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DEVELOPMENT AND CHARACTERIZATION OF POLYMERIC COMPOSITES REINFORCED WITH NATURAL FIBRES AND CARBON NANOTUBES

JORGE DE SOUZA E SILVA NETO

Tese apresentada ao Programa/Curso de Pós-Graduação em Engenharia Mecânica e Tecnologia dos Materiais - PPEMM, do Centro Federal de Educação Tecnológica Celso Suckow da Fonseca, CEFET/RJ, como parte dos requisitos necessários à obtenção do título/certificado de Doutor em Engenharia Mecânica e Tecnologia dos Materiais

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RESUMO

O DESENVOLVIMENTO E CARACTERIZAÇÃO DE COMPÓSITOS POLIMÉRICOS REFORÇADOS COM FIBRAS NATURAIS E NANOTUBOS DE CARBONO

Os compósitos poliméricos reforçados com fibras naturais (NFRCs) tem demonstrado grande potencial para diversas aplicações em vários setores industriais (esporte, automobilístico e têxtil), devido às suas vantagens em relação aos compósitos reforçados por fibras sintéticas, como, por exemplo, baixo impacto ambiental (ex: gasto energético de produção) e baixo custo. No entanto, uma das desvantagens é que os NFRCs apresentam propriedades mecânicas baixas e absorção de umidade relativamente altas devido à característica hidrofílica da fibra natural. Um método para aumentar o desempenho é a hibridização ou adição de partículas (micro ou nano). Portanto, entender as propriedades e o potencial do uso de materiais de múltiplo reforço é de grande interesse no desenvolvimento de compósitos híbridos. O principal objetivo desta tese é o desenvolvimento e caracterização de compósitos poliméricos reforçados com fibras naturais e nanotubos de carbono. Primeiramente, a eficiência do processo de sonicação e concentração de nanotubos de carbono de paredes múltiplas (MWCNTs) na resina epóxi foram investigadas. As propriedades mecânicas e térmicas desses nanocompósitos foram analisadas. Três potências de sonicação (25, 50 e 75W) foram usadas para dispersar os MWCNTs (0,2%, 0,4% e 0,6%) na matriz epóxi. Ensaios de tração foram usados para determinar as propriedades mecânicas dos nanocompósitos, enquanto as propriedades térmicas foram determinadas pela análise termogravimétrica (TGA) e pela Calorimetria Diferencial de Varredura (DSC). Verificou-se que a adição de nanotubos de carbono à matriz epóxi e os parâmetros do processo de sonificação afetam as propriedades mecânicas e térmicas dos nanocompósitos. Um aumento de 14% na resistência à tração e 15% do módulo de Young, quando comparado à matriz epóxi pura, o melhor caso encontrado foi para potência de sonicação de 75W e porcentagem de 0,6 wt% de MWCNTs.

Na segunda parte, estudou-se o efeito do envelhecimento por radiação ultravioleta e spray d’água nas propriedades mecânicas de compósitos de fibras naturais e compósitos híbridos. Os compósitos: juta pura, juta híbrida/vidro e compósitos reforçados com fibra

de vidro foram fabricados. Todos esses tipos de compósitos foram modificados com 0,6wt% em peso de nanotubos de carbono de paredes múltiplas (MWCNTs) e seu comportamento mecânico foi comparado aos corpos de prova não modificados. Testes de tração e flexão foram usados para medir as propriedades mecânicas dos corpos de prova não envelhecidos (controle) e envelhecidos.

Análise de Microscopia Eletrônica de Varredura (MEV) foi usada para examinar as superfícies de fratura dos corpos de prova testados. Verificou-se que o processo de envelhecimento afetou as propriedades mecânicas dos compósitos estudados de diferentes maneiras. Para os compósitos juta e juta + MWCNT as propriedades diminuíram com o aumento do tempo de exposição. Os compósitos híbridos de juta/vidro (não modificado e modificados por MWCNT) foram menos afetados pelo envelhecimento e apresentaram uma alteração insignificante na resistência à tração. Os compósitos híbridos + MWCNT, apresentaram um aumento de aprox. 7% no módulo de Young (1000h) e 9% (500h) e 17% no módulo de flexão (1000h) quando comparado aos corpos de prova sem exposição. Já o MWCNT possuiu efeito positivo nas propriedades mecânicas das amostras envelhecidas de vidro + MWCNT.

Na terceira parte, analisou-se a compatibilidade da fibra de curauá com adição de nanotubos de carbono em compósitos. Os compósitos foram feitos por duas técnicas de produção: adição de nanotubos na matriz e revestimento da fibra. Os compósitos foram caracterizados por ensaios mecânicos (tração e flexão) e caracterizados termicamente por TGA. Por fim, os resultados mostraram que a fibra de curauá apresentou uma melhor compatibilidade adicionando o nanotubo de carbono na fibra comparado com o compósito de curauá puro e com adição de nanotubo na matriz.

Palavras-chave: Fibras naturais, Nanotubos de carbono, Compósitos e resina.

ABSTRACT

DEVELOPMENT AND CHARACTERIZATION OF POLYMERIC COMPOSITES REINFORCED WITH NATURAL FIBRES AND CARBON NANOTUBES

Natural fibre reinforced polymer composites (NFRCs) have demonstrated great potential for many different applications in various industries due to their advantages compared to synthetic fibre-reinforced composites, such as low environmental impact and low cost. However, one of the drawbacks is that the NFRCs present relatively low mechanical properties and the absorption of humidity due to the hydrophilic characteristic of the natural fibre. One method to increase their performance is hybridization. Therefore, understanding the properties and potential of using multiple reinforcement materials to develop hybrid composites is of great interest.

The main objective of this thesis is the development and characterization of polymeric composites reinforced with natural fibres and carbon nanotubes. First, the efficiency of the sonication process and of multi-walled carbon nanotubes (MWCNTs) content on the mechanical and thermal properties of an epoxy matrix was investigated. Three different sonication powers (25, 50 and 75W) were used to disperse the MWCNTs (0.2%, 0.4% and 0.6%) in the epoxy matrix. Tensile tests were performed to determine the mechanical properties of the nanocomposites, while the thermal properties were determined by the thermogravimetric analysis (TGA) and the Differential Exploratory Calorimetry (DSC). It was found that the addition of carbon nanotubes to the epoxy matrix and the parameters of the sonication process affect the mechanical and thermal properties of nanocomposites. An increase of 14% in tensile strength and 15% of Young's modulus, when compared to the pure epoxy matrix was found for 75W sonication power output and 0.6% MWCNTs weight percentage. The thermal analysis indicated that the presence of MWCNTs increased the T_{onset} of the nanocomposites when compared to pure epoxy resin. Finally, increasing the sonication power output leads to higher T_g of the nanocomposites studied here. For the specific materials studied here, the best results were obtained for the 0.6 wt.% MWCNTs and 75W sonication power output case.

The effect of aging by ultraviolet radiation and water spray on the mechanical properties of natural fibre and hybrid composites was studied in the second part of the research. Pure jute, hybrid jute/glass, and glass fibre-reinforced composites were fabricated. All these

types of composites were further modified with 0.6 wt% of multi-walled carbon nanotubes (MWCNTs) and their mechanical behavior was compared to the unmodified specimens. Tensile and flexural tests were used to measure the mechanical properties of unaged (control) and aged specimens. A SEM analysis was used to examine the fracture surfaces of the specimens tested. It was found that the aging process affected the mechanical properties of the composites studied in different ways. For jute and jute + MWCNT composites the properties decreased with increased exposure time. The hybrid jute/glass composites (unmodified and MWCNT modified) were less affected by aging and showed an insignificant change in tensile strength. The hybrid + MWCNT composites, showed an increase of approx. 7% in Young's modulus (1000 h) and 9% (500 h) and 17%, (1000 h) in flexural modulus when compared to the unexposed specimens. The MWCNTs had a positive effect on the mechanical properties of the glass + MWCNT aged samples.

In the third and last phase of the research, the compatibility of curauá fibre with the addition of carbon nanotubes in composites was analyzed. The composites were made by two production techniques: addition of nanotubes in the matrix and fibre coating. The composites were characterized by mechanical tests (tensile and flexural) and thermal characterized by TGA test. Finally, the results showed that the curauá fibre showed better compatibility by adding the carbon nanotube in the fibre compared with the pure curauá fibre composite and with the addition of the nanotube carbon in the matrix.

Keywords: Nature Fibre, Composite, Nanotubes and Resin.

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List of Publications

1. Neto, J., Queiroz, H., Aguiar, R., Lima, R., Cavalcanti, D., & Banea, M. D. (2022). A Review of Recent Advances in Hybrid Natural Fiber Reinforced Polymer Composites. ***Journal of Renewable Materials***, *10*(3), 561. https://doi.org/10.32604/jrm.2022.017434
2. Neto, J. S., de Queiroz, H. F., Aguiar, R. A., & Banea, M. D. (2021). A Review on the Thermal Characterisation of Natural and Hybrid Fiber Composites. ***Polymers***, *13*(24), 4425. https://doi.org/10.3390/polym13244425
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Chapter 1

1. Introduction

In the last decade, the natural fibre reinforced composite (NFRC) has gained space in several sectors of the industry. Many of these sectors, automobile, aerospace, civil and sports, have sought to reduce the dependence of products or oil from petroleum [1, 2]. Therefore the need is linked to society's awareness of understanding and increasingly implementing the circular economy cycle in processes and products [3, 4]. The principal virtues of using these fibres are abundance in nature, low production cost, low density, good insulation (thermal and sound) and biodegradable [5, 6]. However, natural fibres have some limitations, such as variation in mechanical properties, problem of interfacial adhesion between fibre-matrix, dimensional variation, and durability in hostile environments (example: high humidity) [7-9].

To minimize these effects that affect the properties of composites, two types of methods can be applied: hybridization and particle incorporation. Hybridization consists of using two or more types of reinforcements in the matrix, mainly synthetic fibres (glass or carbon) [10]. The implementation of these fibres modifies the mechanical and thermal properties, similarly to improving the durability of these materials [11].

Furthermore, another method described in the literature to reduce this effect and improve performance of the incorporation of nanofiller (Carbon nanotube (CNT's), TiO_2 and SiO_2) with dimension in the range 1 to 100 nm. These materials can be incorporated into the matrix, fibre or both, the main advantages of using these materials are the improvement in the fibre-matrix interface, gain in mechanical, thermal and electrical properties, and reduce the effect of degradation in composites [12-15]. However, one of the main factors in limiting the use of nanofillers is the concentration, cure kinetics and dispersion method [2, 16, 17].

Among the types of existing nanofillers, carbon nanotubes (CNT's) are one of the most used nanofillers in the prevention of degradation. These materials can be divided into three types: single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT) and multi-walled carbon nanotube (MWCNT) [18, 19]. The difference between them are the graphene numbers wrapped around their structure.

However, MWCNTs are the most studied due to two factors: lower chemical inertia for functionalization and better dispersion in the matrix reducing the manufacturing cost [18, 19]. In this context, the objective the present work to study the effect of carbon nanofillers in composites reinforced by natural fibres and epoxy resin, analyzing the mechanical and thermal properties and the effect of durability.

1.1 Motivation

The natural fibres reinforced composites have conquered a growing market over the years. The implementation of natural fibres decreases 63% energy consumption when compared to glass fibre reinforced composites during the life cycle [3, 20]. Moreover, natural fibres have lower density than synthetic fibres (glass and carbon), the cost of production is one of the factors that contribute to the application of these fibres in various sectors of the industry, such as natural fibre (200-1000 US$/ton), synthetic fibre (carbon – 12500 US$/ton) [21]. However, natural fibres reinforced composites have limitations in application in hostile environments. Furthermore, NFRC's are susceptible to water absorption due to their hydrophilic capacity that affects the interface between fibre-matrix [1, 2, 22]. Thus, to improve the mechanical and thermal properties and minimize the effect in hostile environments, nanofillers can be added or apply hybridization [11, 20, 22-25].

1.2 Objectives

The main objective of this thesis is the development and characterization of polymeric composites reinforced with natural fibres and carbon nanotubes.

The specific objectives are:

1. Investigate the effect of carbon nanotubes on the mechanical and thermal properties of nanocomposites.

2. Investigate the effect of aging by ultraviolet radiation (UV) and water spray on natural and hybrid fibre reinforced composites.
3. Analyze the mechanical and thermal properties of natural fibres with difference types of functionalized with carbon nanotubes.

1.3 Research methodology

The objectives of this thesis were achieved by following the methodology:

- In the first stage a review of the effect of hybridization in the mechanical and thermal properties of NFRCs was made. The effect of type of fibres, matrix, and surface treatments in natural fibres (physical and chemical) on the mechanical and thermal properties were discussed. Finally, water absorption was addressed and how this affects the mechanical and thermal properties of NFRCs.
- Second stage: a study was carried out on the effect of carbon nanotubes on epoxy resin. The influence of the nanotube concentration and the power used for dispersion was evaluated, and how this affects the mechanical and thermal properties of the nanocomposites.
- In the third stage, the durability of natural fibres reinforced composites and carbon nanotubes was analyzed. The materials were degraded by water spray and ultraviolet radiation, and tensile and bending tests were performed on these materials, in addition to a visual analysis of the UV effect on the color of the composites.
- In the four stage, the influence of carbon nanotube incorporated into the matrix and fibre of composites reinforced with natural fibres was investigated.

1.4 Thesis structure

This thesis consists in:

- **Chapter 1** - Introductory chapter consisting of introduction, motivation, objectives, research methodology and thesis structure.
- **Chapter 2** –is based on the article: Neto, J., Queiroz, H., Aguiar, R., Lima, R., Cavalcanti, D., & Banea, M. D. (2022). A Review of Recent Advances in Hybrid Natural Fiber Reinforced Polymer Composites. ***Journal of Renewable Materials***, *10*(3), 561. Literature review of composites, types of fibre and matrices, physical and chemical treatments, mechanical and thermal properties of nature fibre and hybrid composites.
- **Chapter 3** – is based on the paper Neto J, Banea M, Cavalcanti D, Queiroz H, Aguiar R. Analysis of mechanical and thermal properties of epoxy multiwalled carbon nanocomposites. ***Journal of Composite Materials***. 2020; 54(30): 4831-4840.https://doi.org/10.1177/0021998320939232 .
  The main objective of this study was to investigate the efficiency of the sonication process and of multi-walled carbon nanotubes (MWCNTs) content on the mechanical and thermal properties of an epoxy matrix.
  Three different sonication powers (25, 50 and 75 W) were used to disperse the MWCNTs (0.2%, 0.4% and 0.6 %) in the epoxy matrix. Tensile tests (ASTM D638) were performed to determine the mechanical properties of the nanocomposites, while the thermal properties were determined by the thermogravimetric analysis (TGA) - ASTM E1131 and the Differential Exploratory Calorimetry (DSC) - ASTM D3418.
- **Chapter 4** – is based on the following published article: Neto, J. S., FM de Queiroz, H., KK Cavalcanti, D., AA Aguiar, R., B Pereira, A., & Banea, M. D. (2021). Effect of ultraviolet radiation and water spraying on the mechanical properties of multi walled carbon nanotubes reinforced natural fiber and hybrid composites. Journal of Applied Polymer Science, 51915. https://doi.org/10.1002/app.51915
  The main objective of this study was to investigate the effect of aging by

ultraviolet radiation and water spray on the mechanical properties of natural fiber and hybrid composites. Pure jute, hybrid jute/glass, and glass fiber-reinforced composites were manufactured by compression molding. All these types of composites were further modified with 0.6 wt% (previous work) of multi-walled carbon nanotubes (MWCNTs) and their mechanical behavior was compared to the unmodified specimens. Tensile (ASTM D3039) and flexural (ASTM D790) tests were used to measure the mechanical properties of unaged (control) and aged specimens.

- **Chapter 5** –is based on the paper: J.S.S. Neto, D.K.K. Cavalcanti, H.F.M. de Queiroz, R.A.A. Aguiar, M. D. Banea. Effect of MWCNTs on the mechanical and thermal properties of curauá natural fiber reinforced composites. Submitted to Fibers.

  The main objective of this study was to investigate the effect of the addition of the Multi-walled Carbon Nanotubes (MWCNTs) on the mechanical and thermal properties of curauá fiber reinforced composites. The MWCNTs were added either to the fiber surface or into the resin matrix as the second reinforcing phase. MWCNT modified curauá fibers as well as raw fibers were characterized by single fiber tensile test (ASTM C1557), thermogravimetric analysis - TGA (ASTM E1131) and Fourier-transform infrared spectroscopy FTIR analyses. Further, different composite samples: pure curauá, (curauá + MWCNT) + resin, curauá+ (resin+MWCNT) were manufactured by compression molding and tested to characterize their mechanical and thermal properties.
- **Chapter 6** – presents the conclusions and future works.

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Chapter 2

A Review of Recent Advances in Hybrid Natural Fiber Reinforced Polymer Composites

ABSTRACT

Natural fiber reinforced polymer composites (NFRCs) have demonstrated great potential for many different applications in various industries due to their advantages compared to synthetic fiber-reinforced composites, such as low environmental impact and low cost. However, one of the drawbacks is that the NFRCs present relatively low mechanical properties and the absorption of humidity due to the hydrophilic characteristic of the natural fibre. One method to increase their performance is hybridization. Therefore, understanding the properties and potential of using multiple reinforcement's materials to develop hybrid composites is of great interest. This paper provides an overview of the recent advances in hybrid natural fiber reinforced polymer composites. First, the main factors that affect the performance of hybrid fiber-reinforced composites were briefly discussed. The effect of hybridization on the mechanical and thermal properties of hybrid composites reinforced with several types of natural fibers (i.e. sisal, jute, curauá, ramie, banana, etc.) or natural fibers combined with synthetic fibers is presented. Finally, the water absorption behaviour of hybrid fiber-reinforced composites is also discussed. It was concluded that the main challenges that need to be addressed in order to increase the use of natural-natural or natural-synthetic hybrid composites in industry are the poor adhesion between natural fibers and matrix, thermal stability and moisture absorption of natural fibers. Some of these challenges were addressed by recent development in fibers treatment and modification, and product innovation (hybridization).

KEYWORDS

Natural Fiber Composites (NFC); hybrid composites; mechanical properties; thermal properties; water absorption

1 Introduction

Several industrial sectors (e.g. the automotive and aeronautics), are continuously seeking development of lighter materials with increased resistance with the goal of improving system reliability and efficiency. Therefore, composite materials present an excellent solution to this demand, especially the fiber reinforced polymeric composites, due to their high strength and stiffness, as well as presenting low density [1].

Nowadays, the industry is looking for new characteristics of composite materials, such as renewability, low environmental impact and cost. Consequently, there is an increasing augment in research and innovation in the natural fiber reinforced composite (NFRC) materials, mainly due to the advantages of these materials compared to synthetic fibre-reinforced composites, such as low environmental impact and low cost. However, one of the shortcomings is that the NFRCs present relatively low mechanical properties. One method to increase the mechanical performance of NFRCs to extend their applications is the hybridisation [2, 3]. Hybrid composites use different reinforcement fibers, which can be arranged in a random, layer-by-layer or in-yarn manner [2]. The possible combinations of fibers in hybrid composites include synthetic– synthetic, natural– synthetic and natural–natural fiber types.

It is worth mentioning that the main natural fibers studied and applied in industry (i.e., jute, sisal, oil palm, kenaf, and flax) are well established on the global market with a well-defined production line. However, new promising types of natural fibers are being discovered and used on a smaller scale or are still being used only for research. It is the case of the buriti and curauá fibres, for example, that still need some improvements in their production line to be more commercially affordable and widespread used [4-6]. Another relevant factor in using natural fibers as reinforcement materials in composites is their eco-friendliness associated with lower energy consumption in their manufacturing process [7]. Nevertheless, its recyclable properties depend also on the type of matrices used in the composite production and the management of residuals produced by superficial treatments used to improve the adhesion between fiber/matrix [8].

Natural fiber reinforced polymer composites have demonstrated outstanding potential for many different applications in various industries such as automotive, domestic furniture, food packaging, and agricultural industry [7, 9-11]. The growing importance of natural fiber reinforced composites is reflected by the increasing number of publications (e.g. reviews, patents, book chapters and books) during the recent years

[12-17]. Although there are several reviews concerning the use of natural fibers in the production of natural hybrid composites, this paper provides an overview of the recent advances in both interlaminar and intralaminar hybrid natural fiber composites with natural-synthetic and natural-natural fiber combination in thermoset polymeric matrices. First, the main factors that affect the performance of hybrid fiber-reinforced composites were discussed. The effect of hybridization on the mechanical and thermal properties of hybrid composites reinforced with several types of natural fibers (i.e., sisal, jute, curauá, ramie, banana, etc.) or natural fibers combined with synthetic fibers is presented. Finally, the water absorption behaviour of hybrid fiber-reinforced composites is also discussed.

2 Main factors that affect the performance of hybrid fiber-reinforced composites

The main factors that affect the performance of hybrid fiber-reinforced composites (types of fiber and resin, and the effect of fiber surface treatment), are briefly discussed in this section.

2.1 Type of fiber

The natural fibers are promising renewable alternatives to the traditional human-made fibers (i.e., glass and carbon fibers) in composite materials. Their consumption is increasing in different industrial sectors, such as aeronautical, automotive, civil, and naval, with an average annual growth of 7.5% and an expected global market demand around of 35 million tons by 2022 [16].

The natural fibers can be divided into three main groups regarding their origin: mineral, animal and cellulose/lignocellulose (see Fig. 1). Mineral-based fibers were widely used in composite materials. However, their use presented many human health issues (carcinogenic parts that can be inhaled or ingested), nowadays being forbidden in many countries worldwide. The animal fibers present lower mechanical properties compared to the cellulose fibers, except for the silk fiber that presents high tensile strength. However, the silk fibers are quite expensive and are more used in the textile industries [1]. The animal fibers (i.e., protein fibers such as silk and wool) and the mineral fibers are not covered in this review.

The cellulose/lignocellulose fibers are the most used natural fibers due to their relatively low price and higher mechanical properties compared to other natural fibers. They can also be subdivided into different categories corresponding to the plant part that

originated them.

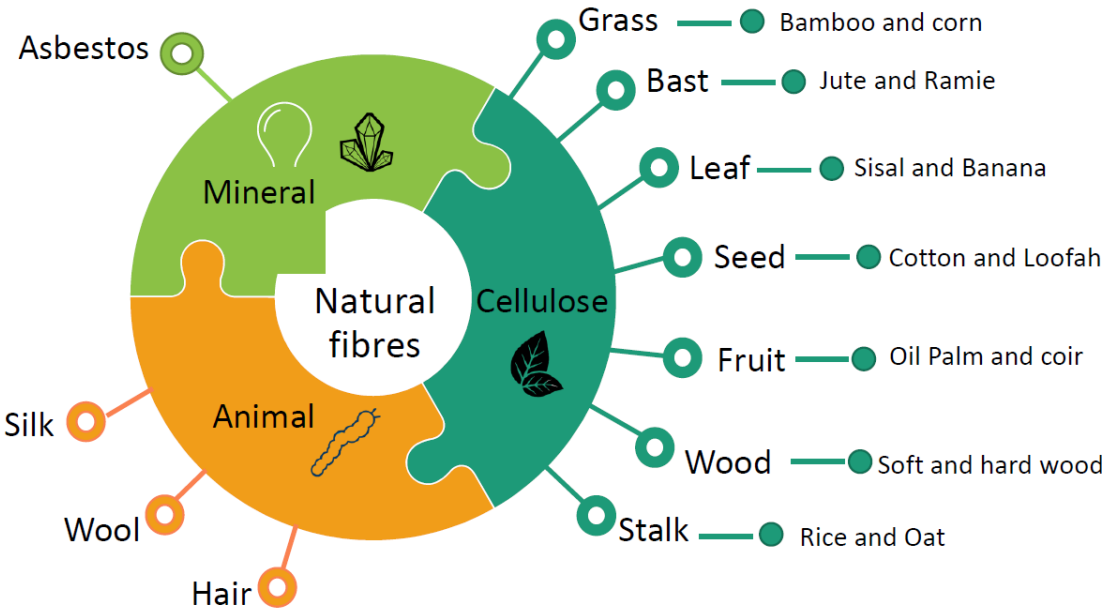


Figure 1: Schematic of natural fibers classification.

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The cellulose/lignocellulose fibers are primarily composed of cellulose (α – cellulose), hemicellulose and lignin [18]. They also present small quantities of waxes in their outer part. The chemical composition and cell structure of cellulose fibers are somewhat complicated [19, 20]. Each fiber is basically a composite in which rigid cellulose microfibrils are embedded in a lignin and hemicellulose matrix. Moreover, the microfibrils are helically wound along the fiber axis to form hollow cells. For instance, the curauá, jute, and sisal fiber morphology are different with distinct lumen diameters (4, 6 and 8 µm, respectively) and cell wall thickness [10, 21]. Besides, they also present different percentages of lignin, cellulose and hemicellulose in their configuration. It is worth mentioning that the amount of cellulose and lignin in the natural fibers depends on the environmental conditions during the plant cultivation, soil properties, irrigation, and extraction techniques (i.e., automatic harvesting or manual extractions) [22]. These characteristics changes the natural fiber's morphology, and consequently, their mechanical and thermal properties [23-27]. The main mechanical properties of the most used natural fibers in hybrid composite materials and their cellulose content are summarised in Table 1. The tensile strengths and Young´s moduli of these natural fibers cover an extensive range of values with typical tensile strength in the range of 100 to 1000

MPa (except for the curauà fibers), which are generally lower than the properties of synthetic fibers (e.g., the tensile strength of E-glass fiber is about 2000–3500 MPa).

Generally, the fibers with higher cellulose contents present higher tensile strength and Young's modulus values (i.e., curauá, sisal and ramie). However, the high variability in fiber quality, which leads to high scattering in the material property values, is still a limitation, showing that many factors can influence their behaviour as the already cited environmental and processing conditions. Therefore, more studies about these parameters are necessary, especially in consideration to the fiber's conservation techniques. Another relevant issue is the lack of detailed information about single-fiber experimental testing procedures, making it difficult to compare the results obtained from different studies. Usually, these results are based on the sample's total cross-section, and its non-corrected measurement can significantly affect the tensile strength results, explaining the different values found in the literature [1].

Synthetic fibers like glass, carbon and aramid are being used in hybrid polymer-based composites mainly because of their high stiffness and strength properties [28]. However, the main drawbacks of using these fibers are their biodegradability, initial processing costs, recyclability, energy consumption, machine abrasion, health hazards, etc.

Table 1: Mechanical properties of several cellulose fibers [10, 18, 22, 29-32].

Fiber	Density (g/cm^3)	Length (mm)	Diameter (µm)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)	Cellulose content (% in weight)
Jute	1.23	0.8-6	5-25	1.5-3.1	187-773	20-55	45-63
Linen	1.38	10-65	5-38	1.2-3	343-1035	50-70	-
Sisal	1.20	0.8-8	7-47	1.9-3	507-855	9-22	50-73
Ramie	1.44	40-250	18-80	2-4	400-938	61.4-128	68.6-76.2
Hemp	1.35	5-55	10-51	1.6-4.5	580-1110	30-60	30-77
Coir	1.20	0.3-3	7-30	15-25	175	6	15-51.4
Kenaf	1.20	1.4-11	12-36	2.7-6.9	295-930	22-60	45-57
Banana	1.50	0.4-0.9	12-30	5-6	529-914	27-32	63
Curauá	0.20	1500	97	4.5-6	1250-3000	30-80	70-73

Pineapple	1.50	1-8	8-41	1-3	170-1627	60-82	81
Abaca	1.50	4.6-5.2	10-30	2.9	430-813	31.1-33.6	56-63
Bamboo	0.6-1.1	1.5-4	88-25	1.3-8	140-441	11-36	74
Nettle	1.51	5.5	20-80	1.7	650	38	53-73
Flax	1.5	5-900	-	2-4	300-800	30-60	30-77
Palm	0.7-1.5	0.59-142	150-500	17-25	150-500	3.24	30
Softwood	1.5	2.8-4.1	28-47	-	1000	18-40	-
Hardwood	1.2	2.67-3.98	31	-	-	37.9	-
Kapok	0.31-0.38	20-32	20	1.2	93.3	4	-

2.2 Surface treatment of natural fibers

Surface treatment of natural fibers is usually performed to enhance the properties of natural fibers, before using them to manufacture a composite material. Fiber surface modification can improve the fiber-matrix interfacial bonding, roughness, wettability and also decrease the moisture absorption of the fibers [33-42]. As a result, better mechanical properties of the resulting composites can be achieved. In this work, the focus will be on natural fibers, since the treatment suffered by the fiber improves the performance of the hybrid composites. The main surface modification methods used for natural fibers (i.e., physical and chemical) are briefly presented in this section.

2.2.1 Physical treatment modifications

The main physical treatments used to modify the surface of natural fibers are as follows: plasma, corona, ultraviolet (UV), heat treatments, electron radiation and fiber beating [15, 42-44]. These treatments improve the adhesion between the fiber and matrix by changing the surface proprieties of the fibers without changing their structural composition [7, 36]. However, physical treatments are more expensive compared to chemical ones, mainly because of the equipment involved in the surface modification processes [7, 15]. The principal effects of physical treatments on the natural fibers are summarised in Table 2.

Table 2: Principal physical treatments used to modify the surface of natural fibers.

