INSTITUTO POLITÉCNICO DE BRAGANÇA

Retting of natural fibers for the manufacturing of filaments

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Dissertation for the degree of **master's in mechanical engineering**

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“If in doubt, Flat out”

Colin McRae

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Resumo

Nos últimos anos, a necessidade imperiosa de mitigar a dependência de polímeros derivados do petróleo, aliada à crescente exigência por materiais ambientalmente sustentáveis, tem fomentado de forma significativa a investigação no domínio dos compósitos biodegradáveis. Entre os biopolímeros disponíveis, o ácido poliláctico (PLA) evidencia-se pela sua proveniência renovável, biodegradabilidade e propriedades mecânicas superiores face a outros polímeros sustentáveis. Contudo, o PLA apresenta limitações intrínsecas, nomeadamente fragilidade e reduzida resistência ao impacto, características que podem ser atenuadas mediante a incorporação de fibras naturais como elementos de reforço.

As fibras lignocelulósicas naturais têm vindo a assumir uma preponderância crescente no setor industrial, devido à sua relação otimizada entre resistência e massa volúmica, elevada biodegradabilidade e impacto ambiental quando comparadas com as fibras sintéticas. Alguns exemplos de fibras naturais muito utilizadas são as do cânhamo e do linho O cânhamo, em particular, distingue-se pela sua robustez estrutural e elevada rigidez, sendo amplamente utilizado nas indústrias automóvel e da construção. O linho, por outro lado, estingue-se pela sua flexibilidade e notável capacidade de absorção a impactos.

O presente estudo visa a investigação, caracterização e otimização da produção de fibras naturais de cânhamo, linho e castanha para a formulação de filamentos destinados à manufatura aditiva, com particular foco na impressão tridimensional. Será realizada uma análise holística das propriedades físicas, químicas e mecânicas dos compósitos obtidos, com o intuito de aferir a viabilidade da substituição de reforços convencionais por fibras naturais. Os resultados do trabalho desta tese contribuirão para o desenvolvimento de soluções compósitas inovadoras, sustentáveis e de elevado desempenho, promovendo alternativas tecnologicamente avançadas e ambientalmente responsáveis em setores industriais estratégicos.

Palavras-chave: *Compósitos biodegradáveis, ácido poliláctio (PLA), fibras lignocelulósicas, cânhamo, castanha, impressão tridimensional*

Abstract

Currently, the persistent need to reduce dependence on petroleum-based polymers, combined with the growing demand for environmentally sustainable materials, has significantly encouraged research into biodegradable composites. Among the available biopolymers, polylactic acid (PLA) stands out for its renewable origin, biodegradability and superior mechanical properties compared to other sustainable polymers. However, PLA has intrinsic limitations, namely instability and reduced impact resistance, characteristics that can be mitigated by incorporating natural fibers as reinforcement elements.

Natural lignocellulosic fibers, namely those from hemp, flax and chestnut, have been assuming increasing preponderance in the industrial sector, due to their optimized ratio between strength and density, high biodegradability and low environmental impact when compared to synthetic fibers. Hemp stands out for its structural robustness and superior rigidity and is widely used in the automotive and construction industries. On the other hand, flax present characteristics, such as flexibility and remarkable absorption capacity.

The present study aims to investigate and optimize the production of natural fibers from hemp, flax and chestnut for the formulation of filaments intended for additive manufacturing, with a particular focus on three-dimensional printing. A holistic analysis of the physical, chemical and mechanical properties of the composites obtained will be carried out, with the aim of assessing the feasibility of replacing conventional reinforcements with natural fibers. The results of this work will contribute to the development of innovative, sustainable and high-performance composite solutions, promoting technologically advanced and environmentally responsible alternatives in strategic industrial sectors.

Keywords: *Biodegradable composites, polylactic acid (PLA), lignocellulosic fibers, hemp, chestnut, three-dimensional printing*

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Abbreviations

CIMO- Centro de Investigação de Montanha

ESTIG- Escola Superior de Tecnologia e Gestão de Bragança

IPB- Instituto Politécnico de Bragança

PLA- Polylactic Acid

CHAPTER 1: INTRODUCTION

1.1 FRAMING

In recent years, the imperative to reduce dependence on petroleum-based polymers, coupled with the growing demand for environmentally sustainable materials, has significantly driven research in the field of biodegradable composites. Among the available biopolymers, polylactic acid (PLA) stands out due to its renewable origin, biodegradability, and high mechanical properties compared to other sustainable polymers [1]. However, PLA exhibits certain intrinsic limitations, notably brittleness and low impact resistance, characteristics that can be mitigated through the incorporation of natural fibers as reinforcing elements [2].

Composite materials can be conceptualized as multiphase systems that exhibit a strong correlation with the properties of their constituent phases [3]. Generally, they consist of two primary phases: the matrix phase and the reinforcement phase. In the current landscape, synthetic materials such as glass fiber and carbon fiber are predominantly used as reinforcement, while the matrix is typically composed of thermosetting resins, namely, epoxy and polyester [4]. Despite their outstanding properties, the use of synthetic fibers and reinforcements in composites involves numerous negative externalities, both environmental and economic [3].

As an environmentally viable alternative to synthetic fibers, the use of natural fibers has gained prominence particularly those whose properties are already well established, such as flax [5]. Lignocellulosic natural fibers exhibit a unique set of attributes, including abundance, biodegradability, low density, non-toxic nature, reduced abrasiveness to processing equipment, and favorable mechanical properties, all while offering significantly lower costs. In this context, they are emerging as excellent candidates to replace current synthetic fibers, especially in strategic sectors such as the automotive and construction industries [5].

Natural fibers have been assuming an increasingly prominent role in the industrial sector, due to their favorable strength-to-density ratio, high biodegradability, and reduced environmental impact compared to synthetic fibers [6]. Hemp has been the subject of numerous scientific studies due to its superior mechanical strength and stiffness and is widely adopted in the automotive and construction sectors [7]. Flax, in turn, is distinguished by its flexibility and impact absorption

capacity, while fibers derived from chestnuts represent an emerging solution with still-unexplored potential, given their lignocellulosic structure like that of other conventional natural fibers [8].

In this context, the work developed in this dissertation aims to explore and optimize the production of natural fibers from hemp, flax, and chestnut. It proposes a holistic evaluation of the physical, chemical, and mechanical properties of the resulting composites, assessing the feasibility of replacing conventional reinforcements with natural fibers, thus contributing to the development of innovative, sustainable, and high-performance technological solutions.

1.2 PROPOSED OBJECTIVES

The main objective of this dissertation is the development of an innovative process for the extraction and integration of natural fibers, namely hemp, flax, and chestnut, into the formulation of filaments for additive manufacturing. Moreover, it will explore and optimize methodologies for the extraction, processing, and incorporation of these fibers into compatible polymer matrices, ensuring a functional, sustainable, and efficient composite for three-dimensional printing applications.

To achieve the proposed objectives, this study will be developed in three main phases:

1) Initially, natural fibers will be extracted from their respective raw materials using chemical and mechanical methods designed to preserve their structural integrity and mechanical properties.

2) Subsequently, tensile tests will be conducted on the extracted fibers to evaluate their mechanical behavior.

3) Finally, a comparative analysis of the extracted fibers will be conducted to identify which extraction method best preserves the desirable characteristics for future applications.

This experimental cycle will be repeated for the three primary fiber sources, hemp, flax, and chestnut, allowing for a comprehensive comparative analysis of the mechanical, thermal, and structural properties of the produced filaments. In this way, it is expected to contribute to the development of innovative and sustainable alternatives to conventional materials used in additive manufacturing, promoting eco-friendly and technologically advanced solutions in the composites sector.

1.3 CONTENT AND ORGANIZATION

This dissertation is structured into six main chapters, organized logically and sequentially to reflect the various stages of the research work, from the theoretical framework to the critical analysis of the results obtained.

Chapter 1 – Introduction: This chapter outlines the general context of the research, detailing the objectives of the study, the motivation behind the selected topic, and its significance within the current landscape of sustainable composite materials research. It also defines the research problem, presents the overarching methodological approach, and describes the structure of the thesis.

Chapter 2 – Theoretical Framework: This chapter presents a comprehensive literature review essential for the development of the study. It addresses key concepts related to natural fibers, including their properties, advantages, and limitations, as well as processing techniques. Additionally, it explores the characteristics of PLA as a biodegradable polymer matrix and the fundamental principles of additive manufacturing.

Chapter 3 – Materials and Methods: This chapter provides a detailed description of the materials employed and the fiber preparation processes, including grinding, drying, defibrillation, and chemical treatments. It also outlines the experimental procedures adopted for mechanical testing, with a specific focus on the tensile tests conducted using the Shimadzu testing machine. Additionally, the methodology for data analysis and the experimental conditions are thoroughly described.

Chapter 4 – Results and analysis: This chapter presents the data obtained from the tensile tests performed on the natural fiber samples processed in the laboratory. It includes the analysis of stress–strain curves, observed failure mechanisms, and comparative assessments between different samples, highlighting the factors influencing their mechanical performance. A comparative analysis with commercial hemp fibers is also conducted, enabling the positioning of the tested natural fibers relative to an established industrial benchmark.

Chapter 5 – Conclusions: This chapter synthesizes the main conclusions drawn from the study, evaluating the results concerning the initially proposed objectives. It identifies the study's

limitations and offers suggestions for future research, with the aim of optimizing the mechanical performance of the composites and enhancing their practical applicability in the production of filaments for 3D printing.

Finally, the bibliography consulted for the development of the work.

CHAPTER 2: THEORETICAL FRAMEWORK

2.1 COMPOSITES

Composite materials are formed by the combination of two or more materials of distinct natures, which complement each other and allow for the creation of a new material with enhanced characteristics and mechanical performance for a specific application, surpassing the individual properties of their constituents. In some cases, the mixtures can generate symbiotic effects, resulting in an exponential increase in the material's properties [9]. The formation of composite material involves the use of a matrix and reinforcements, with the latter constituting a dispersed and discontinuous phase within a continuous phase, the matrix. When a composite material incorporates more than one type of reinforcement with distinct natures, it is referred to as a hybrid composite. It is important to emphasize that, during the formation of the composite, both the matrix and the reinforcements retain their chemical structure intact, with the distribution of stresses throughout the material being ensured by a good interface between the resin and the fibers [9].

The earliest records of the production and use of composite materials date back to antiquity, with the papyrus made by the Egyptians around 4000 B.C. standing out. In addition, there is archaeological evidence demonstrating the use of straw as reinforcement in clay during prehistoric periods. Today, polymer matrix composites have become increasingly relevant, being widely applied in both industry and everyday life, in fields as diverse as sports, construction, aerospace, and transportation [10].

The increasing replacement of conventional materials by composites is due to several reasons, among which stand out their low specific mass, high corrosion resistance, and excellent mechanical properties. Another significant advantage of composite materials is the ability to tailor their properties to the specific requirements of certain applications. Unlike homogeneous materials, such as metals, composites exhibit anisotropic properties, meaning that their mechanical performance varies depending on the direction of the reinforcing fibers. Thus, in the longitudinal direction of the fibers, the properties are superior to those in the transverse direction, allowing for structural optimization and a reduction in the weight of the final part, as material is not used in directions that will not be mechanically stressed. In contrast, metals are isotropic materials, with identical properties in all directions [9].

In addition to these advantages, composite materials allow for the creation of complex shapes, adapting to different functionalities and making them a highly versatile and efficient option. This ability for adaptation and structural optimization makes composites an innovative solution widely used in various industries, replacing traditional materials and contributing to significant advancements across multiple sectors.

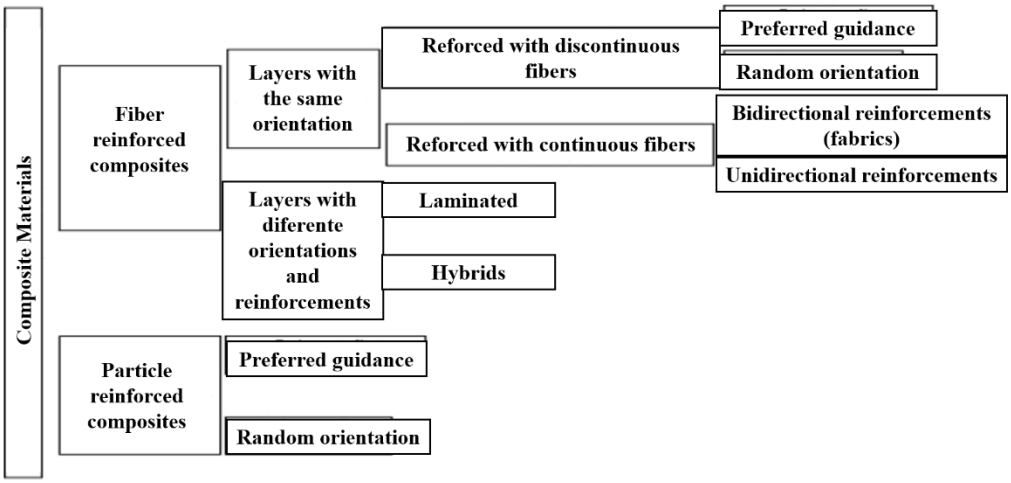


Figure 1-Schematic representation of composites materials. Figure adapted from [11]

Composite materials also offer the possibility of incorporating various additives to optimize specific characteristics, providing them with performance more suited to the specific requirements of each application, as shown in Figure 1. Among the most common additives is sand, frequently used to increase the material's abrasion resistance. Another relevant example is calcium carbonate, which, in addition to contributing to the reduction of the final cost of the composite, significantly improves the surface finish of the parts, making it particularly advantageous when a matte finish is desired.

