

The growth mechanism of carbon nanotubes is still under debate and several models have been proposed by several authors up to date [36-40]. Surprisingly, after more than 20 years from their discovery, there is little knowledge about how the carbon nanotubes grow since several parameters such as type of catalysts, growth temperature and type of hydrocarbon gas influence their growth mechanisms and therefore often contradicting results have been reported. The most widely accepted mechanism to explain the growth of carbon nanotubes catalyzed by metal particles relies on the model for carbon filaments growth proposed by Baker et al. [41], based on the concepts of the vapor-liquid-solid (VLS) theory [42]. After continuous investigations on the morphology and growth of carbon filaments, Baker explains their growth mechanism through a bulk diffusion process. The catalytic decomposition of hydrocarbon gas on the surfaces of the metal particles leads to the release of hydrogen and the resultant carbon dissolves and diffuses through the catalyst through a bulk diffusion mechanism. Considering the type of interaction between the metal particles and the substrate where the metal particles are deposited, Baker [36] proposed two types of growth mechanism known as tip and base growth mechanism, which are represented in Figure 8. When the interaction between the metal particle and the substrate is strong, the metal particle remains attached to the substrate during the growth of the carbon filament (root or base growth mechanism) and when the interaction of the metal particle and the substrate is weak, the catalyst moves away from the support during the growth of the carbon filaments (tip-growth mechanism).

Other commonly accepted mechanism for the growth of carbon nanotubes catalyzed by metal particles was proposed in 1996 by Dai et al.[40], the *yarmulke* mechanism. According to this mechanism, the carbon atoms form a hemispherical graphene cap on the metal catalyst, similar to a yarmulke, and the carbon nanotubes grow from this formed cap.



Figure 8: Baker model mechanisms. Left: Tip-growth mechanism. Right: Base-growth mechanism. Adopted from [36].

As mentioned before, since the growth of carbon nanotubes depend on many variables, such as type and nature of catalysts, growth temperature, type of carbon source, gas flow, etc., there is a great difficulty to understand their growth mechanism and therefore several models have been proposed. Nevertheless, the growth of carbon nanotubes on non-metallic particles contradicts the idea that metal particles are necessary to catalyse the growth of carbon nanotubes under low carbon deposition temperatures. Moreover it represents a promising area of future research with exploration in diverse applications where the presence of metal particles is not desirable, for example in polymer reinforcement, where the presence of metal particles within the carbon nanotubes has shown to accelerate the polymer degradation rate at high temperatures [43, 44].

## 4. HYBRIDS OF GLASS/CARBON FIBERS AND CARBON NANOTUBES POLYMER COMPOSITES

Carbon nanotubes have been reported to grow on a wide variety of substrates, including silica, layered silicate minerals [45-47] as well as fibers, mainly carbon based [48-53]. While there is an extensive study on the CNTs growth on carbon fibers and further incorporation of these hybrid fillers in polymer matrix composites [54-59], there are only a few reports focused on the growth of CNTs on glass fibers [60] and further fabrication of polymer composites [59]. In general, the resulting composites reveal an enhancement of the mechanical properties which is attributed to the presence of carbon nanotubes attached to fibers surface. The carbon nanotubes have shown to improve the interfacial bonding and the efficiency of stress transfer between the fiber and the polymer [56, 59].

Sharma et al. [55] synthesized multiwall carbon nanotubes on carbon fibers by CVD of acetylene in the presence of hydrogen, using a nickel solution as the catalyst precursor. The sizing of the fibers was removed and the fibers were dipped in the catalyst solution and dried. The catalyst particles were formed after a reduction process under hydrogen atmosphere and the carbon nanotubes grew on the formed nickel catalysts covering the surfaces of the fibers. The resultant fibers with carbon nanotubes grown on their surfaces were used to fabricate composites using an epoxy resin. The results showed a significant increase of 43% and 94% in the longitudinal and transversal compressive strength of the resulting composites. In a similar study [54], the same authors observed an increase of 69% in tensile strength of composites made with carbon fibers covered with nanotubes as compared to composites using fibers without carbon nanotubes. Suraya et al. [56] produced multiwall carbon nanotubes on the surface of carbon fibres by a chemical vapour deposition process using ferrocene as the catalyst precursor and benzene as a carbon source. Hydrogen gas was also used during the process. The carbon fibers covered with the carbon nanotubes were compounded with polypropylene and the resulting composites revealed an increase of 52% in tensile strength and 133% in tensile modulus when compared to composites with neat carbon fibers. Kepple et al. [57] were able to grow multiwall carbon nanotubes on woven carbon fiber with the objective of enhancing the properties of epoxy-carbon composites for aerospace applications. After removing the sizing of the woven carbon fiber, the authors deposited iron particles by a thermal evaporation process on both sides of the woven in order to catalyse the growth of the carbon nanotubes. The process was made using a mixture of methane and acetylene as the carbon feedstock under a flow of hydrogen. A thick layer of carbon nanotubes was formed on the surfaces of the woven fabrics which were further used to prepare epoxy composite samples. An increase of 50% in fracture toughness and 5% in the flexural modulus was observed for the resulting composites.

Al-Haik et al. [60] reported the growth of carbon nanofibers on the surface of carbon and glass fibers at 550°C from combustion of hydrocarbon gas ethylene in the presence of oxygen, using palladium as catalyst. After removing the sizing to the fibers they were immersed in the metal solution and subjected to a reduction treatment under hydrogen to form the particles catalysts. Recently, Rahmanian et al.[59] reported the synthesis of carbon nanotubes on glass and carbon fibers by a chemical vapour deposition process using a vaporized solution of ferrocene as the catalyst and benzene as carbon feedstock. The fibers with carbon nanotubes grown on their surfaces were incorporated in polypropylene and the resulting composites revealed superior tensile, impact and flexural properties compared to polypropylene reinforced with the respective neat fibers. Composites containing carbon fibers and glass fibers with carbon nanotubes on the surfaces revealed an increase in tensile modulus of approximately 57% and 40%, respectively. Flexural modulus was increased 51% when using carbon fibers with CNTs and 36% when glass fibers with CNTs were used to produce the composites. Composites with grown CNTs on carbon fibers showed an increase of around 34% in impact energy whereas glass fibers coated with CNTs had an increase of approximately 24%.

#### 5. SINGLE FIBER FRAGMENTATION TEST

As mentioned previously, the performance of fiber-reinforced composites does not only depend on the individual components but also on the fiber matrix-interface properties. Techniques such as single fiber pull-out tests, fragmentation tests, micro-debond and micro-indentation tests are the most common examples of conventional methods used to examine the interface between a single fiber and the polymer matrix. In this work, the single fiber fragmentation test was used to evaluate the CNTs effect on interface properties of the fiber-matrix nanocomposites. The test is relatively simple to perform and can yield considerable information regarding the interactions between the fiber and matrix at the interface.

The single fiber fragmentation test (SFFT) consists of axially embedding a single fiber on a dog-bone polymeric matrix and applying a unidirectional force on the fiber axis direction to the test specimen. The approach of using a single fiber was first used by Kelly and Tyson [61] on a system consisting of a copper matrix and a tungsten fiber. A perfect fiber-matrix interface is assumed by the authors where the matrix behaves as rigid plastic and deformation occurs only by shear while the fiber has a linear elastic behavior and is only exposed to axial strain. A tensile force was applied to the test specimen and while the strain increased in the fiber axis direction it was observed that the tungsten fiber broke into smaller fragments, mainly due to load transfer from the matrix to the fiber by shear stress at the interface of the composite system. The fracture phenomena occurs when the fiber builts enough stress to overcome its maximum tensile strength and failure of the fiber occurs. Considering a geometrical model, as represented on Figure 9, composed by a fiber of finite length and diameter *d* encapsulated by a matrix under tensile load, it is possible to establish a balance of forces acting on the fiber.