Surface Treatment	Treatment effect	Ref.
Plasma	Plasma treatment promotes the removal of contaminants from the fiber surface through ionising gases. Furthermore, this treatment improves the surface roughness by increasing interfacial adhesion between the fiber-matrix.	[4, 42]
Corona	Corona treatment promotes surface fiber change by oxidation process and introduction of polar groups, which results in cleaning of the fiber surface and improving the interfacial adhesion between the fiber (hydrophilic) and matrix (hydrophobic).	[39, 43]
Ultraviolet (UV)	UV treatment affects the polarity of the fiber improving wettability and adhesion between the matrix-fiber. In addition, several bonds are broken (C-C, C-O, C-F, C-Si and C-H) promoting the cleaning of the fibers.	[8, 36]
Ultrasound	Ultrasound process promotes the cleaning of the surface of natural fibers in two ways: micro-jetting and micro-streaming.	[43]
Thermal	Thermal treatment heats the fiber between 100-200°C, affecting their physical and chemical property, cellulose crystallinity, decrease the water percentage and low temperature constituents.	[8, 36]

2.2.2 Chemical treatments

Chemical treatments are a common way of increasing the interface adhesion between the fiber-matrix by chemical bonding or mechanical interlocking at the interface and decreases the water absorption of the fibers [8, 25]. This is achieved by using compounds that promote adhesion by chemically coupling the fibers to the matrix, such as: sodium hydroxide [25, 45-52], silane [8, 23, 29], acetic acid [36, 42, 43, 53], Benzoyl Chloride [43, 54, 55], maleated coupling agents [39, 42, 43], isocyanates [4, 8], peroxide

[31, 56, 57], stearic acid [58] etc. It was shown in the literature that the fiber modification approaches have different levels of efficacy. In general, chemical approaches provide better improvements in properties compared to physical approaches. The improvement in mechanical and thermal properties depends on concentration of the chemical used and exposure time. Combination of treatments with two different chemicals presented better mechanical and thermal properties than the individual treatments in some cases.

Natural fibers that undergo chemical and physical surface modifications presented improved fiber-matrix interfacial adhesion, improved fiber roughness and wettability. In addition, most of the treatments help to minimise the hydrophilic nature and decrease the moisture absorption of natural fibers. The selection of the appropriate fiber modification technique will depend on the particular fiber/matrix used and the composite end-use application. It is essential to understand the interfacial properties and bonding mechanisms of fiber-matrix and this involves significant research efforts in order to maximise NFRCs and hybrid composite applications.

Table 3 presents the most common chemical treatments used to treat/modify the surface of natural fibers.

Table 3: Effect of chemical treatment of natural fibers.

Chemical Treatment	Treatment effect	Ref.
Alkaline	Alkalisation or mercerisation treatment promotes cleaning of impurities, decreases hydrophilicity and fiber constituents. The treatment reduces the diameter and enhances the surface roughness of the fiber and increase the interfacial adhesion of the fiber-matrix.	[4, 38, 59]
Silane	Silane treatment promotes micropore coating on the natural fiber surface. Improves fiber-matrix interfacial adhesion. Pre-treatments are performed, mainly alkalisation, for cleaning existing constituents.	[8, 23, 29]
Acetylation	Acetylation treatment uses acid catalysts (acetic anhydride and acetic acid) for the superficial plasticisation of the natural fiber, increasing interfacial bonding.	[36, 43, 53]

Benzoylation	Benzoylation treatment decreases the hydrophilicity of the natural fiber. Benzoyl Chloride is used to improve the interfacial adhesion between the fiber-matrix and the thermal stability of the fibers. Alkalisation pre-treatment is performed to activate the hydroxyl groups of the fiber.	[43, 54, 55]
Maleated coupling agents	This treatment is used to modify the fiber surface and matrix with the addition of a coupling agent. The maleic anhydride is grafted onto the polymers to increase the compatibility between the matrix and the coupling agent.	[43, 60]
Isocyanate	The treatment is used as a coupling agent in natural fibers, where it can react with the hydroxyl groups found in the fiber, improving interfacial adhesion and increasing water resistance.	[4, 8]

2.3 Type of matrix

The mechanical properties (e.g., tensile, flexural, and impact) of composite materials are directly related to their fiber/matrix interface, where poor adhesion between these elements will result in an inefficient dispersion of loads [1]. Therefore, choosing the correct fiber/matrix combination is fundamental to obtain good composite mechanical and thermal properties. The matrix provides resistance to mechanical and chemical abrasion of the reinforcement fibers, keeps the fibers in the desired position, and is responsible for an efficient load transfer between them [61, 62]. The most common matrices used to produce hybrid natural fiber composites are polymeric (thermoset or thermoplastic) mainly because they can be processed at low temperature and are lightweight [63].

Figure 2 presents a diagram of classification of matrices with the main polymeric matrices types used to produce composites.

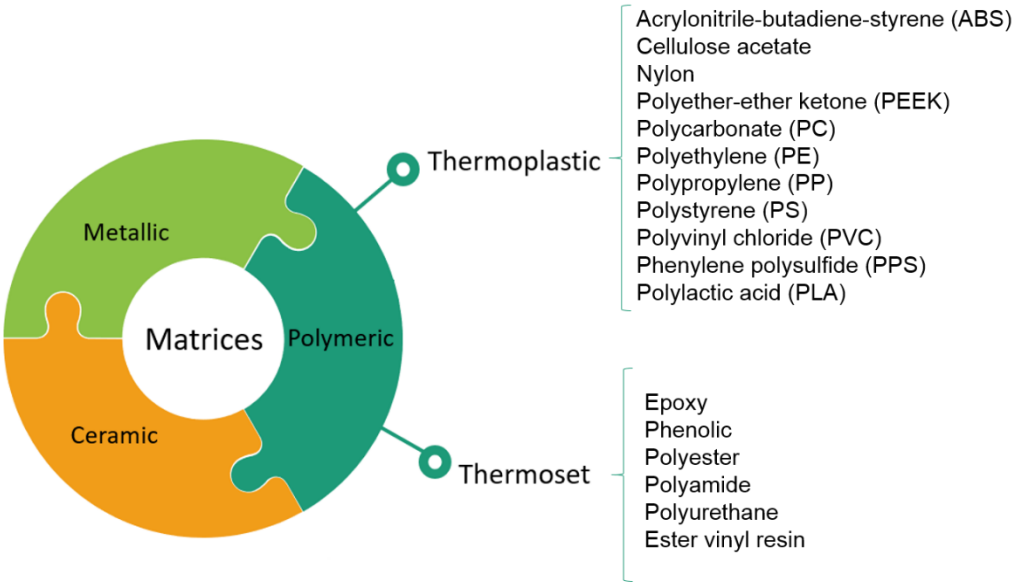


Figure 2: Schematic of classification of matrices with the main polymeric matrices types.

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Thermoplastic polymer matrices can be softened, melted and, also, recycled by the application of heat. However, the continuous reprocessing of these polymers can deteriorate their mechanical and thermal properties [64]. On the other hand, the thermoset matrices (epoxy, urethane, Vinyl Ester, phenolic, polyester, polyimide, polyurethane (PU)) can hardly be recycled or change the shape once the polymerisation (curing) is concluded. These matrices have different chemical structures and undergo different reactivities with the surface molecules of fibers in composites [65].

The main thermoset resins used for hybrid natural composites are epoxy and unsaturated polyesters [66, 67]. Epoxy resins have high mechanical strength and environmental degradation resistance. In general, epoxy resins have excellent adhesion properties, and they are easy to cure and use. In addition, no volatile agents are formed during the curing process, which is an important advantage as compared to phenolic, polyester, and vinyl ester resins. Finally, the shrinkage associated with epoxy resins is lower compared to polyesters. However, one disadvantage is that epoxy resins are relatively brittle, which is detrimental to the interlaminar properties between the matrix and the fiber reinforcement. It is known that epoxy resin cures from liquid to solid through a catalytic chemical reaction, creating extremely strong bonds that cannot be easily reversed or reformed. Because of this, the performance of this matrix material is superior to other matrices; nevertheless their recycling remains challenging. To summarise, as the

majority of natural fibers become unstable at temperatures higher than 200 °C, the matrices that require high processing temperatures are not suitable to manufacture NFRCs or hybrid natural fiber composites.

3 Mechanical properties of hybrid fiber-reinforced composites

Several researches were carried out in the literature to study the mechanical properties of hybrid composites reinforced with several types of natural fibers (i.e. sisal, jute, curauá, ramie, banana, etc.) or natural fibers combined with synthetic fibers [2, 20, 23, 59, 60, 66, 68-84]. The main objective of hybridisation is to balance the deficiency of one specific fiber to achieve sustainability, low cost, and improved performance of the material [2]. Generally, natural hybrid composites are produced by hybridising natural fibers with another either natural or synthetic fiber with superior properties (i.e., higher mechanical strength, chemical stability, nontoxicity, resistance to high temperatures, and thermal or acoustic insulation). Hybridisation of natural fibers with synthetic fibers (i.e., glass, carbon, Kevlar, basalt fibers) can significantly improve the mechanical performance of NFRCs and also their water resistance [20, 71]. The glass fiber is the most used fiber in the hybridisation of NFRCs. Carbon and aramid fibers are also used in NFRC hybridisation but are limited by their high cost and difficult recyclability, thus reducing the main advantage of the hybrid NFRCs (sustainability). Furthermore, the carbon fiber provides stability and high mechanical properties to the hybrid composites but at a much higher cost [85]. For Kevlar, the main use found in literature is for higher impact resistance and in this case, the hybridisation is focused in reducing the number of aramid layers with minimal loss in impact resistance [86]. Finally, another common approach is the substitution of synthetic fibers with natural fibers. This is done with the increase of natural fiber fraction in the hybrid composite. The main purpose is to reduce costs and environmental impact of the composite, while minimizing mechanical property losses [85-87]. Hybrid composites of natural fibers with other natural fibers might not show comparable mechanical enhancements as those hybridised with synthetic fibers, but the natural-natural fibers hybrid composites will be superior in terms of sustainability.

The mechanical properties of fiber reinforced composites are mainly affected by fiber content and orientation [88], stacking sequence [86, 89, 90], hybrid ratio and the fiber-matrix interfacial strength [1, 2, 36]. For example, the tensile strength of hybrid

composites is largely dominated by the reinforcing fiber properties, where the failure begins with the fiber with lower elongation. Considering iso-static loading of all fibers in the hybrid composite the fibers with lower strain at failure will fail first. This results in the failed fibers not participating in carrying the load. Therefore, the fibers with higher elongation will have to carry the brunt of the load. Consequently, the composite should present a compromise between the high and low strain fibers [1, 2]. Figure 3 shows the hybrid effect of a 50:50 wt% LE/HE fiber composite (the hybrid effect is the apparent failure strain enhancement of the LE fiber in a hybrid composite compared to the failure strain of a LE fiber-reinforced non-hybrid composite).

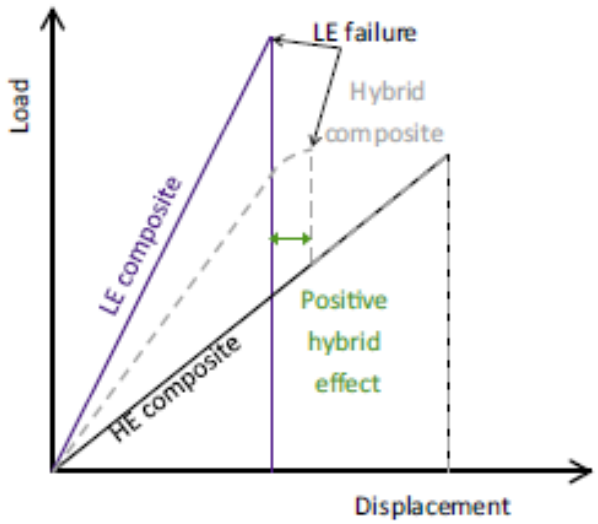


Figure 3: Illustration of the hybrid effect (the apparent failure strain enhancement of the LE fibers, under the assumption that relative volume fraction is 50/50 and that the hybrid composite is twice as thick as the reference composites: LE-low elongations; HE-High elongation). Reproduced with permission from [2].

The volume fraction of each type of fibers has an impact in how the failure will occur. For composites with high strain fiber volume, these fibers will dominate the stress distribution. The resulting stress/strain curve will present a higher secondary peak. If the fiber fraction is reversed, the composite's strength will be limited by the low strain fiber [2]. Another factor that can affect the mechanical properties of hybrid composites is the weight ratio, also known as volume or weight fraction of the reinforcing fiber constituents [1]. By varying the weight ratio/volume of the fibers it is possible to change the composites overall mechanical properties. Therefore, depending on the application

requirements the hybridisation method provides flexibility in fiber selection for achieving the desired materials properties.

For the flexural properties the stacking sequence of the hybrid composite is highly relevant [91, 92]. The tensile and compressive stresses are maximum in the bottom and top faces of a specimen under 3-point bending flexural load, respectively and they linearly decrease towards the neutral line (middle of the specimen). As such the fibers with higher mechanical properties should be placed in the outward most lamina in a composite. This is especially interesting when using synthetic/natural hybrid composites, since most synthetic fibers also present a hydrophobic characteristic, and thus will reduce water absorption [78, 93]. The impact properties of natural hybrid composites was found to vary greatly in the literature. The impact resistance of hybrid composites is strongly linked to the fiber mechanical properties [94, 95], layer stacking sequence [2] and the interfacial adhesion between the fiber and the matrix [23]. Some authors found that the stacking sequence has an insignificant effect on the impact strength, while the fiber orientation in the hybrid composite has a noticeable effect on the impact strength [91].

Table 4 summarises some recent studies on the effect of hybridisation on the mechanical properties of hybrid composites.

Table 4: Effect of hybridisation on the mechanical properties of hybrid composites.

Composite (type of fiber and matrix)	**Fabrication technique and test method**	**Mechanical properties**	**Ref.**
Sisal/jute /glass (Polyester - methyl ethyl ketone)	Hand-lay-up with Compression moulding in a hydraulic press. Tensile, flexural, impact and interfacial shear strength tests	The 20% sisal, 20% jute and 60% of glass-fiber presented the best performance in tensile, flexural and impact properties when compared to the other hybrid composites.	[88]

Banana/ glass /sisal (Epoxy resin - LY556)	Compression moulding. Tensile, flexural and impact tests	The hybrid banana/sisal/glass fiber composite presented highest tensile strength (Glass fiber on the outer layers and in the middle). For flexural strength, the best configuration was found for the banana/sisal composite as a sandwich between layers of glass fiber.	[96]
Sisal/cotton (Isophthalic polyester)	Hand-lay-up. Tensile, flexural and impact tests	The optimal composite presented a percentage of 40% of cotton/sisal reinforcement. Sisal aligned in the load application direction presented better results when compared with the cotton ones.	[69]
Flax/glass (Phenolic)	Compression moulding. Tensile, mode I fracture toughness and short beam tests	For the mode I fracture toughness and the interlaminar shear strength the hybrid composites with higher flax content presented better results when compared with pure glass fiber composites	[58]
Banana/ Kenaf (Unsaturated polyester)	Hand-lay-up. Tensile, flexural and impact tests	The hybridisation process increased the mechanical properties of the single banana and kenaf composites. The superficial treatments improved the tensile, flexural and impact strengths around 10% of the hybrid composites when compared with the untreated condition.	[59].
Twisted kenaf/neem/ glass fibers (Epoxy resin - LY556)	Vacuum assisted compression moulding. Tensile, flexural, impact and double shear tests.	The glass fiber + twisted neem (vertical) + twisted kenaf (inclined) + twisted neem (vertical) + glass fiber hybrid composites presented the best mechanical properties with a tensile ultimate strength around 70 MPa and absorbed impact energy	[97]

		equivalent to 12J.	
Curauá/glass (Polyester)	Compression moulding using a hydraulic press. Barcol hardness and impact tests.	The impact properties and composite hardness increased in the composites with higher percentages of glass fibers, due to better interfacial adhesion of these fibers with polyester resins.	[72]
Banana/jute (Epoxy)	Hand-lay-up. Tensile, flexural, impact and interfacial shear strength tests.	The hybridisation improved the mechanical properties of the studied composites, especially the impact properties. The maximum value of interlaminar shear strength was found for the banana/jute composite with 30 wt% of fiber loading.	[98]
Sisal/bamboo (Polyester resin – methyl ethyl ketone)	Hand-lay-up. Tensile, flexural and impact tests.	The mechanical properties of the hybrid composites increased in the composites with higher weight percentage of bamboo. The alkalinisation process also improved the tensile strength by 30% and the impact energy by 40%.	[71]
Echinoidea spike particles and kenaf (Neem oil blended epoxy)	Hand-lay-up. Tensile, flexural, impact test.	The Neem oil had little impact in the epoxy resin with a slight decline in mechanical properties. The addition of the kenaf fibers had a positive impact in mechanical properties. The addition of the hybrid kenaf- particles increased the mechanical properties of the composite.	[99]
Flax/TiO_2 (Epoxy)	Hand lay-up with compression moulding. Tensile, flexural, impact and short beam tests were carried out.	Improvements in tensile, flexural, impact and ILSS of hybrid composites were approx. 11%, 20%, 10% and 19% when compared to the unmodified samples.	[100]

Jute/nano-clay (Epoxy)	Hand lay-up followed by compression moulding. Tensile, flexural, impact testing.	The best material properties overall were found for the 5% NaOH-treated jute fiber with 5 wt% nano-clay content.	[101]
Pineapple/banana/sisal/TiO_2 (Epoxy)	Compression moulding. Tensile, flexural, impact testing as well as vibrational analysis.	The highest mechanical property increase was observed for the filler content of 3% for all cases (improvements of approx. 20%).	[102]
Jute/Carbon (Epoxy)	Vacuum assisted resin infusion fabrication method. Tensile, flexural, impact testing as well as water absorption.	The highest mechanical properties were reported for the unidirectional fiber orientation compared to the angle and cross-ply hybrid composites. The flexural property varied significantly with stacking sequence. The highest value was reported for the C2J6C2 case. The impact property was not affected by the stacking sequence.	[91]
Jute/ramie, jute/sisal and jute/curauá (Epoxy)	Tensile, flexural and impact testing	The hybridisation had a positive effect in tensile, flexural and impact strength for all studied composites when compared to the non-hybrid. The jute/sisal and jute/curauá presented the best overall mechanical properties (an increase of 68% and 77%, for tensile strength over the simple jute composite, respectively).	[23]
flax/glass and jute/glass fibers (Epoxy)	Vacuum infusion method. Tensile, flexural, Dynamic	Flexural strength increased when glass fiber was placed to the outer layers (“glass/flax/glass” or “glass/jute/glass”) with the increase in jute and flax fiber	[92]

	mechanical analyses	percentage	
carbon, flax, and flax/carbon hybrid (Epoxy)	Tensile, and flexural properties	Flax/carbon fiber hybrid composites exhibited improvement in elongation at break compared to pure carbon composites. Addition of flax fibers decreased the flexural strength of carbon composites due to their inherently lower strength.	[103]

3 Thermal properties of hybrid fiber-reinforced composites

The main techniques used for thermal analysis of hybrid epoxy/synthetic/natural fiber composites are as follows: Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA). The main thermal properties of the composites provided by these techniques are: the crystallisation temperature (T_c), melting temperature (T_m), glass transition temperature (T_g), thermal expansion coefficient (CTE), viscoelastic behaviour and thermal stability (see Fig. 4). It was shown in the literature that several factors can affect the thermal properties of the composite materials, such as: fiber and matrix type, manufacture process, and type of loading [104-106]. In addition, the fiber orientation and volume and chemical treatment of the fibers will also impact the thermal properties of the composites [15].

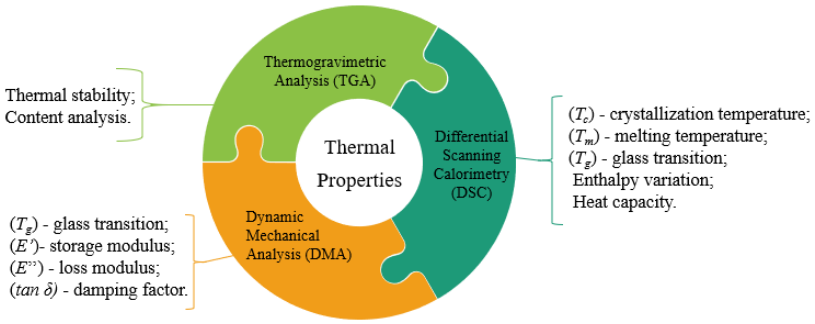


Figure 4: Schematic of the principal methods used to determine the thermal properties of composites with the main thermal properties of the bio composites provided by these techniques.

TGA analysis consists on measuring the weight of a material sample, commonly either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, or other gases [107, 108]. Typical thermogravimetric parameters consist of moisture, volatile substances, loss on ignition or ash. Different temperatures and measurement times are applied in accordance with the matrix type of the composite sample [107-110]. Natural fiber based composites have the thermal stability measured from the decomposition of their constituents (hemicellulose, cellulose, lignin and others) [24, 53, 66, 111-114]. The incorporation of synthetic fibers in natural composites will increase their thermal stability and shift the degradation point of the composites to the right, decreasing its thermal degradation [115]. The thermogravimetric behaviour of hybrid synthetic/natural composites depends on composite constituents (fibers and matrix). For example, similar natural fibers such as jute, sisal, wood and cotton have similar TG/DTG curves and thermal decomposition patterns. The derivative thermogravimetric test (DTG) shows the maximum rate of peak thermal decomposition, and fiber constituents are indicated by peaks in each degradation range. Lignocellulose fibers (i.e., jute, flax, wood, sisal, ramie, curauá and others) present three stages of degradation, the first stage is related to water loss by natural fiber (60°C-100°C). The second stage is related to the loss of the main constituents of the fibers: hemicellulose, cellulose, and lignin (200°C-500°C). Finally, the last stage of degradation is the formation of active coal as a form of residue [53, 111-114]

The DSC determines the material transitions as a function of temperature and time. The endothermic (heat absorption) and exothermic (heat released) peaks and magnitudes indicate the thermal phase transformation of the composites [116, 117]. Thermal data extracted from this analysis are: the glass-transition temperature (T_g), crystallisation temperature (T_c), fusion temperature (T_m), enthalpy variation and heat capacity [118]. The glass transition temperature (T_g) is the temperature band in which a thermoset polymer changes from rigid to a more flexible or 'rubbery' state. There are several factors that can affect the data collected by the DSC analysis, such as: sample size and shape, heat ramp and type of atmosphere. Several authors used the DSC technique to investigate the effect of hybridisation on the glass transition and the peaks (endothermic and exothermic) of hybrid epoxy/synthetic/natural composites [66, 87, 119-121].

The following data can be extracted from DMA: storage modulus (E'), loss modulus (E''), damping factor ($tan\ \delta$=E″/E′) and glass transition temperature (T_g) [118].

The storage modulus (*E*') is associated with the energy storage of the elastic characteristics of the material [24, 105, 122]. It decreases with increase in temperature and is associated with "stiffness" of the composites sample [105, 122]. The loss modulus (*E*'') is associated with the energy dissipation promoted by the viscous part of the composite sample. This dissipation is related to the internal molecular friction of the molecular chains due to the following factors: morphological transformation and relaxation, morphology, and system heterogeneity [105, 108]. The damping factor is defined by dividing the storage and loss modulus (*tan δ= E''/E')* and is associated with the internal mobility of the polymeric molecular chains, showing the influence of the fiber/matrix interactions [24, 105, 123]. A high *tan δ* value shows that the system is dissipating more energy than it is storing due to fiber/matrix interaction quality, while a low *tan δ* value shows that the polymeric chain has lower mobility indicating a good fiber/matrix interfacial interaction. To determine T_g using DMA, measurements of the complex modulus are typically made as temperature is increased at a constant heating rate. The thermal properties of the composites obtained from DMA depends on the physical or structural arrangement of phases such as interface, morphology and the nature of composite constituents. It was shown in the literature that the presence of additive fillers, fiber content, fiber orientation, the chemical treatment of the fibers and the mode of testing governed the dynamic mechanical properties of a composite material [105, 124]. Several researchers used the DMA tests to study the influence of hybridisation on the thermal properties of the hybrid composites [24, 92, 119, 125-129].

Table 5 summarises several recent studies on the effect of hybridisation on the thermal properties of hybrid composites.

Table 5: Effect of hybridisation on the thermal properties of hybrid composites obtained from TGA, DSC and DMA analysis.

Composite	**Method and Parameters**	**Effect hybridisation on the thermal properties**	**Ref.**
Sugar palm /Glass (Polyester)	**TGA –** The temperature was ramped from 30°C to 600°C with a heating rate of 20°C/min, under a Nitrogen Atmosphere with 50 mL/min. The equipment used the GA Q500 from TA Instruments.	**TGA** –the increase in fiberglass decreased the residue percentage**.** **DMA**- the hybridisation and the chemical treatment provided a higher storage	[130]

	DMA -Three-point Bending Test with frequency of 1 Hz. Equipment (DMA Q800 of TA Instruments). The temperature was ramped from 30 to 150 °C with a heating rate of 5°C/min. Rectangular specimens having size 60 mm x 10 mm x 3 mm were used.	and loss modulus, but smaller *tan δ*.	
Cotton/Glass (Polyester)	**DMA -** Three-point Bending Test with Frequency of 1 Hz an Oscillation amplitude of 15 μm. Equipment used DMA 2980 Dynamic Mechanical Analyser. The temperature was ramped from room to 180 °C with a heating rate of 3°C/min. Rectangular specimens having size 60 mm x 10 mm x 3mm were used.	**DMA** –T_g of hybrid composites increased compared to synthetic and natural fiber pure composite.	[131]
Bamboo/Kenaf (Epoxy)	**TMA**–Expansion or Compression test with minimal force of 0.02 N. The temperature was ramped -30 °C to 100 °C with a heating rate of 5°C/min. **DMA-** Three-point bending Test with frequency of 1 Hz an oscillation amplitude of 10 μm and constant current force of 3N. Rectangular specimens having size 45 mm × 10 mm × 3 mm were used. The temperature was ramped from 25°C to 180 °C with a heating rate of 5°C/min.	**TMA/DMA** The expansion coefficient of the hybrid composites (50% bamboo/50% kenaf) was lower when compared to the other cases. T_g and storage modulus results showed an increase in thermal properties.	[126]

Jute/oil palm (Epoxy)	**TGA-** The temperature was ramped from 30°C to 900°C with a heating rate of 20°C/min, under a Nitrogen Atmosphere. Perkin Elmer thermal gravimetric analyser.	**TGA** – The increase of percentage of jute fiber improved the thermal stability of the composite.	[113]
Jute/Coir (Epoxy Novolac)	**TGA** – The temperature was ramped from 30°C to 700°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere with 30mL/min. Equipment DTG- 60 (Schimadzu). **DSC-** The temperature was ramped from 20°C to 400°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere with 50mL/min. Equipment DSC Q10 (TA Instruments). **DMA-** Three-point bending Test with frequency of 10 Hz. Rectangular specimens having size 60 mm × 10 mm × 3 mm were used. The temperature was ramped from 30°C to 200 °C with a heating rate of 5°C/min. Equipment DMA Q800, TA.	**TGA-** The increase in coir fiber percentage increased the onset of degradation temperature of the hybrid composite. **DSC-** Hybrid composites presented higher enthalpy values than the pure resin. **DMA-** The hybrid composite (50% Jute fiber/50% coir fiber) presented the largest storage modulus and the lowest *tan* δ when compared to the other hybrid composites.	[132]
Cocos nucifera sheath (CNS) /Kevlar (Epoxy)	**TGA** – The temperature was ramped from 30°C to 900°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere with 50 mL/min. Equipment Mettler Toledo DSC. **DSC-** The temperature was	**TGA -** The 75%G/25%CNS hybrid presented the highest thermal stability when compared to the other hybrid composites. **DSC-** The DSC results were similar to the TGA. The	[87]

	ramped from 30°C to 900°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere. Equipment Mettler Toledo DSC. **DMA-** Three-point bending test with frequency of 1 Hz. Rectangular specimens having size 60 mm × 12.5 mm × 3 mm. The temperature was ramped from room temperature to 200 °C with a heating rate of 10°C/min. Equipment DMA Q800, TA.	75%G/25%CNS hybrid composites presented lower endothermal peaks when compared to the other studied hybrid composites. **DMA-** Hybridisation with 25% CNS/75% K presented superior storage modulus value when compared to pure Kevlar composite.	
Sugar Palm/Glass (Epoxy)	**DMA- Dual Cantilever Test** with Oscillatory frequency of 1 Hz. Equipment used DMA Instrument Q800 V20.24 Build 43 Module DMA Multi-Frequency. The temperature was ramped from 25°C to 150 °C with a heating rate of 5°C/min.	**DMA-** The hybridisation and Benzoyl treatment increased the storage and loss modulus of the composites.	[133]
Banana/PALF/Glass (Epoxy)	**TGA-** The temperature was ramped from 30°C to 600°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere at a flow rate of 20 mL/min. Samples of around 4.9-8.9 mg. The equipment used was TA TGA Q500. **DMA -** Three-point Bending **Test** with Frequency of 1 Hz. The temperature was ramped from 0-160 °C with a heating rate of 3°C/min.	**TGA-** The group with fiber percentage of 40% presented the best thermal stability within the studied composites. **DMA -** The 30wt % banana-glass fiber hybrid composite presented the highest T_g when compared to the other cases studied.	[134]

Sisal/Glass (Epoxy)	**TGA-** The temperature was ramped from 30°C to 600°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere. Samples of approx. 20 mg. The equipment used was NETZSCH TG 209F3 Tarsus. **DSC** - The temperature was ramped from 30°C to 500°C with a heating rate of 20°C/min, under a Nitrogen Atmosphere at a flow rate of 50 mL/min. Samples of around 20 mg. The equipment used was NETZSCH DSC 00F3 Maia.	**TGA-** The hybridisation increased the thermal stability when compared to the pure sisal. **DSC** -The natural/synthetic hybrid composite presented the lowest endothermic peak when compared to the other hybrid composites studied.	[66]
Kenaf/Pine apple leaf (Phenolic)	**TGA- -** The temperature was ramped from 30°C to 700°C with a heating rate of 20°C/min, under a Nitrogen Atmosphere. The equipment used was TGA Q 500 TA Instrument. **TMA-** The temperature was ramped from 30°C to 200°C with a heating rate of 5°C/min, under a Nitrogen Atmosphere. Square specimens having size 5 mm × 5 mm × 3 mm^3 The equipment used was TA Instrument Q400. **DMA-** Three-point Bending Test. The temperature was ramped from 30-150 °C with a heating rate of 5°C/min. The equipment used was TA DMA Q800.	**TGA-** Hybridisation decreased the onset of degradation temperature of the composites. **TMA-** the composite with 30% Pineapple and 70% Kenaf showed high thermal resistance. **DMA-** The composite with 30% Pineapple and 70% Kenaf showed an increase in storage modulus.	[108]

Jute/Sisal (Epoxy)	**TGA** – The temperature was ramped from 30°C to 800°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere with 20 mL/min. Samples of around 15-25 mg. Equipment Perkin Elmer TGA 4000. **DSC-** The temperature was ramped from 30°C to 400°C with a heating rate of 10°C/min, under a Nitrogen Atmosphere at a flow rate of 20 mL/min. The equipment used was Perkin Elmer model DSC 4000. **DMA-** Three-point bending Test with frequency of 1 Hz. Rectangular specimens having size 50 mm × 13 mm × 3 mm. The temperature was ramped from 30 to 200 °C. Equipment DMA 6100, Seiko.	**TGA-** The thermal stability augmented with the hybridisation and the increase of the jute fiber. **DSC-** All hybrid composites presented benefit in properties: T_g, T_c and T_d. **DMA-** The increment of jute fiber increased the storage modulus, loss modulus and T_g, of hybrid composites.	[119]
Jute/Carbon (Epoxy)	**TGA** – The temperature was ramped from 20°C to 800°C with a heating rate of 20°C/min, under a Nitrogen Atmosphere. Samples of around 5-6 mg. Equipment SDT Q600 Model.	**TGA-** The effect of hybridisation increased the onset and end of the degradation temperatures of the composite.	[135]

To summarise, using natural fibers with low lignin content leads to better thermal performance of composites. The thermal stability of fibers can be enhanced by removing certain proportion of hemicelluloses and lignin constituents by different chemical treatments. The incorporation of synthetic fibers in natural fiber reinforced composites increases their thermal stability. The degradation of natural fibers is an important issue in

the development of hybrid natural fiber reinforced composites in both manufacturing (curing, extrusion or injection moulding) and for the use of these materials in service.

