Mechanical behavior of a composite material using a polyester matrix reinforced with *Guadua angustifolia* bamboo fibers

Eng. MSc. Patricia Luna Tamayo

Faculty of Engineering
Department of Civil and Agricultural Engineering
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Eng. MSc. Patricia Luna Tamayo

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Advisor:
Eng. PhD. Juan Manuel Lizarazo Marriaga
Co-advisor:
Phys. PhD. Alvaro Mariño Camargo

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To Camilo, Mariana and Sebastian ...
the driving force of my life

A Camilo, Mariana y Sebastián ...
el motor de mi vida
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Abstract

Natural fibers have become a valuable resource in the composite industry. Their use as a reinforcement material for polymeric matrices provides multiple benefits for composites, thus showing a remarkable mechanical strength per unit weight and a low production cost per volume unit. Composites’ mechanical behavior is strongly influenced by properties of individual components and the bonding between matrix and fibers. Due to the hydrophilic nature of natural fibers and the hydrophobic behavior of common polymers, there is a physico-chemical incompatibility between them. This incompatibility leads to a poor stress transfer from matrix to fibers, and as a result, to an inadequate mechanical performance of the composite material. Therefore, it is necessary to treat fibers or matrices, in order to improve composites’ final properties. When it comes to industrial applications, natural fibers are commonly treated in order to overcome those incompatibilities.

This research is intended to use Guadua angustifolia bamboo fibers (guadua fibers) as a reinforcement for polyester matrices. In order to increase the compatibility between phases, before composite manufacturing, the fibers were treated employing chemical and physical approaches. As for the chemical approach, alkali (sodium hydroxide) treatments were used to reduce guadua fibers’ hydrophilic features, thus inducing more chemical compatibility with the polyester matrix. Regarding the physical approach, plasma treatments (dry etching) were used in order to increase guadua fibers’ superficial roughness, leading to an increase in the mechanical bonding (frictionally) with the matrix.

This research was focused on the influence of the above compatibilization techniques on the properties (physical, microstructural, chemical and mechanical) of guadua fibers and polyester-guadua composites. The experimental program was focused on the extraction and characterization of guadua fibers, as well as on the characterization of polyester matrices and composites. Results showed that alkali treatments decrease guadua fibers’ tensile strength, around 42% for the highest concentration; in contrast, plasma treatments do not affect considerably their tensile properties. Moreover, both
compatibilization techniques improve polyester-guadua composites' tensile and bending strength, due to an increment in the bonding stress between composite phases. Finally, an analytical model is proposed to describe the macroscopical behavior of the composite material under tensile loads, obtaining differences between the measured and calculated strength is $\pm 3\%$.

This thesis demonstrates the potential of using natural fibers as a reinforcement for composite materials, which could be advised for different engineering applications due to their adequate mechanical behavior.

**Keywords:** Natural fibers, bamboo *Guadua angustifolia*, alkali treatment, plasma treatment, composite materials, mechanical behavior.
Resumen

Las fibras naturales se han convertido en un recurso valioso para la industria de los materiales compuestos. Su uso como refuerzo de matrices poliméricas le proporciona múltiples beneficios al material compuesto, siendo destacable la resistencia mecánica por unidad de peso y el bajo costo de producción por unidad de volumen. El comportamiento mecánico de los materiales compuestos está fuertemente influenciado por las propiedades de los materiales constituyentes y de la unión entre matriz y fibras. Debido a la naturaleza hidrófila de las fibras naturales y al comportamiento hidrófobo de los polímeros comúnmente empleados, existe una incompatibilidad físico-química entre las fases del material compuesto. Esta incompatibilidad trae como consecuencia una deficiente transferencia de esfuerzos desde la matriz hacia las fibras, y por lo tanto, un inadecuado desempeño mecánico del material compuesto. Así, es necesario tratar las fibras o las matrices poliméricas para mejorar las propiedades finales del material compuesto. Tradicionalmente, en aplicaciones industriales los tratamientos están direccionados a la modificación de las fibras naturales.