Figure 9: Schematic representation of the forces represented as stress acting on a fiber segment embedded on a matrix under tensile load where  $\sigma_f$  is the normal tensile stress,  $\tau_{iss}$  is the interfacial shear stress,  $\sigma_M$  is the matrix tensile stress and x the position along the fiber.

The model proposed by Kelly-Tyson assumes that the lack of matrix material at the fiber ends results that all the stress is transferred by shear around the fiber periphery. The normal tensile stress is therefore null at the fiber ends ( $\sigma_f$ =0) and is neglected when establishing a relation between the fiber normal stress ( $\sigma_f$ ) and the shear stress distribution at the interface  $\tau_{ISS}$ . This relation can be expressed in function of the position *x* along the fiber if we consider a constant shear stress, as assumed by the model, and can be expressed as:

$$\sigma_f = \frac{4 \tau_{iss}}{d} x \tag{eq.1}$$

Considering the symmetry of a fiber segment of length l the shear stress will be maximum at the fiber ends where the load is transferred while the fiber normal stress will increase from the fiber ends until a plateau in the middle zone of the fiber. According to the assumptions from the Kelly-Tyson model no load is transferred from the matrix to the fiber within this zone which means that the shear stress is null, Figure 10.



Figure 10: Shear and tensile stress distribution along a fiber of length *l* according to Kelly-Tyson model.

The fiber ultimate tensile strength is, in practice, limited by the statistical nature of fiber flaws. The distribution of defects on the fiber material will ultimately rule the fiber strength since the fiber is as strong as its weakest point. For longer segments the probability of a fracture to occur will be higher than for smaller segments. When a break occurs the tensile stress at the fiber ends becomes null and increases along the new segment obeying to the same principle described before. As the strain of the system increases more breaks will occur and the process repeats itself until the fibers segments are so short that not enough stress in the fiber is built to overcome the fiber failure strength ceasing to induce further breaks, Figure 11.



 $\sigma_3 > \sigma_2 > \sigma_1$ 

Figure 11: Schematic representation of a single fiber successive fragmentations due to increased strain where  $\sigma$  correspond to the fiber ultimate tensile strength. Adopted from [62].

This condition is called the fiber saturation state. According to Kelly-Tyson the minimum length at which the fiber breaks is known as the fiber critical length ( $l_c$ ) and due to variations in strength of the fiber there will be a uniform distribution of fragments with lengths between  $l_c$  and  $l_c/2$ . Oshawa et al.[63] used a statistical approach to relate the critical fragment length to the average length of segments  $\bar{l}$  at the saturation state considering a Gaussian distribution for the same interval. This expression is given by:

$$l_c = \frac{4}{3} \bar{l} \tag{eq.2}$$

The critical length can be related to the interfacial shear stress and fiber stress at critical length by the following expression:

$$\tau_{iss} = \frac{\sigma_{f(l_c)} d}{2l_c} \tag{eq.3}$$

The fiber ultimate strength can be experimentally estimated to a given gauge length by single fiber tensile test and then extrapolated for the critical fragmentation length using Weibull distribution as statistical model.

The fiber strength and adhesion forces at the fiber/matrix interface for a known gauge length will have a direct influence on the number of fragments for that length. A low number of fiber fragments or none at all means that the adhesion forces on the interface are low, the fiber detaches and slides through the matrix and no stress transfer to the fiber occurs unless there is friction between fiber and matrix. However, strong adhesion forces between fiber and matrix will have a positive effect on stress transfer from the matrix to the fiber which is expressed by a higher number of fiber fragments. Another reflection of interfacial adhesion can be characterized by the shape of the breaks. A narrow debonding length (interfacial detachment between fiber and matrix) at fiber ends and a narrow break gap (no fiber slip), are typical evidence of a strong interfacial bonding. Crack propagation into the matrix on such case might also be observed. On the other hand, a wider break gap and debonding length with no crack propagation into the polymeric matrix suggests that the interfacial adhesion strength is weak [64].

The use of cross polarized light during the SFFT can be used to see the photoelastic features such as birefringence caused by the stress state of the matrix particularly in the zone around the fiber break [64, 65]. The birefringence phenomena is a characteristic of anisotropic materials but can also be observed in materials when these are subject to stress and strain. The stress transfer from the polymeric matrix to the fiber causes the fiber to break, and debonding occurs almost simultaneously at the fiber/matrix interface creating a colorful birefringence effect. This feature is more prominent for epoxy rather than polyester materials. The pattern is typically symmetrical but the extension of the birefringe may vary depending on the interfacial debonding that occurs during the test, as shown in Figure 12. A narrow birefringence effect suggests a strong interfacial adhesion and almost no debonding phenomena. On the other hand a long and flat pattern indicates a considerably debonding length at the fiber/matrix interface and a weak interfacial adhesion. This can also be confirmed by the presence of a more intense color at the interface next to the fiber tips. The pattern can change during the test since a continuous applied strain after break might increase the debonding length [64].



Figure 12: Schematic illustration of birefringence pattern around a fiber break without debonding (top) and with debonding (below). Adopted from [64].

These events can be observed in situ by the use of optical microscope equipped with cross polarizers and focal lenses from low to high magnification so that information concerning

the segments and details on the fibers breaks can be assessed. It is therefore essential for the procedure that the polymeric matrix is relatively transparent.

Other techniques have been combined with the SFFT like for instance the use of Raman spectroscopy on which is possible to trace strain profiles along a composite reinforced fiber, typically carbon and Kevlar. The use of glass fibers on the SFFT does not allow the use of such method.

The procedure for the single fiber fragmentation test and estimation of the interfacial shear stress in this work is based on the model proposed by Kelly-Tyson[61]. However, it should be pointed out that several studies have reported inaccuracies on the output data such as disregard of micromechanical events that occur during the test, local plastic flow, matrix cracking and debonding at fiber/matrix interface which compromises the assumption of a constant shear stress. The complexity involving the mechanics of load transfer between fiber and matrix as well as the stress state around fiber break is well-known, nevertheless this model can yield reasonable results which can be used for comparative studies between samples.

The relation given by eq.3 is also debatable since it considers that the fiber fragmentation length distribution is symmetrical within the interval  $l_c$  and  $l_c/2$ , when in fact this is rarely observed [66]. Another issue is related to the critical length. Lacroix et al. [67] support that the critical length is not a material parameter but depends on the transfer load model considered. On the other hand, Feillard et al. [68] defend that there is no actually analytical relationship between the mean fragment length and critical length. With these finding in mind, the mean fragment length is used in this work, as an input parameter in the following calculation of the interfacial shear strength.

#### EXPERIMENTAL PROCEDURE

Carbon nanotubes were grown on the surfaces of fibers by CVD of ethylene under different experimental conditions. The selected fibers were embedded in two different types of polymeric matrices, and the fiber-matrix interfacial properties were studied by single fiber fragmentation tests and photoelasticity analyses. In the following sections are described the experimental procedures adopted to synthesize the carbon nanotubes on the surfaces of the fibers (Section 1) and the embedment of the resulting selected fibers into epoxy resin and PETG (Section 2).

#### 1. SYNTHESIS OF CARBON NANOTUBES ON GLASS AND CARBON FIBERS:

E-glass fibers (UTS 200 UD) and carbon fibers (PAN based Tenax HM 35) with diameters of 14  $\mu$ m and 7  $\mu$ m respectively, were used for the synthesis of the carbon nanotubes on their surfaces by a chemical vapour deposition process. The preparation of the fibers consisted in the following steps:

**STEP 1:** Glass and carbon fibers underwent a pre-heat treatment at 450°C at atmospheric conditions for 30 min, in order to remove the sizing of the fibers. Since the sizing consist in a polymeric material, this temperature should be adequate to cause its degradation. Afterward the fibers were soaked in acetone and washed with alcohol to remove any residues. Finally they were dried at 100°C for 3h.