5 Water absorption behaviour of hybrid fiber-reinforced composites

The affinity to absorb moisture by natural fibers and its composites, is widely known and reported in the available literature [12, 13, 25, 66, 136-138]. The absorption of moisture into a fiber-reinforced polymer composite leads to poor fiber-matrix interfacial adhesion, which will lead to an increasingly poor load-transferring efficiency from the matrix to the reinforcement fiber. In particular, for natural fibers, there is also the aggravating factor that water uptake within the fiber leads to the degradation of its physical, thermal and mechanical properties due to the leeching of water-soluble components [139].

Moisture diffusion in polymeric composites is governed by three different mechanisms [140]. The first involves diffusion of water molecules inside the micro gaps between polymer chains. The second involves capillary transport into the gaps and flaws at the interfaces between fiber and the matrix. This is a result of poor wetting and impregnation during the initial manufacturing stage. The third involves transport from microcracks in the matrix arising from the swelling of fibers (particularly in the case of natural fiber composites) [35] (see Fig. 5). According to these mechanisms, there are three types of diffusion behaviour of polymeric composites: Fickian diffusion model, anomalous or non-Fickian, and an intermediate case between Fickian and non-Fickian [140].

It was shown in the literature that moisture diffusion in hybrid composites depends on a variety of parameters: fiber volume fraction, fiber orientation and stacking sequence, fiber nature, voids, temperature, presence of fillers, fiber surface treatments and immersion time. For instance, higher immersion times, natural fiber volume fraction and voids increase the composite moisture uptake [13, 141, 142]. As well, at higher temperature of immersion, moisture uptake behaviour is accelerated and the moisture saturation time is considerably shortened [1]. On the other hand, the fiber stacking sequence (e.g. placing the hydrophobic fiber fabrics on the outer layers), as well as the fiber orientation (e.g. 0^o orientation of the natural fiber) was shown to lower the water uptake of the composites [143, 144].

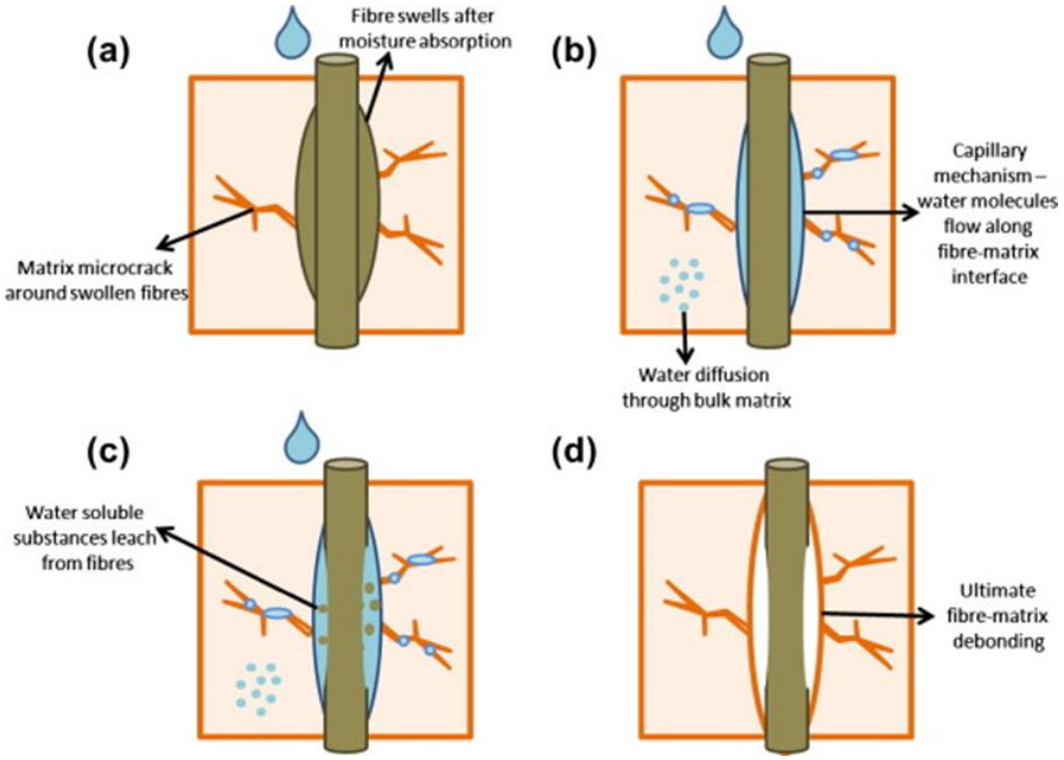


Figure 5: Effect of water on fiber–matrix interface: (a) Formation of micro-cracks due to fiber swelling; (b) water molecules diffuse in the bulk matrix and flow along the fiber-matrix interface (c) water soluble substance leaching; and (d) debonding of fiber-matrix interface. Reproduced with permission from [35].

One solution to reduce the water uptake in natural fiber composites is the fibers' surface treatments [31, 34-42, 145]. The main surface modification methods used for natural fibers (i.e., physical and chemical) were presented in section 2.2 of this review. Another approach to decrease the water absorption in polymeric composites is to incorporate synthetic fillers which can fill the voids and better distribute the internal stresses in the composites [100, 146-148]. For example, a number of researchers have investigated the effects of the incorporation of TiO_2 nanofiller and glass powder in the polymer matrix with the objective of delaying the effect of water absorption on composites [100, 149].

Several studies have been carried out in the literature concerning the moisture absorption behaviour of hybrid composites, both natural-natural and natural-synthetic fibers reinforced composites [12-14, 54, 71, 91, 95, 143, 144, 150-159]. Table 6 summarises some recent studies on the effect of hybridisation on the water absorption characteristics of hybrid composites. In general, the natural-synthetic hybridisation technique coupled with choosing an optimum fiber content, stacking sequence and fiber

orientation, can drastically reduce the moisture content at saturation and decrease the diffusivity coefficient. Therefore, the moisture degradation and composite material property impact is reduced. The water uptake behaviour of natural - natural hybrid composites vary significantly as a function of reinforcement fiber, as different natural fibers present different contents of hydrophilic groups, porosity, crystallinity among other parameters, their water uptake behaviour changes. As such, the natural - natural hybridisation methods provide a viable technique so that a balance may be found in terms of cost/performance regarding its uses in moisture-rich environments.

Table 6: Effect of hybridisation on the water absorption behaviour of hybrid composites.

Composite	**Details of the process**	**Effect of hybridisation on the water absorption**	**Ref.**
Hemp/jute Hemp/flax Hemp/jute /flax (Epoxy matrix)	Bi-directional woven mats. Hand lay-up compression technique.	Hemp/jute/epoxy, hemp/jute/flax/epoxy and hemp/flax/epoxy absorbed 4.5%, 3% and 2.8% water respectively	[12]
Kenaf/Jute Kenaf/Hemp Kenaf Jute Hemp (Epoxy)	Vacuum infusion technique. Interwoven hybrid fabrics.	Both kenaf/jute and kenaf/hemp hybrids absorbed less water than the single fiber composites. A reduction of moisture uptake of up to 64% was reported.	[13]
Kenaf/sisal Kenaf Sisal (Epoxy)	Plain woven kenaf and sisal fabrics. Hand lay-up compression moulding fabrication. Stacking sequence was varied.	Small variation was observed in moisture uptake as a function of hybridisation. The sisal/kenaf/sisal case presented the highest water absorption (~3.5%)	[14]
Kenaf/jute (Epoxy)	Jute and kenaf fiber mats Hand lay-up technique. Two stacking sequences	The water uptake behaviour varied significantly as a function of stacking sequence. The kenaf/jute/kenaf (KJK) case	[156]

	were fabricated.	presented the lowest water absorption (~3.8%).	
Date Palm Leaf (DPL)/glass (Epoxy)	Hand lay-up fabrication. Alkaline treated short fibers. Glass fiber fraction was maintained while the DPL percentage was varied.	The rate of water absorption of the composites increased by adding more DPL fiber. Maximum water uptake was found for the 30 wt % of DPL.	[160]
Jute/carbon (Epoxy)	Plain woven jute fibers was used along with unidirectional carbon fabric. Vacuum assisted resin infusion fabrication method was applied. The stacking sequence and fiber orientation was varied.	Similar pattern of water absorption behaviour was observed for all cases or fiber orientation. The stacking sequence proved to be the most significant variable, with the synthetic layers on the outside of the natural core. The S4 ($C_2J_6C_2$) case absorbed the least amount of moisture.	[91]
Full flax fiber Full glass fiber Flax/glass fiber (Epoxy)	Vacuum assisted resin infusion method.	Water absorption for the flax–fiber composites was found to be 12 times higher than for the glass–fiber composites.	[151]
Flax/glass (Vinyl Ester)	Bi-directional flax and glass fiber fabrics were used. Hand lay-up and vacuum infusion fabrication.	Significant decrease in water absorption was observed as a function of hybridisation. The outer synthetic layers play a significant role in diminishing the moisture saturation content of hybrid composites.	[152]
Jute/glass/ Carbon	Plain weave bi-directional jute fabrics	Significantly lower absorption of moisture was reported for the	[143]

(Epoxy)	were used along with chopped glass mats and twill weave carbon fabrics. The hand lay-up process was used and the stacking sequence was varied.	inter-ply hybrid composites compared to the neat jute.	
4 harness satin woven carbon fibers and flax fibers (Epoxy matrix)	Compression molding	By covering the inner core of flax fiber/epoxy with an external layer of carbon fiber/epoxy the water absorption was kept to 4.8–8.3%.	[144]
Flax fiber laminates Glass fiber Flax–glass composites (Epoxy)	Compression moulding Different stacking sequences	The hybridisation of flax and glass fibers improved the moisture resistance of the flax fiber laminates by reducing the water absorption and the diffusion coefficient as well as the thickness swelling at room temperature.	[161]
Jute/glass fiber reinforced (Polyester)	Pultrusion. Different stacking sequences: JJ, GJJG, CGJJGC and SGJJGS	The pure jute group displayed a moisture content at saturation of 47.65%, while the glass reinforced hybrid case (GJJG) presented a content of 13.31%.	[154]

6 Challenges, market trends and perspectives

The global awareness of environmental issues is at an all-time high and NFRCs are nearing the point to become competitive with classical synthetic fiber-reinforced

composites. This is leading advancements in nearly every industry as they seek the integration of biodegradable and more cost-efficient materials. However, there are still many challenges and a wide scope for improvement to extend their applications. The main challenges identified as potentially detrimental to market growth are supply logistics, moisture sensitivity and weak interfacial bond of NFRCs. In addition, the natural origin of these fibers, which result in variations in their properties produce large variations in properties, long-term stability and durability of NFRCs. Some of these challenges were addressed by recent development in fibers treatment and modification, and process or product innovation (hybridization). Moreover, intense research efforts are in progress to address these limitations.

In this context, there are many exciting market trends going forward in many different industries. For example, tri-dimensional hybrid natural fiber reinforcement preforms have been used recently by sports cars manufacturers such as Porsche and even McLaren in Formula 1 [162]. This application involved the use of flax fibers in a specific 3D architecture to increase stiffness and toughness, lower weight and reduce debris in a crash. It has been successful used in F1 car seats, and the front crash absorbing structure (crash box). Similarly, many other car manufacturers such as Tesla and BMW have been investigating the use of this technique in structural components of the vehicle with promising results. These advances were made commercially available by companies such as Bcomp® and Ycom® [162, 163]. Nowadays, Audi, Volkswagen, Toyota, Daimler-Benz, Volvo, Ford use NFRCs to produce components such as: seat back, interior door paneling, noise insulation panels, instrumental panel support, engine insulation, and internal engine cover. The continually growing demands for lightweight and fuel-efficient vehicles will further push the growth of NFRCs in the automotive market.

In the defence industry, natural fibers are used as an alternative in replacing Kevlar fibers. For instance, they were used in the Multilayered Armour System (MAS) due to their high impact energy absorption, low-weight, and efficiency in capturing splinters from the ceramic plate typically present in MAS [164]. The curauá based natural fibers reinforced composites, for example, are up-and-coming solutions for these applications as they are being intensely studied recently to be applied in military equipment mainly due to their excellent relationship between weight and strength [165, 166].

Another booming area involving natural fibers is the application of natural reinforcements in additive manufactured parts. The advantages using additive manufacture to produce NFRCs and hybrids are the design flexibility to fabricate complex

geometry parts or functionally graded composites with local-specific performance and functionality. The use of natural fibers can bring many advantages to single or dispensable production such as production of tailored, non-toxic, renewable, and recyclable parts. The advantages of natural fibers compared to synthetic fibers are especially relevant when considering their lower toll on both printer durability and production cost. However, using natural fibers and additive manufacture (AM) still presents significant challenges such as: composite filament preparation, porosity/void formation and fiber orientation and large amount of moisture. These issues can be solved by modifying the AM process parameters, hardware and feed stock quality. As the demand for more sustainable material options grows in the general global marketplace, natural fibers coupled with novel processing techniques (e.g. additive manufacturing) can lead to the advancement of many industries towards a smart eco-conscious future.

7 Conclusions

The main challenges that need to be addressed in order to increase the performance and consequently the use of NFRCs composites in industry are mainly the poor adhesion between natural fibers and matrix, fiber quality inconsistency, thermal stability and moisture absorption of natural fibers. Intense research efforts are continuously made and some of these challenges were addressed by recent advancements in fibers treatment and modification, exploration of new natural fibers and hybridization. The fiber modification techniques provide improved fibre-matrix interfacial adhesion, improved fibre roughness and wettability and depends on the particular fiber/matrix used and the composite application, while the hybridization methods provide flexibility in fibers selection for the materials properties according to the end-use application requirements. Exploration of new natural fibers, especially, natural fibers with higher strength and modulus, such as curauá or nano-scaled cellulosic fibers, offer a promising potential for expanding the application of these composites. In addition, can diversify fiber sources and reduce material cost. Although, hybridization of natural fiber composites with other natural fibers may not provide comparable mechanical or thermal properties improvements to those hybridized with synthetic fibers, this approach may have noteworthy value in terms of sustainability. The hybridisation of natural fibers composites with other fibers characterised by low moisture absorption tendency is an effective method to improve the water absorption resistance of natural hybrid composites. Fiber´s treatment and addition of fillers are also solutions to reduce moisture absorption of these composites. The

application of natural and hybrid fibers composites, particularly in automotive, civil industry and sports is quite promising and will significantly increase in the future due to the significant pressure on reducing costs and increasing demand for material recyclability.

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Chapter 3

Analysis of Mechanical and Thermal Properties of Epoxy Multiwalled Carbon Nanocomposites

ABSTRACT

The main objective of this study was to investigate the efficiency of the sonication process and of multi-walled carbon nanotubes (MWCNTs) content on the mechanical and thermal properties of an epoxy matrix. Three different sonication powers (25, 50 and 75 W) were used to disperse the MWCNTs (0.2%, 0.4% and 0.6 %) in the epoxy matrix. Tensile tests were performed to determine the mechanical properties of the nanocomposites, while the thermal properties were determined by the thermogravimetric analysis (TGA) and the Differential Exploratory Calorimetry (DSC). Finally, a SEM analysis was used to investigate the morphology of the tensile fractured surface and the dispersion of the nanotubes in the polymeric matrix, since the quality of dispersion influences the mechanical and thermal properties of nanocomposites. It was found that the addition of carbon nanotubes to the epoxy matrix and the parameters of the sonication process affect the mechanical and thermal properties of nanocomposites. An increase of 14% in tensile strength and 15% of Young's modulus, when compared to the pure epoxy matrix was found for 75W sonication power output and 0.6% MWCNTs weight percentage. The thermal analysis indicated that the presence of MWCNTs increased the T_{onset} of the nanocomposites when compared to pure epoxy resin. Finally, increasing the sonication power output leads to higher T_g of the nanocomposites studied here. For the specific materials studied here, the best results were obtained for the 0.6 wt. % MWCNTs and 75 W sonication power output case.

INTRODUCTION

Carbon nanotubes (CNTs) can act as an excellent filler for polymer matrix reinforcing its mechanical, thermal and electrical properties [1-4]. Several researchers have studied the incorporation of nanoparticles, nanofibers and CNTs into polymeric matrices for the manufacture of nanocomposites [5, 6].

The single wall nanotubes (SWNTs) and multiwall nanotubes (MWCNTs) have attracted great interest from the academic community in searching methods to increase the performance of polymeric materials. They are used as reinforcement elements due to its carbon structure and the fact that exhibit good thermal and mechanical (high strength and good flexibility) properties and high electrical conductivity of approximately 10^6 S/m [3, 7, 8]. In principle, SWNTs have superior properties than MWCNTs, but multi-layer nanotubes are widely used due to their better dispersion within the matrix, which results in lower manufacturing costs [2, 7, 8]. It is well known that the properties of nanocomposites depend on the dispersion of the nanoparticles and the interaction between nanoparticles and the polymer matrix. Homogeneous dispersion and good interfacial adhesion can transfer mechanical loads effectively to carbon nanotubes and improve the properties of the nanocomposites. Thus, the efficiency of the nanocomposites is related to the non-agglomeration of CNTs, as high concentration rate of nanotubes (volume >1-2%) causes reduction of the mechanical properties [9-11]. Various methods are used to prevent nanotubes from joining, such as: sonication, high-shear mixing and chemical modification [6, 7, 9]. Lau et al. [1], investigated the sonication dispersion of SWNTs for various types of solvent (acetone, Ethanol and dimethyl formamide-DMF) in an epoxy matrix, and the results indicated that the solvents impacted the healing reaction of the nanocomposites and their thermal properties, while mechanical properties indicated that the solvent with acetone has the best results. Vahedi et al [11], analyzed the mechanical and electrical properties of various percentages (0.05, 0.1, 0.25 and 0.5%) of MWCNTs in an epoxy matrix. It was found that both tensile strength and flexural modulus reach a maximum value at 0.1% and 0.25% mass fraction of MWCNTs. Suave et al. [12], studied the sonication effect on the mechanical and thermal properties of casted epoxy nanocomposites reinforced with carboxylic-functionalized single-walled carbon nanotubes (c-SWNT). The results showed an increase in Young's modulus (up to 30%) with the addition of 0.25 wt% c-SWNT. However, the tensile strength and elongation at break results, suggested that dispersion and/or c-SWNT/matrix adhesion should be

enhanced to achieve more satisfactory mechanical properties. The tensile strength of the nanocomposites was increased after sonication at a high amplitude for a short period of time (20 min). Shokrieh et al. [13], studied different concentrations (0.05, 0.1 and 0.5%) of MWCNTs in a polyester matrix using mechanical agitation and sonication technique to disperse the nanotubes in the polymeric matrix, and the results showed that for 0.05% improved tensile and bending strength were obtained.

Several studies investigated the thermal properties of nanocomposites through the mechanical dynamic tests (DMA), the Differential Exploratory Calorimetry (DSC) and the thermogravimetric analysis (TGA). Her et al. [14], investigated the incorporation of different percentages of MWCNT (0.3, 0.5, 0.8 and 1%) in epoxy matrices. The results showed that the concentration of 1% provided an increase in the Young's modulus and tensile strength. The thermal analysis indicated that increasing the concentration of nanotubes increased the glass transition temperature and the storage modulus of the nanocomposites. Montarezi et al [15], investigated the effects of duration (15, 45 and 135 min) and power (25, 50 and 100 W) for the sonication dispersion process of 0.5% MWCNTs concentration in an epoxy matrix, using mechanical testing and dynamic mechanical analysis (DMTA). They state that depending on the desirable mechanical properties, optimum power and time vary. Alam et al. [16], studied the effect of different concentrations of MWCNTs in a saturated polyester resin on the mechanical and thermal properties of nanocomposites. They showed that the incorporation of nanotubes increased the glassy transition temperature (T_g) and the melting temperature of the material in relation to pure resin, and also improve the thermal stability of the nanocomposites.

The main objective of this study was to investigate the effect of output power of sonication on the mechanical and thermal properties of different mass fraction of multi-walled carbon nanotubes (MWCNTs) in an epoxy matrix. Tensile tests were performed to analyze the mechanical properties, while TGA and DSC analysis were used to evaluate the effect of nanotubes and the output power of sonication process on the thermal properties of the nanocomposites. Finally, scanning electron microscopy (SEM) was used to analyze the fracture surface of the tensile specimens and the dispersion of nanotubes in the polymeric matrix.

MATERIALS AND METHODS

Materials

The nanotubes selected in this research are of the MWCNT type, supplied by Nanostructured & Amorphous Materials, USA. They have an average purity of 95%, an external diameter of 50-100 nm, an internal diameter of 5-10 nm and an average size of 5-10 μm. The mechanical properties of MWCNTs are described in Table 1 (data provided by supplier).

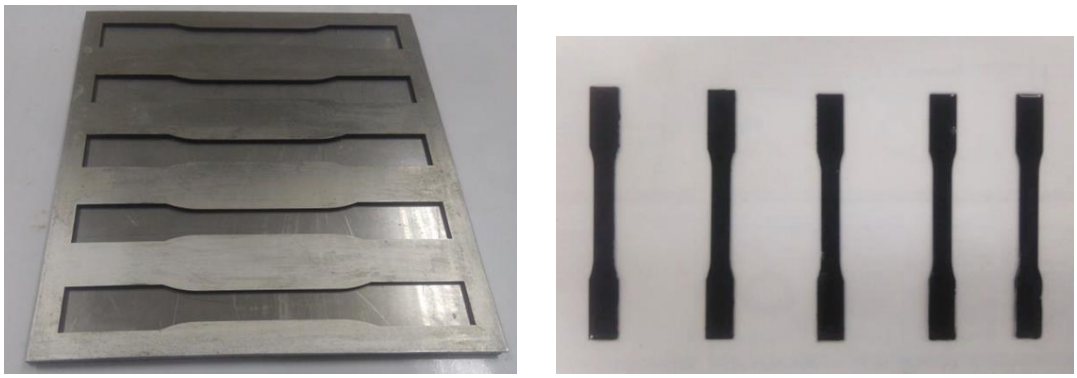
The resin used in the research was a bi-component epoxy HEX 135 slow supplied by Barracuda Advanced Composites (Rio de Janeiro, Brazil), in the 100/33 fraction for epoxy resin/hardener.

Table 1. MWCNTs properties.

Property	**MWCNT**
Density (g/cm³)	1.8
Tensile strength (GPa)	10-60
Young's modulus (GPa)	0.3-1
Thermal stability in air (°C)	700

Specimen Preparation

The manufacture of nanocomposites with different percentages of MWCNTs by weight (0.2%, 0.4% and 0.6%) in the polymeric matrix was as follows: first, the nanotubes were added to the Hex 135 epoxy resin. Then, the process continue using a sonicator (Eco-Sonics, São Paulo, Brazil) with a 4 mm diameter probe. Three different output powers (25, 50 and 75 W) were used for 40 minutes and a frequency of 20 kHz. The time and energy of sonication are important to disperse the particles and break the agglomerations, without damaging the carbon nanotubes [13, 15, 17]. After the dispersion of the MWCNTs in the polymeric matrix the hardener is added and mixed for 5 minutes for homogenization and after that the mixture was poured into a metallic mold with the size of the test specimen, as shown in Fig. 1. All samples were cured inside an oven (Lucadema –São Paulo, Brazil) at 80 °C during 6h as per manufacturer guidelines.



a) b)

Figure 1. Photo of: a) Metallic mould; b) Tensile test specimen.

Test methods

Tensile tests

The universal Instron 5966 (Norwood, Massachusetts, USA) machine with a 10kN load cell, available in the Laboratory of Adhesive and Composite Materials (LADES) of CEFET/RJ, Rio de Janeiro, Brazil, was used for the tensile tests. Five samples for each case were tested according to the ASTM D638 standard with a test speed of 1 mm/min.

Thermogravimetric analysis (TGA)

TGA was performed in a NETZSCH TG 209 F3 Tarsus machine present in the Laboratory of Adhesives and Composites Materials (LADES) of CEFET-RJ, Rio de Janeiro, Brazil. Each sample was tested in the temperature range of 30°C - 600°C at a constant heating rate of 10°C / min under nitrogen atmosphere (20 ml min^{-1}) according to ASTM E1131.

Differential Exploratory Calorimetry (DSC)

DSC was performed in a NETZSCH DSC 200 F3 Maia equipment, also present in LADES, CEFET-RJ (Rio de Janeiro, Brazil). The experiments were conducted with a heating rate of 10 K min^{-1}, in the temperature range of 30–300°C with a nitrogen flux of 50 mL min^{-1} according to ASTM D3418 with sample weights of approx. 8-10 mg.

SEM analysis

The morphological analysis of the fractured tensile samples was done using the microscope JEOL model - JSM-7100F available at "The characterization laboratory and materials" (NANOFAB) of the State University of Rio de Janeiro (UERJ), Rio de Janeiro – Brazil, under an acceleration voltage of 3KV. The samples tested were fixed by a conductive tape for surface visualization.

RESULTS AND DISCUSSION

Tensile tests

Figure 2 shows representative tensile stress-strain curves of the specimens as a function of sonication power output and MWCNT weight percentage. From these curves the tensile properties of the nanocomposites were calculated. The effects of the sonication power output and MWCNT weight percentage on the tensile properties (tensile strength, Young's modulus and tensile strain) of the nanocomposites are summarized in Fig. 3 (a-c) and Table 2.

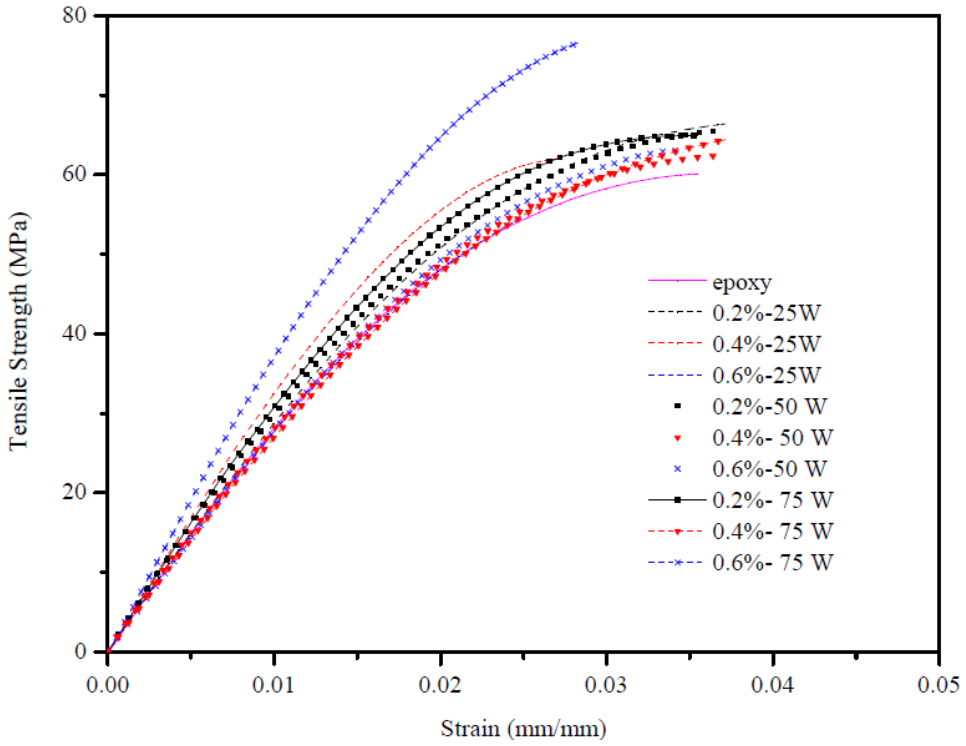


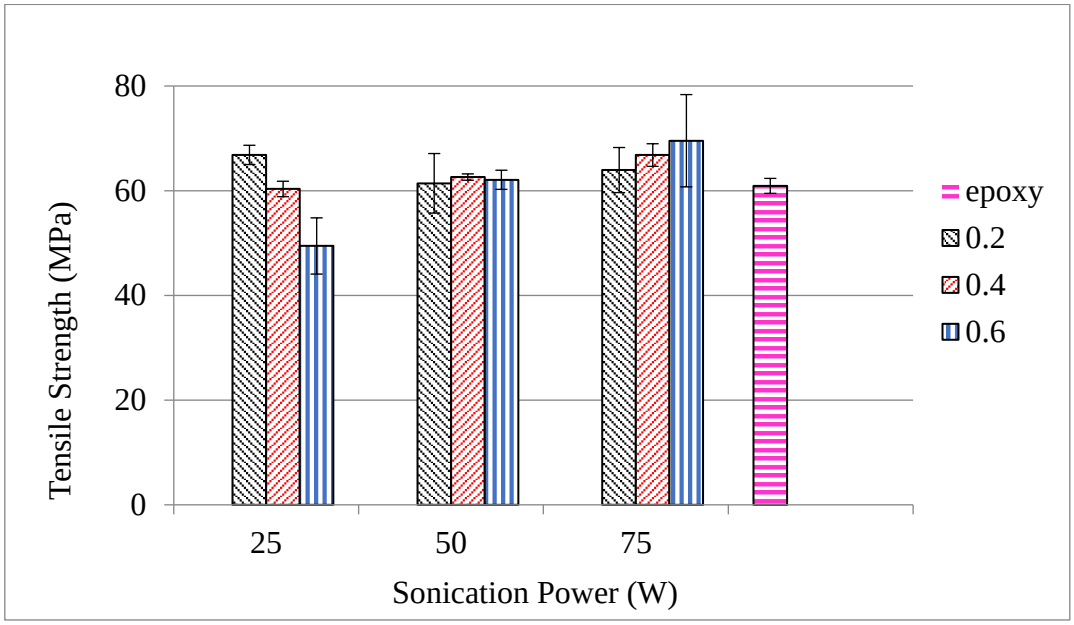
Figure 2. Representative tensile stress-strain curves as a function of MWCNTs weight percentage and sonication power output.