To reinforce impact resistance, elastomeric-based pigments, commonly referred to as impact modifiers, can be incorporated. In addition to these, various other additives play a key role in the formulation of composite materials, such as ultraviolet radiation absorbers, flame retardants, pigments responsible for the final coloration of the material, additives that improve corrosion resistance, and those that minimize shrinkage of the part during processing. The selection and incorporation of these additives allow for the adjustment of composite properties to meet the

specific needs of each application, making them highly versatile and efficient materials for a wide range of industrial sectors [11].

Most composites consist of two distinct phases: the matrix, which constitutes the continuous phase, and the dispersed phase, commonly referred to as the reinforcement. The matrix's function is to surround and support the reinforcement, ensuring the material's cohesion and the efficient distribution of applied stresses. The interaction between these two phases is essential to ensure the mechanical and functional performance of the composite, as illustrated in Figure 2.

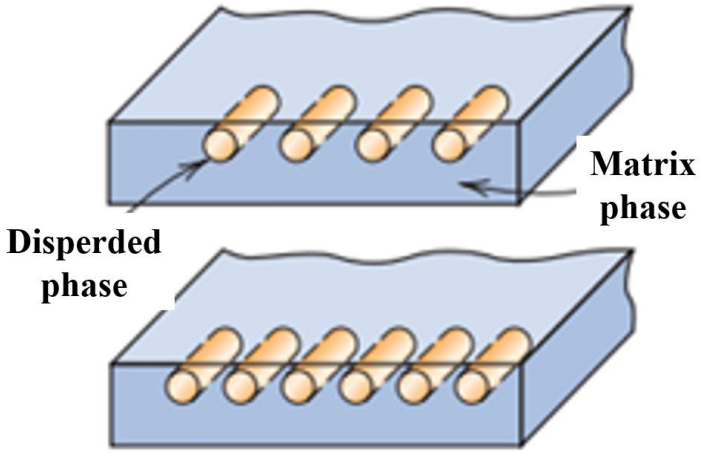


Figure 2-Example schematic of phases in a composite. Figure adapted from: [3]

2.1.1 MATRIX

The matrix in composite materials can be made from various types of materials and plays a fundamental role in the composite's structure. Its main function is to bond the dispersed phases and transfer the applied loads between them, ensuring the material's structural integrity and mechanical performance. However, the matrix also has other essential functions, such as maintaining the desired orientation and location of the fibers in fiber-reinforced composites, protecting the reinforcement from adverse environments and damage caused by temperature, humidity, chemicals, abrasion degradation, transferring interlaminar shear forces, improving the composite's transverse properties, increasing impact and fracture resistance [12].

Composites can be classified based on the type of material used in their matrix phase. Thus, three main classes of composites can be distinguished [13]:

- Metal matrix composites

Characterized by the incorporation of ceramic materials, cemented carbides, high-strength and high-stiffness fibers, as well as other metals, into a metallic matrix. This type of composite is widely used in applications that require high mechanical and thermal resistance, such as in the aerospace and automotive industries.

- Ceramic matrix composites

They represent the least common category due to the difficulties associated with processing ceramics. However, they stand out for their high resistance to heat and corrosion, being used in extreme environments, such as gas turbine components and refractory coatings.

- Polymer matrix composites

Polymer matrix composites are the most widely used, especially due to their versatility and ease of processing. Thermosetting resins, such as epoxy and polyester, are the most common in this category, often combined with fiber reinforcements to enhance mechanical properties. In thermoplastic polymers, the matrix can incorporate powders as a dispersed phase, imparting specific characteristics to the final material.

The matrix phase is crucial for the behavior of the composites, as it not only directly influences the material's mechanical, thermal, and chemical resistance, but also plays a key role in energy dissipation and stress relief. The choice of matrix type depends, therefore, on the application's requirements, considering factors such as temperature resistance, impact, fatigue, and composite durability. Furthermore, the interaction between the matrix and the reinforcement is a critical factor for optimizing the material's properties, with good adhesion between the phases being essential to avoid premature failures.

Thus, the matrix not only provides structural cohesion and stress distribution but also contributes to the durability and overall performance of composites, making it a fundamental element in materials engineering and the development of innovative solutions for various industries.

2.1.2 REFORCEMENT

Reinforcements play a crucial role in defining the mechanical properties of composite materials, being the main contributors to their strength and stiffness. The selection of reinforcement fibers to be used primarily depends on the final application of the product, considering factors such as density, mechanical properties, compatibility with the matrix, ease of processing (closely related to permeability), and the cost associated with the fibers available on the market. These fibers can come in different forms, namely short, long, or continuous. The use of reinforcement fibers provides the composite material with high strength in the longitudinal direction, allowing, from a design perspective, the mechanical properties to be adjusted in different directions. Thus, it becomes possible to orient the fibers in the directions where the composite will experience the highest mechanical stresses in service, thereby optimizing its structural performance [14].

Composites can also be classified based on the type of reinforcement used, which is a determining criterion for their characterization. However, in addition to the reinforcements, the matrix phase also plays an essential role in the structure of composite materials. The matrix's function is to surround and protect the reinforcement fibers, ensuring the material's cohesion and transferring mechanical loads to the fibers. Matrices can be polymeric, metallic, or ceramic, with polymeric matrices being the most used due to their ease of processing, low cost, and good mechanical properties in combination with high-performance fibers. Among polymeric matrices, thermoplastics and thermosets stand out, with the latter, such as epoxy and polyester resins, being frequently used due to their high chemical and thermal resistance [3].

According to Figure 3, composites can be classified based on their reinforcement [3].

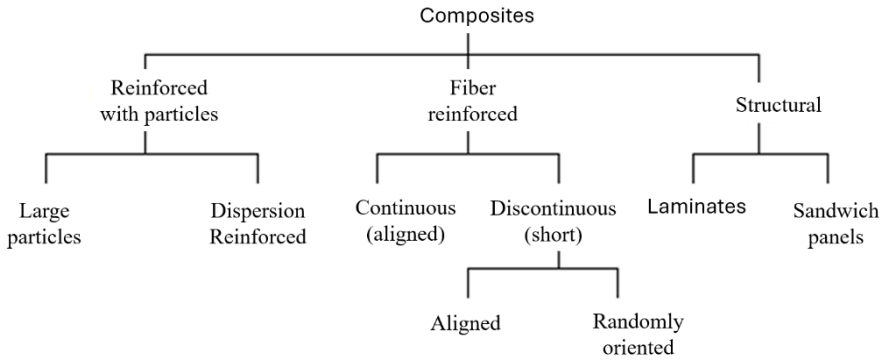


Figure 3-Classification of composites. Figure adapted from:[3]

This classification divides composites into three main classes: particle-reinforced composites, fiber-reinforced composites, and structural composites. The first type has a dispersed phase made up of particles that are approximately equiaxed, meaning they have similar dimensions in all directions. This type of composite is often used to enhance properties such as hardness and wear resistance. Fiber-reinforced composites, on the other hand, have a dispersed phase in the form of fibers, whose length is significantly greater than their diameter, thus providing high strength and stiffness, particularly in the longitudinal direction of the fibers. Finally, structural composites are made up of combinations of composites and homogeneous materials, designed to maximize structural efficiency through the optimized arrangement of their layers or components.

The interaction between the matrix and the reinforcement is crucial for obtaining a material with superior properties, as the adhesion between these phases directly influences the efficiency of load transfer. Optimizing the matrix-reinforcement interface, through surface treatments or chemical modifications, can significantly improve the mechanical properties of the final composite, ensuring greater strength and durability. Therefore, the proper selection of the matrix and reinforcement, as well as their compatibility, is essential for developing composite materials with optimized performance for demanding structural applications [3].

2.1.3 INTERFACE BETWEEN THE MATRIX AND THE REINFORCEMENT

The interface between the constituent phases of a composite material (Figure 4) plays a decisive role in defining its final properties, directly influencing the material's mechanical, thermal,

and chemical performance. Although the primary materials, matrix and reinforcement, are generally insoluble in each other, it is essential that there is good chemical affinity between both phases to ensure efficient adhesion. This interaction is crucial to ensure the composite's structural cohesion and to allow effective stress transfer between its phases, thereby maximizing the material's mechanical strength and durability [15].

The quality of the interface can be improved through various surface treatments on the reinforcement, such as chemical functionalization, the application of coupling agents, or physical modifications, which increase compatibility and promote more effective adhesion between the matrix and reinforcement. The presence of a weak interface can significantly compromise the composite's performance, leading to premature failure under mechanical loads. On the other hand, a well-optimized interface contributes to the efficient dissipation of stresses and the material's structural integrity, making it a crucial factor in the design of composites intended for demanding structural applications [15].

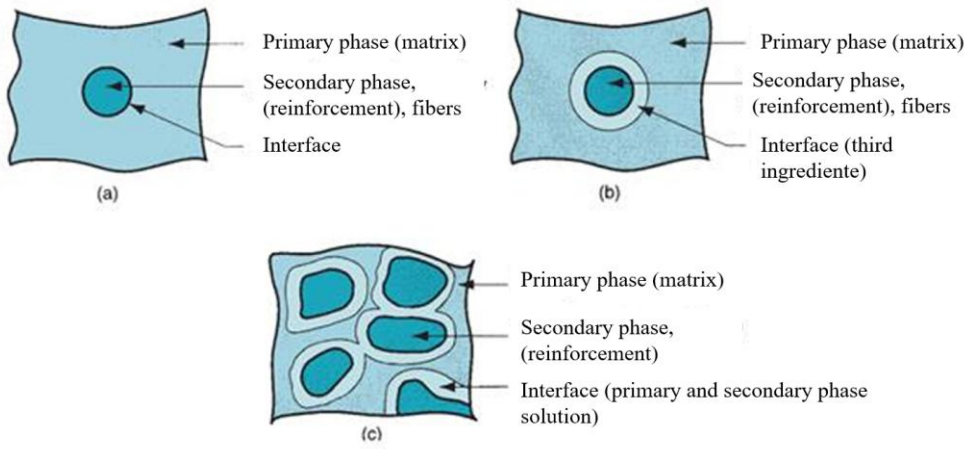


Figure 4--Interfaces and interphases in a composite material: (a) direct bond between the primary and secondary phases; (b) addition of a third ingredient to join the primary and secondary phases and form an interphase; (c) formation of an interphase by the dissolution of the primary and secondary phases at their boundary. Figure adapted from [13]

When there is a strong chemical affinity at the interface between matrix and reinforcement, an intermediate phase or interphase is formed, establishing a bond between the two phases of the composite, as illustrated in Figure 4. This intermediate phase results from the interaction between intermolecular forces and surface free energy, being distributed throughout the material's structure.

The quality of this interphase is a determining factor for the composite's performance and depends on various variables such as moisture, chemical reactions between matrix and reinforcement, residual stresses, surface morphology, and the roughness of the materials [16].

2.2 TYPES OF FIBERS

Fibers can be classified according to their origin (Figure 5) and are produced from a wide variety of materials. However, the most used fibers in industry and research are natural fibers and synthetic fibers, due to their mechanical properties, availability, and applicability across different sectors.

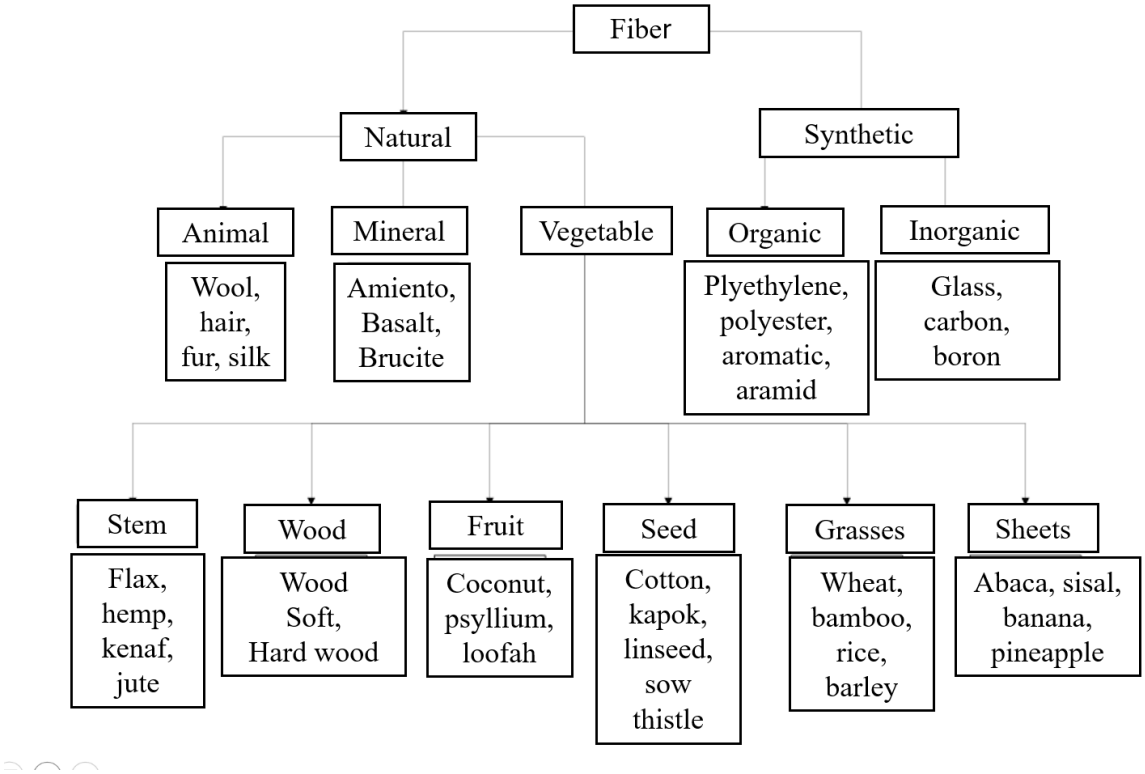


Figure 5-Classification of fibers. Figure adapted from [17]

2.2.1 SYNTHETIC FIBERS

Synthetic fibers play a fundamental role in reinforcing composite materials and are widely used due to their exceptional mechanical properties. Their high tensile strength, stiffness, and corrosion resistance make these fibers indispensable in highly demanding sectors such as the

aerospace and aeronautical industries. Among the most used are carbon, glass, and aramid fibers, whose application provides outstanding structural performance to composites [17].