**STEP 2:** In order to study the effect of iron metallic particles on the yield and quality of carbon nanotubes synthesized on the different fibers, deposition of iron was made on their surfaces by an impregnation method. A batch of fibers was prepared as follows: glass and carbon fibers were impregnated in an iron metal salt solution with concentration of 0.25M, which has been reported to yield suitable catalysts for the growth of carbon nanotubes. After 2h, the fibers were pulled out and allowed to drain for 30 min. Afterwards they were dried in the oven at 110°C and subjected to a calcination process during 4.5h at 450°C. These conditions have been shown to yield suitable particles for the synthesis of carbon nanotubes [45]. Note that the fibers without deposition of iron catalysts did not undergo this step.

**STEP 3:** Carbon nanotubes were synthesized on the surfaces of the glass and carbon fibers by chemical vapour deposition of ethylene. Different parameters were varied during the chemical vapour deposition process, namely time of deposition, temperature and pre-reduction treatment under hydrogen in order to evaluate their effect on the yield and quality of carbon nanotubes formed. The different samples are summarized in Table 4, where GF and CF stands for glass fiber and carbon fiber respectively and the prefix Fe means the fiber was first impregnated in the iron solution (STEP2) in order to form iron particles to catalyse the growth of carbon nanotubes.

SAMPLE	Fe - CNT- GF1	CNT-GF2	CNT-GF3	CNT-GF4	CNT-GF5	CNT-GF6	Fe - CNT- CF1	CNT- CF2
T (°C)	750	750	750	650	550	650	750	750
Time (h)	2	2	2	2	2	1	2	2
$H_2$	+	-	+	+	+	+	+	+

Table 4: Samples prepared under different conditions (time, temperature and reduction process).

The fibers were inserted in a ceramic boat and put into the oven ensuring it was placed in the middle heated zone of the oven. Argon was allowed to flow through the tube reactor at room temperature to reduce the atmospheric gases present in the tube and afterward hydrogen (500 sccm) was introduced into the tube. With exception of sample CNT-GF2, all the samples were subjected to a reduction treatment at 650°C for 2h under a flow of hydrogen. Afterwards, a mixture of ethylene and hydrogen with a flow of (60:60 mL.min<sup>-1</sup>) was introduced into the oven. The temperature of carbon deposition varied between 550°C and 750°C, and the synthesis of carbon nanotubes was carried out for periods of 1h and 2h. Finally, the ethylene gas was closed and argon was allowed to flow during the cooling process.

The experimental system used in this work is shown in Figure 13. It consists of a Horizontal Tube Furnace, Single-Zone, Model R 40/500/12, Naberthem, equipped with an outer quartz tube with diameter of 40 mm and a length of 1 m and an inner quartz tube with diameter

of 28 mm and a length of 500 mm. A gas flow system supplies the furnace with ethylene, hydrogen and argon, from Air Liquide and AGA.



Figure 13: Chemical vapour deposition experimental setup used in this work.

#### 2. PRODUCTION OF GLASS FIBER-CNTS POLYMER COMPOSITES:

According to the results obtained in the first section related to the production of CNTsfibers, the selected samples (CNT-GF4, CNT-GF5 and CNT-GF6) were embedded in epoxy resin and PETG. The reasons of this selection will be presented after the results discussion in the next part of this work.

## 2.1 GLASS FIBER-CNT EPOXY SPECIMEN

Dog-bone shape specimens for mechanical and interfacial studies were produced using silicon open moulds, Figure 14. The silicon used was Elastosil M4511 which was mixed with catalyst T21 at a ratio of 100:5, respectively, and poured in a negative mould with a PTFE sprayed layer to assist the mould removal after a curing process for 2 days. The negative mould consisted of an aluminium machined plate with five aligned dog-bone shape negatives with slots at each end. These slots will allow the fibres to be placed aligned in the middle position of the specimen, Figure 14. The mould was cut into individual pieces with the negative shape for easier handling during fiber embedment. The specimen dimensions can be seen on Figure 15.



Figure 14: Silicon mould of dog-bone specimens with open slots.



Figure 15: Test specimen dimensions.

Each single fibre was placed in the silicon mould and anchored in the ends with 2g of adhesive mass, as it can be seen in Figure 16. The weight of the mass confers a pre-tension to the fibres that not only prevents the fibre to float when the polymer is poured into the mould, but also can partly compensates the compressive stress introduced by the polymer shrinkage during the curing process. The weights are removed after the epoxy pre-curing stage. The polymer matrix in this experiment consists of the thermoset epoxy resin Pro-set 117 mixed with 226-hardener from the same brand, at a ratio of 100:39. The curing process of the specimens was divided in a pre-curing time of 16h at room temperature and further 16h at 50°C. Dog-bone shaped specimens with no fibres were also made in order to obtain the characteristic stress/strain curve of the epoxy.



Figure 16: Embedded fibers under pre-tension during epoxy resin curing.

Since the samples were produced in open moulds a convex meniscus is formed during the curing process, yielding a varying transversal cross-section thickness of the specimen, which has to be removed by polishing, Figure 17. Therefore, a metal fixture was machined with the shape of the specimen with the desired sample thickness where the specimen was fixed and polished with until a uniform thickness of approximately 1.5 mm was achieved. Drawings of the fixture can be found in the *Appendices* section of this work, [A1].



Figure 17: Schematic representation of a convex meniscus after resin curing stage.

#### 2.2 GLASS FIBER-CNT PETG SPECIMEN

The thermoplastic polymer polyethylene terephthalate glycol (PETG), commercially designated as VIVAK PETG Transparent 099, was supplied by Vink as sheets of 1mm thickness. These sheets were cut into smaller plates of (100x80) mm to fit a purpose made aluminium closed mould (drawing shown on *Appendices* section of this work, [A2]). The fibers were placed in between the PETG sheets and adhesive was used at the fibers ends to assist their right positioning, Figure 18. A polymeric release foil was placed between the mould and the sheets to facilitate the mould removal without damaging the final composite. The mould was closed tight with the use of several bolts to produce as much compressive pressure as possible and then put in an oven for 60 min at 250°C. These parameters were found by trials in order to homogenously melt the PETG around its melting point temperature, without lowering its viscosity excessively in order to prevent it from escape though small gaps and bolt holes. Moreover, by reducing the flow of material inside the mould could prevent major displacements of the fibers. Finding the correct temperature window is crucial since the polymer degradation is also to be avoided.



Figure 18: a) Bulk production of PETG with embedded fibers.b) Single specimen after water jet cut.
The resulting PETG composites were cut in the shape of the dog-bone test specimen by water jet cutting with the same dimensions as showed on Figure 15 apart from the thickness which on PETG specimens is 2mm. Afterwards the specimens were polished in order to prevent potential propagation of surface cracks when tensile load is applied.

## 2.3 SINGLE FIBRE FRAGMENTATION TEST

For the single fiber fragmentation test (SFFT) the same apparatus is used for both the Epoxy and PETG embedded fiber specimens. The setup, Figure 19, consist of a micro-tensile machine (detail on Figure 20) with an electric controller box is fixed to an optical microscope stage having an aperture that allows light to be transmitted through the specimen to be tested. For the cross polarized images, a custom polarizer was made and placed next to the source light while the analyser was placed at the top of the microscope next to a mounted video camera for the capture of images.



Figure 19: Single fiber fragmentation test setup.



Figure 20: Micro-tensile machine with test specimen.

Width and thickness of the PETG and epoxy composite samples were measured using a calliper. Each specimen was placed in the micro-tensile machine locked by grip holders, and preloaded until a small tensile load was detected on the sensor. A number of five specimens for each sample were tested using the micro-tensile machine, Figure 20, with a speed rate of 0.5mm/min in order to have a low strain rate to avoid early failure of the specimen. Since it was not possible to get an accurate elongation reading during the test since no clip gauge was available, a load limit value was established inside the elastic limit of the stress-strain curves for the Epoxy and PETG samples. The stress-strain curves were obtained using an Instron tensile machine model 5944, Figure 21, by testing blank specimens for each system according to standard ASTM D638-03. The load limit established for the different polymeric materials was used to stop the SFFT on the micro-tensile machine, leaving the specimen under constant tensile load. Pictures of the broken segments as well as high magnification pictures of the breaks with and without cross polarized light were taken for later measurements and interpretation. Software registers the time and load during the tensile test.