El objetivo de esta investigación es usar fibras de bambú *Guadua angustifolia* (fibras de guadua) como refuerzo de matrices de poliéster. Para aumentar la compatibilidad entre las fases, antes de la fabricación del material compuesto, las fibras de bambú se trataron usando enfoques químicos o físicos. En el enfoque químico, se utilizaron tratamientos alcalinos (con hidróxido de sodio) para reducir las características hidrófilas de las fibras de guadua, lo que induce una mayor compatibilidad química con la matriz de poliéster. En el enfoque físico, se usaron tratamientos plasma (de grabado en seco) para aumentar la rugosidad superficial de las fibras de guadua, aumentando así el agarre mecánico (por fricción) con la matriz.

Así, en esta investigación se estudió la influencia de las dos técnicas de compatibilización en las propiedades (físicas, microestructurales, químicas y mecánicas) de las fibras de guadua y del compuesto guadua-poliéster. El programa experimental se enfocó en la extracción y caracterización de fibras de guadua, así como en la caracterización de la matriz de poliéster y del compuesto. Los resultados obtenidos muestran que
los tratamientos alcalinos disminuyen la resistencia a tracción de las fibras de guadua cerca de un 42% para la concentración más alta. En contraste, los tratamientos con plasma no afectan considerablemente la resistencia a tracción de las fibras. Además, ambas técnicas de compatibilización mejoran la resistencia a tracción y flexión de los compuestos guadua-políester, debido al incremento en la adherencia entre las fases del material compuesto. Finalmente, se propone un modelo analítico para describir el comportamiento macroscópico del material compuesto ante cargas de tracción, obteniendo diferencias cercanas al ±3% entre los valores medidos y los calculados.

Esta tesis demuestra la potencialidad del uso de fibras naturales como refuerzo de materiales compuestos, los cuales pueden ser usados en diversas aplicaciones de ingeniería debido a su adecuado desempeño mecánico.

**Palabras clave:** Fibras naturales, bambú *Guadua angustifolia*, tratamiento alcalino, tratamiento plasma, materiales compuestos, comportamiento mecánico.
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Preface

During the research progress, many scientific topics of great interest were broken down into several journal papers and conferences. A list of the most relevant contributions is listed below.

Papers marked with (*) are presented in Appendix B.

Journal papers:


Conference proceedings:


Oral presentation:


Introduction

According to Ashby (1992), engineering materials can be classified into six categories: metals, polymers, elastomers, ceramic, glasses and composites. Composite materials are made out of two or more constituents of the other categories, with significantly different physical and/or chemical properties that, in combination, result in a material with features not found in its constituents (Meyers and Chawla, 2009).

In general terms, three phases can be distinguished regarding composite materials: a continuous phase commonly called matrix, a discontinuous phase called reinforcement, and the interfacial region or interface which occurs between the reinforcement and the matrix, as a consequence of the physico-chemical interactions between composite constituents (Daniel and Ishai, 1994). Therefore, composite properties depend on the properties of its constituents, its geometry, the distribution between phases and the properties at the interface. Moreover, according to some authors (Jang-Kyo and Yiu-Wing, 1998; Bank, 2006b; Zhou et al., 2016), a well-established interface linkage is mandatory in order to ensure an adequate composite performance, since the properties at the interface determine the stress transfer from matrix to fibers.

Ceramics, metals and polymers are commonly used as matrices of composite materials. Common ceramic matrices are made out of silicon, alumina and concrete, the latter highly used in the construction industry. In the case of metallic matrices aluminum, magnesium, titanium and copper are frequently used. Polymers include thermoplastic resins (commonly polystyrene, polyethylene, nylon and polycarbonate) and thermoset resins (commonly epoxy, polyamide, polyester, and phenolic). Ceramics and metallic matrices are mostly employed in the aerospace industry. According to Askeland et al. (2013), polymers are the most employed matrices in the composite industry, due to their versatility, ease of manufacturing and low cost. In respect of the polymer material family, thermosets are the mostly used polymeric resins (Vison and Sierakowski, 2004).