However, despite the advantages they offer, their use entails significant challenges. The high production cost, the environmental impact associated with their manufacturing and eventual disposal, as well as the loss of mechanical properties at extreme temperatures, are factors that must be carefully considered when choosing these materials as reinforcement [17].

Thus, the selection of fibers for composites requires a balance between mechanical performance and environmental sustainability. Although glass and carbon fibers are widely recognized for their excellent structural behavior, it is essential to consider alternatives that minimize environmental impacts, promoting more sustainable solutions for materials engineering.

2.2.2 NATURAL FIBERS

Natural fibers can be classified according to their origin into three main categories: plant, animal, or mineral fibers, as shown in Figure 5. Plant-derived fibers are predominantly composed of cellulose (Figure 6) and are therefore referred to as lignocellulosic fibers. Animal fibers, on the other hand, are primarily made up of proteins, such as wool, silk, and hair [18].

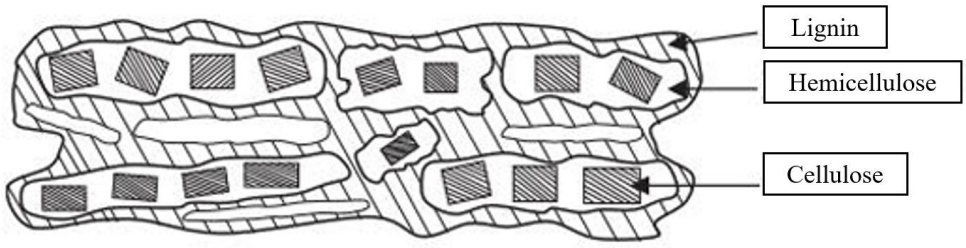


Figure 6--Organizational structure of the cell wall of a lignocellulosic fiber. Figure adapted from [18]

This study will focus exclusively on plant-derived fibers. Therefore, the term "natural fibers" will be used throughout this work solely to refer to fibers extracted from plants. These fibers can be obtained from different parts of the plant, namely the bark, stem, seeds, leaves, and fruits.

This type of fiber is characterized by the presence of cellulose fibrils embedded in a lignin matrix. The cellulose fibrils are aligned along the length of the fiber, as shown in Figure 7,

providing it with high tensile and flexural strength, as well as significant rigidity. The effectiveness of the reinforcement provided by natural fibers is directly related to the nature of the cellulose and its degree of crystallinity [19].

Natural fibers are primarily composed of cellulose, hemicellulose, lignin, pectin's, and waxes, and the proportions of these components influence their mechanical and chemical properties.

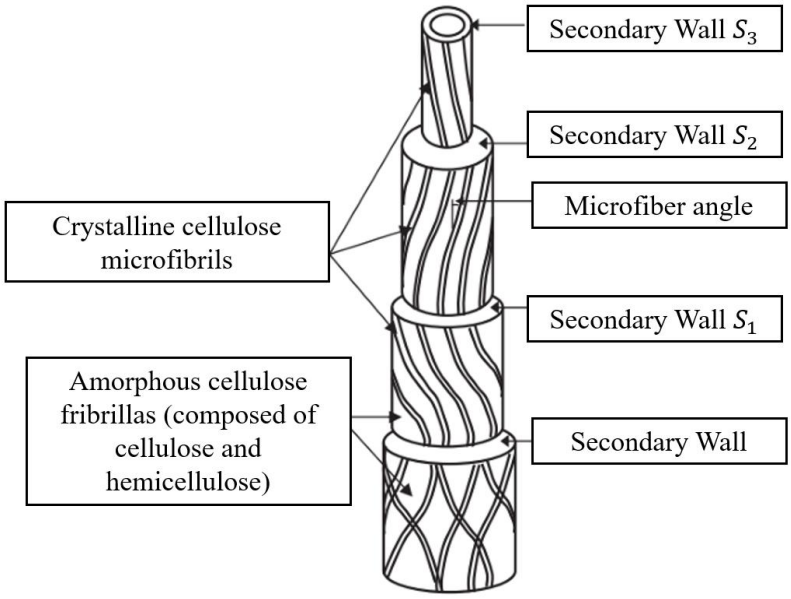


Figure 7-Genetic structure of natural fibers. Figure adapted from [18]

The use of natural fibers as reinforcement offers several advantages, including their abundance, biodegradability, and renewability. In addition to these characteristics, plant-based fibers are generally lighter, more economically accessible, and resistant to corrosion when compared to synthetic fibers, such as glass, carbon, and aramid [19].

These properties have sparked increasing interest from the industry, as they enable satisfactory structural performance at a reduced cost, while simultaneously promoting more sustainable solutions for engineering [20].

The following table highlights the main advantages and disadvantages between natural fibers and synthetic fibers.

Table 1-Advantages and disadvantages between Natural fibers and Synthetic fibers. Table information of [2]

Advantages	***Disadvantages***
Recyclable	High moisture absorption
Low density	Dimensional instability
Negative CO2 emissions	Flammable
Better mechanical properties compared to glass fibers	Lower strength and thermal resistance compared to glass fibers
Non-abrasive processing	Anisotropic behavior
Does not produce toxic components during processing	Sensitivity to UV light, microbial action, and fungi
Lower energy consumption compared to glass fibers	Limited processing temperature compared to glass fibers

2.3 FIBER PANORAMA IN PORTUGAL

Portugal has a centuries-old tradition in the cultivation and use of natural fibers, notably hemp (*Cannabis sativa*), flax (*Linum usitatissimum*), and chestnut (*Castanea sativa*). Historically, these fibers played a fundamental role in the country's economic and cultural development, being widely employed across various industries and artisanal practices. In recent decades, there has been a renewed interest in these raw materials, driven by increasing environmental concerns and the search for sustainable alternatives to synthetic materials.

Hemp, cultivated in Portugal since the 14th century, was traditionally used in the production of ropes, fabrics, and sails for ships. By the 18th century, Portugal was one of the leading European producers of this fiber. However, in the 20th century, with the advent of synthetic fibers and legal restrictions linked to Cannabis sativa, hemp cultivation declined significantly. Currently, its use is expanding across multiple sectors, including textiles, cosmetics, food, paper, and construction, despite existing legislation posing barriers to the growth of the national industry [21].

Flax has a long-standing tradition in Portugal, particularly in northern regions where its cultivation and processing gave rise to a well-established artisanal culture. Flax fibers are recognized for their strength and durability, being used in the production of fine fabrics, clothing,

and household items. The industrialization and spread of synthetic fibers led to a sharp decline in flax production, nearly causing the extinction of this traditional crop. Nevertheless, the growing demand for eco-friendly products has fostered initiatives aimed at revitalizing flax cultivation, combining traditional knowledge with technological innovations to enhance fiber quality and improve global market competitiveness [22] .

The chestnut tree, an autochthonous species of the Iberian Peninsula and of particular importance in the mountainous northern and central regions of Portugal, is primarily known for its nutritional value. Its by-products have historically been used in the production of natural dyes and tanning agents for the leather industry. Recent research has underscored the potential of chestnut as a source of biomaterials, particularly through the valorization of its bark fibers to produce biodegradable films, thereby positioning it within the broader context of circular economy and sustainability initiatives. However, chestnuts are not considered a fibrous plant in the traditional sense of the textile industry.

While chestnut belongs to the group of native plants, flax and hemp are exotic species that have naturalized in Portugal and played a decisive role in textile fiber production [23]. Flax was likely introduced during antiquity and was intensively cultivated in regions such as *Minho* and *Trás-os-Montes*, being used to produce lightweight fabrics and clothing. The flax cultivation cycle involved complex communal practices from sowing to weaving [24]. Hemp, introduced between the 14th and 15th centuries, was crucial during the Portuguese Age of Discoveries due to its robust fibers, ideal for producing ropes, sails, and industrial fabrics. Following the decline of sailing ships and the implementation of legal restrictions on recreational use, hemp cultivation significantly decreased. However, in recent decades, it has experienced a resurgence driven by sustainability and bioconstruction initiatives, with research increasingly focused on its applications in paper production, textiles, and eco-friendly materials.

The distinction between native and exotic plants is now particularly relevant in conservation policies and biodiversity valorization in Portugal. Chestnuts are integral to the protection of native ecosystems, whereas flax and hemp represent introduced species that have become part of the country's agricultural and textile identity. The rediscovery and valorization of these natural fibers reflect a growing environmental awareness and a commitment to economic

diversification, projecting a future where tradition and innovation converge to address contemporary challenges.

2.3.1 HEMP

The cultivation of hemp (*Cannabis sativa*) in Portugal dates to the 14th century and played a key role during the Age of Discoveries, particularly in the production of ropes and sails for ships. After a period of decline, interest in this crop has resurfaced due to its multiple industrial applications and sustainable potential.

Recent studies have focused on the extraction and characterization of hemp fibers for textile use, investigating sustainable plant pre-treatment methods to optimize fiber quality. Additionally, the determination of the mechanical properties of hemp fibers has been a subject of research [22].

Another relevant aspect is the comparison of the mechanical properties of hemp fibers with those of other natural fibers, such as flax. The effectiveness of different chemical treatments, such as alkaline treatment and acetylation, has been studied to improve the properties of hemp fibers, aiming at their application in polymer composites [25].

These studies highlight the potential of hemp as a sustainable alternative in the textile industry and other applications, contributing to the diversification of the Portuguese economy and the promotion of more environmentally friendly agricultural and industrial practices.

Figure 8-Hemp cultivation IPB

2.3.2 FLAX

Flax (*Linum usitatissimum*) is a herbaceous plant from the Linaceae family, cultivated in Portugal since prehistoric times, with traces dating back to 2000 BC in the Serra de Monchique. Historically, flax cultivation had significant economic and social importance, especially in the regions of *Minho* and *Trás-os-Montes*, where its production was intertwined with cultural practices and community traditions.

Flax fibers are extracted from the plant's stem and are highly valued for their strength, durability, and absorbency, characteristics that make them ideal to produce high-quality fabrics. Studies indicate that, from one ton of flax straw, approximately 160 kg of tow (long fibers) and 100 kg of scutch (short fibers) can be obtained. Additionally, the processing of the straw results in about 13% long fibers for cloths and threads, 16% short fibers used in oilcloths and mats, 40% woody fragments, 13% seeds, and 18% various residues [26].

In Europe, flax production has experienced significant growth. This increase in production reflects the growing demand for natural and sustainable fibers in the textile industry, driven by the appreciation of eco-friendly agricultural practices and consumer preference for environmentally responsible products.

In Portugal, although flax production has declined over the centuries due to competition from other fibers and industrialization, there is a renewed interest in revitalizing this crop. The implementation of new technologies and more efficient cultivation methods can increase the profitability and sustainability of flax production, contributing to the diversification of national agriculture and the preservation of the cultural heritage associated with this plant [27].

Thus, flax represents a multifaceted crop with the potential to contribute significantly to the Portuguese economy, combining tradition and innovation in the search for sustainable and high-quality solutions.

Figure 9-Flax. Figure adapted from:[33]

2.3.3 CHESTNUT

Chestnuts are better known for their nutritional value, but the by-products of their processing, such as shells and husks, have great potential for fiber production. Recent research projects have explored the reuse of these residues with the aim of creating new materials, promoting sustainability, and encouraging innovation in the use of natural resources. The valorization of by-products from *Castanea sativa*, such as the reuse of shells and husks, can generate materials of interest for various industries, including textiles and biomedicine. These advancements reinforce the idea that the valorization of agro-industrial waste can have a significant impact on reducing waste and promoting the circular economy [28].

Portugal holds a rich and diverse heritage in the cultivation and use of natural fibers, ranging from traditional textile applications to innovations in emerging sectors. The rediscovery of these fibers reflects a combination of factors, including the appreciation of cultural heritage, the need for sustainable alternatives, and economic diversification.