Figure 21: Instron 5944 tensile machine with test specimen loaded.

## **RESULTS AND DISCUSSION**

This part is divided in two main sections. The first section is dedicated to the synthesis of fibers-CNTs hybrids. The different fibers produced were characterized by energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), Raman Spectroscopy and termogravimetric analyses (TGA), and the respective results are presented and discussed. The second section is dedicated to the evaluation of fiber/matrix interfacial properties, when the selected glass fibers were embedded in PETG and epoxy resin. The results obtained by single fiber fragmentation tests and photoelasticity analyses are presented and discussed.

#### 1. CHARACTERIZATION OF HYBRIDS OF GLASS FIBERS AND CARBON NANOTUBES

## 1.1 ENERGY DISPERSIVE X-RAYS (EDX) ANALYSES

The elemental composition of the as-received glass fibers (GF) and after the pre-heat treatment at 450°C for 30 min and glass fibers-carbon nanotubes (GF-CNTs) hybrids was assessed by EDX analyses. EDX analyses were done in order to verify the amount of metallic species within the constitution of the fibers that could contribute to the catalytic synthesis of carbon nanotubes, the effective removal of the sizing after the treatment of the fibers, and the successful deposition of carbon on their surfaces after the chemical vapour deposition process.

The results of the elemental composition of the glass fibers, in weight%, before and after the sizing removal, are shown respectively in Table 5 and Table 6. Oxygen, silicon, aluminium, boron, magnesium, iron and calcium are identified as the main elements within glass fibers composition. Since the amount of iron present in the glass fibers is very small (less than 1%) it should hardly contribute to the formation of suitable sites which may possibly catalyze the growth of carbon nanotubes. In the case of the as received fibers, the EDX analyses indicate a considerable amount of carbon within its composition which is mainly attributed to the polymeric protecting layer of the fibers, Table 5. After the heat treatment at 450°C and the washing step, the amount of carbon drops considerable, Table 6, since typical glass fibers do not contain any carbon within their composition [15]. However, its presence is still identified

although in a lower amount which is most probably due to the carbon tape used to hold the samples.

After chemical vapour deposition of ethylene, EDX analyses show that the amount of carbon is considerable increased due to the growth of carbon filaments on the surfaces of the fibers, as it can be seen in the further scanning electron microscopy analyses. An example is shown in Table 7, which corresponds to the elemental composition of sample CNT-GF4.

Spectrum	В	С	0	Mg	Al	Si	Ca	Fe
Spectrum 1	4.54	28.26	44.36	3.01	6.18	13.52	0.03	0.10
Spectrum 2	4.38	28.67	43.76	3.02	6.26	13.55	0.03	0.32
Spectrum 3	3.71	24.53	45.67	3.24	6.73	14.95	0.04	1.13
Mean	4.21	<b>27.15</b> 2.28	44.6	3.09	6.39	14.01	0.04	0.52
Std. Deviation	0.44		0.98	0.13	0.29	0.82	0.01	0.54

Table 5: Elemental composition of the as received glass-fibers.

Spectrum	В	С	0	Mg	Al	Si	Ca	Fe
Spectrum 1	-	5.98	52.27	5.12	10.74	25.80	0.03	0.05
Spectrum 2	-	6.01	52.61	5.12	10.68	25.55	0.03	-
Spectrum 3	-	7.00	51.73	5.07	10.63	25.52	0.04	-
Mean	-	6.33	52.20	5.10	10.68	25.63	0.03	0.02
Std. Deviation	-	0.58	0.44	0.03	0.05	0.16	0.01	0.03

Table 6: Elemental composition of the glass-fiber after sizing removal.

Spectrum	В	С	0	Mg	Al	Si	Ca	Fe
Spectrum 1 Spectrum 2 Spectrum 3	4.93 - 4.75	33.67 22.72 32.39	37.52 45.99 38.02	3.03 4.03 3.15	6.19 8.06 6.33	14.61 19.17 15.27	$0.05 \\ 0.04 \\ 0.04$	$0.00 \\ 0.00 \\ 0.05$
Mean Std. Deviation	3.23 2.79	<b>29.59</b> 5.99	40.51 4.75	3.40 0.55	6.86 1.04	16.35 2.46	$0.04 \\ 0.01$	0.02 0.03

Table 7: Elemental composition of GF-CNTs hybrids, sample CNT-GF4.

#### **1.2 SCANNING ELECTRON MICROSCOPY ANALYSES**

The morphology of the glass and carbon fibers before and after the sizing removal procedure, and after the chemical vapour deposition of ethylene, was evaluated by scanning electron microscopy analyses and the images are shown in the following sub-sections:

## 1.2.1 Raw and pre-treated fibers

Figure 22 and Figure 23 show the morphology of the as received glass and carbon fibers before and after the removal of the sizing, respectively. In Figure 22(a) and Figure 23(a) the layer of polymeric material that covers the fibers is observable. After the heat treatment and washing step with acetone, the sizing is completely removed, as shown in Figure 22(b) and Figure 23(b). The removal of this thin layer before the deposition of carbon by CVD procedure is important since residual carbonaceous resultant from polymer degradation may lead to deposition of amorphous carbon along the surfaces of the fiber and it might result in a further non-controllable parameter in the growth of CNTs.



Figure 22: SEM image of as received glass fibers (a) and after the sizing removal (b).



Figure 23: SEM image of as received carbon fibers (a) and after the sizing removal (b).

The images of the glass and carbon fibers coated with iron solution and after the calcination treatment under atmospheric conditions at 450°C for 4.5h are shown in Figure 24 and Figure 25, respectively. As it can be seen from the SEM images for both fibers, after their immersion in the iron solution, a non uniform film is formed on the surface of the fibers and after the calcination process large thick layers remain attached to the surfaces.



Figure 24: SEM images (a-b) of glass fibers coated with iron after the calcination process.



Figure 25: SEM images (a-b) of carbon fibers coated with iron after the calcination process.

## 1.2.2 Fibers after chemical vapour deposition of ethylene

#### CONDITIONS:

- Glass and carbon fibers pre-immersed in iron solution;
- Temperature of deposition: 750°C;
- Time of carbon deposition: 2h;
- Presence of hydrogen during CVD.

The glass and carbon fibers coated with iron lead to the formation of non-uniform sites covered with carbon filaments, as seen in Figure 26(a) and Figure 27(a) respectively. The deposition of carbon is preferential on iron particles due to their ability to interact with hydrocarbon molecules and catalyze the growth of carbon nanotubes as mentioned in the *Introduction* part of this work. Agglomerates of carbon nanotubes are observed due to a poor dispersion of iron particles. On both types of fibers, Figure 26(b) and Figure 27(b) it is also possible to observe the presence of carbon nanofibers and amorphous carbon.



Figure 26: SEM images of iron coated glass fibers after CVD (a-b), sample Fe-CNT-GF1.



Figure 27: Different magnification SEM images of iron coated carbon fibers after CVD (a-b), sample Fe-CNT-CF1.

#### CONDITIONS:

- Temperature of deposition: 750°C;
- Time of carbon deposition: 2h;
- Absence of hydrogen during CVD;

Figure 28 corresponds to the SEM images of the glass fibers subjected to the chemical vapour deposition of ethylene at 750°C during 2h and in the absence of hydrogen. The carbon filaments do not grow on the surfaces of the fibers and amorphous carbon deposited in the fibers is observable in some parts of the fibers, as it can be seen in Figure 28. The presence of hydrogen has been shown to be fundamental for the growth of carbon filaments.