A large variety of fibers can be used as composite reinforcement. Fibers like glass, kevlar, carbon, boron and metallic fibers (Liu et al., 2013) have been conventionally
used. However, due to the increment of environmental awareness, nowadays natural fibers have become a valuable resource for the composite industry (Pickering et al., 2015; Senthilkumar et al., 2019). In this sense, since 1990’s natural fiber-reinforced materials have been manufactured for their use in automotive, furniture, packing and construction applications, where a high load carrying capacity is not required (Alsaeed et al., 2013a; Sanjay et al., 2016, 2018). Fernandes et al. (2015) made a statistical analysis of the scientific publications in the area of natural fiber-reinforced polymer composites since January 2000 through May 2014, which revealed that the interest in the developing ecologically viable materials, especially with less environmental impact, with the use of raw materials from natural sources, like natural fibers, has grown in the last decade. Furthermore, according to Grand View Research (2018), the global market of natural fiber-reinforced composites was valued at USD 4.46 billion in 2016, and a 12% growth is expected from 2016 to 2024.

Accordingly, abaca (Ramadevi et al., 2012; Cai et al., 2016), coconut (de Carvalho et al., 2015; Sharma et al., 2015a), cotton (Koyuncu et al., 2016), fique (Hidalgo-Salazar and Correa, 2018), flax (Marais et al., 2005; Bozaci et al., 2013), jute (Seki et al., 2010; Sever et al., 2011), pineapple leaf (Senthilkumar et al., 2019) and bamboo (Yu et al., 2014; Chunhong et al., 2016; Huang and Young, 2019) are some examples of natural fibers that have been used as reinforcement of polymer matrices. Peças, P.; Carvalho, H.; Salman, H.; Marco (2018) made a bibliometric analysis that revealed that between 2016 and 2018 cotton was the natural fiber with a higher number of publications by the research community, with 427 papers in the Science Direct database, followed by pineapple (379 papers) and bamboo (275 papers). In contrast, natural fibers like abaca (9 papers) and ramie (20 papers) are the ones with less scientific papers published between these years. According to the authors of the research, the differences in publication frequency could be explained by the origin and amount of plant areas available throughout the planet, the product readiness to be used as a composite reinforcement material and the overall mechanical properties.

Bamboo is a giant arborescent grass that belongs to the Gramineae (Poaceae) family, Bambusoideae subfamily (Singh et al., 2017). There are approximately 75 genera and 1300 species (Liese and Köhl, 2015), distributed in tropical and temperate zones of different parts of the globe, occupying habitats from sea level to high mountains (Singh et al., 2017). Bamboos include some of the fastest growing plants in the world, due to their unique rhizome dependent system (Hidalgo, 2003), which is one of their most interesting features as a forest resource. According to related literature, bamboo is considered an important plant fiber which has a great potential to be used in the
composite industry, due to its structural variation, mechanical and thermal properties (Abdul et al., 2012). However, various authors agree that the most interesting feature for its use as a reinforcement for different matrices is its high strength to weight ratio (Osorio et al., 2010; Peças, P.; Carvalho, H.; Salman, H.; Marco, 2018; Scherer and Bom, 2019).

The most important bamboo specie in Latin America is the *Guadua angustifolia*, native from Colombia, Venezuela and Ecuador (Morán, 2015). Particularly in Colombia, this bamboo specie has been related to the folklore, ecosystem, social customs and in general to the socio-cultural development of the western region in the country (Cruz, 2009). In its raw form, it has been massively used in Colombia as a construction material since pre-Columbian times (Estrada, 2016). As a laminated construction material, there are fewer real applications, but there is a lot of research carried out (Correal and Ramirez, 2009, 2010; Luna and Takeuchi, 2012; Takeuchi, 2013; Luna et al., 2014b; Luna and Takeuchi, 2014; Correal et al., 2014). In contrast, there is a limited research about its fibers (Osorio et al., 2010; Fuentes et al., 2011; Tolosa et al., 2014; Trujillo et al., 2014; Espitia-Nery et al., 2018), and even less on fiber extraction (Obando, 2010; Estrada, 2010; Luna and Lizarazo-Marriaga, 2016).