Figure 10-Ilustrative figure of Chestnut. Figure adapted from: [34]

2.4 RETTING TECHINIQUES

Retting techniques, as illustrated in Figure 11, refer to a set of processes applied to plant fibers to separate the useful fibers from the woody material or the surrounding bark. These techniques are essential in the preparation of fibrous raw materials such as flax, hemp, or jute, and can be classified into five main categories: microbiological, enzymatic, mechanical, physical, and chemical [29].

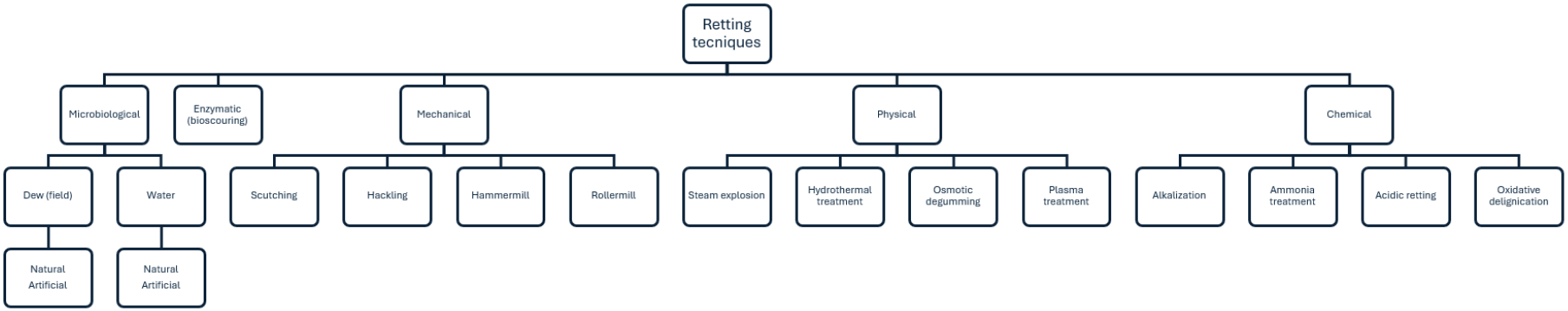


Figure 11-Retting techniques

Microbiological retting is based on the activity of microorganisms (bacteria and fungi) that degrade pectin, a substance responsible for holding the fibers together with the woody part of the plant. Within this category, two main subtypes stand out: dew retting and water retting. Dew retting can occur naturally by leaving the stalks in the field exposed to weather conditions, thereby promoting natural microbial colonization, or artificially, in controlled environments such as greenhouses, with optimized parameters to accelerate the process. Water retting follows the same principle and can be carried out naturally in bodies of water such as lakes and rivers, or artificially in tanks with stagnant water under controlled temperature and oxygenation. Although these techniques are more environmentally sustainable, they are generally slower and heavily dependent on climatic conditions [29].

Enzymatic retting, also known as bio scouring, involves the controlled application of enzymes, such as pectinases and cellulases, which act selectively on the components of the cell wall. This technique offers significant advantages in terms of precision, selectivity, and sustainability, as it avoids the use of harsh chemical products. However, it requires investment in biotechnology and may involve higher operational costs, making it particularly suitable when the goal is to preserve the integrity and quality of the fibers [29].

Mechanical retting involves the physical separation of fibers through mechanical action, without the use of chemical or biological agents. Common methods include scutching (removal of woody material by impact), hackling (combing to align and separate the fibers), hammer milling (use of rotary hammer crushers), and roller milling (pressing the stalks through rollers to release the fibers). These methods are fast and easy to implement on an industrial scale, but they carry the risk of mechanically damaging the fibers, which may compromise their final quality [29].

Physical retting uses methods based on physical energy, such as heat, pressure, or plasma treatment, to facilitate the separation of fibers. Among the most relevant approaches are steam explosion, which subjects the stalks to high-pressure steam followed by a sudden depressurization; hydrothermal treatment, which involves the use of hot pressurized water; osmotic degumming, which takes advantage of osmotic pressure gradients to remove gums and pectins and plasma treatment, where gaseous plasma is applied to modify the surface of the fiber. These techniques have shown high effectiveness and offer greater control over the process, although they involve significant costs in terms of equipment and energy consumption [29].

Finally, chemical retting employs chemical compounds to dissolve the substances that bind the fibers to the non-fibrous parts of the plant. The most common methods include alkalization (typically using sodium hydroxide), ammonia treatment, acidic retting (with acids such as sulfuric acid), and oxidative delignification (using peroxides or other oxidizing agents). These techniques are particularly effective and fast, making them widely used in industrial contexts. However, they raise environmental and safety concerns due to the generation of toxic effluents and the potential risk of fiber degradation [29].

Besides the retting process, it is important to consider that natural fibers, despite their advantages such as low density and relatively low cost, present significant limitations, with high polarity being one of the main ones. These characteristic compromises compatibility and interfacial adhesion with most polymer matrices, which negatively affects the performance of composites. To mitigate this issue, chemical surface modification treatments are frequently applied, which, although increasing the raw material cost, significantly improve the interfacial interaction between the fiber and the matrix, as well as reduce the material's hygroscopicity. Thus, these treatments play a fundamental role in modifying the properties of natural fibers, making them more suitable for advanced applications, such as in high-performance composite materials [5].

The present study aimed to extract fibers to mechanically reinforce PLA in filaments intended for 3D printing. To identify the most efficient extraction method, several chemical treatments were carried out to separate the fibers from the plant. For this purpose, an alkaline solution containing of sodium hydroxide (NaOH, Absolve, Australia), sodium carbonate (Na_2CO_3, V.P., Lisbon, Portugal), and DIADAVIN detergent (Grupo ADI, Santo Tirso, Portugal) was used, all subjected to a temperature of 80 ºC. These treatments were conducted in two different systems: open circuit and closed circuit. After fiber extraction, tensile tests were performed to evaluate their mechanical properties.

While the present dissertation employed alkaline treatment for the extraction of hemp fibers aimed at their application as mechanical reinforcement in PLA based composites for 3D printing, a previously published thesis focused predominantly on biological and enzymatic methods, such as water retting and enzymatic retting using pectinases [22] . Although this approach is sustainable and effective in removing non-cellulosic components, it requires longer processing times and more controlled conditions, making it more suitable for textile spinning applications

where preserving the fiber's surface structure is essential. In contrast, the alkaline treatment used in this study, combining sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and detergent at 80 °C, enabled a more aggressive and efficient removal of lignin and hemicelluloses, facilitating fiber separation and promoting a more reactive surface for polymer adhesion. This methodological choice is justified by the need to maximize interfacial compatibility between the fiber and the polymer matrix, reducing the polarity and hygroscopicity of the natural fiber, critical factors for the mechanical integrity and durability of composite filaments intended for 3D printing. Thus, although it slightly increases the cost and environmental impact of the process, the alkaline treatment proves to be more suitable for structural applications in composite materials than the biological methods described in the referenced thesis.

2.5 TENSILE TESTING FOR FIBERS CHARACTERIZATION

Tensile testing is one of the most used methods in engineering to evaluate the mechanical behavior of a material when subjected to a uniaxial tensile force. This type of test allows the determination of fundamental properties such as tensile strength, elastic modulus (or Young's modulus), yield strength, and elongation at break. Through the controlled application of an increasing force, the material is stretched until the point of rupture, while the deformation experienced over time is recorded.

During the test, the specimen is fixed in a tensile testing machine using grips that apply an increasing axial load. This force is measured simultaneously with the elongation of the sample, enabling the construction of a stress-strain curve. The shape of this curve provides valuable information regarding the material's ductility, stiffness, and strength.

Tensile testing is standardized by various international norms. In the case of fibers, ASTM D3822 is commonly used and will be adopted in this study for the tensile tests of hemp fibers, ensuring the reproducibility and reliability of the results. It is widely used in the characterization of metals, polymers, composites, and natural fibers, being essential for the development, selection, and validation of materials in engineering projects [30].

In addition to its technical importance, tensile testing is also a fundamental tool for scientific research, as it allows for the understanding of the relationship between the microscopic structure of materials and their macroscopic behavior underloading.

CHAPTER 3: MATERIALS AND METHODS

This chapter presents the materials used and the methods applied for the extraction and characterization of natural fibers. Three main materials were selected: hemp, flax, and chestnut shells, each with distinct origins and conditions. The procedures adopted for the preparation of each material, as well as the methods used for fiber extraction, including both chemical and mechanical approaches, are described.

In the case of hemp, multiple fiber extraction methods were evaluated to determine the most effective technique. For flax, commercially available and pre-processed material, only characterization tests were conducted. Chestnut shells, sourced from an industrial process and already in a state of decomposition, were subjected to a single fiber extraction procedure.

Additionally, all fibers obtained were analyzed under a microscope and subjected to tensile testing, to assess structural changes and the mechanical properties resulting from the different methods applied. The specific details regarding the materials, experimental steps, and characterization techniques are presented throughout this chapter.

3.1 CHEMICAL TREATMENTS FOR FIBER SEPARATION

3.1.1 HEMP FIBERS

The chemical separation of hemp fibers was carried out to facilitate the removal of the lignocellulosic matrix that binds the fibers, thereby promoting their individualization. For this purpose, a solution containing alkaline reagents and a detergent was prepared.

The solution was prepared in a 500 mL round-bottom flask by dissolving 2 g/L of NaOH, 0.5 mL/L of DIADAVIN detergent, and 2 g/L of Na_2CO_3 in distilled water. The mixture was manually stirred until the reagents were fully dissolved.

The treatments were performed with an exposure time variation from 30 to 90 minutes with the alkaline solution, aiming to identify the most effective duration for fiber separation without compromising their integrity. The temperature of the mixture gradually increased until it reached 80 °C, at which point the treatment time was recorded. This approach ensured that all samples were subjected to equivalent thermal conditions during the extraction process.

After the specified treatment time, the samples were carefully removed from the solution, thoroughly rinsed with distilled water to eliminate any chemical residues and then left to dry at room temperature (23-25 °C). The analysis of the results allowed for the evaluation of the impact of each treatment for duration on the quality and integrity of the fibers obtained.

3.1.1.1 MATERIALS

For this study, hemp (*Cannabis sativa*) was hand-harvested in Bragança (Portugal) during the vegetative growth stage, from non-commercial fields that had received no prior chemical treatments. The plants were naturally air-dried in the field for several weeks and had not undergone any curing or industrial processing. No signs of fungal or pest contamination were observed after this time.

The hemp is composed of several parts, namely seeds, long fiber bales, short fiber bales and hurds (Figure 12). Only the stem was used in the experiments, as this is the part of the plant where the target fibers are concentrated—both the short and long bundles located in the layer between the epidermis and the central woody cylinder, as illustrated in Figure 12. Leaves and inflorescences were removed before the experimental procedures began.

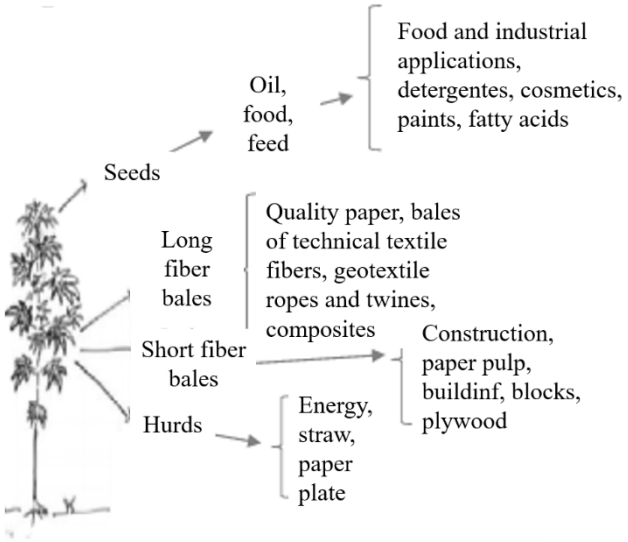


Figure 12-Diagram of various applications of cannabis sativa. Figure adapted from: [22]

The stems were cut into segments approximately 7 cm in length (Figure 13), using scissors to standardize the samples and facilitate handling during the subsequent chemical and mechanical treatments. Each segment retained the full structural integrity of the stem, including the outer bark, to preserve the material's natural condition at the time of fiber extraction.".

Figure 13-Cut hemp

The harvesting of the hemp and the time elapsed before conducting the experiments varied for each assay, allowing for the study of environmental exposure on the quality of the extracted fibers:

1) The hemp was harvested the day before the treatment and was therefore in a fresher state.

2) The material had been harvested eight days before testing.

3) The hemp had been harvested twenty-one days earlier.

4) Twenty-eight days had passed between harvest and treatment.

5) Fibers from the fourth trial were reused to assess the effects of a second treatment on previously treated fibers.

6) Hemp harvested forty-two days before the treatment was used, allowing for the analysis of prolonged environmental exposure on fiber quality.

The chemical treatment was carried out using an Alkaline Solution (AS), Figure 14, composed of 2 g/L of NaOH, 2 g/L of Na_2CO_3, and 0.5 mL/L of DIADAVIN detergent dissolved in distilled water. The solution was stirred until the reagents were fully dissolved and then heated

to 80 °C. From this point, the treatment time was recorded, which varied across samples to assess the influence of duration on the fiber separation process.