Figure 28: Low (a) and high magnification (b) SEM images of CNT-GF2.

#### CONDITIONS:

- Temperature of deposition: 750°C;
- Time of carbon deposition: 2h;
- Presence of hydrogen during CVD;

The morphology of the glass fibers with a temperature of carbon deposition of 750°C during 2h but with the presence of hydrogen is shown in Figure 29. The fibers show the presence of carbon filaments on their surfaces which are difficult to be identified due to their irregular shape and size.



Figure 29: Low (a) and high magnification (b) SEM images of sample CNT-GF3.

MASTER THESIS

#### CONDITIONS:

- Temperature of deposition: 650°C;
- Time of carbon deposition: 2h;
- Presence of hydrogen during CVD;

Reducing the temperature to 650°C, the SEM images in Figure 30 show a significant increase of carbon nanotubes on the surfaces of the fibers and with considerable greater length. This indicates that the reduction of the temperature during the chemical vapour deposition process facilitates the formation of carbon nanotubes. A possible explanation may be related to the decomposition of the ethylene before reaching the surfaces of the glass fibers. At higher temperature (750°C), the decomposition of ethylene is initiated in the tube reactor entrance which may lead to carbon deposition on the walls of the reactor.



Figure 30: Low (a) and high magnification (b) SEM images of CNT-GF4.

#### CONDITIONS:

- Temperature of deposition: 550°C;
- Time of carbon deposition: 2h;
- Presence of hydrogen during CVD;

In the SEM images of the glass fibers under CVD of ethylene at 550°C during 2 h are shown in Figure 31. It is observable a great amount of carbon nanotubes covering the surfaces of the fibers, Figure 31 B), however they seem to be not so finely dispersed when compared to fibers subjected to a deposition temperatures of 650°C, under the same time of deposition, Figure 30 A) and Figure 31 A).



Figure 31: Low (a) and high magnification (b) SEM images of CNT-GF5.

#### CONDITIONS:

- Temperature of deposition: 650°C;
- Time of carbon deposition: 1h;
- Presence of hydrogen during CVD;

In Figure 32, it is shown the SEM images of the glass fibers subjected to a carbon deposition temperature of 650°C for 1h. The surface of the glass fibers seem very similar to sample CNT-GF4 and by SEM analyses was not possible to differentiate the two samples.



Figure 32: Low (a) and high magnification (b) SEM images of CNT-GF6.

In all the samples, some parts of the fibers are absent of carbon nanotubes due to the placement of the fibers on the ceramic boat. The proper separation of the fibers precluded the experiment since they easily flew from the holder, and therefore they needed to be placed in small bundles. This fact led to small parts without carbon nanotubes where the fibers were touching each other.

One interesting observation in this work resides on the fact that carbon nanotubes were grown on glass fibers without the use of metal catalysts, contrary to carbon fibers where carbon nanotubes were not grown in the absence of catalysts (not shown). The glass fibers comprise a very low amount of iron within its composition, as revealed by EDX analyses, which could hardly be responsible for the catalytic synthesis of carbon nanotubes. The growth of carbon nanotubes without using metal catalysts on silica substrates have been reported recently and the growth of carbon nanotubes on the surface of glass fibers without previous deposition of metal catalysts on their surfaces has never been reported before. In a similar work, Liu et al.[35] reported the growth of carbon nanotubes on a silica oxide substrate without a catalyst. Likewise, the authors observed a strong dependence of the carbon nanotubes growth and the gas environment, concluding that the annealing treatment of silica oxide substrate under hydrogen was essential to synthesize the carbon nanotubes on its surface.

In this work, since the growth of carbon nanotubes was possible in the glass fibers with and without the use of catalysts, it was decided to continue the investigations only focused on the glass fibers. Therefore, the quality and yield of carbon nanotubes synthesized on the surface of the glass fibers under different experimental conditions, was further evaluated by Raman spectroscopy and thermogravimetric analyses, respectively.

#### **1.3 RAMAN SPECTROSCOPY ANALYSES**

Raman Spectroscopy investigations were made in order to estimate the quality of the carbon nanotubes grown on the glass fibers under different CVD conditions, and the results are shown in Figure 33. For comparison, the Raman spectrum of a glass fiber with the sizing removed (GF-SR), is also presented.

In the Raman spectrum is possible to observe two main peaks, a peak around 1300 cm<sup>-1</sup> and another at 1600 cm<sup>-1</sup>. The peak at higher frequencies is attributed to the G band, also called graphitic band, which is related to the tangential stretch modes of the carbon atoms and it is present in sp<sup>2</sup> carbon materials. The peak around 1300 cm<sup>-1</sup> corresponds to the D-band, also called the defect induced band, and it is related to defects and finite size effects in the graphitic structure [69]. The crystalline quality of the carbon nanotubes structure can be estimated by the intensity ratio of these two bands,  $I_D/I_G$ , and the ratio values for the different samples are summarized in Table 8.

As expected, in the case of the glass fiber with the sizing removed, GF-SR, no intense peaks are distinguishable in the Raman spectrum, indicating the absence of carbon nanotubes. Likewise, sample CNT-GF2 do not present any peaks, indicating that the deposition of carbon did not occur in this sample. These results support the SEM investigations of CNT-GF2 where it was not possible to observe the presence of carbon nanotubes.

Sample Fe-CNT-GF1 reveals the lowest  $I_D/I_G$  ratio, of approximately 0,811, indicating the presence of carbon nanotubes with superior quality. When compared to sample CNT-GF3 which was subjected to the same CVD conditions but without the use of iron catalysts, sample CNT-GF3 shows a slight increase of 4.7% in the intensity ratio  $I_D/I_G$ . Since the difference between the intensity ratios  $I_D/I_G$  of these two samples is too small, the presence of iron seem to have no significant effect on the quality of carbon nanotubes produced.

In the absence of iron metal catalysts and for the same time of carbon deposition in the presence of hydrogen, sample CNT-GF4 contains carbon nanotubes with superior crystalline quality. When compared to sample CNT-GF4, sample CNT-GF3 shows a minor increase in the intensity ratio  $I_D/I_G$  of approximately 1,3% which indicates that the temperatures of deposition of 750°C and 650°C yield carbon nanotubes of similar crystalline quality. On the other hand, sample CNT-GF5 shows a visible increase in the intensity ratio  $I_D/I_G$  of approximately 16%

when compared to sample CNT-GF4. This fact is attributed to the temperature used to run the experiments which may be insufficient to properly decompose the ethylene which leads to the development of amorphous carbon species. Comparing the quality of carbon nanotubes produced at the same carbon deposition temperature under hydrogen and using different times of carbon deposition, sample CNT-GF6 shows a slight increase in the intensity ratio  $I_D/I_G$  value of around 4,7%. The time of deposition seems to have no considerable effect on the quality of carbon nanotubes produced.



Figure 33: Raman spectra for the glass fibers after chemical vapour deposition of ethylene at different experimental conditions.

	Fe-CNT-GF1	CNT-GF2	CNT-GF3	CNT-GF4	CNT-GF5	CNT-GF6
	(750°C,2h,H <sub>2</sub> )	(750°C,2h,-H <sub>2</sub> )	(750°C,2h,H <sub>2</sub> )	(650°C,2h,H <sub>2</sub> )	(550°C,2h, H <sub>2</sub> )	(650°C,1h, H <sub>2</sub> )
D/G	0,811	-	0,849	0,838	0,974	0,878

Table 8: Raman results for the different samples (D/G ratios).

#### **1.4 THERMOGRAVIMETRIC ANALYSES**

In order to verify the complete removal of the sizing from the fibers before the CVD process, thermogravimetric analyses (TGA) were made for the as received glass fibers and after the sizing removal procedure. The results, shown in Figure 34, indicate a single mass drop of approximately 3% for the glass fibers as received (GF0) and which corresponds to the decomposition of the polymeric material that covers the glass fiber (sizing). On the other hand, the glass fiber subjected to the sizing removal (GF-SR) maintains nearly constant mass which indicates that the sizing was effectively removed.