There are multiple technical advantages from using natural fibers as a reinforcement for polymeric matrices, from which it can be highlighted their low density, high specific strength and stiffness, abundant availability, corrosion resistivity, low cost and non-abrasive processing features. However, there are some disadvantages from using them, such as their high property variability and moisture absorption variability, low strength and durability and poor fiber/matrix bonding (Pickering et al., 2015; Sanjay et al., 2018; Halip et al., 2019). According to some authors (John and Anandjiwala, 2008; Alsaeed et al., 2013a; Rohit and Dixit, 2016; Hashim et al., 2017; Sanjay et al., 2018; Peças, P.; Carvalho, H.; Salman, H.; Marco, 2018; Halip et al., 2019), the poor fiber/matrix bonding is the main disadvantage from using natural fibers as a reinforcement for polymers. The weak adhesion between composite phases is a consequence of the incompatibility between the hydrophilic natural fibers and the hydrophobic polymer matrices. This limitation can be overcome by modifying the physico-chemical properties of polymer matrices or natural fibers (Valadez-Gonzalez et al., 1999). Regarding industrial applications, the modification of the fiber’s physico-chemical properties is commonly used (Summerscales et al., 2010; Luna et al., 2016a). Thereby, the modification of the fiber’s properties can be accomplished through chemical or physical methods (Bledzki et al., 1996; Faruk et al., 2012; Islam et al., 2013; Fernandes et al., 2015). The main purpose of chemical methods is to reduce the hydrophilic features
of natural fibers, thus inducing more compatibility with polymer matrices (George et al., 2001; Sanjay et al., 2018). On the other hand, physical methods change the fiber’s structural and surface properties, mainly affecting the mechanical (frictionally) bonding with polymers (Bledzki et al., 1996; Halip et al., 2019). The chemical modification involves alkali, silane, benzylation and acetylation treatments among others (Halip et al., 2019), from which, according to Li et al. (2007) and Fernandes et al. (2015), alkali treatments are the most used ones. Physical modifications can be carried out through plasma, vacuum ultraviolet irradiation, ozone, corona, γ-ray and laser treatments (Sanjay et al., 2018).

Thus, this thesis is intended to provide technical and scientific elements for using natural fibers as a reinforcement for composite materials. In this way, it was proposed to characterize some physical, microstructural, mechanical and chemical properties of Guadua angustofila bamboo fibers (fibers) and polyester-fiber composites. Fibers’ physico-chemical properties were modified in order to improve the bonding with the polyester matrix. These modifications accomplished by using chemical and physical methods. As for the chemical method, alkali treatments were used. The physical modification was achieved through a novel plasma technique.

The principal aim of this research project was to establish the mechanical behavior of the P/BG composite material made using Guadua angustifolia bamboo fibers, embedded into a polyester matrix.

In order to reach this aim, three objectives were developed:

- To develop a Guadua angustifolia bamboo macrofiber extraction method, and characterize its physical, mechanical and chemical properties.
- To evaluate the effect of the treatments by using alkali or argon plasma on the physical, mechanical and chemical properties of Guadua angustifolia bamboo fibers, and on the physical and mechanical properties of the P/BG composite.
- To establish an analytical model to describe the macroscopic behavior of the P/BG composite material under tensile loads.

This document is divided into three parts, each of them related to fibers, polymers and polymer composites, respectively. This arrangement was made due to the necessity of presenting the results and discussion of each part independently. It is expected that this methodology will help the reader to understand the progression of the work, which involved an integration of many concepts related to composite material science.
The first part of the research was focused on the extraction and characterization of *Guadua angustifolia* bamboo fibers. The technical aspects related to the classification, chemical composition, properties and extraction methods of natural fibers are presented in Chapter 1. This chapter also describes some general aspects related to the anatomy of bamboo plants and highlights the state of art of bamboo fibers. Chapter 2 is related to the establishment of the methodology for extracting *Guadua angustifolia* bamboo fibers. Chapter 3 describes the experimental work and results obtained from the characterization of extracted fibers. Chapter 4 presents the most relevant conclusions for this part of the research.

The aim in the second part of the research was to characterize the polyester matrix used for the manufacturing of the P/BG composite material. Chapter 5 presents a brief description of some relevant engineering aspects and characteristics of polymers that could affect the behavior of composite materials. Chapter 6 presents the experimental programme and results obtained from the characterization of the polyester resin used in the research. Chapter 7 highlights the most relevant conclusions in the second part of the research.