The MWCNT weight percentage affected the mechanical properties of the nanocomposite when compared to the pure resin. For the 25W power output case, the samples modified with 0.2% of MWCNTs presented an increase of approximately 10% in tensile strength when compared to the pure resin. For the samples modified with 0.4% of MWCNTs no significant difference in tensile strength was found. However, the samples modified with 0.6% of MWCNTs presented a decrease of approximately 19%, in tensile strength, when compared to the pure resin (60.92 ± 1.42 vs. 49.44 ± 5.36 MPa). This might be explained by the fact that the 25 W power output of the sonication process was not enough to effectively disperse the nanotubes, creating regions of agglomerations that lead to points of concentrations which may lead to rapid crack propagation that affect the mechanical properties of the nanocomposite [13]. In addition to agglomerates, poor MWCNTs /matrix interfacial adhesion might also be associated with low tensile strength of nanocomposites. For the 50W power output case, the samples modified with 0.2%, 0.4 % and 0.6% MWCNTs weight percentage presented an insignificant variation on the tensile strength compared to pure epoxy resin (a slight increase up to 4% was found). Finally, for the 75W power output case, an increase in the tensile strength of approximately 5% for the 0.2% wt. MWCNTs, 10% for 0.4% wt. MWCNTs and 14% for 0.6% wt. MWCNTs was found, when compared to the pure resin. This may be explained by the fact that the increase in sonication power output affected the MWCNTs' dispersion in the polymeric matrix by decreasing the agglomerations as observed in the SEM analysis (see Fig. 9). Zhou et al. [18], reported that when MWCNTs are well dispersed, the nanotubes tend to change the crack propagation, which can increase the tensile strength of the composites.

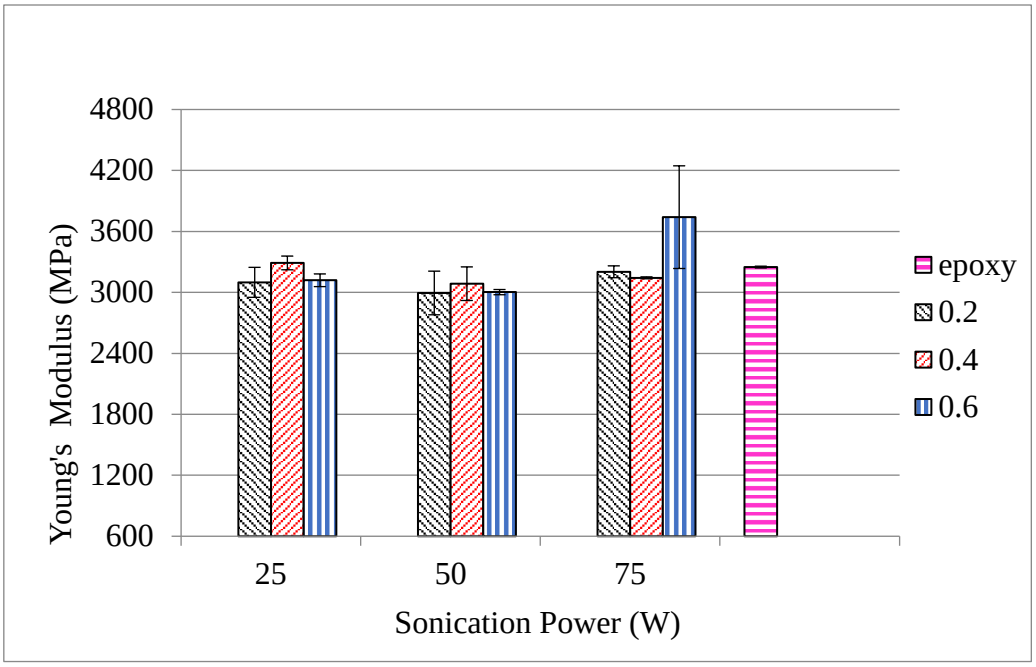
Similar to the tensile strength, the Young's modulus was also affected by the MWCNT weight percentage and sonication power in different ways. The Young's modulus slightly decreased for almost all the cases studied here when compared to the pure resin. The exception was, for the 75W power output case and 0.6 % of MWCNTs where an increase in rigidity of 15% was found when compared to the pure resin. The increase in the sonication power output causes a decrease in the entanglement of the MWCNTs and as a result, a better dispersion of the nanotubes in the epoxy matrix.

The elongation at break of the nanocomposites was also affected by the MWCNT weight percentage. For the 25W power output case, an increase in elongation at break of approximately 8% was observed for the 0.2% MWCNT weight percentage, when compared to the pure resin. On the other hand, the MWCNT weight percentage of 0.4%

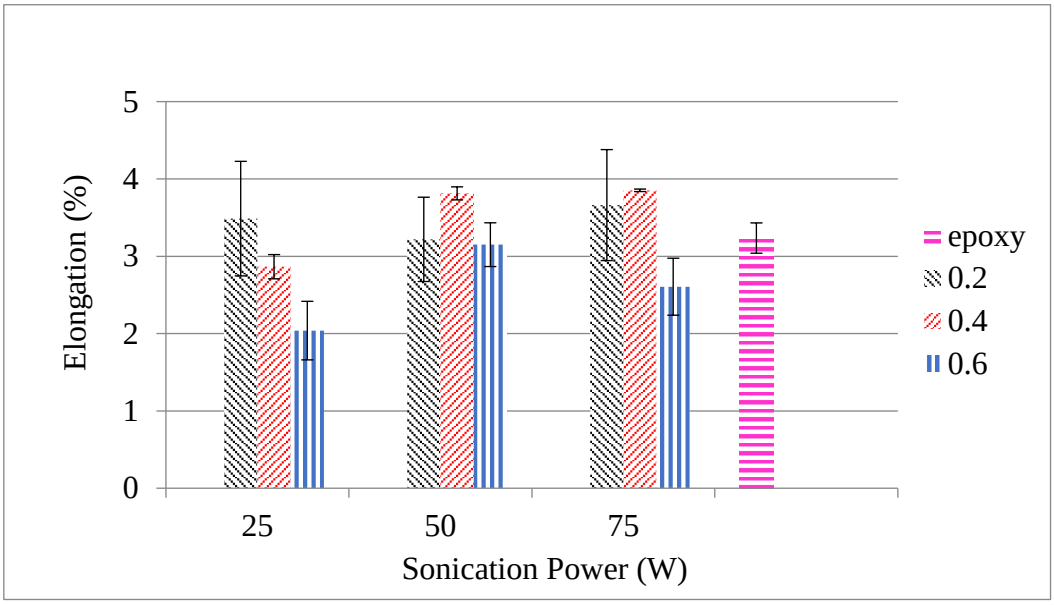
and 0.6% presented a decrease of approximately 11% and 37%, respectively, when compared to the pure resin. This trend is similar to that observed for the tensile strength at low power output. For the 50W power output case, the elongation at break of the MWCNT weight percentage of 0.4% indicates an increase of 18% in relation to the pure resin. Furthermore, the MWCNT weight percentage of 0.2% and 0.6% presented a decrease of 1% and 3%, respectively, in relation to pure resin. Finally, for the 75W power output case, an increase in the elongation at break of approximately 13% was observed for the 0.2% wt. MWCNT modified samples and 19% for 0.4% wt MWCNTs respectively, in relation to the pure resin. This might be explained by the increase of the interfacial adhesion of the nanotubes with the polymeric matrix, as reported by Gonjy et al. [12].



a)



b)



c)

Figure 3. Tensile data as a function of sonication power output and MWCNT weight percentage: a) Tensile strength b) Young's modulus; c) Elongation at break.

Table 2. Tensile test data.

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
Pure Epoxy	60.92 ± 1.42	3250 ± 80	3.23 ± 0.20
Epoxy + 0.2 % MWCNTs - 25W	66.83 ± 1.84	3100 ± 150	3.84 ± 0.30
Epoxy + 0.2 % MWCNTs - 50W	61.41 ± 5.68	2990 ± 200	3.21 ± 0.54
Epoxy + 0.2 % MWCNTs - 75W	63.94 ± 4.30	3200 ± 60	3.66 ± 0.72
Epoxy + 0.4 % MWCNTs - 25W	60.33 ± 1.47	3290 ± 70	2.86 ± 0.15
Epoxy + 0.4 % MWCNTs - 50W	62.60 ± 0.60	3080 ± 160	3.81 ± 0.08
Epoxy + 0.4 % MWCNTs - 75W	66.81 ± 2.16	3150 ± 90	3.85 ± 0.01
Epoxy + 0.6 % MWCNTs - 25W	49.44 ± 5.36	3120 ± 60	2.04 ± 0.38
Epoxy + 0.6 % MWCNTs - 50W	62.08 ± 1.82	3000 ± 260	3.14 ± 0.28
Epoxy + 0.6 % MWCNTs - 75W	69.54 ± 8.81	3740 ± 510	2.60 ± 0.36

Thermogravimetric analysis (TGA)

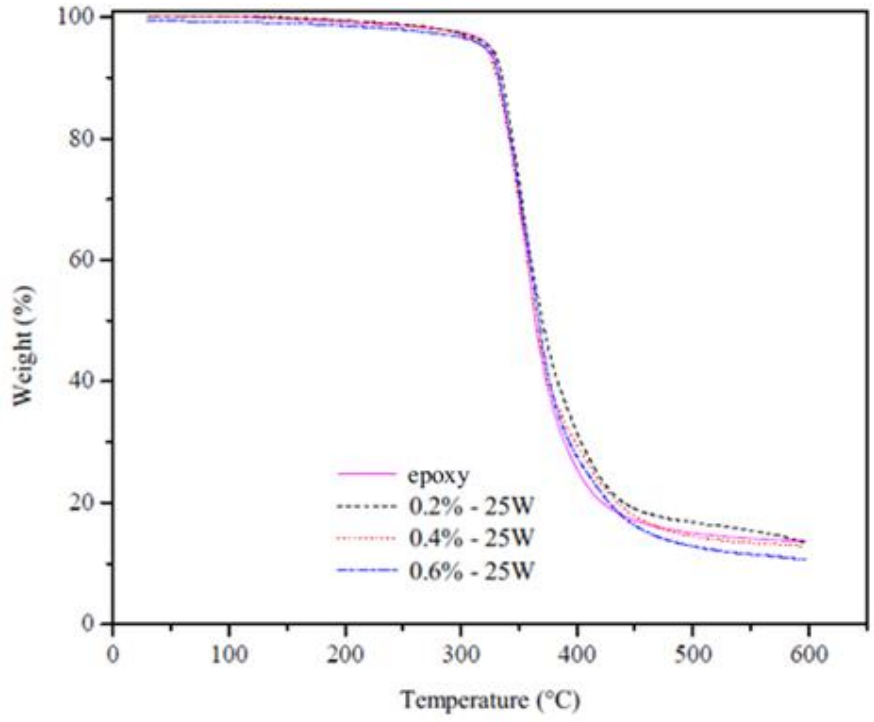
TGA analysis was performed to determine the influence of nanotubes addition on thermal stability and decomposition process of the composites studied here as a function of sonication power output and the MWCNT weight percentage and the results are presented in Fig. 4 to Fig. 6 (a-b) and Tables 3. It can be seen that the addition of the MWCNTs positively affects the thermal stability of the nanocomposites. For instance, for 25 W power output case, by the incorporation of 0.2 % MWCNTs, the onset temperature increased by 8 ºC, while for MWCNT percentage of 0.4 %, increased by 14 ºC. Finally, for MWCNT percentage of 0.6% %, an increase of 40°C in onset temperature was obtained when compared to the pure resin. It was shown in the literature that the incorporation of nanotubes in epoxy matrices influence the decomposition temperature of the nanocomposites, since carbon presents good thermal properties [3, 19].

Figure 5 (a-b) presents the TGA analysis data for the 50W power output case. From the analysis, it can be seen that the MWCNT percentages of 0.2%, 0.4% and 0.6% increased the onset temperature of the modified samples by approximately 17° C, 13 °C and 19° C respectively, when compared to the pure resin. This increase is attributed to the addition of carbon nanotubes that prevent the mobility of the polymeric matrix during

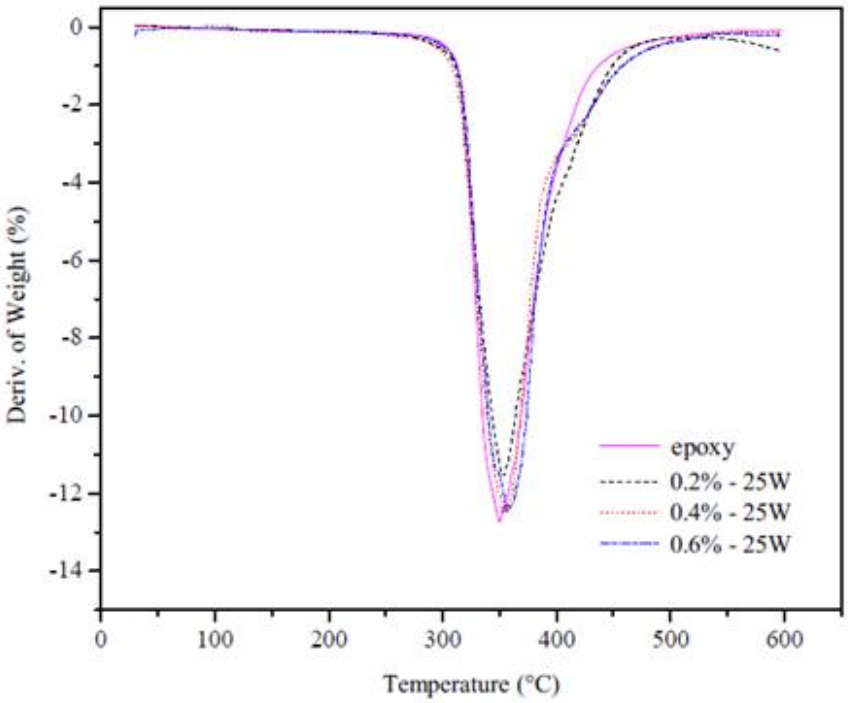
the decomposition process [20-22].

Finally, for the 75W power output case (see Fig 6 and Table 3), the MWCNT percentages of 0.2%, 0.4% and 0.6% increased the onset temperature by 21° C, 27 °C and 20° C respectively, when compared to the pure resin.

The rate of decomposition of the nanocomposites show lower values when compared to the pure epoxy (control sample), and this indicates that the presence of MWCNTs in the polymeric matrix structure acts as a flame retardant in the material [23]. Finally, the char residue after thermal analysis indicates that the incorporation of nanotubes decreases the percentage of active coal [24].

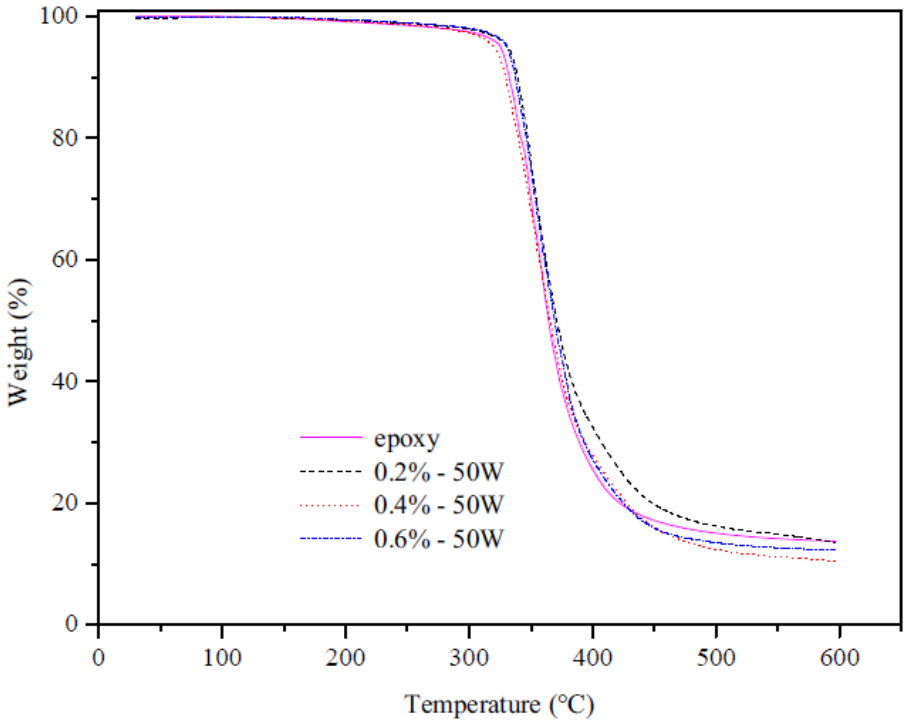


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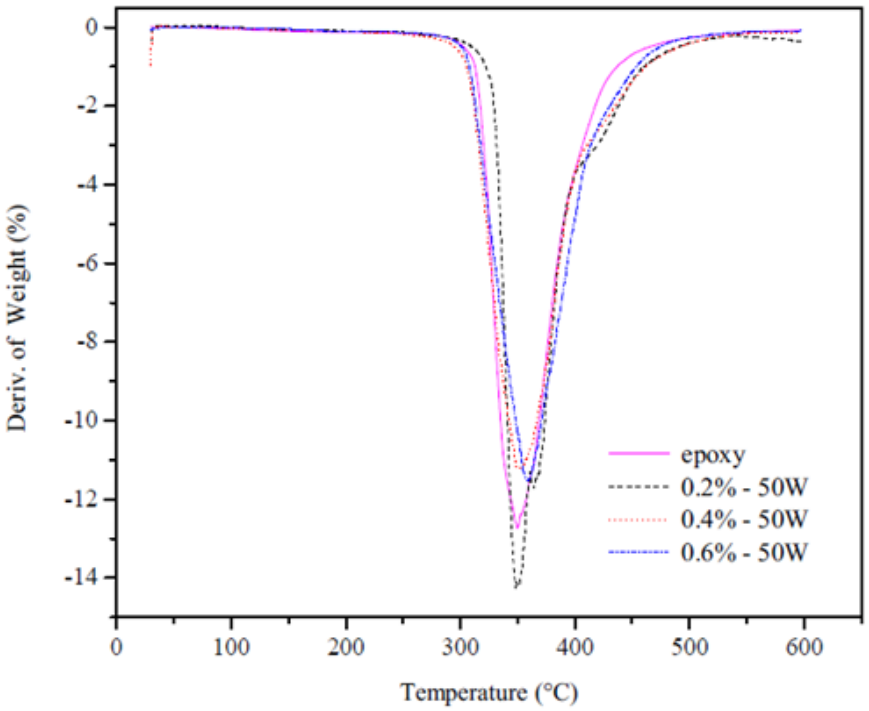


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Figure 4. Thermogravimetric analysis data for the 25W power output case: a) TG curves; b) DTG curves.

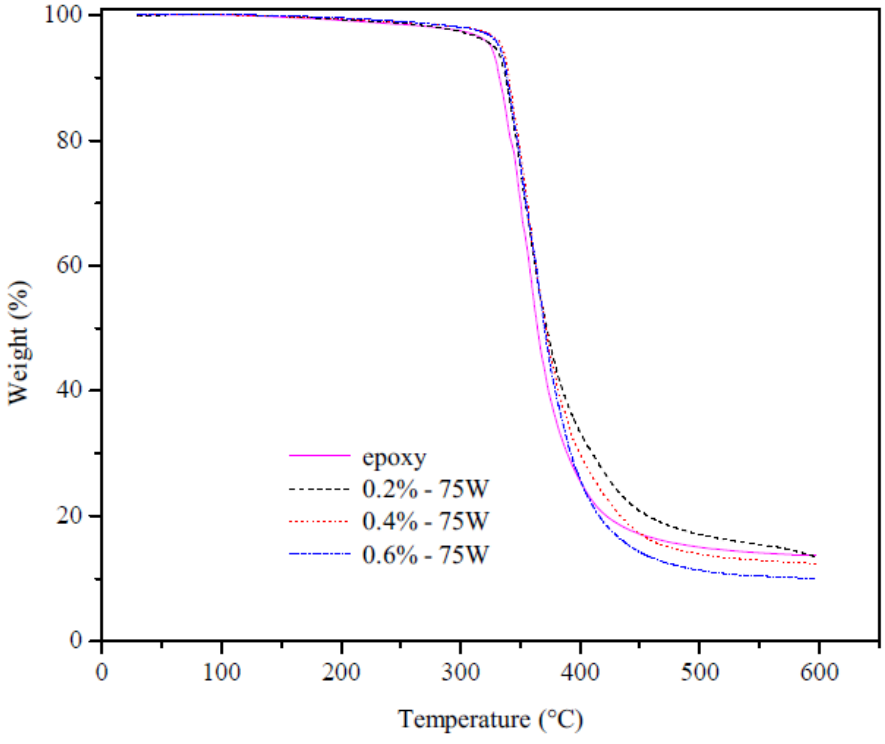


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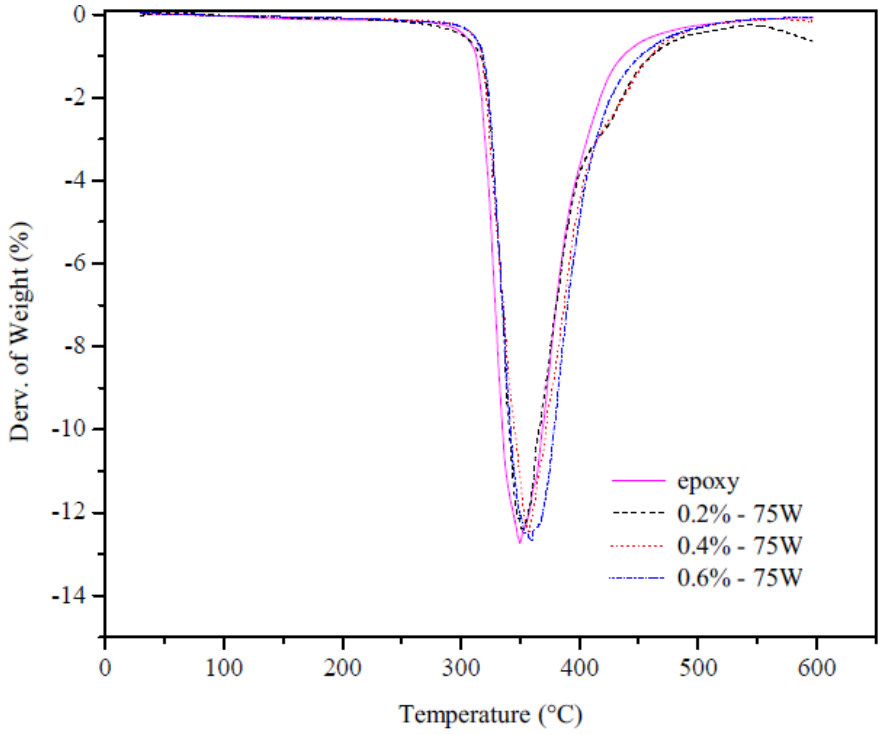


b)

Figure 5. Thermogravimetric analysis data for 50W power output case: a) TG curves; b) DTG curves.



a)



b)

Figure 6. Thermogravimetric analysis data for 75 W power output case: a) TG curves;

b) DTG curves.

Table 3. TGA analysis data.

Composite	Onset temperature (°C)	Weight Loss (%)	Char Residue (%)
Epoxy	328.80	74.56	13.70
Epoxy + 0.2% MWCNTs - 25W	336.90	71.85	13.40
Epoxy + 0.4% MWCNTs - 25W	342.60	70.87	12.81
Epoxy + 0.6% MWCNTs - 25W	368.40	73.96	10.61
Epoxy + 0.2% MWCNTs - 50W	346.30	68.81	13.49
Epoxy + 0.4% MWCNTs - 50W	341.60	71.28	10.51
Epoxy + 0.6% MWCNTs - 50W	347.60	76.13	12.25
Epoxy + 0.2% MWCNTs - 75W	350.00	66.89	13.39
Epoxy + 0.4% MWCNTs - 75W	356.30	72.96	12.32
Epoxy + 0.6% MWCNTs - 75W	348.50	76.48	10.00

Differential Exploratory Calorimetry (DSC)

The glass transition temperature (T_g) of the nanocomposites as a function of sonication power output and MWCNTs weight percentage are presented in Table 4. The value found for the glass transition of the pure epoxy was 83° C and is in accordance with the value informed by the manufacturer. The T_g of the nanocomposites was affected by the MWCNTs weight percentage in different ways depending on the power output. For the 25W power output case, the T_g of the samples modified with MWCNTs decreased when compared to the pure resin (by approximately 7°C, 3°C and 2°C for 0.2, 0.4 and 0.6% of MWCNTs). This might be explained by the decrease of the crosslink and the disorder of the matrix cure reaction by the presence of the nanotubes [10, 12, 25]. However, as the MWCNT weight percentage increases, the T_g increases.

For the 50W power output case, the T_g slightly increased by approximately 1°C for the samples modified with 0.2wt. MWCNTs, 2.5°C for the samples modified with 0.4 wt. MWCNTs, and 6°C for the samples modified with 0.6 wt. MWCNTs respectively, when compared to the pure resin. This is a sign that the output power affected the distribution of the nanoparticles in the polymeric matrix. Finally, for the 75W power output case, the T_g of the nanocomposites remained practically constant as a function of MWCNT weight percentage.

The maximum increase in T_g was observed for the samples modified with 0.6% wt. MWCNTs (i.e approximately 6°C and 5.5°C for the 50W and 75W power output). The T_g increase observed in these samples relative to the pure epoxy sample is due to an increase in cross-link density, mechanical reinforcement arising from a percolated MWCNTs morphology, and/or restriction of segmental relaxation of chain segments near the MWCNTs [26]. Cross-linking density is related to the dispersion and amount of nanoparticles in the composites. The strong adhesion between the resin and the MWCNTs restricts the motion near the interface, which may shorten the polymer chain causing an increase in the thermal stability. Thus, the presence of the MWCNTs enhances the T_g values in the composites as polymer chain confinement effect is increased. Therefore, the modified samples can be used at higher temperatures than the non-modified epoxy. Any changes in mechanical properties are due to the physical presence of the MWCNTs and also to the change in the polymeric network structure [27]. Roy et al. [28], reports that the presence of nanotubes influences the alignment of polymeric chains and thus increase the T_g of the nanocomposites. Ciecierska et al. [29], also found an increase of T_g of 4° C

for composites modified with 1% of MWCNTs.

Table 4. Glass transition temperature (T_g) of the nanocomposite samples.

Composite	T_g (°C)
Epoxy	83.0
Epoxy + 0.2% MWCNTs - 25W	76.3
Epoxy + 0.2% MWCNTs - 50W	83.7
Epoxy + 0.2% MWCNTs - 75W	88.1
Epoxy + 0.4% MWCNTs - 25W	79.9
Epoxy + 0.4% MWCNTs - 50W	85.5
Epoxy + 0.4% MWCNTs - 75W	88.3
Epoxy + 0.6% MWCNTs - 25W	81.5
Epoxy + 0.6% MWCNTs - 50W	89.1
Epoxy + 0.6% MWCNTs - 75W	88.5

Finally, if we compare the T_g of the samples as a function of the sonication power output we can see that increasing the power output increased the T_g for all the MWCNTs weight percentage. For instance, for 0.2 % wt. of MWCNTs, the T_g increased by approximately 12 ºC for 0.6 % wt. and by approximately 7ºC for 0.4 % wt. Similar trend to increase the T_g for higher sonication powers was found for 0.4 and 0.6 % wt. of MWCNTs (with a maximum increase of around 9 ºC). Therefore, increasing the sonication power output leads to higher T_g of the nanocomposites studied here.

SEM analysis

Figure 7 presents the fracture surface of the pure epoxy sample and shows a typical brittle fracture morphology specific to epoxy resins [9, 30].