Figure 34: Thermogravimetric results for glass fibers before and after sizing removal.

TGA analyses were also made for the glass fibers produced in order to compare the yield of carbon nanotubes within the different samples. The TGA results are shown in Figure 35 and the values of masses loss before and above 500C are summarized in Table 9.

The carbon nanotubes content was determined by the mass losses in each sample at temperatures above 500°C. Several studies have shown that the mass losses at temperatures

above 500°C correspond mainly to the decomposition of carbon nanotubes and/or carbon nanofibers while the mass losses below this temperature is attributed to the decomposition of amorphous carbon species which typically occur between 200°C and 400°C [70, 71]. Sample CNT-GF2 do not show any mass loss, implying that no deposition of carbon occurred on the surfaces of the glass fibers during the chemical vapour deposition process, as supported by the previous analyses.

It is possible to observe that there is no significant difference in the amount of carbon nanotubes produced in the samples without iron catalysts, Table 9, with mass loss values between 2.1% and 5,4%. On the other hand, sample Fe-CNT-GF1 reveals a considerable amount of carbon nanotubes of approximately 19.4% by weight. This noticeable difference in the yield of carbon nanotubes between the samples without iron particles and sample Fe-CNT-GF1 is related to the ability of iron particles to catalyse the growth of carbon nanotubes contributing to a higher amount of carbon nanotubes formed.



Figure 35: TGA results of the hybrids glass fibers-carbon nanotubes subjected to different experimental condisitons.

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SAMPLES	Mass loss (<500°C)	Mass loss (≥500°C)
Fe-CNT-GF1 (750°C, 2h, H <sub>2</sub> )	0.5	19.4
CNT-GF2 (750°C, 2h, -H <sub>2</sub> )	-	-
CNT-GF3 (750°C, 2h, H <sub>2</sub> )	0.8	2.8
CNT-GF4 (650°C, 2h, H <sub>2</sub> )	1.1	5.4
CNT-GF5 (550°C, 2h, H <sub>2</sub> )	3.3	2.3
CNT-GF6 (650°C, 1h, H <sub>2</sub> )	1.7	2.1

Table 9: Values of the mass losses before and after 500°C for the different samples.

Based on the results obtained in this section, three samples were selected to continue our experiments, namely samples CNT-GF4, CNT-GF5 and CNT-GF6. These three different samples revealed simultaneously the presence of carbon nanotubes, a more uniform dispersion of those through the fibers surface, and CNTs with superior length.

# 2. CHARACTERIZATION OF GLASS FIBERS-CARBON NANOTUBES PETG AND EPOXY COMPOSITES

The single fiber fragmentation test was performed in order to evaluate the effect of CNTs, grown under different parameters on the surface of glass fibers, on the matrix/fiber interfacial shear strength for two polymeric systems, namely PETG and epoxy resin. The test yields quantitative data for the calculation of the interfacial shear stress at critical length by measuring the broken segments for each specimen. The distribution of the different segments length was plotted and the mean length estimated by Weibull statistics. Pictures of the breaks for the different samples at different magnifications, with and without the use of cross polarized light, are also presented for interpretation in the last part of this section.

## 2.1 SINGLE FIBER FRAGMENTATION TEST ANALYSES

In order to know the behaviour of the matrix materials, the stress/strain curves of blank dog-bone specimens of PETG and Epoxy were assessed by tensile tests using a Instron 5944 tensile machine, since no accurate strain values are provided by the micro-tensile machine used in this work.

The characteristic stress/strain curves for the PETG and Epoxy resin specimens are presented in Figure 36 and Figure 37. PETG specimens showed a maximum tensile stress of approximately 42MPa for a strain of 6%, and strain at break values of around 6,5%. In the case of the epoxy specimens, the maximum tensile stress was found to be approximately 53MPa at a strain of 4,2%, and the strain at break was measured to 4.3%.

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Figure 36: Characteristic stress-strain curve for PETG specimens.

Figure 37: Characteristic stress-strain curve for epoxy specimens.

A strain value in the limit of the linear region was selected for the different samples. The strain limit for the PETG and epoxy were fixed at 4% and 3%, which corresponds to a tensile stress of 36MPa and 43,7MPa, respectively, calculated from the linear region of the stress-strain curves.

#### 2.1.1 NEAT AND CNTS-GLASS FIBERS EMBEDDED IN PETG:

The fragmentation test was made for the PETG composite specimens and Figure 38 shows the typical stress/time curve obtained. Note that the fragmentation test was suspended at the value of stress 36 MPa which corresponds to a strain value of 4%, as explained previously. In order to verify that the fiber reached the saturation state during the test, the number of breaks in the fiber was registered at the selected stress (36 MPa) and when the specimen started to fail (approximately at 40 MPa). Since the number of breaks was exactly the same, this fact is a strong indication that the fiber reached its saturation state at the limited imposed (36 MPa).



Figure 38: Stress-time curve for a typical PETG-CNT-GF specimen during the SFFT.

When the fragmentation test was completed, the number and length of the fragments for each specimen was measured. Figure 39 shows the cumulative distribution for the fragments length obtained for samples PETG-CNT-GF4, PETG-CNT-GF5 and PETG-CNT-GF6. The fragment length distribution may give an indication of the adhesion between the fiber and the matrix, where the shift to lower fragments length is indicative of a good adhesion [72]. From the cumulative distribution plot it is not possible to clearly distinguish the different samples, since the curves obtained are very similar. The respective mean length was calculated using Weibull statistics in order to determine the critical fragment length and the interfacial shear stress for the different samples, according to equations 2 and 3, respectively, described in the *Introduction* part. The results are summarized in Table 10.

Due to equipment limitations it was not possible to obtain experimentally the fiber tensile strength ( $\sigma_f$ ) at critical length. Therefore an experimental value was adopted from [65], for a similar critical length, and assuming that the properties of the fiber remained constant and were not affected by the temperature treatment used to run the experiments or by the presence of carbon nanotubes. This value was used to calculate the fiber interfacial shear strength ( $\sigma_{iss}$ ) at critical length, for all the samples. Nevertheless it should be remarked that the measurements of

the fiber ultimate tensile strength for each fiber used in this work should have been experimentally calculated in order to fairly compare the results obtained.

The number of segments for the different samples in the gauge length selected is nearly the same, of about 50 breaks, Table 10. Among the PETG-CNT-Glass fibers composites samples, it is observed that sample PETG-CNT-GF4 show the smallest critical length of approximately 582,9 $\mu$ m, followed by samples PETG-CNT-GF6 and PETG-CNT-GF5 with critical lengths of 614,8  $\mu$ m and 632,4  $\mu$ m, respectively. Using equation3, sample PETG-CNT-GF4 has the highest interfacial shear stress of 45MPa. This indicates that this sample has possibly the highest adhesion at the interface fiber/matrix. This fact may be related with the presence of possible longer carbon nanotubes on the surface of this fiber that could lead to a better physical interlocking of polymer chains with the CNTs. A large variation is observable on the segments length in the different samples which may be attributed to a non uniform dispersion of the CNTs on their surfaces.



Figure 39: Cumulative distribution of fragments lengths for samples PETG-CNT-GF4, PETG-CNT-GF5 and PETG-CNT-GF6.

Samples	Average No.	Average length	<i>l<sub>c</sub></i> (µm)	σ <sub>f</sub>	$ au_{iss}$
	Segments	or segments (µm)		(MPa)	(Mpa)
PETG-CNT-GF4 (650°C, 2h)	52	437,2 ± 17,9	582,9 ± 23,9	3750	45
PETG-CNT-GF5 (550°C, 2h)	49	474,3± 31,9	632,4 ± 42,5	3750	41,5
PETG-CNT-GF6 (650°C, 1h)	51	461,1 ± 21,9	614,8 ± 29,3	3750	42,7

Table 10: Average No. and length of segments, critical length, fiber ultimate tensile strength and interfacial shear stress values for the PETG-CNT-GF composites.