Finally, the third part of the research was focused on the characterization of the P/BG composite material developed in this research. Thus, Chapter 8 shows a brief description of some important aspects related to the mechanical performance of composite materials. Also, in this chapter, it was included a section for composites reinforced using natural fibers, which presents a discussion on the compatibilization treatments that could be used to modify the physico-chemical properties of natural fibers, remarking on the treatments employed in this research. Chapter 9 explains the experimental procedure used for treating guadua fibers and the manufacturing process employed for the fabrication of the P/BG composite material. Also, this chapter describes the experimental methodology used for the characterization of treated fibers and the P/BG composite material. Chapter 10 shows the obtained results from the experimental characterization of treated fibers and the P/BG composite. Chapter 11 presents the proposed analytical model to determine the P/BG composite material’s tensile strength. Finally, Chapter 12 highlights the main outcomes of this part of the research.

Although essential conclusions are provided at the end of each part of the document, Chapter 13 presents the main key conclusions and findings of this research. In this, the limitations of the work carried out are stated and considerations about future work are presented.
It’s worth mentioning that for the development of this research, an international research internship at the *Pontificia Universidade Católica do Rio de Janeiro, PUC RIO* was carried out during the second semester of 2017. The main objective of the internship was to explore some different techniques for the physical characterization of bamboo culms and fibers. The internship supervisor was the Prof. Khosrow Ghavami, leader of the Non-Conventional Materials and Technologies (NOCMAT) research group.
Part I
Fibers

This first part of the research is focused on the mechanical characterization of *Guadua angustifolia* bamboo fibers that could be used, in general, as reinforcement of composite materials. The first chapter outlines important topics related to the classification, chemical composition, properties and extraction of natural fibers and highlights the state-of-art of bamboo fibers. Also, the description of general aspects related to the anatomy of bamboo plants was included in this chapter. The second chapter describes the research work carried out on the establishment of an extraction methodology of *Guadua angustifolia* bamboo fibers. This chapter presents a brief description of the proposed methodology to determine the cross-sectional area of *Guadua angustifolia* bamboo fibers, that was already published in a scientific journal, as well as the system compliance for the machine used on the mechanical testing. The third chapter presents the characterization of the extracted fibers. Finally, the fourth chapter points out the most relevant conclusions of this first part of the research.
Chapter 1

Review on the state-of-art of natural fibers

In general, fibers can be defined as a unit of matter characterized by flexibility, fineness and a high length/thickness ratio. In mechanics, they can be described as anisotropic material which is, in most cases, strong and stiff along its length but may bend under its own weight (Fangueiro and Rana, 2016).

In tropical regions, natural fibers are found in abundance and many of them are suitable to be used in many engineering applications (Rohit and Dixit, 2016). Natural fibers are constituted by long and chain-like molecules of organic nature, known as macromolecules or natural-polymers. These molecules are able to pack together closely to each other resulting in crystalline regions. On the other hand, there are other regions where molecules do not hold together, forming random arrangements or amorphous regions. The crystalline regions provide strength and rigidity to the fibers, while amorphous regions are responsible for flexibility and reactivity (Kabir et al., 2013; Fangueiro and Rana, 2016).

This chapter describes the principal engineering aspects of natural fibers. Considering that this research makes use of fibers extracted from *Guadua angustifolia* bamboo culms (guadua), the first part of this chapter describes some general aspects related to the anatomy of bamboo plants. Since natural fibers encompass all forms of fibers ranging from woody plants, grasses, fruits, agriculture crops, seeds, water plants, palms, wild plants, leaves, animal feathers to animal skins (Ansell and Sapuan, 2014), this chapter is restricted only to the state-of-art of plant-based fibers.
1.1 Fiber sources and classification

Traditionally, the primary source of natural fibers has been wood (Fernandes et al., 2015), but they can be obtained also from non-woody plants such as bamboo (Estrada, 2010). Depending on their use, plants can be classified as primary and secondary. Primary plants are those grown to obtain their fiber content, while secondary plants are those from which fibers are produced as a second product (Faruk et al., 2012). Cotton, flax, jute, sisal, curauá and hemp are examples of primary plants. Corn, rice, sugarcane, pineapple, banana and coconut are examples of secondary plants.