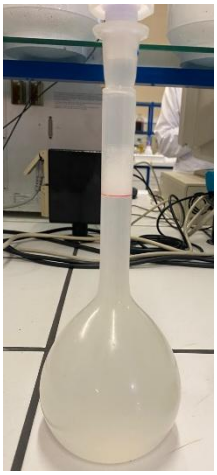


Figure 14-Alkaline solution

After the treatment, some samples were rinsed with distilled water to remove chemical residues and then left to dry in a ventilated environment, Figure 15, ensuring the preservation of the fibers' natural properties. This procedure optimizes hemp fiber extraction while preserving fiber integrity for microscopic analysis and mechanical testing.

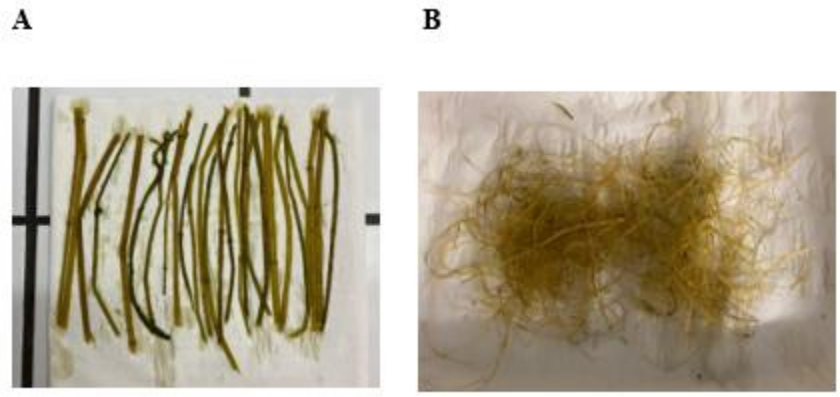


Figure 15-A- Fiber drying immediately after removal from the solution; B- Drying of the combed fibers

3.1.1.2 METHODS

Between October 2024 and April 2025, a series of laboratory experiments were conducted using hemp fibers and chestnut shells to evaluate the chemical behavior of these materials, promote the removal of impurities, and optimize their properties for future technological applications. Table 2 summarizes the main steps, conditions, and distinguishing features of each experiment. In the case of hemp, six tests were carried out using fibers harvested at different time intervals (ranging from 1 to 42 days after harvesting) and processed in either open- or closed-loop systems. Some experiments included prior mechanical treatment, notably Experiment 4, which combined water immersion with a roll-bending process using a manual plate rolling machine. The chemical process was repeated in Experiment 5 to assess the cumulative effects of multiple treatments.

The first experimental stage with freshly harvested hemp fibers took place on October 30th, 2024. The fibers were immersed in an SA solution inside a glass flask, placed in a water bath over a heating plate in an open-loop system. Heating began at 2:35 p.m., gradually reaching 80 °C, the point at which the solution began to boil at approximately 4:10 p.m. This temperature was maintained for 30 minutes to ensure the reagents acted effectively on the fiber structure, Figure 16. After treatment, the fibers were removed from the solution and dried in a controlled environment for 24 hours to eliminate residual moisture, preparing the samples for subsequent physicochemical analysis, Figure 16.

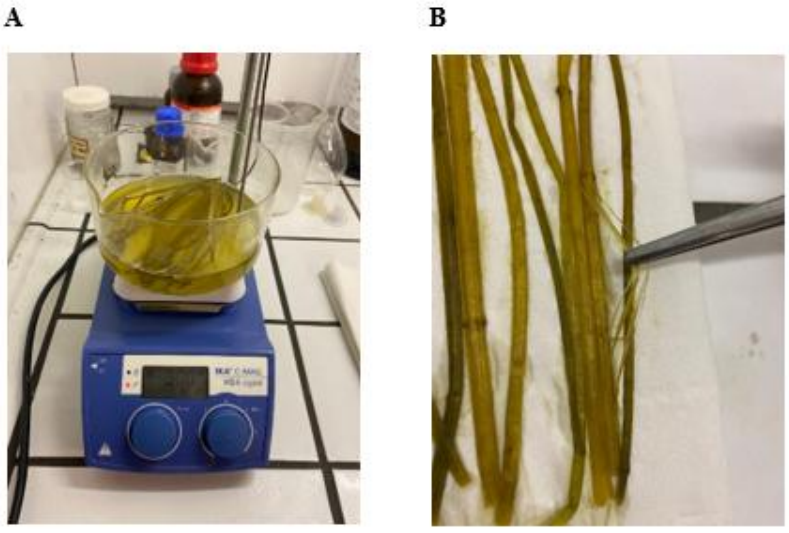


Figure 16-A-Chemical process with the fibers; B-Fibers after the chemical process, ready for drying

On November 6th, 2024, the second laboratory experiment was conducted using hemp harvested eight days earlier to evaluate its chemical behavior and improve the fiber properties. The fibers were treated in an SA solution heated in an open system, reaching 80 °C and maintained for 1 hour and 30 minutes. After treatment, the fibers were washed with hot distilled water and dried in a controlled environment for 24 hours to remove residual moisture and prepare the samples for further analysis, Figure 17.

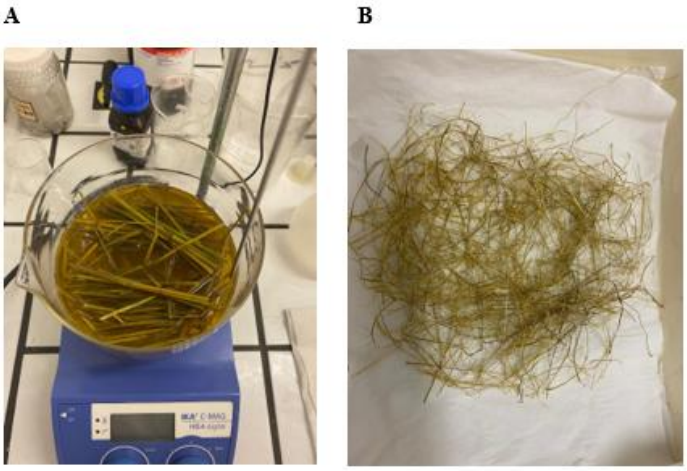


Figure 17-A-Chemical process with the fibers; B-Fibers after the chemical process, ready for drying

On November 19th, 2024, the third laboratory experiment was carried out using fibers harvested 21 days earlier to assess their chemical behavior and remove impurities for material optimization. The treatment employed a closed-loop system with an SA solution heated in a 500 mL distillation flask connected to a 40 cm condenser and warmed by a heating mantle starting at 10:20 a.m. Boiling was reached at 10:27 a.m., with boiling inhibitors added to prevent excessive turbulence. The temperature was maintained for 1 hour until 11:30 a.m., after which the system was turned off and the fibers were allowed to cool before further analysis, Figure 18.

A B

Figure 18-A-Chemical process with the fibers, B-Fibers after the chemical process, ready for drying

On November 26th, 2024, the fourth laboratory experiment was conducted using hemp fibers harvested 28 days earlier. After being submerged in distilled water at room temperature for seven days, the fibers underwent a mechanical treatment using a roll bending machine to compress and stretch them, improving their structure for subsequent chemical treatment. The chemical process was performed in a closed-loop system with an SA solution heated in a 500 mL distillation flask connected to a 40 cm condenser and heated by a mantle starting at 2:30 p.m. Boiling reached at 2:40 p.m., with boiling inhibitors added to control the intensity. The treatment lasted 1 hour and 30 minutes, ending at 4:10 p.m., followed by system cooling. Afterwards, the fibers were soaked in distilled water from November 27th to December 5th to remove chemical residues, then dried in a controlled environment, preparing them for further analysis, Figure 19.

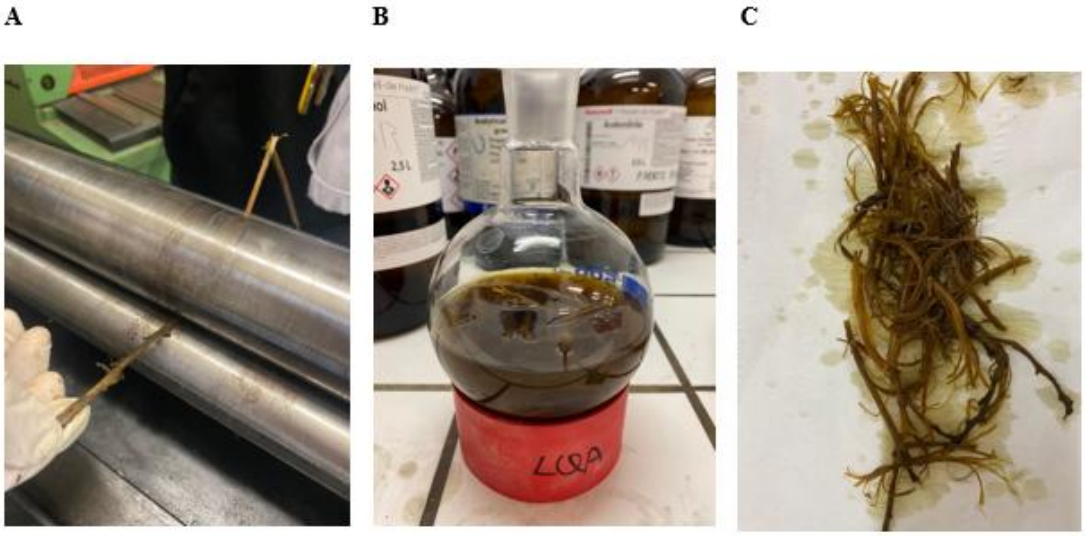


Figure 19-A- Mechanical calendaring process; B-Chemical process with the fibers; C-Fibers after the chemical process, ready for drying

In the December 5th experiment, we used the hemp fibers resulting from Experiment 4 and repeated the entire chemical process from the beginning. The hemp was therefore subjected to a mechanical treatment followed by two chemical treatments, aiming to evaluate the cumulative effect of these processes on the fiber properties, Figure 20.

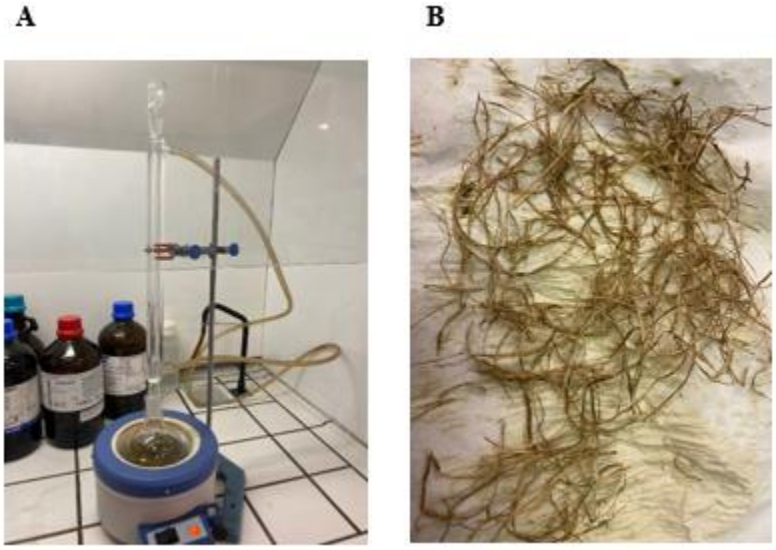


Figure 20-A-Chemical process with the fibers, B-Fibers after the chemical process, ready for drying

The sixth laboratory experiment was conducted on December 10th, 2024, to evaluate the chemical behavior of hemp fibers harvested 42 days earlier and to promote impurity removal for property optimization. The test was performed in a closed-loop system using an SA solution. The solution was placed in a 500 mL (Schott brand) flask connected to a 40 cm condenser and heated with a heating mantle. The fibers were introduced at 10:05 a.m., and the solution reached boiling at 10:16 a.m. The temperature was maintained at 80 °C for 1 hour and 30 minutes, with the process ending at 11:40 a.m. The system was then left to rest until the fibers cooled to room temperature, Figure 21.

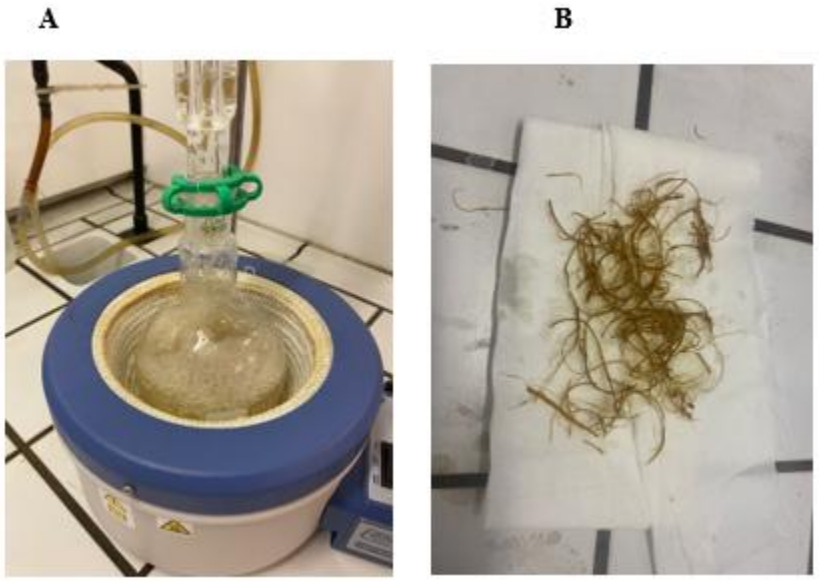


Figure 21-A-Chemical process with the fibers, B-Fibers after the chemical process, ready for drying

As for the chestnut shells, two distinct categories were evaluated: one thermally pre-treated and the other in a state of natural decomposition. Both were subjected to chemical treatments in a closed-loop system, allowing for a comparison of how preservation conditions influenced the final material properties.