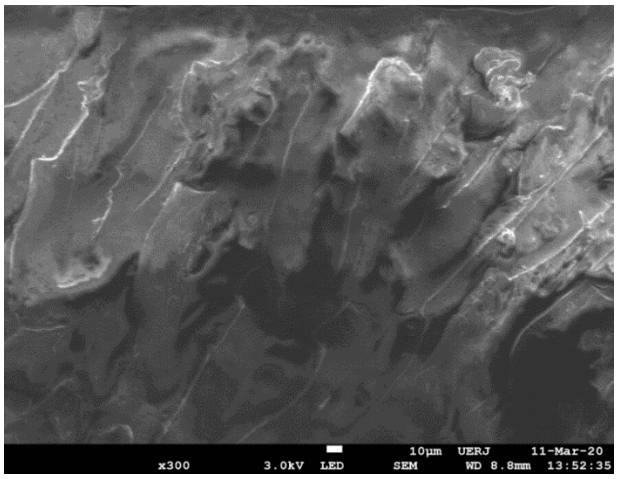
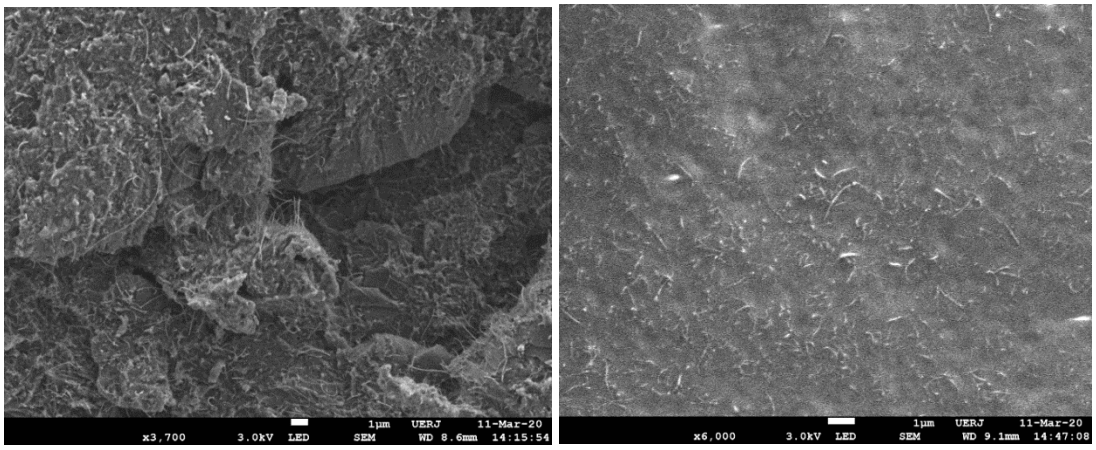
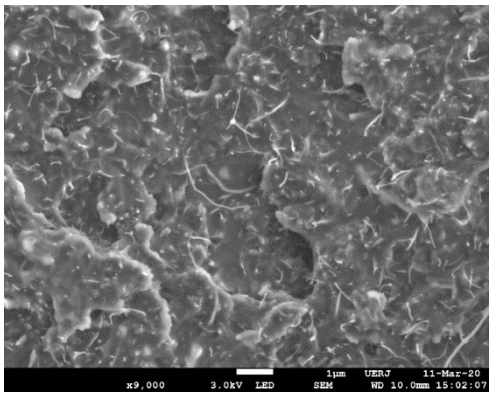


Figure 7. SEM images of pure epoxy sample.

Figure 8 presents the SEM images of tensile samples as a function of MWCNT weight percentages for the 25W power output case. It is known that the agglomerations act as stress concentration and thus crack initiation [15]. The SEM micrographs of the fractured surface of tensile specimens show that the cracks usually initiate from agglomeration. A better dispersion leads to less agglomeration as well as smaller average size of agglomerates with less stress concentration.



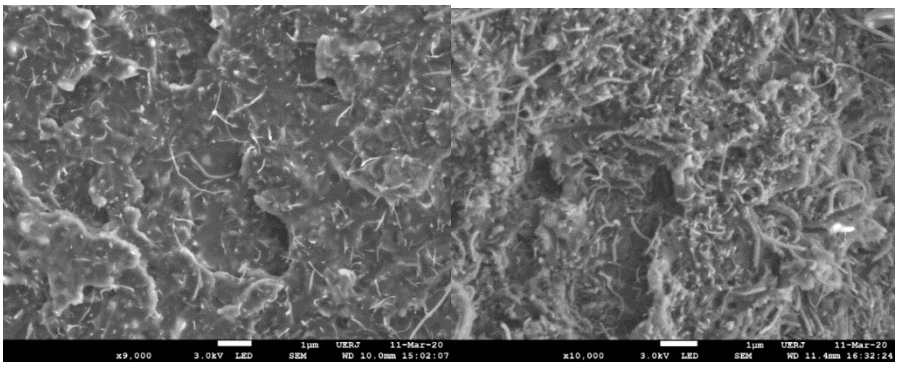
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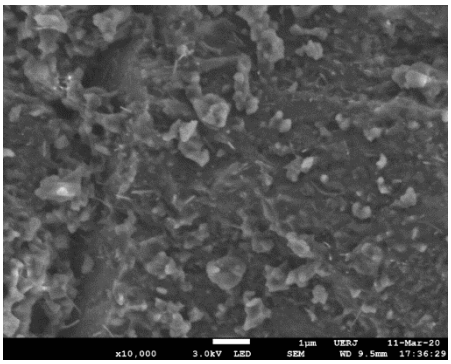
c)

Figure 8. SEM images of tensile specimens as a function of MWCNT weight percentages for the 25W power output case: a) 0.2%, b) 0.4% and c) 0.6%.

Figure 9 (a-c) shows the SEM images of the epoxy+0.6% MWCNTs weight percentage tensile specimens as a function of sonication power output. It can be seen that the dispersion of the MWCNTs is quite uniform and homogeneous. A difference in surface aspect for the 75 W power output can be observed which is due to the shortening of MWCNTs, which facilitates their dispersion within the polymer matrix due to the decreasing degree of physical interaction between them (as the length of the MWCNTs diminishes, the contact area between them becomes lower and decreases the number of physical entanglements between nanotubes). It was shown in the literature that the increase in the sonication power output causes a decrease in the entanglement of the MWCNTs and as a result, a better dispersion of the nanotubes in the epoxy matrix [10, 15, 31]. In line with the results presented in Table 2, the best dispersion was accomplished for the samples modified with 0.6% of MWCNTs and 75 W power output.



a) b)



c)

Figure 9. SEM images of the 0.6% MWCNT weight percentage case as a function of power output: a) 25W, b) 50W and c) 75W.

Conclusions

In this paper, the effect of sonication power output on the mechanical and thermal properties of an epoxy matrix modified with different mass fraction of multi-walled carbon nanotubes (MWCNTs) was investigated. It was found that the addition of MWCNTs to the epoxy matrix and the sonication process affect the mechanical and thermal properties of nanocomposites. The maximum increase in tensile properties was found for 75W sonication power output and 0.6% wt. MWCNTs content (an increase of approximately 14% in tensile strength and 15% of Young's modulus, compared to the pure epoxy matrix). The variations in tensile strength and Young's modulus were less significant at 50W sonication power output compared to low power (25W) and relatively high power (75W). The thermal analysis indicated that the presence of MWCNTs increased the T_{onset} of the nanocomposites when compared to pure epoxy resin. Increasing the sonication power output leads to higher T_g of the nanocomposites studied here.

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Chapter 4

Effect of UV and water spraying on the mechanical properties of multi-walled carbon nanotubes reinforced natural fibre and hybrid composites

ABSTRACT

The main objective of this study was to investigate the effect of aging by ultraviolet (UV) radiation and water spray on the mechanical properties of natural fibre and hybrid composites. Pure jute, hybrid jute/glass and glass fibre-reinforced composites were fabricated. All these types of composites were further modified with 0.6wt% of multi-walled carbon nanotubes (MWCNTs) and their mechanical behaviour was compared to the unmodified specimens. Tensile and flexural tests were used to measure the mechanical properties of unaged (control) and aged specimens. A scanning electron microscopy (SEM) analysis was used to examine the fracture surfaces of the specimens tested. It was found that the ageing process affected the mechanical properties of the composites studied in different ways. For jute and jute + MWCNT composites the properties decreased with increased exposure time. The hybrid jute/glass composites (unmodified and MWCNT modified) were less affected by ageing and showed an insignificant change in tensile strength. The hybrid + MWCNT composites, showed an increase of approx. 7% in Young´s modulus (1000h) and 9% (500h) and 17%, (1000h) in flexural modulus when compared to the unexposed specimens. The MWCNTs had a positive effect on the mechanical properties of the glass + MWCNT aged samples.

KEYWORDS: Aging, degradation, fullerenes, graphene, mechanical properties, nanotubes, non-polymeric materials and composites.

1. INTRODUCTION

In recent years, the move to less harmful, biodegradable products has been in the vanguard of industrial interests as a means to reduce dependency on petroleum-based products [1-3]. For this reason, the use of natural fibres has been intensified in the production line of various sectors of industry, such as: automotive, aerospace, civil, sport, and maritime [1, 4-7].

Natural fibres present a great alternative to the reduction of the use of synthetic fibres, due to their main advantages: low cost of production, low density, renewable resource, biodegradable and good insulation to both sound and heat [5, 8]. However, natural fibres have several disadvantages, such as the variation of their mechanical and dimensional properties, low interfacial adhesion between the fibre (hydrophilic) and polymeric matrix (hydrophobic) and high moisture absorption capacity [1, 9]. To mitigate these shortcomings several methods can be used, of these, the hybridization is of note [10, 11]. Hybridization consists in the use of two or more different reinforcement agents in the same matrix [1, 12]. This will in turn modify the mechanical properties of the resulting composite, with the integration of the positive characteristic of each reinforcement [10, 11, 13]. Composite materials are subjected to hostile environments in service (i.e. high temperature, humidity and ultraviolet radiation (UV)), which may negatively affect their performance [14-16]. For example, the effect of UV radiation induces decomposition by photo-oxidation of macromolecular chains, leading to irreversible changes in the molecular structure of materials [16, 17], which modifies the surface morphology of composites, such as colour, brightness, induce cracks, etc. [16, 17]·[18]. Yan et al. [14] analysed the combined effect of UV radiation and spray water on flax fibre-reinforced composites and found that the tensile strength and Young's modulus decreased by 29.9% and 34.9%, respectively, when compared to the control case (without exposure). The authors stated that the reduction in the properties was caused by the degradation of the interfacial zone between the fibre/matrix.

One method used in the literature to reduce the effect of UV on the performance of composite materials is by using of various types of nanofillers which can be incorporated into resin, fibre or both [19-21]. The function of these nanofillers is to absorb, prevent or delay the material degradation [19, 20]. Carbon nanotubes (CNTs) are one of the nanofillers used for this purpose and they are divided into three types: single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT) and multi-walled carbon nanotube (MWCNT) [22-24]. The difference between the types of

CNTs is the amount of graphene numbers rolled into their structure [24]. However, MWCNTs are the most studied because of two factors: lower chemical inertia for functionalization and better dispersion in the matrix reducing the cost of fabrication [22, 25, 26]. The main advantages of using nanotubes are the increase of mechanical, electrical, thermal, UV absorption capacity and ability to reduce moisture and oxygen permeability of the composites [23, 24, 27]. However, this improvement in properties is related to several factors, such as, concentration and dispersion of the nanoparticles, cure kinetics and the interactions between nanoparticles and the matrix [22, 28-31].

Several researchers have studied the effect of CNTs on the properties of natural, synthetic and hybrid (natural and/or synthetic) composites [22, 27, 32, 33]. Awad et al. [27], investigated the influence of UV radiation on epoxy resin of type hydrogenated diglycidyl ether of bisphenol A (HDGEBA) with exposure time of 1-6 months. Two cases were studied: pure resin and resin filled with 0.5% of multi-walled carbon nanotube (MWCNT). They found that the composites modified with MWCNTs showed a lower loss in mechanical properties when compared to pure resin. The thermal properties of the nanocomposites (i.e. the onset of temperature (T_{onset}) and the glass transition (T_g)) decreased by increasing the exposure time of the material. On the other hand, the T_{onset} and T_g of nanocomposites increased when compared to pure resin. The authors report that MWCNTs reduce the negative effects resulting from UV radiation and moisture. Costa et al. [31], studied the effect of the functionalization of Graphene Oxide (GO) on curauá fibre-reinforced composites. Four cases were studied: the first case without the presence of GO, for the second case only the fibre was functionalized by GO, the third case GO was added in the resin and the fourth case both the resin and fibre were functionalized. They found that the functionalization of the resin presented better performance in tensile strength when compared to other cases. Shen et al. [34], investigated the effect MWCNTs (0wt%, 0.2wt%, 0.4wt% and 0.6wt%) on the mechanical properties of ramie fibre-reinforced composites. They found that the incorporation of MWCNTs increased the tensile and flexural strength of the modified specimens when compared to the unmodified composite specimens. It was found that the specimens modified with 0.6% MWCNTs performed better when compared to the other cases. Ismail et al. [32], analysed the effect of MWCNTs (0wt%, 0.5wt%, 1wt%, 1.5wt% and 2wt%) on epoxy resin, pure flax composites and three types of hybrid composites (flax-glass, flax-carbon and flax-Kevlar) and found that the presence of MWCNTs reduced the mechanical properties of the hybrid composites. However, for pure flax composite the mechanical properties were preserved

at the percentage of 1wt%, while for the resin the mechanical properties increased with the percentages of 0.5wt% and 1wt%. The authors report that above 1wt% of MWCNTs, they have the tendency to agglomerate, decreasing the mechanical properties of the composites. Chennareddy et al. [33], studied the effect of UV radiation on glass fibre-reinforced composites (GFRP) modified with MWCNT in weights of 0.25%, 0.5% and 1%. They found that pure GFRP and 0.25% MWCNT-GFRP specimens showed a decrease in mechanical properties when compared to unexposed cases, while the 0.5% MWCNT-GFRP and 1% MWCNT-GFRP showed an increase in mechanical properties when compared to unexposed composites. Although several studies regarding aging of composites are available in the literature, the effects of aging and the extent of those effects on properties of these materials are still not fully understood. Thus, there is still a lack of data related to the durability of composites based on natural fibres and this is one major challenge that needed to be addressed prior to the widespread acceptance of natural fibre reinforced polymer composites in industry.

The main objective of this work was to investigate the effect of aging by ultraviolet radiation (UV) and water spray on the mechanical properties of different type of composites: unmodified natural, hybrid and glass fibre composites and the same composites modified with MWCNTs. Tensile and flexural tests were used to measure the mechanical properties of unaged (control) and aged specimens. A scanning electron microscopy (SEM) analysis was used to examine the fracture surfaces of the specimens tested.

2. MATERIALS AND METHODS

2.1 Materials

Pure jute fibre, glass fibre and interlaminar hybrid jute/glass fibre composites were fabricated using bidirectional glass and jute fibre plain woven fabrics. The jute fabrics (T4) were supplied by Sisalsul (São Paulo, Brazil), while the glass fabrics (RE200P) were supplied by Barracuda Advanced Composites (Rio de Janeiro, Brazil). The bi-component epoxy resin HEX 135 SLOW with the 100/33 fraction for epoxy resin/hardener, supplied by Barracuda Advanced Composites (Rio de Janeiro, Brazil) was used as matrix. The MWCNT nanotubes with an average purity of 95%, an external diameter of 50-100 nm, an internal diameter of 5-10 nm and an average size of 5-10 μm were supplied by Nanostructured & Amorphous Materials, USA.

2.2 Specimen Preparation

The composites were fabricated using the compression moulding technique (the cure was done using a steel mould and a heated plate hydraulic hot press, Solab SL 20 (São Paulo, Brazil)). All composites were fabricated with 11 layers in total. For the interlaminar hybrid composites 6 layers of glass fibre and 5 of jute fibre were used (the jute layers was enveloped by 3 layers of glass fabrics on each side) [35]. The fibre weight percentage was kept at around 30% and the resin + hardener (100:33) at 70% of the final composite weight. For the fabrication of the MWCNTs-modified composites, the fillers were first added to the neat epoxy resin and mixed manually for a few minutes. Next, the fillers were dispersed in the matrix via the ultrasonication technique with the use of a 100 W and 4 mm diameter probe ultrasonicator Eco-Sonics (São Paulo, Brazil). The percentage of MWCNTs (0.6% wt.) and the dispersion procedure followed the author's previous work [22]. The specimens were cut from the composite plates with the aid of a tungsten carbide saw according to the standard geometry of the ASTM D3039 and ASTM D790 for the tensile and flexural tests, respectively. The specimen geometry for tensile testing was 220 mm x 13 mm x 5 mm and for flexural testing was 180 mm x 13 mm x 5 mm for the natural and hybrid composites. The neat glass composites presented a lower thickness of approx. 2 mm. The three-point bending test was done according to a span to depth ratio of approx. 32:1.

2.3 Accelerated weathering by UV irradiation and moisture

The composites were exposed to UV fluorescent light using a QUV/spray Accelerated Weathering Tester chamber, present at Mechanical Testing Laboratory of the Centre for Mechanical Technology and Automation (TEMA) of the University of Aveiro (see Fig. 1). The ageing (cycle configuration) followed the following steps: (i) 12h exposure to UV at 60°C, (ii) exposure at room temperature (RT) for 3h with condensation, (iii) spraying water on the exposed surface and exposure to UV for 6h at 60°C, and (iv) exposure at RT for 3h before restarting the entire procedure. The total exposure time was 1000h with irradiation fixed at 0.89 w/m^2 at 340 UVA.



(a) (b)

Figure 1. a) QUV/spray Accelerated Weathering Tester chamber and b) specimens in the chamber.

2.4 Tensile and flexural tests

The tensile and flexural tests were performed at RT using a universal Shimadzu AG-100kN testing machine (Shimadzu, Tokyo, Japan). Five samples for each case were tested with a test speed of 1 mm/min, according to the ASTM D3039 and ASTM D790 standard. The tensile and flexural tests were performed at three different times: unexposed samples (control) and aged samples after 500h and 1000h of exposure.

2.5 SEM analysis

Two distinct SEM microscopes were used for the analysis of the failure surfaces of tensile specimens: JEOL model - JSM-7100F microscope available at The Mechanical Testing Laboratory of the Centre for Mechanical Technology and Automation (TEMA) of the University of Aveiro, Portugal (An acceleration voltage of 15 KV was used) and a Quanta FEG 450 microscope available at Nanotechnology Characterization Laboratory (CENANO) of the National Institute of Technology (INT), Rio de Janeiro, Brazil (an acceleration of 10KV). All samples were coated with a platinum layer with surface density equal to 21.53 g/cm^3.

3. RESULTS AND DISCUSSION

3.1 Effect of UV on colour of natural, hybrid and synthetic composites

The natural, hybrid and synthetic composite samples were visually exanimated before and after the aging process (see Fig. 2a-f).

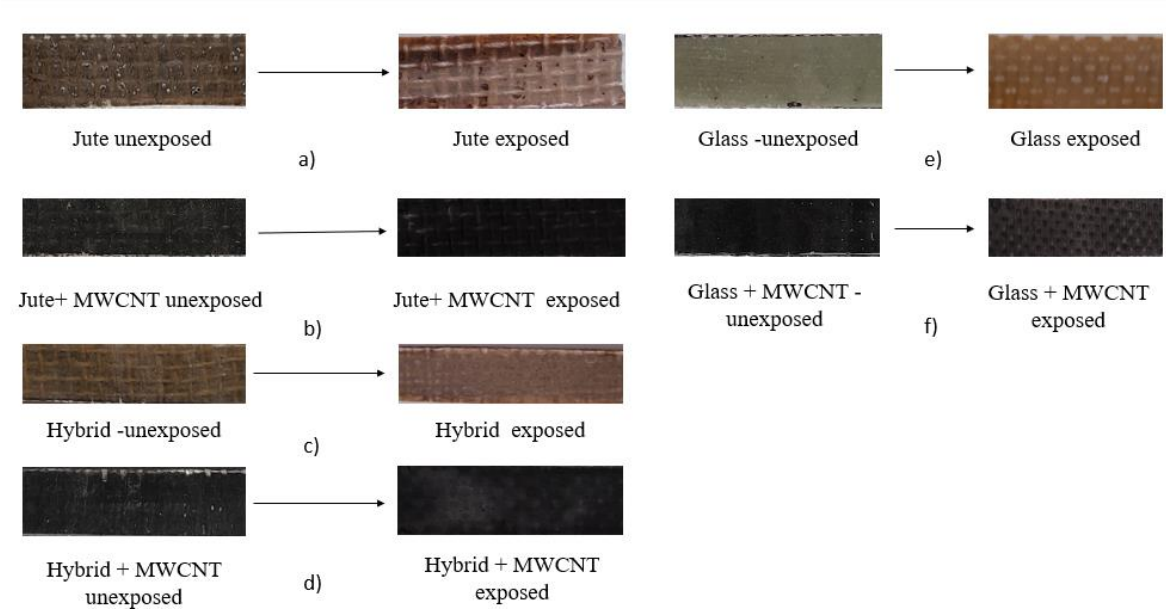


Figure 2. Effect of ultraviolet radiation (UV) on the colour of composites: a) Jute control, b) Jute + MWCNT, c) Hybrid control, d) Hybrid + MWCNT, e) Glass control and f) Glass + MWCNT.

From Fig. 2a it can be seen that the jute exposed samples presented a change in the coloration of natural fibres, due to the moisture absorbed from the water spray and the photo degradation of matrix from the UV irradiation. It was shown in the literature that the ageing causes physical-chemical changes of the fibre and matrix [36]. However, the composites modified with MWCNTs (see Fig. 2b, 2d and 2f) presented only a slight change in their colour. It was shown in the literature that MWCNTs present a photo stabilization effect similar to carbon black nanoparticles, and this type of reinforcement is commonly used to reduce the effect of degradation caused by UV radiation [33]. Finally, the glass composite samples (Fig. 2e) presented a higher change in its colour after ageing when compared to the other cases studied. The initial white coloration of the glass composite changes to yellow and brown tones after the aging process. This is also seen in Fig. 2c for the hybrid composite samples because of the outer layers of glass fibres. This might be explained by the change of the macromolecules of these polymers due to chain splitting caused by the effect of degradation and this phenomenon is described in the literature as photoreaction of the polymer [33, 37].

3.2 Tensile tests

Figure 3a-f shows representative tensile stress-strain curves of the specimens as a function of exposure time. From these curves the tensile properties of the natural, hybrid and synthetic composite were calculated and the results are presented in Fig. 4.

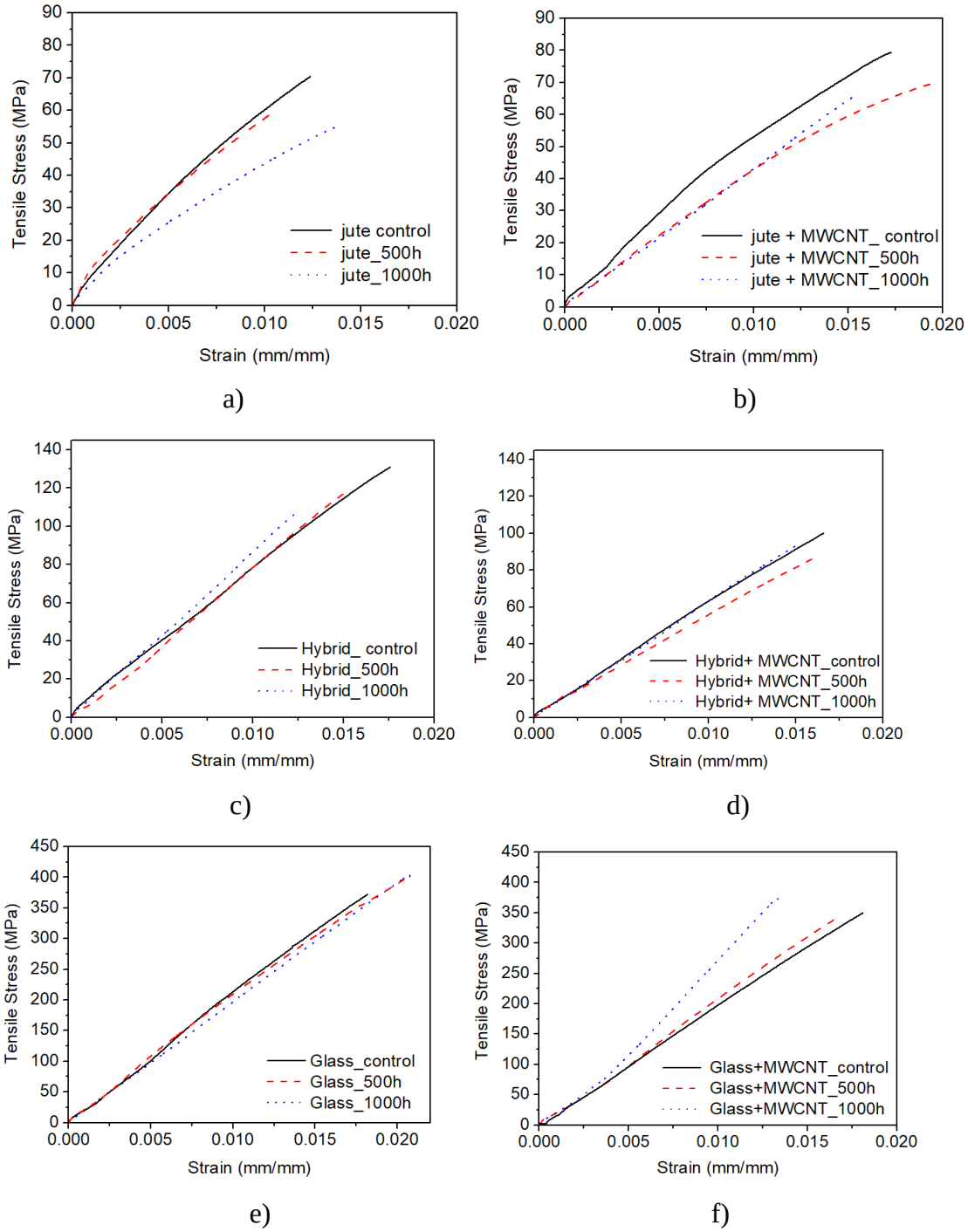


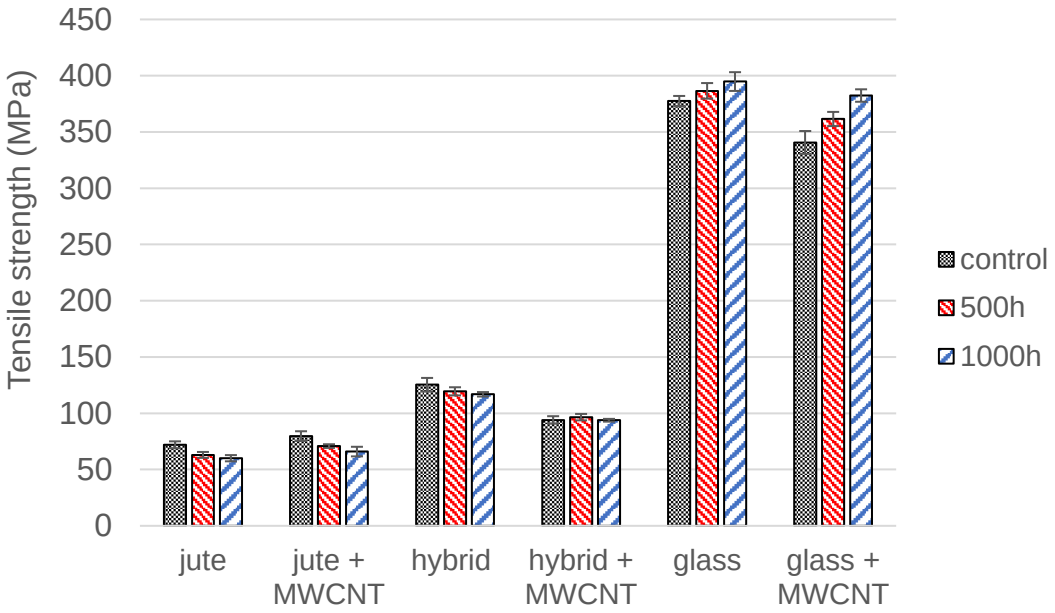
Figure 3. Representative tensile stress-strain curves as a function of composite type and ageing: a) Jute, b) Jute+ MWCNT, c) Hybrid, d) Hybrid + MWCNT, e) Glass and f) Glass + MWCNT.

It can be seen that the behaviour of the jute specimens varied significantly for the 1000h ageing case but remained relatively similar for 500h. For the jute + MWCNT composites similar behaviour at 500h and 1000h is found (see Fig. 3b), while for the hybrid and hybrid + MWCNT composite, relative stability in tensile behaviour was observed despite the ageing process (see Fig. 3c-d).

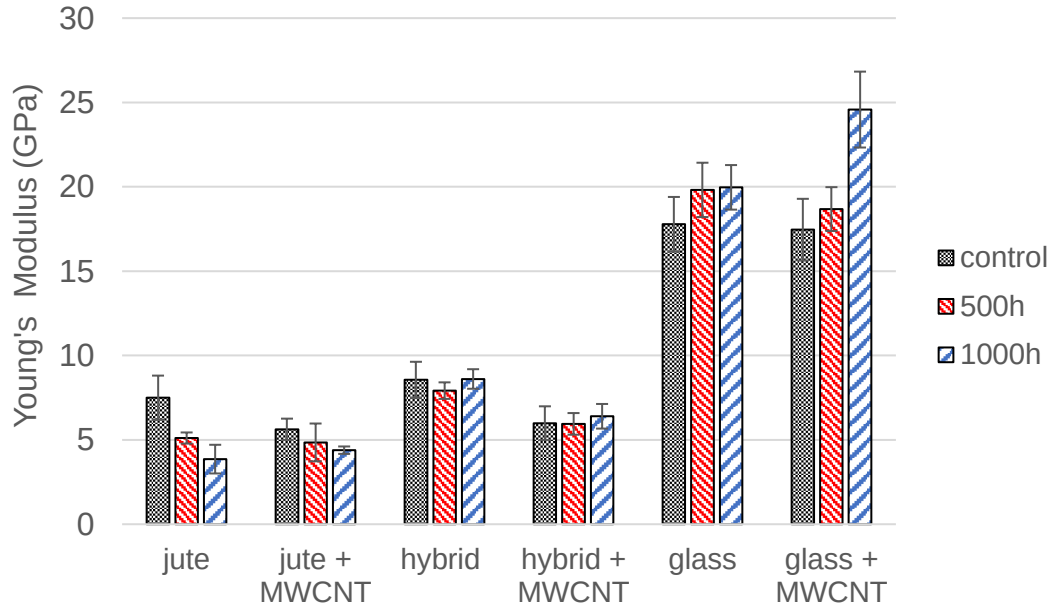
3.2.1. Effect of MWCNT on the tensile properties of composites

The addition of MWCNT affected the mechanical properties of natural, hybrid and synthetic composites in different ways (see Fig. 4). For instance, the jute + MWCNT composite showed an increase of approx. 11% in tensile strength when compared to the case of pure jute composite (see Fig. 4a). Li et al. [38], reports that carbon nanotubes increase the interfacial bonding between natural fibre and matrix. Sumesh et al.[39], also reported that the addition of filler decreases surface fiber abnormalities and reduces the gaps between fibre/matrix. However, the hybrid + MWCNT and glass + MWCNT composite showed a decrease of approx. 25% and 10% in tensile strength compared to the unmodified the hybrid and glass composite, respectively. Song et al.[40], reported that well dispersed carbon nanotubes increase mechanical properties, however poorly dispersed nanotubes help cracks to propagate easily resulting in a decrease in mechanical properties.