The single fragmentation test was also made for PETG composites with the as received glass fibers, i.e., glass fibers with the fabric sizing. However, the measurement of the fragments length in the specimens was not possible due to a high concentration of cracks present along the fiber, as shown in Figure 40, when compared to the PETG-CNT-GF composites, Figure 41. In order to be able to accurately measure such small segments, an X-Y table under the microscope would be necessary in order to control the exact displacement of the micro-tensile machine. The high crack density observed on the as received fibers embedded in PETG may be related to a good adhesion between the fiber and the matrix promoted by the sizing. Although the segments length was not possible to determine and thus the critical length and interfacial shear stress, the presence of a high crack density in the fibre is a strong indication of good adhesion between the fiber and these observations, the sizing treated fibers have a better fiber/matrix adhesion when compared to fibers with CNTs grown on their surfaces.







#### 2.1.2 NEAT AND CNTS-GLASS FIBERS EMBEDDED IN EPOXY:

During the single fragmentation test of the epoxy composites, it was not possible to reach the previously stipulated stress value of 43,7 MPa, as seen in Figure 42 which shows a typical stress-time curve for the epoxy composites specimens. After a certain amount of applied load, the specimens' shoulders started to deform and slip from the grips of the micro-tensile machine, as it can be seen in Figure 43, and therefore compromising the test results. Since the target load was not achieved, only a few breaks were observed, depending on the point where the test started to fail. Since the fiber did not reach the saturation state, the number and length of segments were not registered. Nevertheless, optical microscopy images were taken of the breaks present in the epoxy specimens and they will be presented and discussed in the next section.





Figure 42: Stress-time curve for a typical Epoxy-CNT-GF specimen during the SFFT.

Figure 43: Specimen shoulder deformation during the SFFT.

## 2.2 BREAKS AND PHOTOELASTICITY ANALYSES

Optical microscope images of the breaks after the SFFT were taken with and without the use of cross-polarized light. The results obtained for the PETG and epoxy composites are shown and discussed in the following sub-sections 2.2.1 and 2.2.2 respectively.

#### 2.2.1 NEAT AND CNTS-GLASS FIBERS EMBEDDED IN PETG:

Figure 44 a), Figure 45 a) and Figure 46 a) are typical images of the breaks occurring during the SFFT for the different samples of fibers with CNT's embedded in PETG matrix. These images were taken during the pause of the fragmentation test at the selected target load, where the load slightly decreases due to matrix stress relaxation, as seen in Figure 38, during the optical microscopy analyses.

In all the samples, a gap caused by fiber breakage is observable when the fiber tensile stress reaches its failure strength. The stress is transferred to the fiber by means of shear at the interface fiber/matrix. If the interfacial shear stress is high enough it may cause the matrix to deform and delaminate due to cracking and interfacial debonding, Figure 44, as it can be seen for all PETG-CNT-GF samples. This is an indication of a good adhesion between the fiber and matrix most likely attributed to the ability of CNTs to entangle with the polymer chains.

On the pictures where cross polarized light was used, Figure 44 b), Figure 45 b) and Figure 46 b) a symmetrical birefringence effect can be seen in all samples which is produced by the stress field around the fiber break. By analysing the breaks in the samples of fibers with CNTs there is no clear difference in the birefringe pattern. A bright red zone which has been reported to be a zone were interfacial debonding between fiber and matrix occurs [64], was also visually perceptible in the optical microscope images for all the PETG-CNT-GF samples.

## PETG-CNT-GF4 (650°C, 2h)



Figure 44: Optical micro. images (20x) of a break in PETG-CNT-GF4 (a) using cross-polarized light (b).



## PETG-CNT-GF5 (550°C, 2h)



Figure 45: Optical micro. images (20x) of a break in PETG-CNT-GF5 (a) using cross-polarized light (b).



Figure 46: Optical micro. images (20x) of a break in PETG-CNT-GF6 (a) using cross-polarized light (b).

Although the observations of the breaks for the fibers with CNTs on their surfaces did not allow the differentiation between them, a noticeable difference was observed when the as received glass fibers were used. The optical microscope images of the as received fibers embedded in PETG taken after the SFFT, with and without the use of cross-polarized light, are shown in Figure 47. As mentioned on the previous section, a large crack density was observed along the fiber which is likely attributed to the fabric sizing which improves the adhesion between matrix and fiber. Compared to the PETG-CNT-GF samples, the cracks observed in the samples with as-received fibers are noticeably larger. The sizing may produce a brittle interphase region around the fiber with high modulus and low fracture toughness. This high modulus increases the shear stress transfer at the fiber interface but the lower fracture toughness of the created interphase induces the cracks propagation into the polymeric matrix from the fiber interface [73]. An early stage of the cracks propagation, with and without the use of crosspolarized light, is shown in Figure 48. Moreover, the birefringence pattern in the interface between the fiber and the matrix is not observed, Figure 47 b), which strongly indicates that interfacial debonding did not occur when the as received sized fibers were used.



Figure 47: Optical micro. images (40x) of breaks in the specimen PETG-GF0 (a) and using cross-polarized light after SFFT.

## PETG-GF



Figure 48: Optical microscope images (40x) of breaks in the specimen PETG-GF0 (a) and using crosspolarized light in an early stage of crack propagation.

#### 2.2.1 NEAT AND CNTS-GLASS FIBERS EMBEDDED IN EPOXY:

Microscopy images of typical fiber breaks for the samples Epoxy-CNT-GF4, Epoxy-CNT-GF5 and Epoxy-CNT-GF6 can be seen in Figure 49 a), Figure 50 a) and Figure 51 a), respectively. No significant difference can be seen between samples Epoxy-CNT-GF4 and Epoxy-CNT-GF6. However, the break gap seems to be wider for the Epoxy-CNT-GF5 sample and since no obvious deformation or cracking of the matrix is seen, it suggests that the fibers may have slipped during the test, Figure 50 a).

The respective microscopy images of the samples using cross-polarized light are shown in Figure 49 b), Figure 50 b) and Figure 51 b). Similar to the PETG samples, it is observable the colourful birefringence effect caused by the stress areas around the break with a more intense pattern on the fiber surface next to the fiber ends. In the case of sample Epoxy-CNT-GF5 this pattern is more pronounced which suggests a poorer adhesion of this fiber and the matrix, when compared to samples Epoxy-CNT-GF4 and Epoxy-CNT-GF6. The fiber used to produce the sample Epoxy-CNT-GF5 contained the highest amount of amorphous carbon, as revealed by thermogravimetric analyses, and this fact may explain the poor adhesion between the fiber and the epoxy. However, since the SFFT was paused before the fiber saturation and thus only few breaks were analysed, no definitive conclusions can be made.

For the epoxy samples with as-received fibers, no breaks were observed, as it can be seen in Figure 52. This may indicate that debonding at the interface occurred and no load was transferred from the matrix to the fiber making it to slip from the matrix during the SFFT. When compared with the fibers with CNTs on their surfaces, this fact could suggest that the presence of carbon nanotubes on the fibers surface enhanced the interfacial bonding between fibre and matrix. However, for the reasons mentioned previously, no conclusions can be definitely drawn.

#### EPOXY-CNT-GF4 (650°C, 2h)



Figure 49: Optical microscope images (10x) of a break in Epoxy-CNT-GF4 (a) using cross-polarized light (b).



Figure 50: Optical microscope images (10x) of a break in Epoxy-CNT-GF5 (a) using cross-polarized light (b).



## EPOXY-CNT-GF6 (650°C, 1h)

Figure 51: Optical microscope images (10x) of a break in Epoxy-CNT-GF6 (a) using cross-polarized light (b).