This set of tests enabled a comprehensive analysis of the various factors affecting the quality of the treated materials, providing a solid basis for more efficient decisions in industrial and technological applications. Table 2 summarizes the main stages and key characteristics of the laboratory experiments conducted with hemp fibers and chestnut shells between October 2024 and

April 2025. The tests aimed to evaluate the chemical behavior of the materials, facilitate the removal of impurities, and optimize their properties for future technological use.

Table 2-Summary of Chemical Procedures and Samples

Material	Date	Sample condition	Treatment	Fibers submerged in distilled water	Roll bending process	Duration/ Temperature	Type of system	Final observations
Sample 1 Hemp	30/10/2024	1 day	Alkaline Solution	0 days	No	80ºC/ 30 minutes	Open	24 hour drying
Sample 2 Hemp	06/11/2024	8 days	Alkaline Solution	0 days	No	80ºC/1h e 30 minutes	Open	Washed in distilled water and dried for 24 hours
Sample 3 Hemp	19/11/2024	21 days	Alkaline Solution	0 days	No	80ºC/1h	Close	24 hour drying
Sample 4 Hemp	26/11/2024	28 days	Alkaline Solution	7 days	Yes	80ºC/1h e 30 minutes	Close	24 hour drying
Sample 4 Hemp[1]	05/12/2024	28 days	Alkaline Solution	0 days	Yes	80ºC/3 horas	Close	24 hour drying
Sample 5 Hemp	10/12/2024	48 days	Alkaline Solution	0 days	No	80ºC/1h e 30 minutes	Close	24 hour drying
Sample 1 Chestnut	19/03/2025	Thermal shock	Alkaline Solution	0 days	No	80ºC/1h	Close	Washed in running water and dried for 24 hours
Sample 2 Chestnut	09/04/2025	State of decomposition	Alkaline Solution	0 days	No	80ºC/1h	Close	Washed in running water and dried for 24 hours

1 sample already subjected to chemical treatment on 26/11/2024

3.1.3 MECHANICAL CHARACTERIZATION

Fiber mechanical properties were evaluated through uniaxial tensile testing, a standard materials science method that quantifies tensile load response. This method involves subjecting a specimen to a controlled, monotonically increasing axial load until failure, thereby generating detailed data on the material's deformation and fracture behavior. The tensile test provides critical mechanical parameters such as ultimate tensile strength (UTS), which defines the maximum stress the material can withstand before rupture; elongation at break, indicating ductility and toughness; Young's modulus (or modulus of elasticity), representing the stiffness or elastic response of the fiber under load; and the fracture point, marking the precise moment of structural failure. For natural fibers like hemp, these parameters are fundamental for evaluating their suitability as reinforcements in composite systems or bio-based materials, where mechanical integrity and compatibility with matrices are essential.

In the context of this research, the fibers under investigation were chemically treated hemp fibers subjected to an experimental protocol designed to enhance their mechanical properties through controlled chemical modifications. The chemical treatments aimed to remove impurities, improve fiber-matrix adhesion potential, and optimize the fiber's microstructural characteristics, all of which could impact mechanical performance. To accurately assess these changes, uniaxial tensile testing was selected due to its ability to provide direct measurement of fundamental mechanical properties and enable comparison with literature values and industry standards.

The tensile testing was conducted using a Shimadzu AGS-X universal testing machine (Figure 22), a highly sophisticated instrument recognized worldwide for its precision, reliability, and adaptability across a diverse range of materials. This universal testing machine can perform multiple test types, including tensile, compressive, flexural, and cyclic tests, making it highly versatile for research involving metals, polymers, composites, and increasingly, natural fibers. The AGS-X is equipped with an advanced digital control system and high-resolution load and

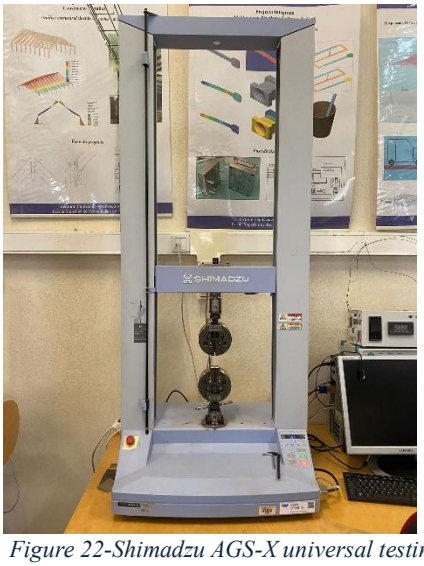


Figure 22-Shimadzu AGS-X universal testing machine

displacement sensors, ensuring data integrity and reproducibility.

For this study, a 20 kN load cell was selected, chosen specifically to accommodate the expected load range associated with hemp fiber failure. Natural fibers typically exhibit relatively low tensile strength compared to engineering materials like metals, making sensitivity crucial. The 20 kN load cell balances the need for sufficient load capacity to prevent sensor saturation while maintaining high sensitivity to detect subtle load variations, particularly in the initial elastic region of the stress-strain curve. Precise measurements are necessary to correctly determine Young's modulus and identify early damage/anomalies in tests.

Sample preparation was meticulously executed (Figure 23) to ensure test result reliability. Individual hemp fibers, each representing a single filament extracted from the bulk material, were carefully mounted on custom-designed specimen holders. These holders were engineered to provide rigid but gentle clamping, preventing slippage or premature damage while maintaining perfect axial alignment of the fibers along the load axis. The avoidance of misalignment is critical as even slight angular deviations can introduce bending stresses or uneven load distribution, leading to inconsistent or invalid results. The mounting process also minimized any pre-loading or stress concentration at the gripping points, which could otherwise initiate early failure.

Figure 23-Sample preparation

A gauge length of 7 cm was standardized for all specimens. This length was chosen after considering practical constraints, the dimensional uniformity of the fibers, and existing recommendations from the literature and testing standards such as ASTM C1557 – 03 (Reapproved 2008). The gauge length must be long enough to reduce the influence of gripping effects and to allow uniform strain distribution, yet short enough to prevent fiber buckling, slippage, or lateral deflection during testing. The 7 cm length provides a reliable compromise that facilitates precise strain measurement while maintaining specimen stability [31].

Tensile loading was applied at a controlled, constant crosshead displacement rate of 2 mm/min, corresponding to a strain rate of approximately 8×10^{-6} m/s. This rate was deliberately chosen to align with ASTM C1557 guidelines, ensuring that deformation occurs under quasi-static conditions. Maintaining a low, constant displacement rate is critical to avoid dynamic effects such as inertial forces, which could distort the stress-strain response or cause premature failure. Moreover, the selected speed ensures that fiber fracture occurs within a reasonable time frame (less than 30 seconds), which is necessary for the validity and repeatability of the results according to the standard. Deviating from this rate could compromise the accuracy and comparability of mechanical parameters, especially in brittle or viscoelastic natural fibers where strain rate sensitivity is significant [31].

During each test, the Shimadzu AGS-X continuously recorded load and displacement data at high sampling frequencies, enabling the generation of precise stress-strain curves. These curves capture the full mechanical response of the fiber, from initial elastic deformation, through any yielding or plastic deformation (if present), to final fracture. Ultimate tensile strength was identified as the peak stress prior to failure, while Young's modulus was calculated as the slope of the initial linear portion of the stress-strain curve, representing the elastic stiffness. The elongation at break was determined from the strain corresponding to the fracture point. This detailed data enabled comprehensive comparison between treated and untreated fibers, providing insight into the effects of chemical modifications on mechanical performance.

Cross-sectional area measurements, a key parameter for accurate stress calculation, were performed using optical microscopy combined with digital image analysis software. High-magnification images of the fiber cross-sections were captured with precise focus and clarity to allow accurate tracing and area measurement. Given the irregular and often non-cylindrical geometry of natural fibers, this approach is essential to avoid over- or under-estimation of the cross-sectional area, which directly affects the accuracy of calculated mechanical properties. Multiple measurements were taken for each fiber to account for variability and ensure statistical reliability.

While the tensile tests were not conducted in a strictly climate-controlled environment, steps were taken to mitigate the influence of ambient temperature and humidity fluctuations, both of which can significantly affect natural fiber mechanical properties due to their hygroscopic

nature. Tests were scheduled on days with stable environmental conditions and during periods when temperature and humidity were relatively constant. This approach, though not ideal, is an accepted compromise in experimental setups lacking specialized climate chambers. The consistency of environmental conditions contributed to the repeatability and validity of the experimental data.

Overall, this comprehensive testing methodology, combining careful specimen preparation, controlled loading protocols, precise instrumentation, and rigorous data analysis, provided a robust and detailed mechanical characterization of chemically treated hemp fibers. The results serve as a critical foundation for assessing the potential of these natural fibers in sustainable composite applications and advancing the understanding of their mechanical behavior under tensile loading.

CHAPTER 4: RESULTS AND ANALYSIS

The results obtained allowed for a clear evaluation of the parameters under study, highlighting relevant trends and significant differences between the variables analyzed. The information gathered throughout this chapter will be essential for the discussion and final interpretation of the data, enabling consistent conclusions in the following chapter.

4.1 FIBERS

Before presenting the results of the different treatment methodologies applied to plant fibers, it is essential to provide a detailed framework that justifies the selection of the analyzed variables, as well as the criteria adopted for their evaluation. Table 3 summarizes the tests carried out on samples of hemp fibers and chestnut shells, subjected to distinct physicochemical processes, with the aim of optimizing their application in composite materials.

The focus of this analysis lies in the removal of lignin and other structural impurities that compromise the compatibility of the fibers with polymeric matrices, particularly polylactic acid (PLA). The effectiveness of each treatment was assessed based on direct microscopic observations, which allowed for the identification of significant morphological variations in the fibers, such as presence or absence of shell residue, thickening of the cell walls, structural fragility, and exposure of the inner cell wall.

To ensure a rigorous and comparable evaluation, the treatments were grouped according to the type of process involved (open-circuit, closed-circuit, thermal treatment, and combined methods). Optical microscopy images supported the qualitative analysis, making it possible to distinguish between treatments with low, moderate, or good effectiveness. It is important to note that the classification of treatment effectiveness was not based solely on visual appearance, but rather on the integration of multiple criteria: observable reduction of lignin content, preservation of the fiber's structural integrity, absence of residual particles, and the degree of shell separation (in the case of chestnut samples).

Therefore, Table 3 provides a clear and organized synthesis of the treatments applied, along with corresponding microscopic observations and an overall classification of each method's

effectiveness. This analysis represents an essential step for interpreting the subsequent data and defining the optimal conditions for potential industrial applications.

Table 3 – Results of the chemical treatments

Assay	Treatment	Microscopic observations	Treatment effectiveness
Sample 1 Hemp	Chemical (open circuit)	High lignin content; agglomeration with PLA unfeasible	Low
Sample 2 Hemp	Chemical (open circuit)	Reduced lignin content compared to Experiment 1, but still unfeasible for PLA	Moderate
Sample 3 Hemp	Chemical (close circuit)	Lower lignin content; thicker fibers	Good
Sample 4 Hemp	Mechanical+ Chemical (closed circuit)	Thicker and drier fibers; more lignin than in Experiment 3	Moderate
Sample 4 Hemp[1]	Repetition of experiment 4	Fragile fibers; no significant improvement in lignin removal	Low
Sample 6 Hemp	Chemical (close circuit)	Fibers decreased in size; more lignin than in Experiment 3	Moderate
Sample 1 Chestnut	Thermal+ Chemical (treated chestnut)	Bark still attached; structural fragility	Low
Sample 2 Chestnut	Thermal+ Chemical (decomposed chestnut)	Bark attached; lower effectiveness in decomposed chestnuts	Low

[1]Sample already subjected to chemical treatment on 26/11/2024

Table 3 of results systematically summarizes the different treatments applied to hemp fibers and chestnut shells detailing the methodologies used, the observations obtained through microscopic analysis, and the evaluation of each procedure's effectiveness.

Regarding the hemp fibers, six distinct experiments were conducted, applying variations of chemical treatment processes (open and closed circuit), and in some cases, combining them with prior mechanical treatment stages. The main objective was the removal of lignin and other impurities to optimize the fibers' properties for future industrial and scientific applications particularly their compatibility with polymers such as PLA. It was observed that treatments conducted in a closed-circuit system (notably Assay 3) provided greater efficiency in lignin removal, resulting in fibers with better structural performance. However, subsequent experiments (such as 4, 5, and 6) revealed limitations in the control of fiber morphology, with variable results

including excessive thickening, structural fragility, and shrinkage indicating the need for further refinement of the operational parameters, Figure 24.