Similar to tensile strength, the Young's modulus was also affected by the addition of MWCNT (see Fig. 4b). For the condition unexposed, the jute + MWCNT composite showed a decrease of approx. 25% in Young's modulus when compared to the case of pure jute composite. For the hybrid + MWCNT composite a decrease of approx. 30%, in Young's modulus, when compared with the unmodified hybrid composite was found. The incorporation of filler in the matrix reduces the voids found between the fibre-matrix and improves the transfer of loads between the reinforcement and matrix. However, the filler percentage influences the mechanical properties of the composite owing to the possible negative effects of high filler concentrations leading to a decrease in the overall properties when compared to lower filler concentration cases[35, 41]. Thus the percentage of the MWCNT used in this study seems be the reason of the reduction in the tensile proprieties for the modified specimens. Finally, the glass + MWCNT composites showed no significant variation in Young's modulus when compared to the unmodified specimens.



a)



b)

Figure 4. Average tensile properties by reinforcement type and aging: a) Tensile strength and b) Young's modulus.

3.2.1. Effect of ageing on the tensile properties of composites

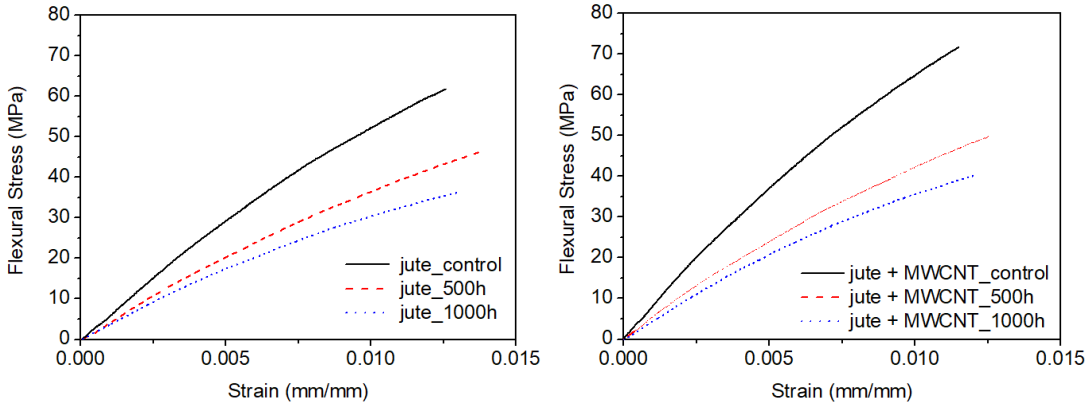
Form Fig 4a it can be seen that the jute composite with 500h and 1000h of exposure showed a decrease of approx. 12% and 20% in tensile strength, when compared to the unexposed jute composite. This can be explained by the photochemical degradation mechanism caused by the UV effect [18, 42]. The spray process can cause the fibre swelling by absorbing water molecules causing fragility of the fibre-matrix interface (see Fig. 7a) [42]. The jute + MWCNT composite with 500h and 1000h exposure times also showed a decrease of approx. 11% and 20% in tensile strength, when compared to the unexposed jute + MWCNT composite. The hybrid composite with 500h and 1000h of exposure presented only a slightly decrease in tensile strength (approx. 5% and 7%), when compared to the unexposed hybrid composite. Mayandi et al. [43], reports that for hybrid composites (natural + synthetic) UV rays can penetrate through the synthetic layer and this effect can cause the degradation of the natural fibre constituents and the weakening of the fibre-matrix interface (see Fig. 7i). On the other hand, the hybrid + MWCNT composite with 500h and 1000h of exposure showed no significant variation in tensile strength when compared to the unexposed hybrid + MWCNT composite. This can be explained by the fact that nanoparticles can absorb UV rays [43]. Finally, the glass composite samples with 500h and 1000h of exposure, presented an increase in tensile strength of approx. 2% and 5%, when compared to unexposed glass composite, while the glass + MWCNT composite with 500h and 1000h of exposure showed an increase of approx. 5% and 12% in tensile strength, respectively, when compared to the unexposed glass + MWCNT composite. The addition of MWCNT minimizes the plasticizing effect and prevents the creation of cracks caused by moisture and radiation [44]. The results found are similar to other studies found in the literature [26, 33].

Similar to the tensile strength, the Young's modulus was also affected by exposure time and addition of MWCNT (see Fig. 4b). The jute composite with 500h and 1000h of exposure showed a drop of more than 50% in Young's modulus when compared to the unexposed jute composite. This drop in rigidity is attributed to photochemical degradation, fissure, plasticization and water molecules in the interface between fibre-matrix [42, 45]. However, the addition of MWCNT in the jute composite produced a reduction in rigidity of approx. 16% after 500 and 28% after 1000h exposure, when compared to the unexposed jute + MWCNT. The hybrid composite with 500h and 1000h exposure time showed an insignificant variation in Young's modulus when compared to the unexposed hybrid composite. The hybrid + MWCNT composite with 500h exposure, also presented no significant variation in Young's modulus. However, the hybrid +

MWCNT composite with 1000h showed an increase of approx. 7% in Young's modulus when compared to the unexposed composite. Finally, the glass composite with 500h and 1000h of exposure showed an increase of approx. 2% and 7% in Young's modulus, respectively, when compared to the composite unexposed. The glass + MWCNT composite with 500h and 1000h of exposure presented an increase of approx. 6% and 12% in Young's modulus, when compared to unexposed glass + MWCNT composite. It was found in the literature that incorporation of MWCNT higher than 0.5wt% enhanced the mechanical properties of composites after UV aging [33].

3.3. Flexural Tests

Figure 5a-f shows representative flexural stress-strain curves of the composite specimens as a function of ageing. For the jute and jute + MWCNT composite specimens, similar behaviour and rigidity range from highest (control) to lowest (1000h) was observed (see Fig. 5a-b). For the hybrid and hybrid + MWCNT composites (see Fig. 5c-d), the behaviour was similar, however, for the aged filler modified specimens, the failure occurred earlier (compressive failure). Finally, for the glass and glass + MWCNT composites, a significant change in the flexural behaviour as a function of ageing was observed (see Fig. 5e-f). The range of rigidity was similar with the neat specimens presenting the lowest values, however, the trend for 500h and 1000h was inversed between the neat and filler reinforced specimens. It is also possible to see the compressive failure behaviour near the end of the curves.



a) b)

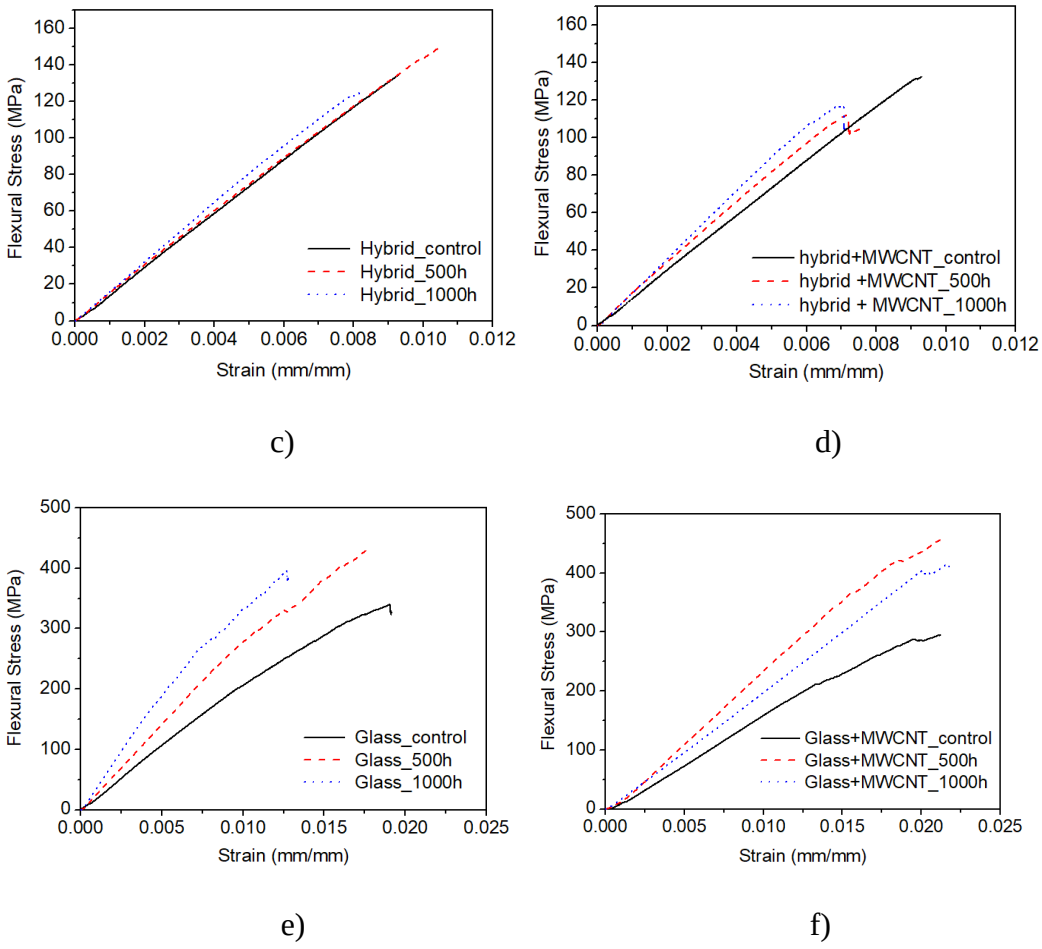
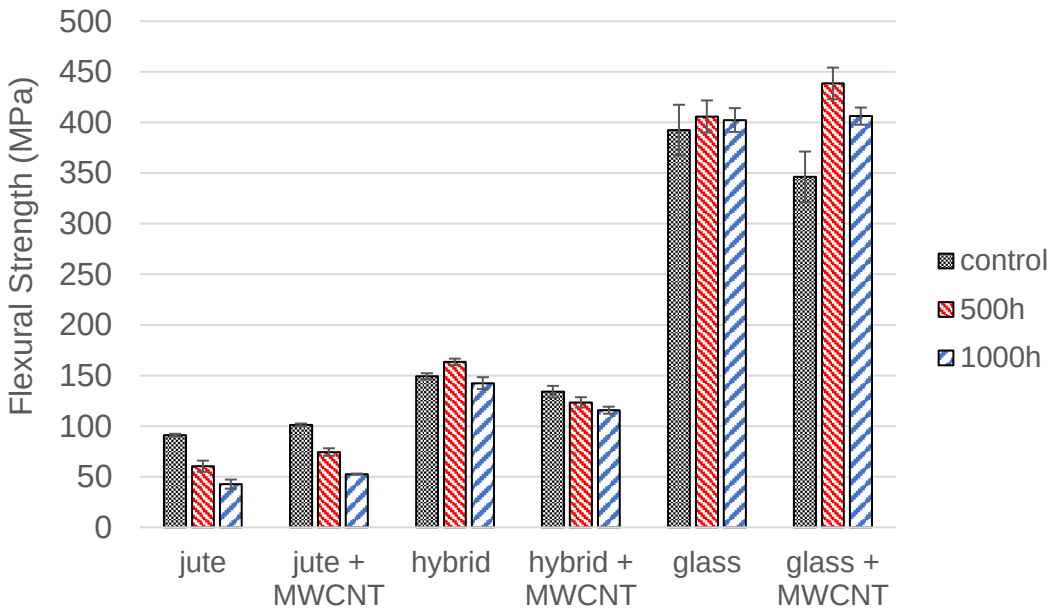


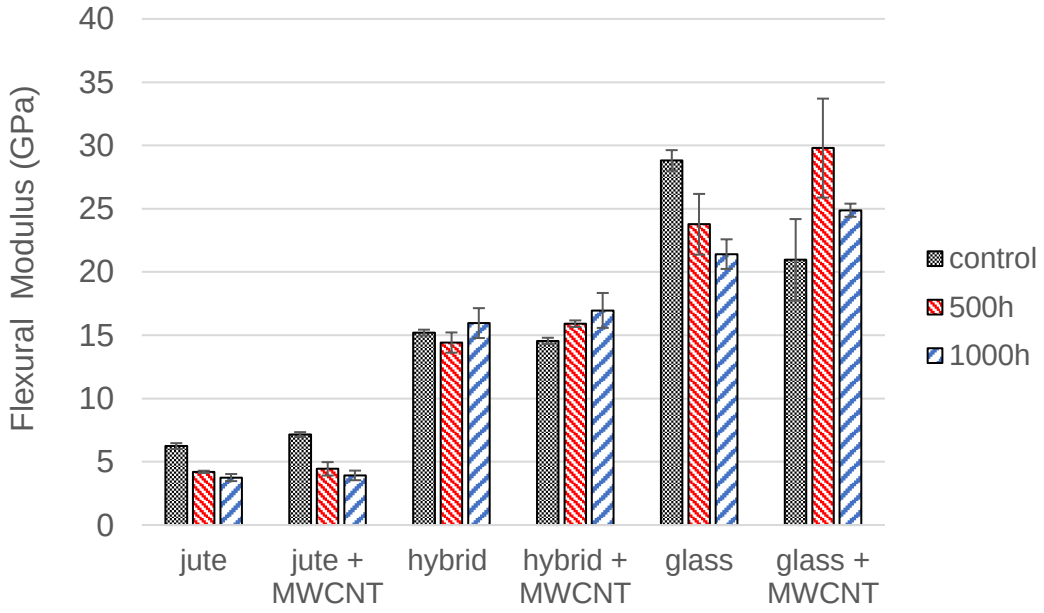
Figure 5. Representative flexural stress-strain curves as a function of composite type and ageing: a) Jute, b) Jute+ MWCNT, c) Hybrid, d) Hybrid + MWCNT, e) Glass and f) Glass + MWCNT.

3.3.1 Effect of MWCNT on the flexural properties of composites

The addition of MWCNT to the matrix of the composites affected the flexural properties of natural, hybrid and synthetic composites (see Fig. 6a-b). For the condition unexposed, the jute + MWCNT composite showed an increase of approx. 11% in flexural strength when compared to the unmodified pure jute composite. It was shown in the literature that the incorporation of filler in the matrix reduces the formation of voids found between the fibre-matrix, improving the transfer of loads between the reinforcement and matrix. Moreover, higher filler content decreases the chance of crack progression, resulting in an increase in mechanical properties[46]. However, the hybrid + MWCNT composite and glass + MWCNT composite showed a decrease of approx. 10% and 12% in flexural strength compared to the unmodified hybrid and glass composite, respectively.



a)



b)

Figure 6. Average flexural properties by reinforcement type and aging: a) Flexural strength and b) Flexural modulus.

Similar to the flexural strength, the flexural modulus was also affected by addition of MWCNT (see Fig. 6b). For the control condition (without exposure), the jute + MWCNT composite showed an increase of approx. 15% in flexural modulus when compared to unmodified pure jute composite. The hybrid + MWCNT composite also

presented no significant variation in flexural modulus, while the glass + MWCNT composite, presented a decrease of approx. 27% in flexural modulus when compared to the unmodified glass composite.

3.3.2 Effect of ageing on the flexural properties of composites

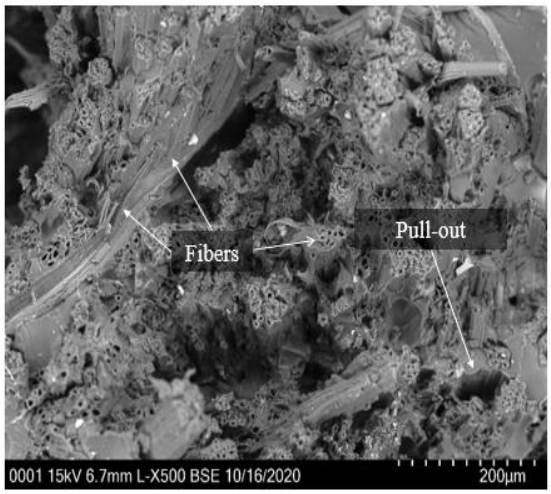
The jute composite with 500h and 1000h of exposure showed a decrease of approx. 34% and 114% in flexural strength, respectively, when compared to the unexposed jute composites. This can be explained by the fact that the UV irradiation process and spraying over time, deteriorate the matrix and produce delamination between fibre-matrix [47]. Furthermore, the addition of carbon nanotubes in the composites showed a deceleration effect on the mechanical properties (the jute + MWCNT composite with 500h and 1000h exposure showed a decrease of approx. 18% and 93% in flexural strength, when compared to the unexposed jute + MWCNT composite). The hybrid composite with 500h of exposure showed an increase of approx. 9% in flexural strength when compared to the unexposed hybrid composite. However, the hybrid composite with 1000h of exposure presented a decrease of approx. 5% in flexural strength when compared to the unexposed hybrid composite. The hybrid + MWCNT composite with 500h and 1000h of exposure presented a decrease of approx. 5% and 16% in flexural strength, respectively, when compared to the unexposed hybrid + MWCNT composite. The glass composite with 500h and 1000h of exposure showed no significant variation when compared to the unexposed glass composite, while the glass + MWCNT composite with 500h and 1000h of exposure showed an increase of approx. 27% and 85% in flexural strength, respectively, when compared to the unexposed glass + MWCNT composite. Similar results have been reported in the available literature [26, 33].

Similar to the flexural strength, the flexural modulus was also affected by the ageing process. The jute composite with 500h and 1000h showed a drop of approx. 30% in flexural modulus when compared to the unexposed jute composite. Fiore et al. [48], showed that the jute composite presented approx. 30% drop in flexural modulus when it reaches 84 days of exposure. However, the addition of MWCNT in jute composite with 500h and 1000h of exposure, showed that the decrease in flexural modulus was between approx. 38%-55% when compared to the unexposed jute + MWCNT. The hybrid composite with 500h and 1000h exposure time presented no significant difference in flexural modulus when compared to the unexposed hybrid composite. The hybrid +

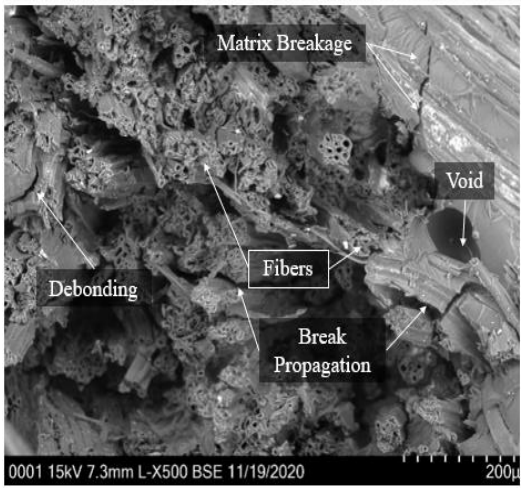
MWCNT composite with 500h and 1000h exposure, showed an increase of approx. 9% and 14%, respectively, in flexural modulus when compared with the unexposed hybrid composite. The glass composite with 500h and 1000h of exposure showed a decrease of approx. 18% and 35% in flexural modulus, when compared to the unexposed specimens. Finally, the glass + MWCNT composite with 500h and 1000h of exposure showed an increase of approx. 42% and 19% in flexural modulus, respectively, when compared to unexposed glass + MWCNT composite.

3.4 SEM analysis

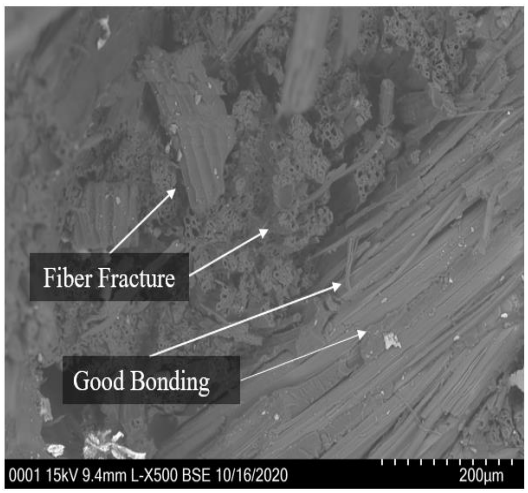
In order to investigate the effect of ageing on the fracture mechanisms and filler morphology, a SEM analysis of the fractured surfaces was performed on the control (unexposed to UV and water spray) and the aged specimens.

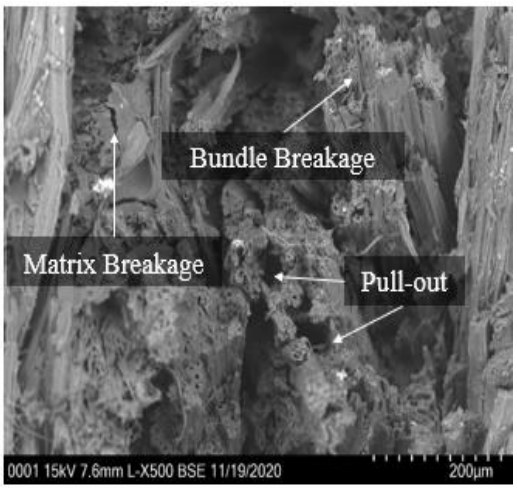


a) Jute unexposed

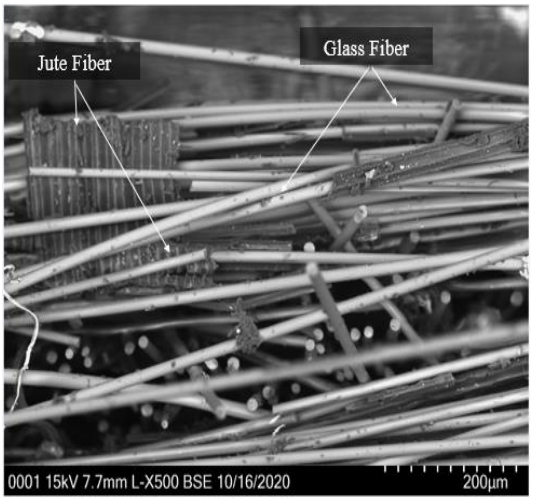


b) Jute exposed

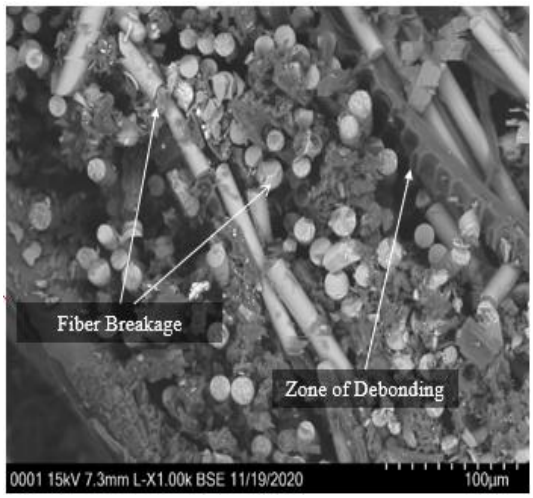




c) Jute+ MWCNT unexposed



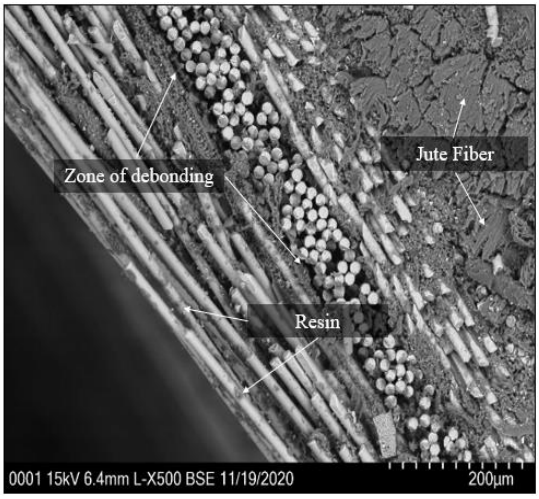
d) Jute + MWCNT exposed



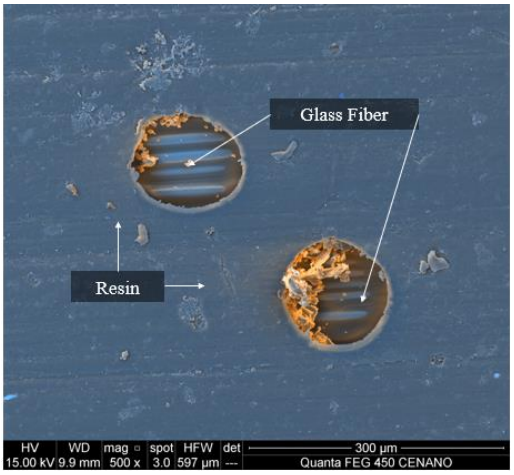
e) Hybrid unexposed



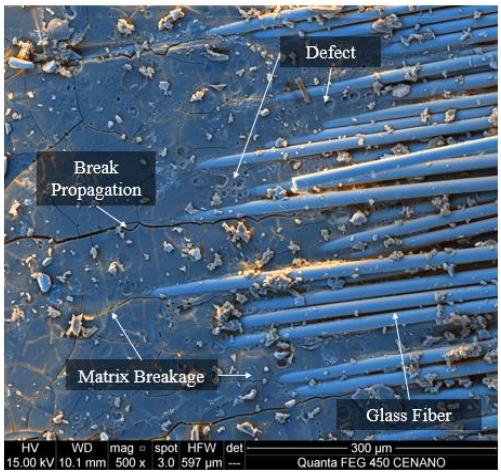
f) Hybrid exposed



g) Hybrid + MWCNT unexposed

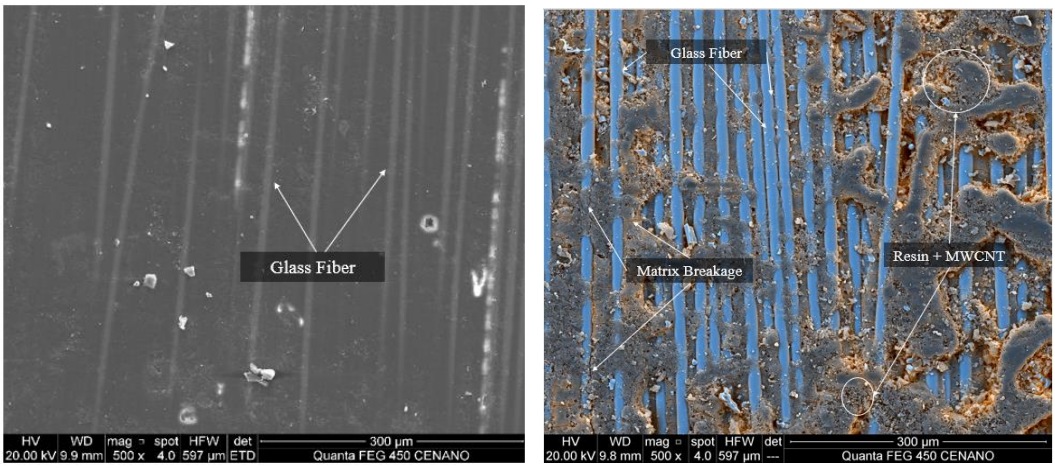


h) Hybrid + MWCNT exposed



i) Glass unexposed

j) Glass exposed



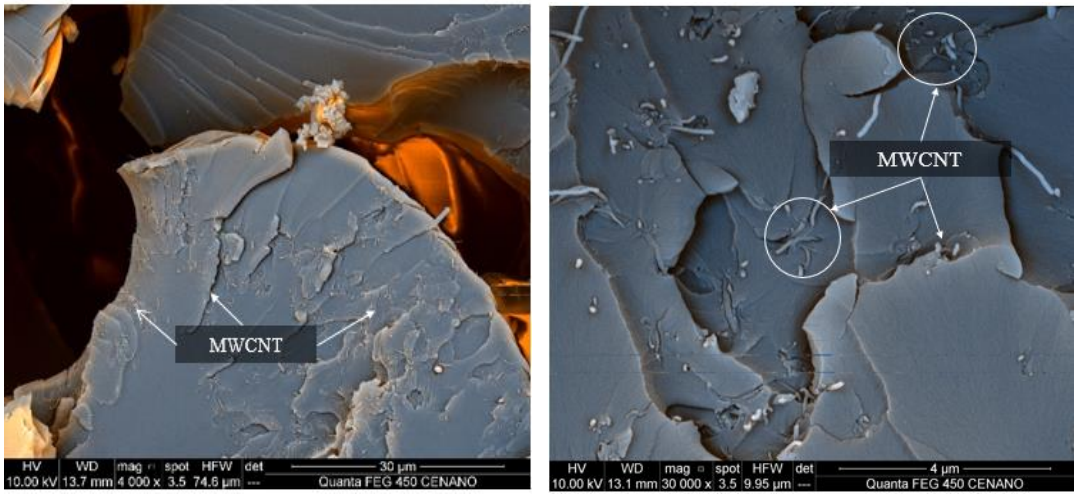
k) Glass + MWCNT unexposed l) Glass + MWCNT exposed

Figure 7. SEM micrographs of unexposed and 500h aged composite tensile specimen fracture surfaces (500x).