## EPOXY-CNT-GF5 (550°C, 2h)

## EPOXY-GF0



Figure 52: Optical microscope images (8x) showing no breaks in Epoxy-GF0 (a) using cross-polarized light (b).

## CONCLUSION AND FUTURE SUGGESTIONS

Carbon nanotubes were synthesized on the surface of glass and carbon fibers under different experimental conditions, namely the presence or absence of iron catalysts, varying the time and temperature of deposition and reduction treatment under an atmosphere of hydrogen. It was envisaged that the presence of carbon nanotubes attached to fibers surfaces could enhance the interfacial bonding between the fibers and the polymer matrix, by interlocking the polymer chains in the surrounding area of the fibers.

SEM analyses showed that glass and carbon fibers coated with iron revealed a considerable amount of carbon nanotubes on their surfaces. This fact is not surprising since it is well known the ability of iron to decompose the carbon species and the ability of carbon to diffuse in the iron metallic particles. Nevertheless the carbon nanotubes were not uniformly distributed throughout the fiber surface and this fact was attributed to a possible non-uniform dispersion of the catalyst particles. For this reason, these fibers were not selected to be embedded in epoxy and PETG matrices, since a poor dispersion of carbon nanotubes could lead to sites with different adhesion properties and stress concentrations that could compromise the single test fragmentation tests. These observations lead us to the conclusion that the impregnation method is not the best procedure to achieve a uniform dispersion of the catalyst particles throughout the fibers surface before the CVD process in order to obtain a more uniform dispersion of the iron catalysts.

In the absence of iron catalysts, the synthesis of carbon nanotubes was not possible on the surface of the carbon fibers contrary to the glass fibers where the presence of carbon nanotubes was observed. For this reason, our studies were further focused on the glass fibers. The growth of carbon nanotubes on glass fibers surface without the use of metal catalyst particles was never reported before and this observation is quite interesting. The detrimental effect of metal particles entrapped in carbon nanotubes is well-known in many applications and their removal is normally necessary which involves delicate procedures that may induce defects on the carbon nanotubes structure. Therefore, the carbon nanotubes attached to glass fibers surface without metal particles may bring several advantages and further studies are highly recommended.

In this work, the presence of hydrogen was indispensable in the synthesis of carbon nanotubes, in accordance with previous works which reported the growth of carbon nanotubes without the presence of metallic catalytic particles [35]. The presence of hydrogen may have a twofold effect: it may be crucial during the annealing process in order to form suitable sites for the further deposition of carbon and it avoids the formation of amorphous carbon by reacting with the radicals formed during the decomposition of the carbon source.

Raman spectroscopy analyses revealed that the presence of iron particles had no significant effect on the quality of carbon nanotubes produced. In the absence of iron catalysts, samples with the temperatures of carbon deposition of 750°C (sample CNT-GF3) and 650°C (sample CNT-GF4) yielded carbon nanotubes of similar crystalline quality. On the other hand, when a carbon deposition temperature of 550°C was used (sample CNT-GF5), the quality of carbon nanotubes is lower when compared to samples CNT-GF3 and CNT-GF4. This fact is attributed to the temperature used during the CVD, which might have been insufficient to properly decompose the ethylene and therefore leading to the formation of amorphous carbon species. The time of deposition had no considerable effect on the quality of carbon nanotubes produced.

Thermogravimetric analysed revealed no significant difference in the amount of carbon nanotubes produced in the samples without iron catalysts. On the other hand, in the presence of iron catalysts (Fe-CNT-GF1) it was detected a significant amount of carbon nanotubes, of approximately 19.4% by weight. This fact is attributed to the ability of iron particles to catalyze the growth of carbon nanotubes contributing to a higher amount of carbon nanotubes formed.

According to the results obtained in the production of hybrids of fibers and carbon nanotubes, three samples (CNT-GF4, CNT-GF5 and CNT-GF6) were selected to evaluate their effect on the fiber/matrix interfacial properties. The effect of the quality and amount of carbon nanotubes within the different samples on the fiber/matrix interfacial strength of PETG and epoxy fiber composites was evaluated by SFFT and photoelasticity analyses.
After the SFFT for the PETG-CNT-GF samples, the number of segments in a gauge length of 26mm was registered and all the samples which revealed nearly the same number of breaks (around 50). The length of the segments was measured and the respective cumulative results showed no significant difference between the samples. The mean length for each sample was calculated using Weibull statistics and the critical fragment length and the interfacial shear stress were further determined. Sample PETG-CNT-GF4 showed the smallest values of critical length of around 582.9µm and therefore a better interfacial shear stress of 45MPa. This may indicate that this sample has better adhesion at the interface fiber/matrix. This fact was attributed to the presence of possible longer carbon nanotubes on the surface of this fiber that could lead to a better physical interlocking between them and the polymer chains. Nevertheless, no definite conclusions can made due to several reasons:

One relies on the fact that an experimental value of the fiber tensile strength at a critical length, calculated by other authors [65], was used to calculate the interfacial shear stress for all the samples. However, single fiber tensile tests must be done to verify that the experimental conditions used to prepare the fibers (heat treatment, carbon deposition time, gas atmosphere, etc.) and the presence of CNTs did not affect the fiber properties.

Another issue is related to the number of specimens used. Due to the geometry of the samples, most part of PETG samples slipped from the micro-tensile machine holders and therefore the results were discarded. A new geometry of the dog-bones and a higher amount of tests would lead to more accurate results.

Nevertheless, the presence of possible longer carbon nanotubes in the sample PETG-CNT-GF4, due to the CVD conditions, may lead to a higher entanglement of carbon nanotubes and polymer chains that would lead to a greater fibre/matrix adhesion. Therefore, further studies concerning the mentioned issues are highly recommended.

The single fragmentation test made for PETG composites with the as received glass fibers, lead to a high concentration of cracks present along the fiber, which is likely attributed to the sizing fabric which enhances the adhesion between the fiber and the matrix.

Microscopy and photoelasticity analyses of the fiber breaks in the PETG-CNT-GF samples did not show clear difference between them. On the other hand, when as-received fibers were used, a high density of cracks was observed and noticeably larger when compared to the fibers with CNTs on their surfaces. Moreover, the birefringence pattern in the interface between

the fiber and the matrix was not observed which strongly indicates that interfacial debonding did not occurred when the sizing fabric was used.

Based on the results obtained for the fibers embedded in PETG, it may be concluded that the sizing treated fibers have a higher fiber/matrix adhesion when compared to fibers with CNTs grown on their surfaces.

Concerning the epoxy fiber composites, it was not possible to conclude the SFFT since all the samples slipped from the grips, therefore compromising the results. However a few amount of breaks was observable before the specimen started to fail. These were considered for analysis. Samples Epoxy-CNT-GF4 and Epoxy-CNT-GF6 revealed the crack propagation going slightly inside the epoxy matrix while no cracking was seen on sample Epoxy-CNT-GF5. In addition, the birefringe pattern was more intense in the sample Epoxy-CNT-GF5. These observations suggest a poorer adhesion of this fiber and the matrix, when compared to samples Epoxy-CNT-GF4 and Epoxy-CNT-GF6, which may be related to the presence of a higher amount of amorphous carbon on its surface. On the other hand, no breaks were observed when the as-received fibers were used, which may indicate a poor fibre/matrix interface.

Based on the microscopy and photoelasticity analyses, the presence of carbon nanotubes on the fibers surface seem to enhance the interfacial bonding between fiber and epoxy. However no conclusion can be made since the SFFT was not possible to conclude and therefore further studies are necessary to evaluate the effect of CNTs on the fiber/matrix interfacial strength.

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**APPENDICES** 





Section A-A

A1: Dog-bone specimen polishing fixture drawing.

MASTER THESIS



A2.

A2: Closed mould drawing for PETG fiber composites production.