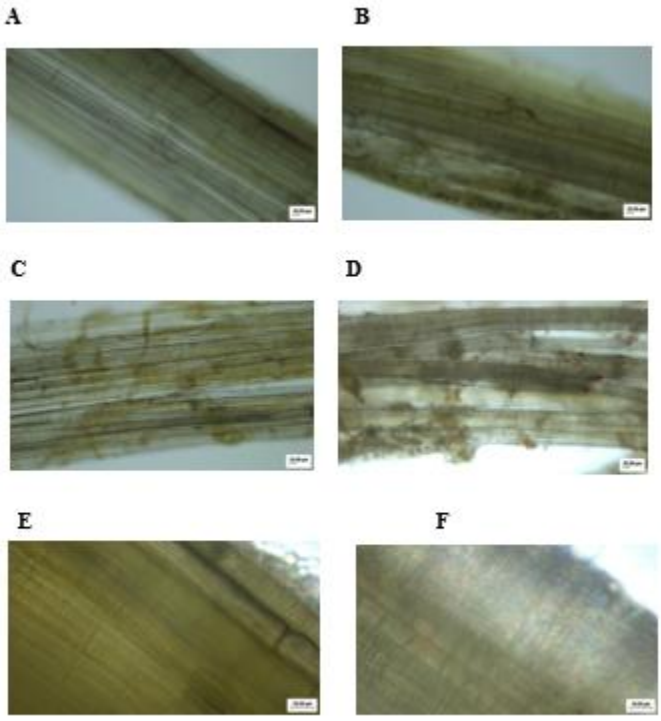


Figure 24- A- Microscopic image-Sample 1; B- Microscopic image-Sample 2; C- Microscopic image-Sample 3; D- Microscopic image-Sample 4; E- Microscopic image-Sample 5; F-Microscopic image-Sample 6

As for chestnut shells, two tests were conducted using samples in different states of preservation: one previously subjected to thermal treatment and the other in an advanced state of natural decomposition, Figure 25. Both procedures used the same closed-circuit chemical treatment system. However, the results showed low effectiveness in separating the shells from the internal fibers. Microscopic analyses demonstrated that, despite the structural fragility induced by the process, complete removal of the shell was not achieved, with visible residues still adhering to the surface. The decomposed sample yielded even more unsatisfactory results, suggesting that biological degradation compromised the fiber's integrity and the effectiveness of the applied treatment.

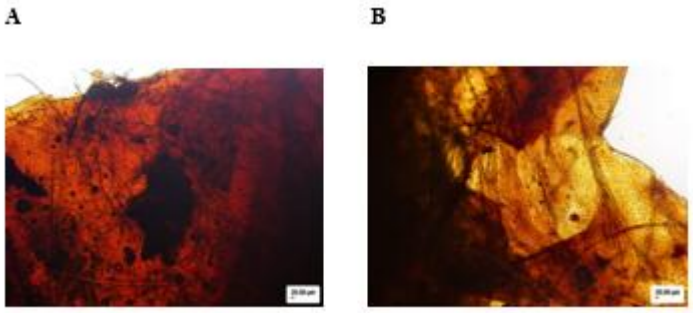


Figure 25- A- Microscopic image-Sample subjected to thermal treatment;
B- Microscopic image-Sample in advanced state of natural decomposition

Thus, the combined analysis of experimental data indicates that closed-circuit treatments are generally more effective in modifying the fibers, although there are still limitations to be overcome particularly regarding the complete removal of lignin and the preservation of the fibers' physical integrity. These results will be crucial in guiding future optimization stages of the processes and the development of composites with enhanced technical performance.

4.2 HEMP TENSILE TEST

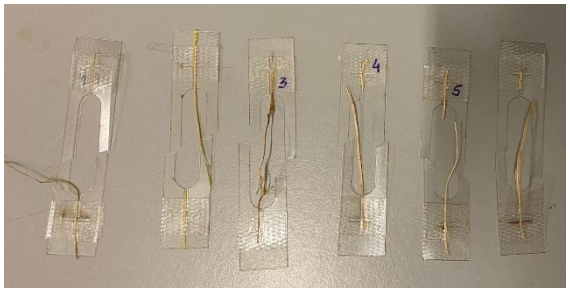
During the tensile tests, force-displacement curves were recorded in real time, enabling the calculation of maximum tensile strength, defined as the ratio between the maximum applied force and the cross-sectional area of the fiber at the rupture zone, and the modulus of elasticity (Young's modulus), derived from the slope of the linear region of the stress-strain curve.

It is important to highlight that only tensile tests on hemp fibers were performed in this work, focusing on the characterization of the intrinsic mechanical properties of the fibers. Pull-out tests, which are typically used to evaluate the fiber-matrix interfacial adhesion in composite materials by measuring the force required to extract the fiber from the matrix, were not conducted. Although pull-out tests provide valuable insights into the fiber-matrix bonding quality, the methodology here concentrated exclusively on the mechanical behavior of the isolated hemp fibers.

Figure 26 shows images of the hemp fibers after the tensile tests, revealing the fracture zones in each sample and highlighting different modes of structural failure. Most specimens failed

within the central gauge section, indicating that failure occurred naturally and was not influenced by imperfections in the gripping areas. In several cases, fibers fractured abruptly and perpendicular to the tensile axis, a behavior typical of natural materials with low plastic deformation capacity, characterizing a predominantly brittle failure mode.

A



B

C

Figure 26 – a) First tensile test; b) Second tensile test; c) Third tensile test

In the Figure 26, indicates potential issues in the impregnation and anchorage of the fibers during the composite manufacturing process. Fiber misalignment observed after testing may indicate residual stress or accumulated deformation prior to fracture.

These qualitative observations are essential to understanding the failure mechanisms of hemp fibers and provide important guidance for optimizing manufacturing processes, particularly concerning uniform fiber distribution, matrix impregnation improvement, and fiber surface treatments to enhance interfacial bonding and overall mechanical performance of composites.

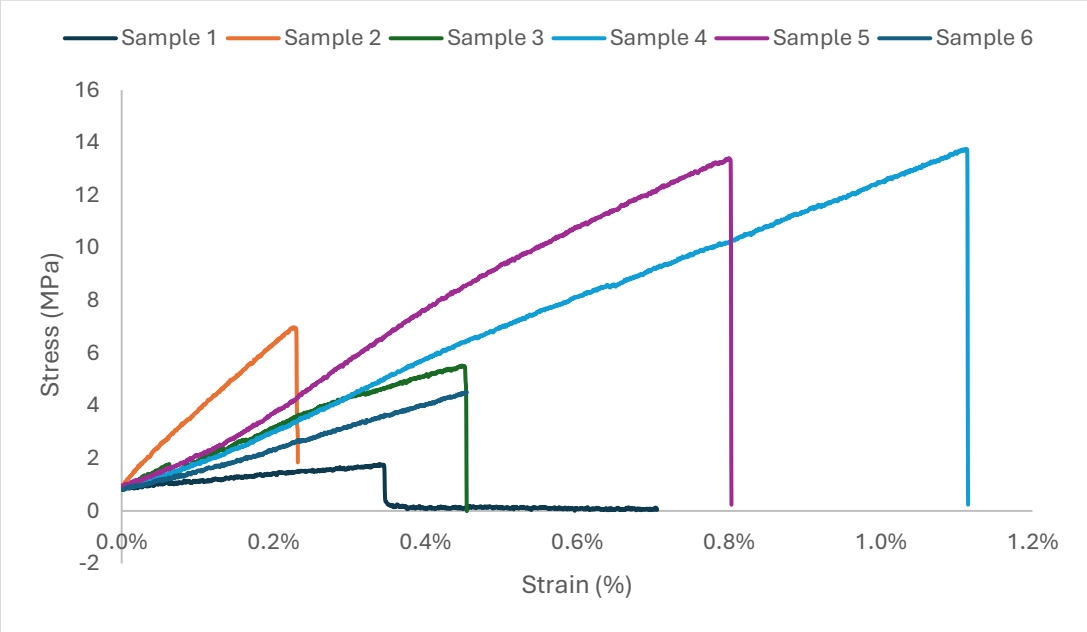


Figure 27- Stress–strain curves obtained from the first test

The graphic (figure 27) presents the stress–strain curves obtained from the first test of the six hemp samples. It can be observed that all samples initially display an approximately linear behavior, which characterizes the elastic region where the relationship between stress and strain follows Hooke's law. From this point onwards, each sample evolves differently, showing significant differences both in terms of maximum strength and deformation capacity prior to failure.

Sample 2 stands out for its premature failure at low strain levels (~0.25%), although it reached a relatively high stress (~7 MPa). This behavior indicates a stiffer yet brittle material, unable to withstand significant deformation before rupture. In contrast, Samples 4 and 5 demonstrated greater ductility, sustaining strains above 0.8% and reaching maximum stresses between 13 and 14 MPa. This performance suggests that these samples have a higher energy absorption capacity up to failure, combining strength with deformability.

Samples 1 and 3 exhibited intermediate behavior, reaching maximum stresses between 4 and 6 MPa and strains in the range of 0.3% to 0.4%. Sample 6 showed a response similar to Sample 5 but failed at a lower strain (~0.8%), which indicates good strength but with a reduced elongation capacity.

Overall, the results highlight the variability in the mechanical behavior of the samples tested. While some presented high strength combined with greater ductility (Samples 4 and 5), others displayed characteristics of brittle materials (Sample 2) or intermediate performance (Samples 1, 3, and 6). This analysis is essential for selecting the most suitable material for specific applications, since different scenarios may require higher strength, greater deformation capacity, or a balance between these properties.

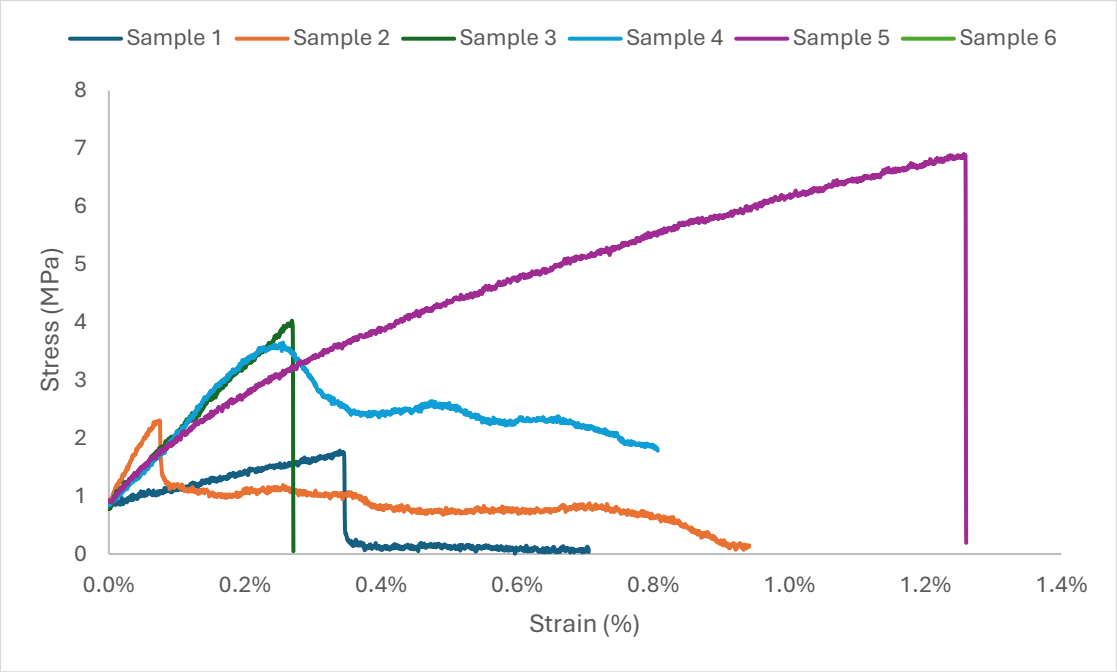


Figure 28- Stress–strain curves obtained from the second test

The graphic (figure 28) presents the stress–strain curves obtained from the second test of the six hemp samples. As in the first test, all samples initially exhibit a nearly linear behavior corresponding to the elastic region, in which stress and strain maintain a proportional relationship. From this stage onward, however, the samples evolve differently, displaying distinct values of maximum stress and deformation at failure.

Sample 2 shows premature rupture, with failure occurring at a very low strain (~0.15%) and a maximum stress of approximately 2.2 MPa. This indicates a material with high stiffness but brittle behavior, incapable of sustaining significant deformation. Similarly, Sample 3 also exhibits an early failure (~0.25%) but at a higher stress level (~4 MPa), suggesting a more resistant yet still brittle response.

Samples 1 and 6 reached intermediate maximum stresses (~1.7 MPa and ~3.8 MPa, respectively), failing at strains around 0.3%. These results indicate materials with modest strength and limited deformation capacity. Sample 4, in turn, sustained higher levels of strain (up to ~0.8%) but with moderate stress (~3 MPa), evidencing a more ductile yet less resistant response.

Sample 5 stands out as the best-performing material in this set of tests. It withstood the highest strain (~1.25%) and the greatest stress (~7 MPa) before rupture, demonstrating a combination of high strength and high ductility.

Overall, these results confirm the variability in the mechanical performance of hemp samples, as already observed in the first test. While Sample 5 once again exhibited superior properties, other samples showed premature failure or only moderate performance, reinforcing the heterogeneous nature of the material and highlighting the importance of sample selection and processing for structural applications.