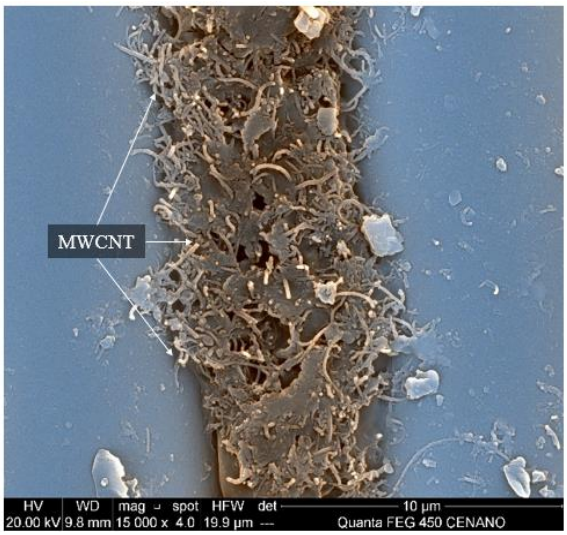
Representative SEM micrographs of the composite specimens as a function of the ageing process are presented in Fig. 7. It can be seen that brittle failure of the jute fibre, voids and internal matrix defects were present in most cases. For the Jute specimens, matrix cracking and higher incidence of fibre pull-out was shown on the fracture surface of the exposed specimens (see Fig. 7b). However, a better fibre/matrix interface was observed for the unaged specimens (see Fig. 7a). Similarly, for the Jute + MWCNT specimens, a better interface as well as less matrix cracking and pull-outs were observed when the unexposed fracture surface is compared to the exposed specimens (see Fig. 7c-d). These observations are likely the cause of the slight decrease in the tensile properties reported in section 3.2. For the hybrid specimens, classical glass fibre longitudinal splitting failure is observed, however, more pronounced matrix cracking and fibre debonding can be observed for the exposed specimens (see Fig. 7e-f). Regarding the hybrid + MWCNT specimens, matrix defects and jute fibre pull-out was observed along with a smoother resin surface (see Fig. 7-g). However, for the exposed specimens, significant matrix cracking can be observed. It is likely that the tensile properties reflect a balance of less pull-out and more matrix cracks for the exposed specimens, balancing the mechanical properties (very low variation, see Fig. 3). Similarly, the glass specimens presented matrix defects for both conditions as well as matrix cracking as a function of the ageing process (see Fig. 7i-j). It was shown in the literature that after the aging process the matrix can present microcracks and loss of resin in the fiber areas.[33] However, given the high mechanical properties of the fibre and the relatively localized environmental

damage (surface boundary layers), the overall mechanical properties did not vary significantly (see Fig. 3). Likewise, for the glass + MWCNT specimens, boundary layer resin debonding was observed for the exposed specimens due to the UV effect when compared to the unexposed specimens.

Figure 8 presents detailed micrographs of the MWCNT fillers in the composite specimens. From Fig. 8a, it can be seen that the resin fracture morphology was globally ductile, with significant multi-level scarps, indicating a complex crack propagation. However, locally, smooth “mirror” (brittle) fracture surface initiation zones can be seen, progressing to mist and hackle zones towards the main scarps, where the fillers acted as crack-blunting mechanisms [44]. For the hybrid + MWCNT specimens (see Fig. 8b), a more brittle/ductile mixed failure mode was observed for the matrix as well as the slender shaped carbon tubes can be seen. Moreover, a good filler/matrix interface can be seen[41]. Finally, from Fig. 8c, a complex structure of entangled (agglomerated) carbon tubes can be seen for the glass + MWCNT specimens. Classically, agglomerations are linked to stress concentrators and lower mechanical properties. However, due to the slender shape of the tubes (high aspect ratio and specific surface area), this is similar to molecular chain crosslinking, where the crack blunting characteristics are elevated. This mechanism is linked to the improved mechanical properties, where even though the resin is more prone to cracking due to exposure, the complex MWCNT architecture acts as significant crack blunting mechanisms, maintaining, and slightly improving the properties.[46]



a) JFRP + MWCNT exposed (4000x) b) Hybrid + MWCNT (30000x)



c) Glass + MWCNTs (15000x)

Figure 8. Detailed micrographs of the MWCNTs modified composite specimens.

Conclusions

In this work, unmodified (control) jute fibre, interlaminar hybrid jute/glass and glass fibre composites and MWCNTs modified composites were exposed to alternating cycles of UV radiation and water spraying in an accelerated aging chamber. The effects of aging on the composites properties were evaluated by tensile and flexural tests. The following conclusions can be drawn:

- The change in colour appearance of the composites studies was evaluated as a function of ageing. The unmodified jute, hybrid and glass fibre composites presented a coloration change which was attributed to photodegradation of samples altered by accelerated ageing. However, this phenomenon was not seen in the composites containing MWCNTs.
- The aging process affected the mechanical properties of the composites studied here in different ways. The jute and jute + MWCNT composites were negatively affected by the ageing process, presenting a decrease in tensile and flexural strength (a decrease in tensile strength of approx. 11% after 500h and 20% after 1000h was found, while the flexural strength was reduced by approx. 34% (500h) and 114% (1000h) for jute and by approx. 18% (500h) and 93% (1000h) for jute + MWCNT). The hybrid composites (unmodified and modified) were less affected by ageing and showed an insignificant change in tensile strength for the

500h and 1000h exposure times. However, an increase in flexural strength for the 500h specimens was found for unmodified hybrid specimens, while for the hybrid + MWCNTs a loss in flexural strength for the 500h and 1000h exposure times was found. The hybrid + MWCNT composites, showed an increase of 9% (500h) and 17%, (1000h) in flexural modulus when compared to the unexposed specimens. The glass fibre composites presented a slight improvement in tensile strength as a function of aging and no significant change in flexural strength. The glass + MWCNTs composite presented an increase in tensile and flexural strength as a function of ageing.

- The incorporation of the nanoparticles had a positive effect on the performance of pure natural fibre composites (the tensile and flexural strength of jute + MWCNT composite increased when compared to unmodified jute composite). However, for the hybrid + MWCNT the tensile and flexural strength slightly decreased when compared to unmodified composites. Finally, for glass + MWCNT composites, the nanotubes had a positive effect only on the properties of the aged samples.
- SEM analysis was used to examine the fracture surfaces of the specimens tested and showed that the aging process affected the fracture and failure mechanisms of the specimens. The SEM images of the aged samples showed the presence of micro cracks and voids in the matrix, in addition to degradation of the material at the fibre/matrix interface. Furthermore, the presence of MWCNTs also indicated changes in the morphology of the composite samples.

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Chapter 5

Effect of MWCNTs on the mechanical and thermal properties of curauá natural fiber reinforced composites

ABSTRACT

The main objective of this study was to investigate the effect of the addition of the Multi-walled Carbon Nanotubes (MWCNTs) on the mechanical and thermal properties of curauá fiber reinforced composites. The MWCNTs were added either to the fiber surface or into the resin matrix as the second reinforcing phase. MWCNT modified curauá fibers as well as raw fibers were characterized by single fiber tensile test, TGA and FTIR analyses. Further, different composite samples: pure curauá, (curauá + MWCNT) + resin, curauá+ (resin + MWCNT) were manufactured by compression molding and tested to get their mechanical and thermal properties. A scanning electron microscopy (SEM) analysis was used to examine the surfaces of the tested fibers. It was found that the addition of MWCNTs on the curauá fibers showed positive effects (an increase in properties was found for the MWCNT-modified fibers and their composites). The addition of MWCNT also increased the thermal stability of natural fibers and composites.

Keywords: Multi-walled Carbon Nanotube (MWCNT), Composites, Thermal properties, Mechanical properties, curauá fiber.

1. INTRODUCTION

The use of natural fibers presents advantages owing to their many positive characteristics, such as: biodegradability, low density, good acoustic isolation and low cost, when compared to the synthetic fibers. However, their main disadvantages are: the variability in fiber quality and absorption of humidity due to the hydrophilic characteristic of the fiber, which leads to low interfacial adhesion between the fiber and the hydrophobic matrix and consequently relatively low mechanical properties [1-3]. Different techniques have been used by researchers to surpass these shortcomings (i.e., chemical treatments of the fibers and the hybridization techniques) [4, 5].

One technique explored in the literature to improve the properties of natural fiber-reinforced composites is the use of filler materials (either on the fiber surface or into the matrix as the second reinforcing phase) [6, 7], [8]. Due to their high specific surface area, good chemical interaction with the hydrophobic matrix and crack arresting capabilities, a synergistic relationship is observed with NFRCs [9]. However, a careful determination of the fabrication and matrix/filler homogenization technique must be done in order to avoid filler agglomeration, which may lead to detrimental effects [10, 11].

Carbon nanotubes (CNTs) are one of the nanofillers used for this purpose and they are divided into three types: single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT) and multi-walled carbon nanotube (MWCNT) [12, 13]. MWCNTs are highly utilized in the modification of polymer composites. These nanotubes consist of multiple layers of rolled graphene sheets, offering exceptional mechanical, electrical, and thermal properties. Due to their unique structure and high aspect ratio, MWCNTs are widely employed as reinforcing agents to enhance the performance and functionalities of polymer composites in various applications. However, a significant challenge in attaining optimal performance lies in the inherent tendency of MWCNT to agglomerate, resulting in inadequate dispersion within the composite, which can have a detrimental effect on the overall performance and mechanical properties of the composite structures.

Several researchers investigated the effect of MWCNTs on the mechanical and thermal properties of composites [11, 12, 14-17]. Zhao et al. [15], investigated the influence of MWCNT mixed in the matrix and fiber for carbon fiber reinforced composites. It was found that the mechanical properties (tensile, flexural and short beam) enhanced with the mixture of the nanotubes in the matrix and fiber. Furthermore, the most promising results

were found for the case of adding the MWCNTs in the fiber. The addition of MWCNTs increased the thermal properties of the composites (the addition of MWCNTs in the resin showed better glass transition (T_g)). Dilfi et al. [17], analyzed the effect of MWCNTs in ramie fiber reinforced composites, using two types of chemical treatments: alkaline and silane to make the coupling of the nanotube with the fiber and reported that the incorporation of nanotubes in the composites showed a significant increase in the mechanical and thermal properties of these materials. Pulikkalparambil et al. [16], investigated the effect of Graphite (Gr) nanoparticles in bamboo fiber reinforced composites. The composites studied were: bamboo fiber reinforced composite (EP/BF), bamboo fiber reinforced composite + 1wt% of Gr (EP/BFGr1), bamboo fiber reinforced composite + 3wt% of Gr (EP/BFGr3), bamboo fiber reinforced composite + 5 wt% of Gr (EP/BFGr5), bamboo fiber reinforced composite + 10wt% Gr (EP/BFGr10). It was found that the mechanical properties (tensile, flexural and hardness) were improved by the addition of nanoparticles. However, this improvement was obtained up to 5% of addition, after reaching this limit the properties were impaired by the process of agglomeration of the nanoparticles. Moreover, the study reports that the addition of nanoparticles presents an increase in the thermal stability of the composites.

Prabhudass et al. [18], investigated the incorporation of MWCNTs in NFRCs. The configurations studied were Bamboo + Epoxy, Kenaf + Epoxy, Bamboo + Kenaf + Epoxy, Bamboo + Kenaf + Epoxy + MWCNT, Bamboo + MWCNT + Epoxy and Kenaf + MWCNT+ Epoxy. The results show that the hybrid composite reinforced by MWCNT presented an improvement in the glass transition temperature (T_g) and a 41% increase in the storage modulus (E') because of the presence of MWCNT.

Neto et al. [11] investigated the effect of MWCNTs in the UV and water spray ageing process of natural fiber and hybrid composites. Jute and glass fiber plain weave bidirectional fabrics were used along with an epoxy resin matrix. The MWCNTs used were 95% purity with 50-100 nm internal diameter and 5-10 nm internal diameter and an average size of 5-10 μm. The compression molding technique was used to fabricate the composite plates. The fillers were first stirred with the resin manually, then sonicated at 100W. The filler weight fraction was 0.6%. The mechanical properties were analyzed via tensile and flexural tests according to ASTM standards. The samples were aged at 500h and 1000h of exposure, respectively. It was reported that for the pure natural fiber composites an improvement in the mechanical properties was observed. However, for the hybrid composites, a slight decrease in tensile and flexural strength was found.

Although several studies on the effect of carbon nanotubes on the mechanical and thermal properties are available in the literature, it have not been fully explored for natural fiber reinforced composites. Therefore, the main objective of this research was to investigate the effect of MWCNT's on the mechanical and thermal properties of curauá natural fibers and their composites. MWCNT coated natural fibers were fabricated, and fiber-reinforced composites were developed using two different methods of filler reinforcement. These methods include direct coating of MWCNTs onto the fibers and incorporating MWCNTs into the resin matrix prior to composite fabrication. Tensile test, FTIR and TGA analysis were used to measure the mechanical, chemical, and thermal properties of the individual curauá fibers (coated with MWCNT and without MWCNT). Tensile and flexural tests were used to measure the mechanical properties of the composites, while the TGA test was used to measure the thermal properties of the composites. A scanning electron microscopy (SEM) analysis was used to examine the surfaces of the tested fibers.

2. MATERIALS AND METHODS

2.1 Materials

The curauá fibers used in this study were supplied in-natura by the Federal Rural University of Amazonia (UFRA, Amazônia, Brazil). The bicomponent epoxy resin HEX 135 SLOW with the 100/33 fraction for epoxy resin/hardener, supplied by Barracuda Advanced Composites (Rio de Janeiro, Brazil) was used as matrix. The MWCNT nanotubes with an average purity of 95%, an external diameter of 50–100 nm, an internal diameter of 5–10 nm and an average size of 5–10 μm were supplied by Nanostructured & Amorphous Materials, USA.

2.2 Specimen Preparation

MWCNT coated curauá fibers were fabricated, and fiber-reinforced composites were developed using two different methods of filler reinforcement. These methods include direct coating of MWCNTs onto the curauá fibers and incorporating MWCNTs into the resin matrix prior to composite fabrication.

2.2.1. MWCNT coated natural fibers

The curauá natural fibers were coated with MWCNTs (see Fig. 1a) by using the following procedure. First the fibers were dried in an oven for 1h at 80ºC. After this step the natural fibers were immersed in a solution of distilled water (100ml) containing carbon nanotubes

for 1.5 h and mixed by the sonification process. Further, the fibers were dried again for 1.5 h at 100 °C.



Figure 1. Schematic of the coating process of curauá fibers with MWCNT.

2.2.2 MWCNT-modified composites

The fabrication process of Curauá + (MWCNT + resin), (Curauá + MWCNT) + resin composite specimens was as follow: the MWCNTs were first added to the neat epoxy resin and mixed manually for a few minutes. Next, the fillers were dispersed in the matrix via the ultrasonication technique. The percentage of MWCNTs (0.6% wt.) and the dispersion procedure followed the author's previous work [19]. The fiber weight percentage was kept at around 30% and the resin + hardener (100:33) at 70% of the final composite weight. The composites were fabricated using the compression moulding technique (the cure was done using a steel mold and a heated plate hydraulic hot press, Solab SL 20 (São Paulo, Brazil). The specimens were cut from the composite plates with the aid of a tungsten carbide saw according to the standard geometry of the ASTM D3039 and ASTM D790 for the tensile and flexural tests, respectively. The specimen geometry for tensile testing was $220 \times 13 \times 5\ mm^3$ and for flexural testing was $180 \times 13 \times 5\ mm^3$.

2.3 Test methods

2.3.1. Fourier-transform infrared spectroscopy (FTIR)

The FTIR technique was used to investigate the possible influences of MWCNT on the functional groups of the curauá fibers. The Spectra-Two model spectrophotometer (Perkin Elmer, USA): FTIR spectroscopy available at Pontifical Catholic University of Rio de Janeiro (PUC – Rio) was used. For all samples, the same mass quantities of 2 mg of fiber were used.

2.3.2. Single fiber test

The single curauá natural fibers were characterized by a tensile test according to ASTM C1557. To produce the specimens a template paper (80 × 40 mm) was used, in which the curauá fiber was fixed by the application of a fast-curing cyanoacrylate adhesive. Thereafter, an adhesive tape was used at the paper's ends to facilitate the attachment of the test piece to the test machine. Fifteen specimens were produced and tested. It is important to highlight that the reduced dimensions of the specimens are due to the difficulty of obtaining single, long fibers. The simple multi-axis hydraulic machine Instron® 5966 with load cell (1 kN) (Norwood, Massachusetts, USA) was used with a test speed of 0.2 mm/min.

2.3.3 Tensile and flexural tests

The universal Instron® 5966 (Norwood, Massachusetts, USA) machine with a 10kN load cell, available in the Laboratory of Adhesive and Composite Materials (LADES) of CEFET/RJ, Rio de Janeiro, Brazil, was used for the tensile and flexural tests. Five samples for each case were tested according to the ASTM D3039 and ASTM D790 standard with a test speed of 1 mm/min.

2.3.3 Thermogravimetric analysis (TGA)

TGA was performed in a NETZSCH TG 209 F3 Tarsus machine (Netzsch-Gerätebau GmbH, Germany). Samples of approximately 8-10 mg for fiber and 20-30 mg for composite samples, were used to make the measurements. An alumina (Al_2O_3) crucible was used. Each sample was tested in the temperature range of 30 °C – 600 °C at a constant heating rate of 10 °C / min under nitrogen atmosphere (20 ml min^{-1}) according to ASTM E1131.

2.3.2 SEM analysis

Quanta FEG 450 microscope available at Nanotechnology Characterization Laboratory (CENANO) of the National Institute of Technology (INT), Rio de Janeiro, Brazil (an acceleration of 10KV) was used for the SEM analysis of the surfaces of the fibers. All samples were coated with a platinum layer with surface density equal to 21.53 g/cm^3.

3. RESULTS AND DISCUSSION

3.1 Mechanical and thermal properties of fibers

3.1.1. FTIR

The curauá fiber and MWCNT- modified curauá fiber were characterized by FTIR spectroscopy to confirm the reactions occurring between the MWCNT and curauá fiber, and the spectra are shown in Figure. 2. The curauá fiber presents absorption bands spectrum for lignocellulosic materials: cellulose (3327, 2905, 1636, 1318, 1012, and 894 cm^{-1}), lignin (1603, 1510, 1423, 1364, and 1248cm^{-1}), hemicelluloses (1724, 1154, and 1021cm^{-1}) [17, 20]. The absorption bands of the curauá fiber spectrum can be seen as: 3379 cm^{-1}, which is related to the elongation of OH groups present in cellulose and water. The 2916 cm^{-1} band can be attributed to the symmetrical and asymmetrical stretching (C–H) of the aliphatic chain, 1736 cm^{-1} corresponding to the acid elongation vibration (C=O); 1430 cm^{-1} (aliphatic C–H vibration) and 1110 cm^{-1} from the elongation vibration of the ether groups [21]. Other bands refer to the existence of high content of oxygen functional groups on the MWCNT surface, such as (–C–O–C) groups—oxides of structural, oxygen bridges, etc.) are present in the FTIR transmission spectra of multiwall carbon nanotubes [22]. As a result of functionalization, the decreasing relative intensity of the –OH band assigned to the associated water (3289 cm^{-1}) and the appearance of an additional peak (near 3000 cm^{-1}) confirms the presence of various hydroxyl at the carbon surface. Moreover, the decrease in intensity of peaks corresponds to the -OH stretching and bending vibrations also suggested the grafting of CNT onto the surface of curauá fiber. The peaks observed at 1688 cm^{-1} and 1490 cm^{-1} in the MWCNT-fiber cases were due to the carbon skeleton vibrations of MWCNT [22]. The findings indicate that there have been alterations in the relative intensities of certain bands, indicating a possible connection between the MWCNT molecule and functional groups mentioned earlier. This connection seems to have caused a significant reduction in the intensities observed throughout the spectrum. The experimental results demonstrate notable variations in the relative intensities of specific bands, suggesting a potential binding interaction between the MWCNT molecule and the functional groups. These interactions appear to have induced a substantial attenuation in the overall intensity of the spectrum.

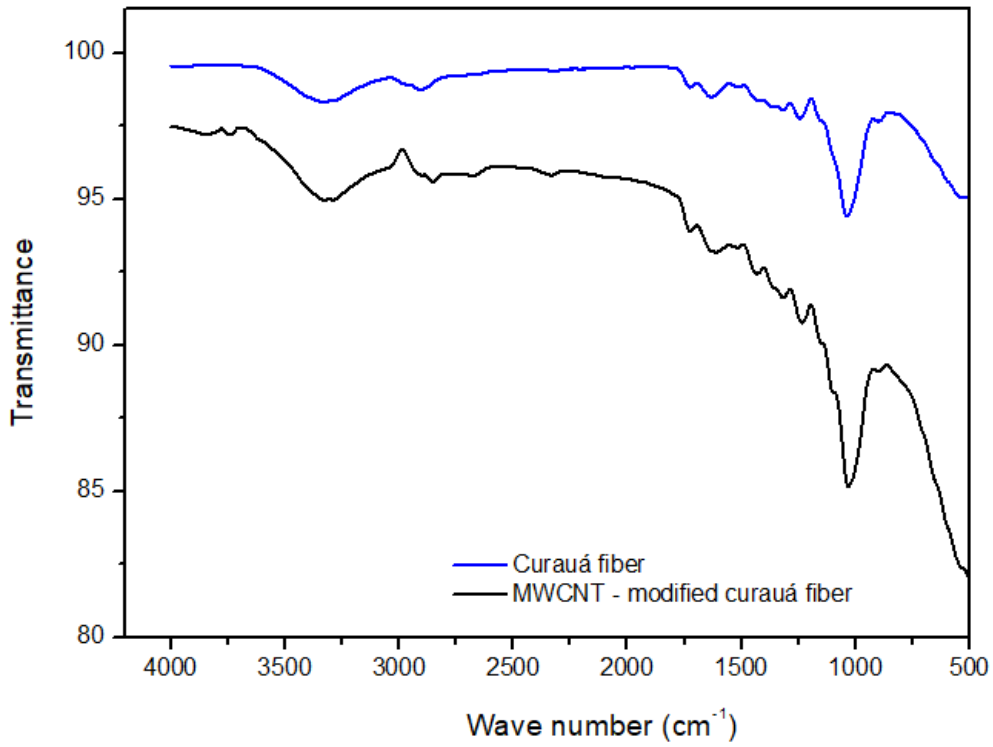
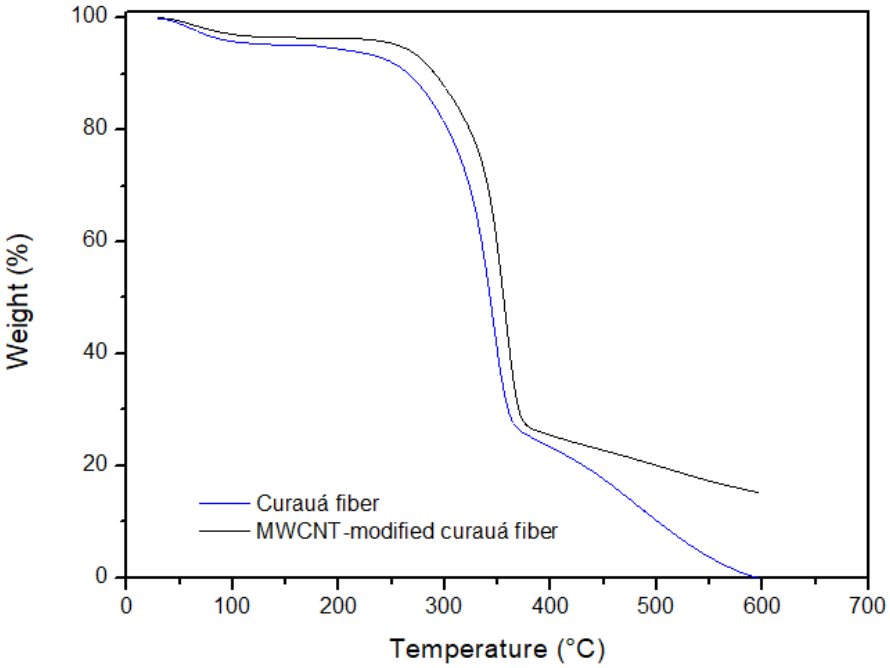


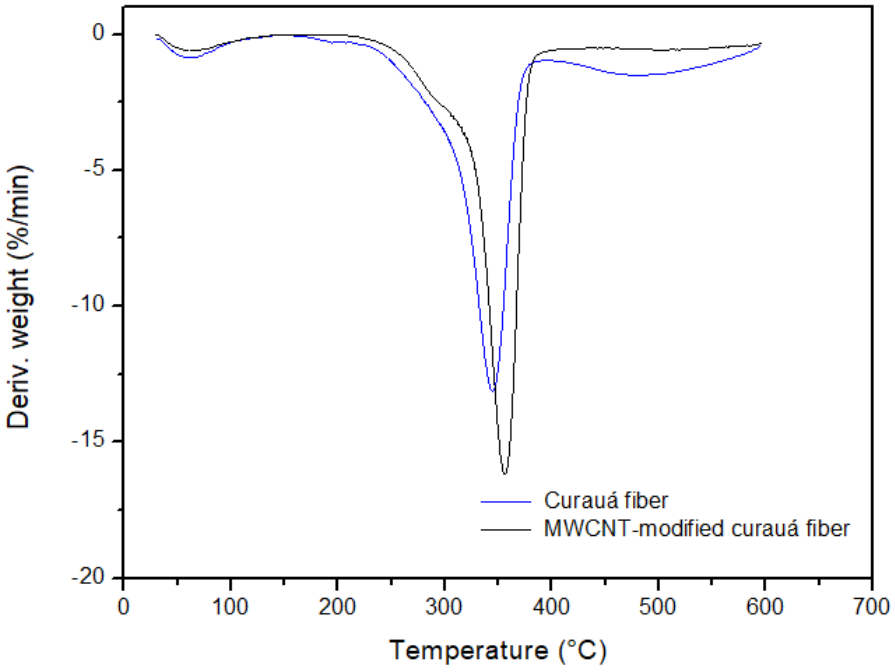
Figure 2. FTIR spectra of curauá fiber and MWCNT-modified curauá fiber.

3.1.2. Thermal properties of fibers

TGA analysis was performed to determine the influence of nanotubes addition on thermal stability and decomposition process of the fibers studied. Curauá fiber and MWCNT-modified curauá fibre specimens were analyzed, and the results are presented in Fig.3a-b and Table 1. The initial decomposition temperature (T_{IDT}), final decomposition temperature (T_{FDT}), derivative thermogravimetric (T_{DTG}) and char residue were extracted from the TG and DTG curves for each case studied. These parameters describe the thermal stability of the composites [23]. The curauá fiber presented mass loss at $T_{100°C}$ higher than the MWCNT-modified curauá fiber, with the respective values of 4.22% and 2.96%. The literature shows that between 60 - 150 °C, the evaporation of moisture retained in the natural fiber take place [23]. On the other hand, the T_{IDT} of MWCNT-modified curauá showed an increase in thermal stability when compared to unmodified curauá fiber, respectively, 331°C and 313°C (see Fig.3a). Finally, the residual rate of MWCNT-modified curauá indicated a considerable increase by the presence of MWCNTs (Table 1).



a)



b)

Figure 3. Thermogravimetric analysis data for the curauá fiber: (a) TG curves; (b) DTG curves.

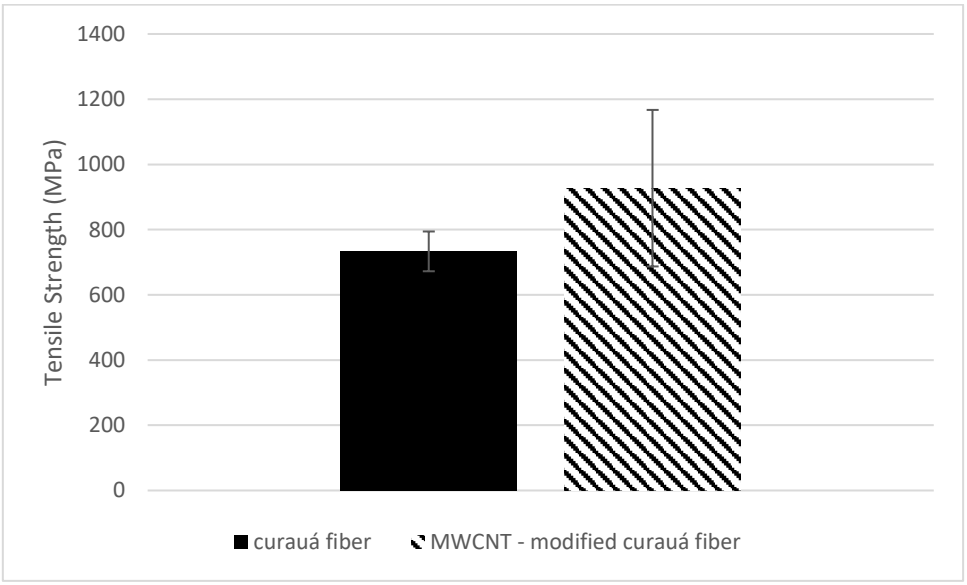
Table 1. TGA analysis data.

Fiber	$T_{(100\ °C)}$ (%)	T_{IDT} (°C)	T_{FDT} (°C)	Residual Mass (%)	T_{DTG} (°C)
Curauá	4.22	313.1	359.8	0.04	344.8
MWCNT-modified Curauá	2.96	331.1	369.5	15.2	356.3

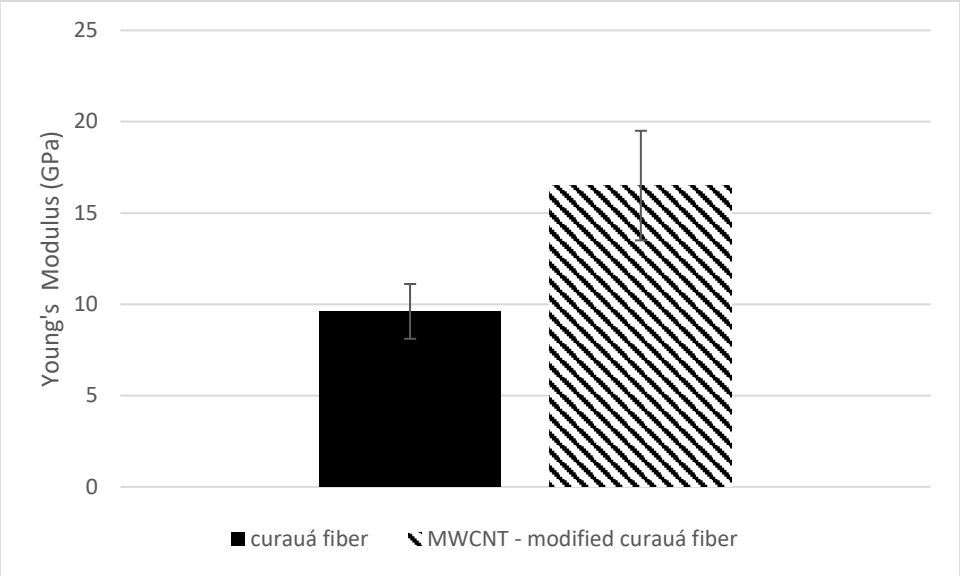
3.1.3 Single fiber test

The addition of MWCNTs nanoparticles affected the tensile properties of curauá fibers (Fig. 4a-b). It can be seen that MWCNT-modified curauá fiber showed an increase in tensile strength of approx. 26% and approx. 21% in Young's modulus when compared to pure curauá fiber. This is explained by the fact that the MWCNTs presented good adhesion on the surface of the curauá fibers (the MWCNTs were bonded to many individual fiber fibrils as can be seen in Fig. 10b).