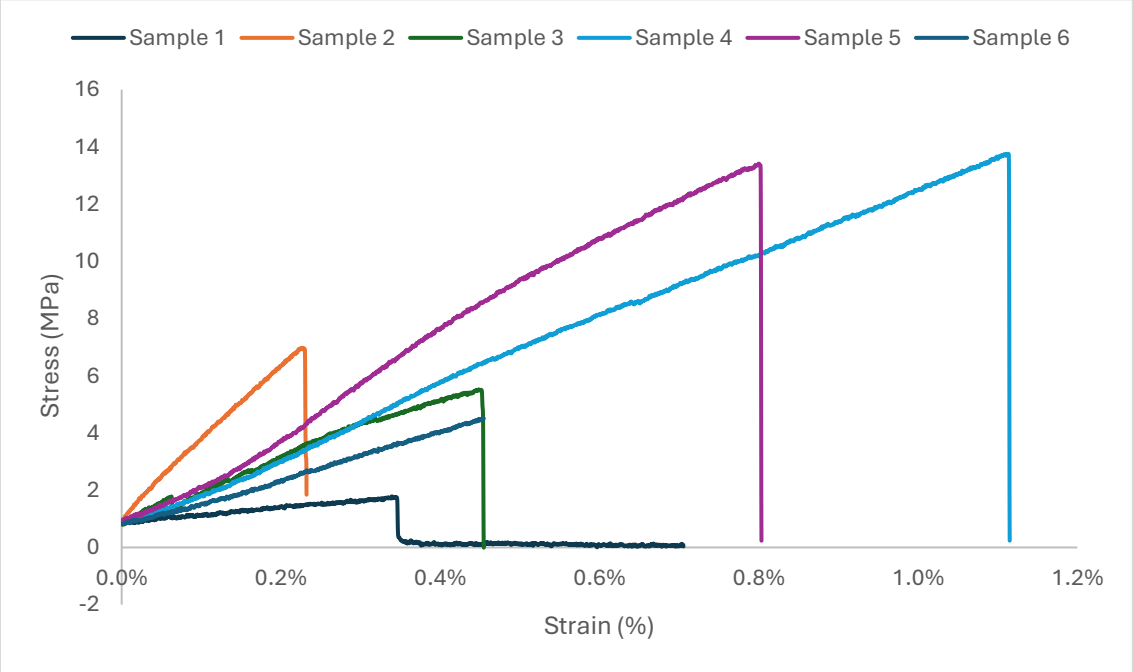


Figure 29- Stress–strain curves obtained from the third test

The graphic (figure 29) presents the stress–strain curves obtained from the third test of the six hemp samples. As in the previous tests, all samples initially exhibit a nearly linear response, corresponding to the elastic region where stress and strain are proportional. From this region

onward, however, the samples evolve differently, showing marked variations in both maximum strength and deformation at rupture.

Sample 2 exhibits premature failure at low strain (~0.25%), although it reached a relatively high stress (~7 MPa). This behavior indicates a material with greater stiffness but brittle characteristics, unable to accommodate significant deformation. Similarly, Samples 1 and 3 also show early rupture, with maximum stresses in the range of 4–5 MPa and strains around 0.3–0.4%. These results suggest materials with moderate strength but limited ductility.

Samples 5 and 6 demonstrated superior performance compared to the other samples. Sample 5 sustained stresses of approximately 13 MPa with a strain of ~0.8%, while Sample 6 reached the highest values, resisting stresses of nearly 14 MPa at strains above 1.1%. These results indicate that both samples combine high strength with considerable ductility, particularly Sample 6, which shows the best overall performance in this test series.

In summary, the third test confirms the heterogeneous mechanical behavior of the hemp samples. While Samples 5 and 6 exhibited a favorable balance between strength and ductility, Sample 2 behaved as a stiff but brittle material, and Samples 1 and 3 demonstrated intermediate performance. This variability emphasizes the need for careful material selection and processing to ensure reliable mechanical performance in structural applications.

These findings are consistent with the results reported in article [32] who conducted an extensive tensile analysis of raw hemp fibers and demonstrated a high degree of variability in their mechanical properties due to natural defects, diameter fluctuations, and microstructural inhomogeneities. Their statistical analysis, based on Weibull and normal distributions, revealed that even at the fiber level, material inconsistency significantly affects mechanical behavior. [32].

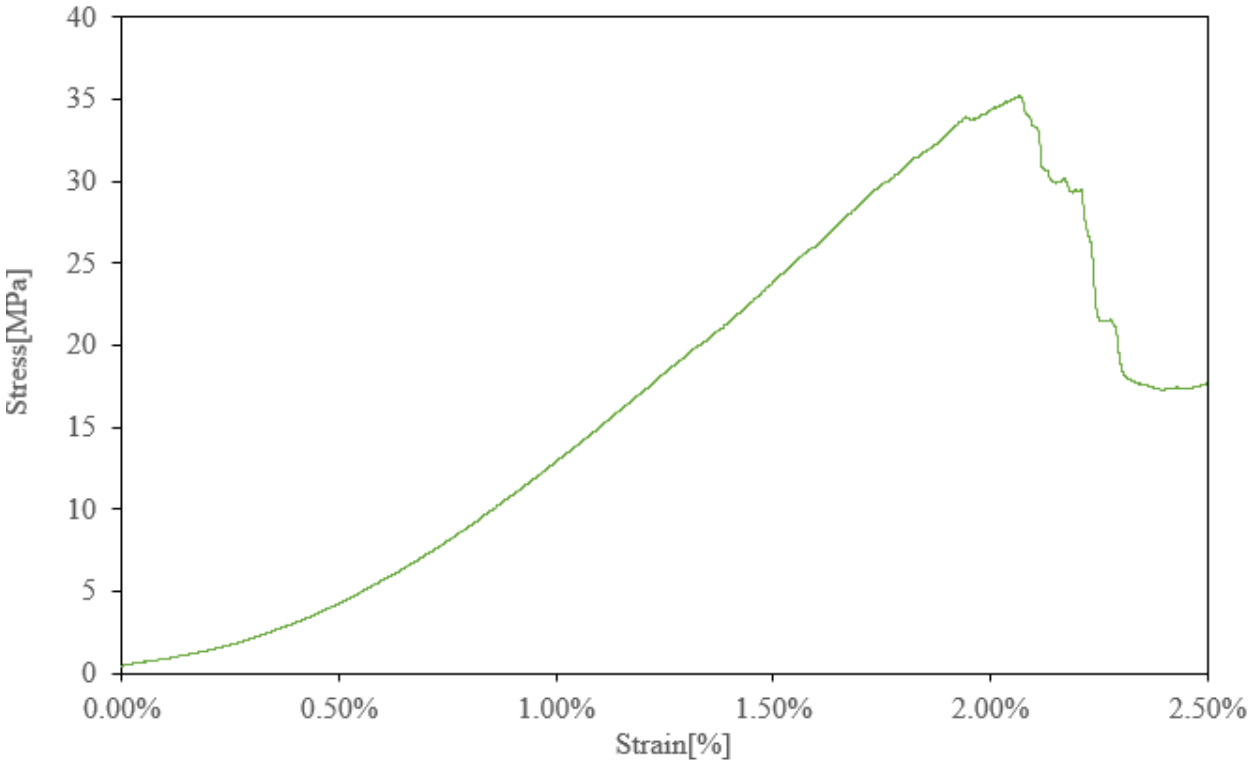


Figure 30- Stress- Strain graph of the commercial hemp tensile test

The curve shown in Figure 28 represents the tensile test performed on processed commercial hemp fibers, which are also natural fibers. In this study, hemp fibers were processed, and six samples were prepared for the tensile test, allowing for a direct comparison with results obtained from untreated natural fiber. The commercial fiber was presumably subjected to standard industrial processes (such as washing, bleaching, or softening) but was used as received, without any additional chemical modifications or treatments before the test.

From the start of loading, the behavior of the processed commercial fibers stands out due to its smooth and continuous progression without abrupt oscillations, demonstrating a more homogeneous structure free of internal defects. Stress increases approximately between 0.75% and 2% strain, reaching a maximum peak of around 35 MPa, significantly higher than what was observed in untreated natural fibers.

In contrast, tests conducted on treated natural fibers (Figure 27) revealed stress-strain curves with multiple discontinuities, partial ruptures, and intermittent failures reflecting the typical mechanical behavior of brittle materials. The average maximum stress values in these cases ranged between 5 MPa and 15 MPa, with strains generally below 0.25%, indicating a much more limited deformation and strength capacity.

After the maximum point on the curve, the processed commercial fibers still show substantial differences, although there is an abrupt drop in the ultimate stress, the material retains some residual load-bearing capacity, indicating a degree of toughness and energy dissipation capacity, qualities absent in untreated natural fibers, which almost always failed suddenly and completely. This behavior can be explained by the industrial treatments applied to the commercial hemp fibers, which promote better alignment and compaction of fiber bundles, removal of impurities and heterogeneities, or the use of capitalizing agents that reinforce the fiber–polymer matrix interface.

These improvements result in a material with superior structural performance and greater predictability in mechanical behavior, both essential aspects for industrial applications.

Table 4 – Comparison between natural fibers and commercial hemp

Parameter	Native fiber (mean)	Commercial Hemp
Maximum stress (σmáx) [MPa]	5 – 15 MPa	~35 MPa
Strain at break [%]	0,15 – 0,25 %	~2,1 %
Type of failure	Bittle, abrupt	Semi-ductile, progressive
Fracture	Multiple local failures	Clear, centralized rupture
Structural quality	Irregular, with defects	Uniform, industrial
Post-fracture behavior	Null	With residual load-bearing capacity
Applicability	Experimental, limited	Commercial, high

The analysis of the data presented in Table 4 confirms the mechanical superiority of commercial hemp compared to manual chemical fibers. The maximum tensile strength is nearly three times higher, and the strain at break is approximately eight times greater, reflecting not only increased strength but also a more stable and predictable structural response. The failure mode observed in commercial fiber, progressive and maintaining partial integrity after rupture, contrasts with the abrupt fracture seen in natural fibers, highlighting greater toughness and structural quality in the industrial material.

These results underscore the decisive role of industrial processing, such as fiber alignment, defect elimination, and the application of compatibilization treatments in enhancing the mechanical properties of natural materials. Thus, while natural fibers present significant limitations for structural applications, commercial hemp emerges as a viable and efficient alternative for contexts that require consistent and reliable mechanical performance.

CHAPTER 5: CONCLUSION

This dissertation aimed to evaluate the technical feasibility of using natural fibers, hemp, flax, and chestnut, as reinforcement in PLA-based polymer matrix composites, with applications in additive manufacturing, specifically in filaments for 3D printing. The research systematically addressed the extraction, preparation, and functionalization of the fibers, as well as the mechanical characterization of the resulting composites.

Figures 27, 28, and 29 present the stress–strain curves obtained from three successive tensile tests performed on six hemp samples. In all cases, the samples initially exhibit an approximately linear response corresponding to the elastic region, after which the curves diverge, reflecting distinct mechanical behaviors in terms of maximum strength, ductility, and failure mode.

A consistent trend across the three tests is the premature failure of Sample 2. In every case, this sample shows rupture at very low strain levels (~0.2–0.25%), despite reaching relatively high stresses (6–7 MPa). This indicates that Sample 2 behaves as a stiff but brittle material, with limited capacity for deformation before failure. Similarly, Samples 1 and 3 show modest strength (4–6 MPa) and limited elongation (0.3–0.4%), classifying them as materials of intermediate performance.

On the other hand, Samples 5 and 6 consistently demonstrate superior properties. In the first and third tests, they reach the highest maximum stresses (13–14 MPa) and sustain strains up to ~0.8–1.2%, combining strength with ductility. In the second test, Sample 5 still outperformed the others, with ~7 MPa and ~1.2% strain, whereas Sample 6 achieved ~3.8 MPa and ~0.25% strain, suggesting that its performance may be more sensitive to test conditions or sample preparation. Sample 4 exhibited moderate behavior across the tests, showing higher ductility than Samples 1–3, but lower strength compared to Samples 5 and 6.

Taken together, the three tests reveal the heterogeneous mechanical response of hemp samples. While Samples 5 and 6 generally display the best balance of strength and deformability, Sample 2 repeatedly demonstrates brittle behavior, and Samples 1, 3, and 4 occupy intermediate positions depending on the test. The variability observed between tests further highlights the influence of material heterogeneity and experimental conditions on the mechanical performance

of hemp, reinforcing the need for rigorous selection and processing to ensure reproducibility and reliability in structural applications.

Thus, it is concluded that the objectives initially set were largely achieved. The study demonstrated the technical feasibility of using natural fibers, especially hemp, as reinforcement in biodegradable materials for 3D printing applications, provided that rigorous treatment and compatibilization processes are employed. The main contributions of this work lie in identifying the technical challenges associated with the application of natural fibers in polymer composites and in proposing guidelines for overcoming them.

In conclusion, this work contributes to the advancement of knowledge on the use of natural fibers as a sustainable reinforcement in composites for additive manufacturing, aligning with the principles of the circular economy and environmental sustainability, and paving the way for future technological innovations with practical feasibility and positive impact.

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