Lima et al. [24], showed that natural fibers have different characteristics among them, such as lumen size, wall thickness, cell quantities and chemical treatment effectiveness. These factors affect the mechanical properties of these materials. It was shown in the literature that curauá fibers with smaller lumen diameter, higher percentage of cellulose presents better performance than jute, sisal, and rami fibers [20, 25, 26].



a)



b)

Figure 4. Tensile data of natural fiber as a function of MWCNT coating: a) Tensile strength and b) Young`s modulus.

3.2 Mechanical and thermal properties of composites

3.2.1 Thermal properties

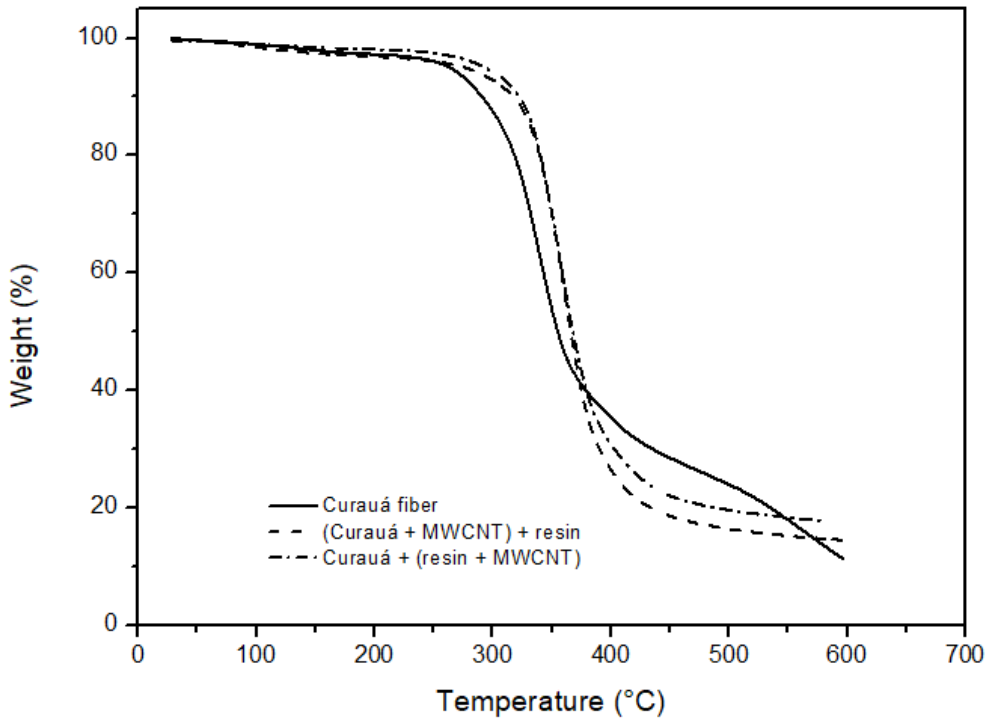
TGA analysis was performed to determine the influence of nanotubes addition on the thermal stability and decomposition process of the composites studied. The initial decomposition temperature (T_{IDT}), final decomposition temperature (T_{FDT}) and char residue of the studied composites were extracted from the TG curves for each case studied. These parameters describe the thermal stability of the composites and the results are presented in Fig. 5a-b, and Table 3. At $T_{100°C}$, the unmodified curauá fiber composite specimens presented a mass loss higher (1.04), compared to the (Curauá + MWCNT) + resin (0.46) and Curauá + (resin + MWCNT specimens (0.96)). It was shown in the literature that between 60 - 150 °C, the evaporation of moisture retained in the natural fiber take place [23]. The incorporation of MWCNT in composites helps to reduce the voids between the fibre-matrix interfaces, limiting the water absorption capacity.

The addition of MWCNT in the composites either to the fiber surface or into the resin matrix as the second reinforcing phase increased the maximum degradation temperature when compared to the pure curauá composite specimens as expected. For instance, the values of T_{IDT} of curauá + (resin + MWCNT) and (curauá + MWCNT) + resin composite

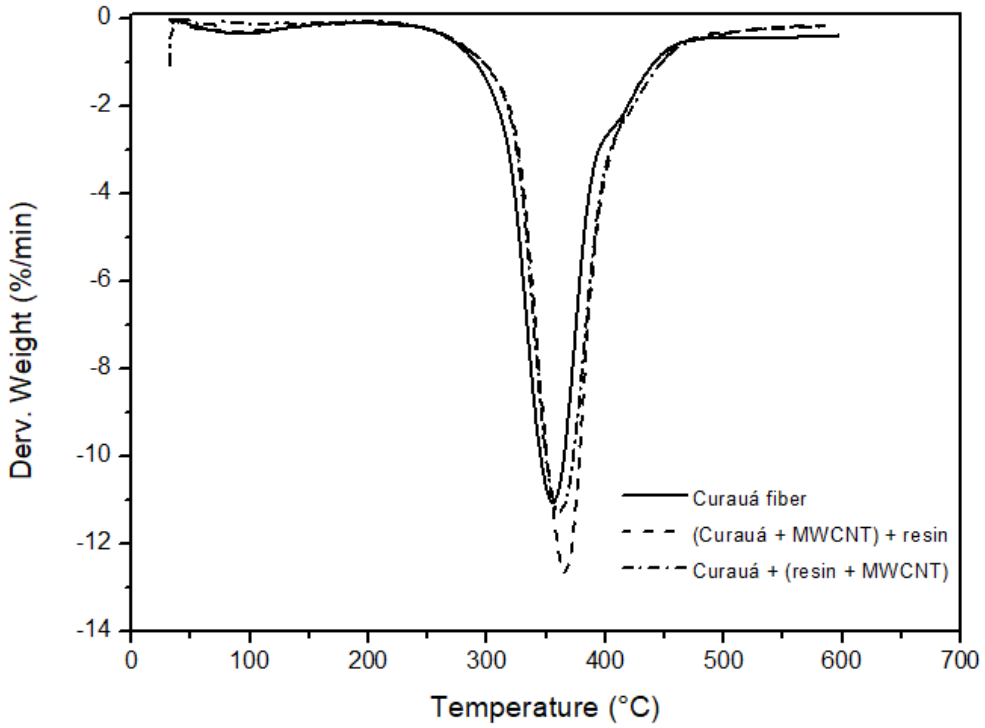
samples was 326.8°C and 331.1 °C, respectively when compared to unmodified curauá composite specimens (304.3 °C). This is in accordance with the literature that shows that nanotubes increase the thermal properties of composites [27].

Another important aspect is the increase in the residual mass of the MWCNT filled composites compared to unmodified samples, due to the incorporation of the particles in the composites (i.e the residual mass (%) was 11.26 for the unmodified curauá fiber composite specimens, 14.43 (Curauá + MWCNT) + resin and 17.50 Curauá + (resin + MWCNT).

Finally, the DTG curve shows the maximum rate of peak thermal decomposition, and fiber constituents are indicated by peaks in each degradation range. For instance, the curauá fiber composites present three stages of degradation. The first stage is related to water loss by natural fiber (60–100 °C). The second stage is related to the loss of the main constituents of the fibers: hemicellulose, cellulose, and lignin (200–500 °C). Finally, the last stage of degradation is the formation of active coal as a form of residue. The value of T_{DTG} (°C), was 338.6 for the unmodified curauá fiber composite specimens, while for (Curauá + MWCNT) + resin was 362.2 and 355.8 for Curauá + (resin + MWCNT specimens.



a)



b)

Figure 5. Thermogravimetric analysis data for the curauá fiber composite: (a) TG curves; (b) DTG curves.

Table 2. TGA analysis data of the composites studied.

Composite	$T_{(100\,°C)}$ (%)	T_{IDT}(°C)	T_{FDT}(°C)	Residual Mass (%)	T_{DTG} (°C)
Curauá	1.04	304.3	369	11.26	338.6
(Curauá + MWCNT) + resin	0.46	331.1	388.6	14.43	362.2
Curauá + (resin + MWCNT)	0.96	326.8	389	17.50	355.8

3.2.2 Mechanical Properties

Tensile Test

Figure 6 shows representative tensile stress-strain curves of the composites studied. From these curves the tensile properties (tensile strength and Young's modulus) were calculated and are summarized in Fig. 7(a-b).

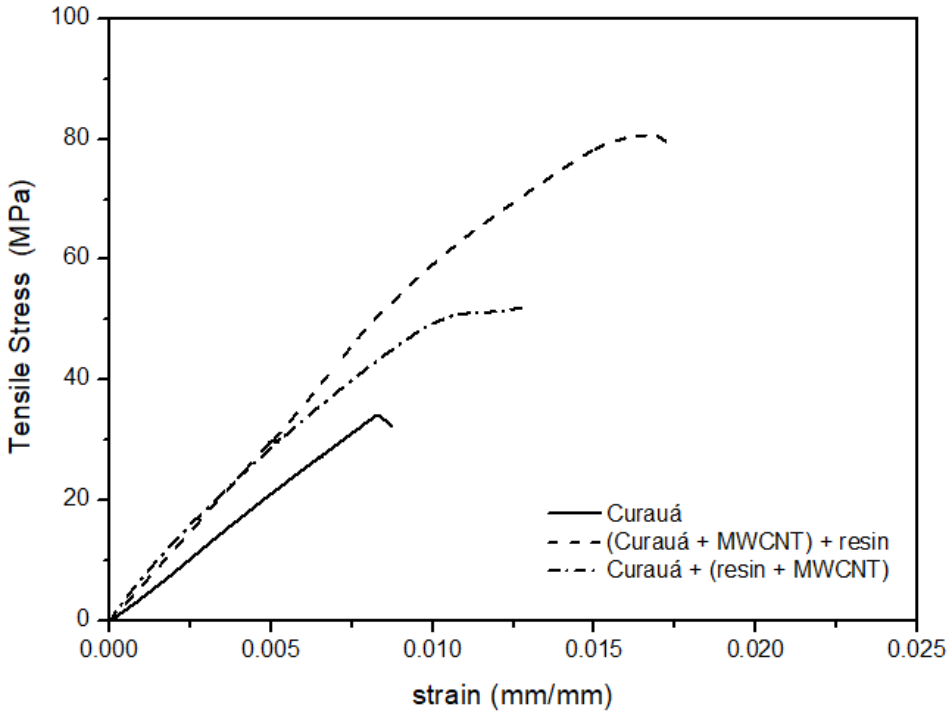
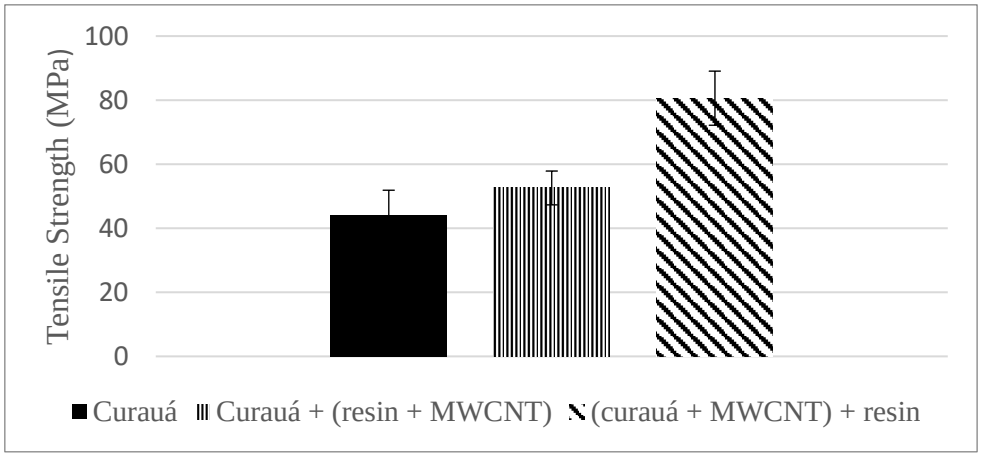
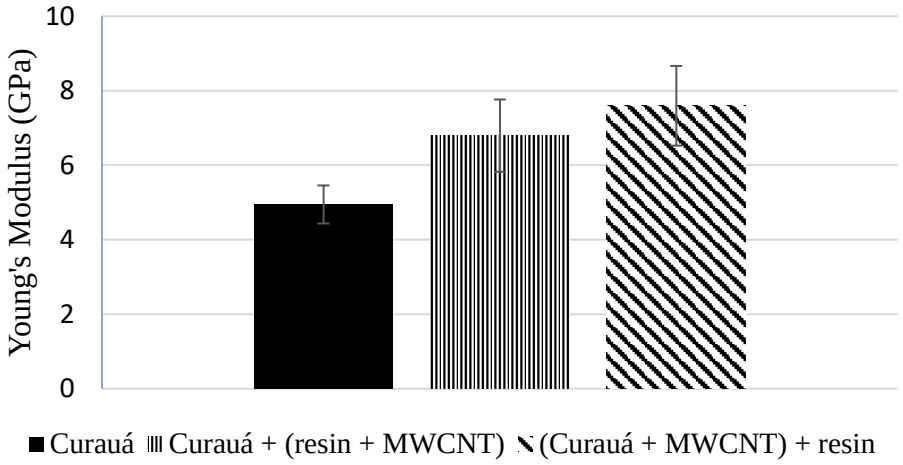


Figure 6. Representative tensile stress-strain curves of the composite specimens.



a)



b)

Figure 7. Average tensile properties as a function of reinforcement methods: a) Tensile strength and b) Young's modulus.

It can be seen that the (curauá + MWCNT) + resin composites an increase of approx. 54% when compared to the unmodified curauá composite specimens, respectively. This can be explained by the fact that the roughness of the curauá fiber seen on SEM (see Fig.10) positively influences the tensile properties of the (curauá + MWCNT) + resin specimens. The curauá + (resin + MWCNT) composites presented an increase of approx. 19% in tensile strength. It was shown in the literature that the incorporation of MWCNT in the matrix reduces the voids found between the fiber-matrix and improves the transfer of loads between the reinforcement and matrix.

Similar to the tensile strength, the Young's modulus was also positively affected by the addition of nanoparticles. For instance, the (curauá + MWCNT) + resin and curauá + (resin + MWCNT) composites showed an increase in Young's modulus, respectively by approx. 54% and 37 %. Yan et. al. [28], reported that carbon nanotubes can strongly adhere to the surface of the fibers and also enter the space between the fibrils of the fibers. Furthermore, Van der Waals forces and the expansion effect can strengthen the interaction between fibers and nanotubes.

Flexural Test

Figure 8 shows representative flexural stress-strain curves of the composite studied. From these curves the flexural properties (flexural stress and flexural modulus) of the composites were calculated and are summarized in Fig. 9 (a-b).

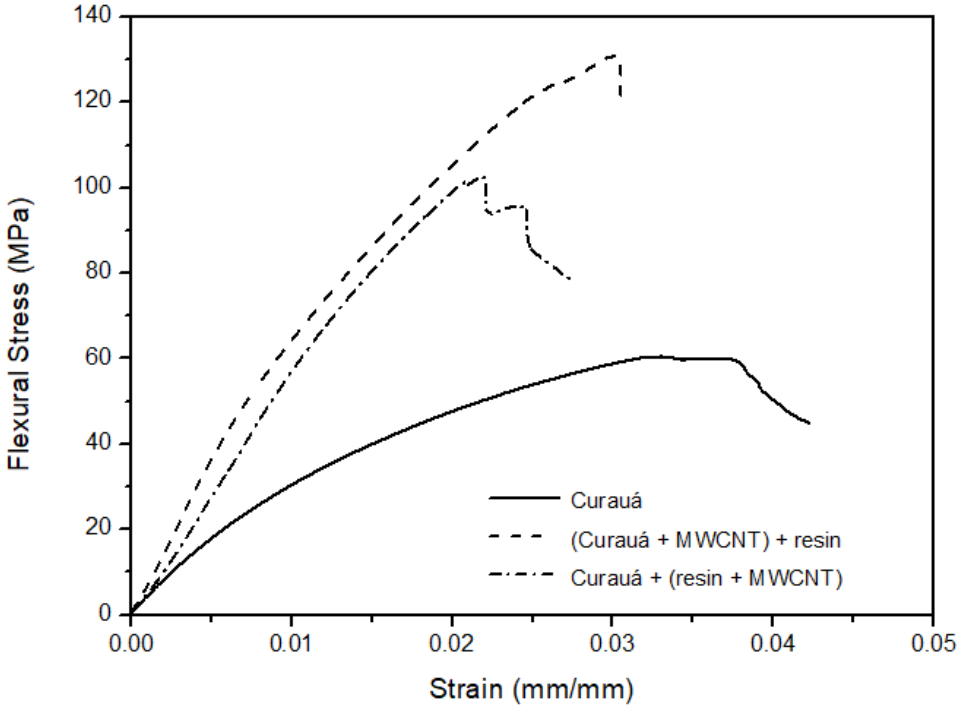
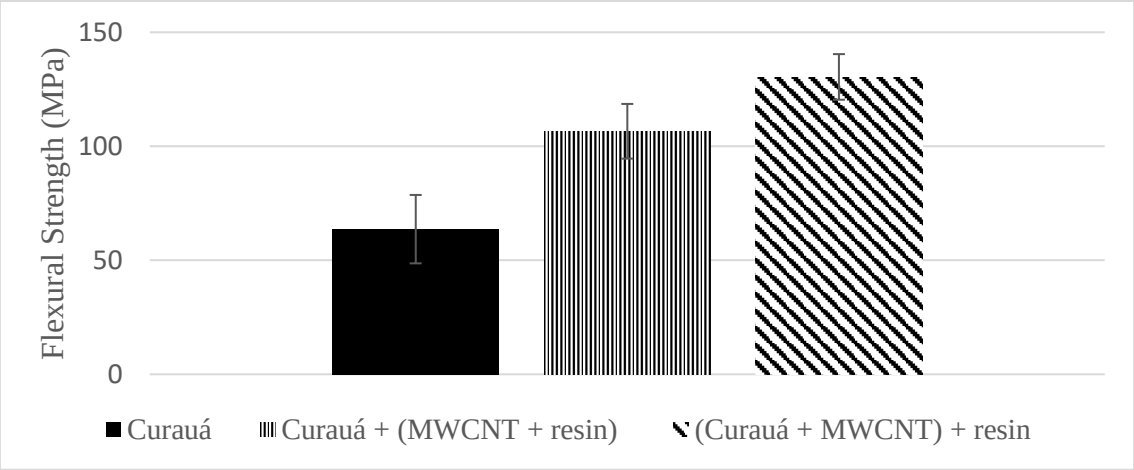


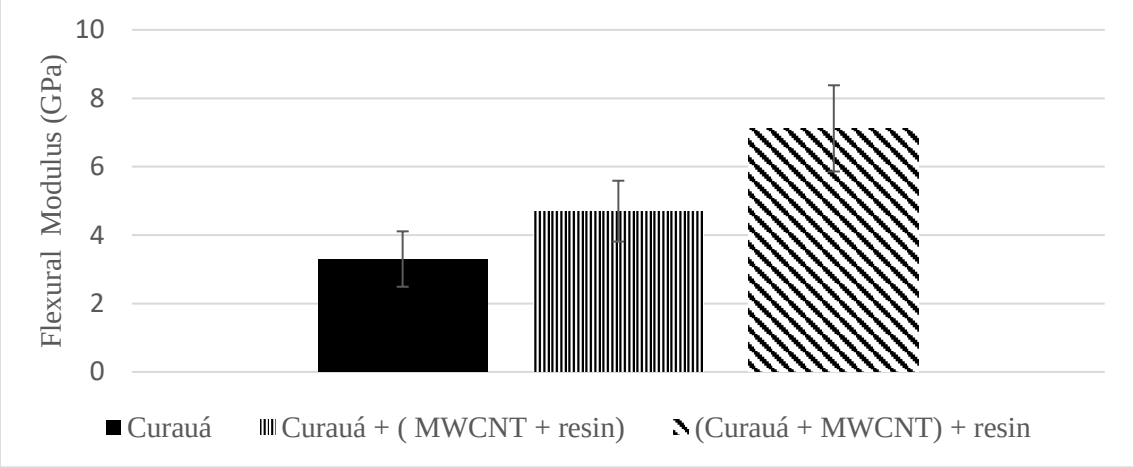
Figure 8. Representative flexural stress-strain curves of the curauá fiber composite specimens.

The addition of MWCNT to the fiber and the matrix of the composites affected the flexural properties of composites. Both, the curauá + (resin + MWCNT) and (curauá + MWCNT) + resin composites presented higher stiffness values when compared to the unmodified curauá composite. The curauá + (resin + MWCNT) composite specimens showed an increase of approx. 67% in flexural strength, while the (curauá + MWCNT) + resin composite specimens indicated an increase of approx. 105% when compared to the unmodified curauá composite, respectively. It was shown in the literature that the incorporation of filler in the matrix reduces the formation of voids found between the fiber-matrix, improving the transfer of loads between the reinforcement and matrix.

Similar to the flexural strength, the flexural modulus was also affected by addition of MWCNT (see Figure 9b). The flexural modulus of the curauá + (resin + MWCNT) composite increased by approx. 42%, while for the (curauá + MWCNT) + resin increased by approx. 116%. The literature demonstrates that integrating fillers into the matrix effectively mitigates void formation between the fiber-matrix interface, thereby enhancing load transfer efficiency between the reinforcement and matrix [11]. The presence of nanoparticles delays the onset of cracking in the polymer, in addition to increasing the composite's flexural strength [29].



a)



b)

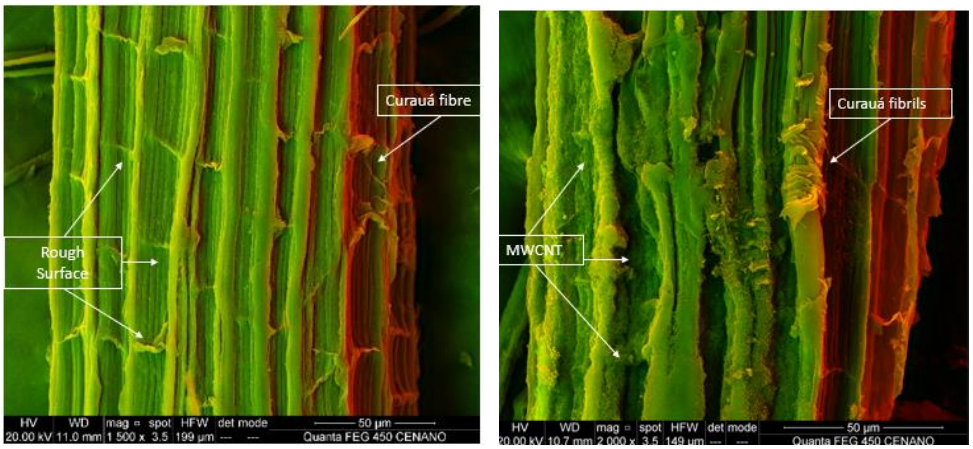
Figure 9. Average flexural properties as a function of reinforcement methods: a) Flexural strength and b) Flexural modulus.

To summarize, the mechanical properties of polymer composites modified with MWCNT are greatly influenced by the interactions between the nanofillers and the polymer matrix.

SEM analysis

In order to investigate the effect of the filler reinforcement on the morphology of the fibers, a SEM analysis was performed on the single fibers. Figure 10 presents the representative SEM images of the curauá fiber morphology for both the neat and modified cases (see Fig. 10a and b). The curauá fibers present a rough yet organized in a star-shaped (cross-sectionally, see Fig. 10a) geometry, where deep grooves are separated by

fiber surface protrusions (microfibrils). This is responsible for the significant mechanical interlocking between the fiber and the matrix [24] (see Fig. 11), the opposite is observed for natural fibres with smooth surfaces such as jute [30]. Patches of MWCNT agglomerations are visible and this is due to the high tendency of nano-scale fillers to clump together [31], however, they tend to be within the grooves, potentially adding to the already significant mechanical interlocking of the fiber/resin interface. This can be clearly seen in Fig. 11, where the partial pull-out of a coated curauá fiber is visible on the SEM failure surface. The curauá fiber cross-section morphology imprint is visible on the resin matrix failure as well as a part of the fiber that was left bonded, indicating good adhesion. The side of the fiber with the superior adhesion likely had more MWCNT deposited within the grooves. These observations are in agreement with the general mechanical properties found in this research, where the MWCNT-modified Curauá specimens presented the most promising results.



a) b)

Figure 10. a) Curauá fiber and b) MWCNT-modified curauá fiber.

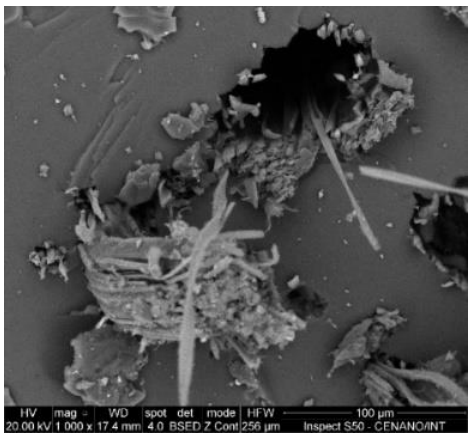


Figure 11. MWCNT-modified curauá composite fiber failure.

Conclusions

In this work, the effect of the addition of the MWCNTs on the mechanical and thermal properties of curauá fiber reinforced composites was investigated. MWCNT coated curauá fibers were fabricated, and fiber-reinforced composites were developed using two different methods of filler reinforcement. These methods include direct coating of MWCNTs onto the fibers and incorporating MWCNTs into the resin matrix prior to composite fabrication. The following conclusions can be drawn:

- The incorporation of the nanoparticles onto the curauá fiber had a positive effect on the tensile properties (The MWCNT-modified curauá fiber presented an increase in tensile strength by approx. 26% and Young's modulus by approx. 21% when compared to unmodified curauá fiber).
- The mechanical performance of curauá fiber composites also was improved by the addition of the MWCNTs onto the fibers or into the resin matrix. The tensile and flexural properties of curauá + (resin + MWCNT) and (curauá + MWCNT) + resin composites increased when compared with unmodified curauá composite specimens. The enhancement of the mechanical properties of the MWCNT modified curauá fiber composites is attributed to improved and strong interfacial interaction between the MWCNTs and the curauá fiber.
- The addition of MWCNT in natural fibers and composites improved the thermal properties. The T_{IDT} e T_{FDT} increasead with the presence of MWCNTs when compared to pure natural fiber specimens. The T_{DTG} values also demonstrate that the MWCNT cause an improvement in the thermal stability of the natural fiber and composites.

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Chapter 6

Conclusions and future works

6.1 Conclusion

In this thesis the effect of carbon nanofillers in composites reinforced by natural fibres and epoxy resin were characterized. In the published articles, the mechanical and thermal properties of nanocomposites with carbon nanotubes were investigated. The effect of durability on natural, hybrid and synthetic fibres reinforced composites were studied as well as the article submitted to investigate the effect of the addition of the Multi-walled Carbon Nanotubes (MWCNTs) on the mechanical and thermal properties of curauá fiber reinforced composites. The main conclusions of this work can be summarized below:

The mechanical and thermal properties of nanocomposites are highly dependent on the concentration and dispersion of carbon nanotubes in the nanocomposites. Furthermore, sonicator power parameters have a significant impact on the traction, TGA and DSC results. In the second article, a study was carried out on the combination of parameters: concentration of nanotubes and sonication power applied to the nanocomposites. This combination determines which percentage and power had the best mechanical and thermal performance. It was found that the most promising parameters were with 75W sonication power output and 0.6% wt. MWCNTs content.

In the third article, the effect of durability of natural, hybrid synthetic fibre reinforced composites were investigated. Moreover, the effect of carbon nanotubes was also studied, as the addition of these nanofillers has a significant impact on the mechanical properties and inhibits the color change of the composites, the concentration and potency for mixing the carbon nanotube used were defined in article second. It was observed that the incorporation of nanotubes increased the mechanical properties of nature composites, however the degradation effect was more intense in the composite without MWCNT than the composite with the presence of MWCNT. However, for the hybrid + MWCNT the tensile and flexural strength slightly decreased when compared to unmodified

composites. Finally, for glass + MWCNT composites, the nanotubes had a positive effect only on the properties of the aged samples.

In the fourth article, the effect of the addition of the Multi-walled Carbon Nanotubes (MWCNTs) on the mechanical and thermal properties of curauá fibre reinforced composites was investigated. Moreover, the method of addiction of carbon nanotubes was also studied, as the addition of nanofillers has significant impact on the mechanical and thermal properties of the composites. The curauá fibre showed great compatibility with carbon nanotubes and, the method that presented the best result was the direct coating of the MWCNT's on the fibre. The presence of carbon nanotube by both methods showed an increase in the thermal properties of the composites. The concentration and potency for mixing the carbon nanotube used were defined in article 1. The curauá fiber has excellent properties and it may be interesting to replace the commercial jute fibre in the third article. However, this fiber has not yet reached a mature commercial scale.

6.2 Future works

The composites reinforced by natural fibres and nanofiller presents some little explored themes, some proposals will be discussed below.

The study of nanofiller dispersion in composites reinforced by natural fibres, could define which natural fibres have good compatibility with the type of nanofiller used and the dispersion method. Furthermore, another area that nanofillers can be applied as reinforcements of 3D filaments. Another proposed study is the influence of nanofiller on mechanical and thermal properties, requested to delay the effect of degradation caused by hostile environments (salt spray, oil and other aggressive media to composites).