Table 1-1 shows the world production of the most used natural fibers in different applications, especially in the composite industry.

Table 1-1: Natural fibers world production (Adapted from Rowell et al. (1997); Faruk et al. (2012); Rohit and Dixit (2016))

<table>
<thead>
<tr>
<th>Fiber source</th>
<th>World production ($10^6$ ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>1750</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>75</td>
</tr>
<tr>
<td>Bamboo</td>
<td>30</td>
</tr>
<tr>
<td>Cotton</td>
<td>15</td>
</tr>
<tr>
<td>Hemp</td>
<td>3</td>
</tr>
<tr>
<td>Jute</td>
<td>2.3</td>
</tr>
<tr>
<td>Sisal</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Natural fibers can be classified into three main categories depending on the part of the plant from which they are extracted (Jawaid and Abdul, 2011). According to Azwa et al. (2013), bast fibers provide the most appropriate properties for structural applications, because they are cheaper, but have low weight and good strength and stiffness.

- Bast or stem fibers: jute, flax, hemp, ramie, kenaf, bamboo, etc.
- Leaf fibers: sisal, banana, pineapple, etc.
- Seed fibers: cotton, coir, oil palm, etc.
1.2 Non-woody plants and bamboo

Among the non-woody species that exist in Colombia, it is very common to find bamboo plants (Estrada, 2010). Bamboos are giant arborescent grasses that belong to the *Gramineae (Poaceae)* family, *Bambusoideae* subfamily (Singh et al., 2017). They grow mostly in tropic areas and are native of all continents, except Europe (Grosser and Liese, 1971; Jit et al., 2016). There are about 75 genera, divided into approximately 1300 species, covering 25 million hectares around the world (Liese and Köhl, 2015). They have a wide range of heights, from a few centimeters (specie *Arundinaria pusilla*) to 30 m height (specie *Dendrocalaus giganteus*) (Freire and Beraldo, 2003).

Bamboo plants are constituted by rhizome, culm, branches and leaves (Figure 1-1.a). The culm, branches and leaves form the aerial part of the plant, while the rhizome forms the subterranean part. The rhizome plays a vital role in the plant development: it is the responsible for the asexual reproduction of bamboo, has the function of storage and nutrient transport and is the support of the aerial part of the plant (Hidalgo, 2003).

Culms are formed by nodes and internodes alternating simultaneously (Figure 1-1.b), whose cells have strongly differentiated characteristics in terms of orientation, size and quantity. In the internodal zone, the cells have an axial orientation and in the nodal region they are transversally oriented, to facilitate the nutrients and liquids transport (Liese, 1998). Generally, the external diameter, the wall thickness and internodal length change along the culm. According to Ghavami and Marinho (2005), as to the guadua species, the external diamater and wall thickness decrease linearly from base to top, varying from around 100 mm to 30 mm as for the external diameter and from 20 mm to 5 mm as for the wall thickness. On the other hand, the internodal length of the base and top of the culm, is shorter than that at the central part; the minimum value is 150 mm and the maximum one 350 mm.

Bamboo is a natural composite material, formed by long fibers aligned into a ligneous matrix (Ghavami, 2005). Anatomically, the culm is mainly conformed by vascular bundles embedded in a parenchyma tissue. The size, shape and density of vascular bundles vary from the base to the top of the culm, and from the outer to the inner section (Grosser and Liese, 1971; Nogata and Takahashi, 1995; Ghavami et al., 2003; Montiel et al., 2006; Osorio et al., 2009), thus bamboo is known as a functionally graded material (Ray et al., 2005). As shown in Figure 1-1.c, on the outer section of the culm wall, the vascular bundles are small and their density is higher than in the middle and inner part of the wall. Parenchyma tissue is mainly composed by cellulose and hemicellulose cells. Vascular bundles are formed by two large metaxylem vessels,
Figure 1-1: Bamboo *Guadua angustifolia* structure: a) plant parts; b) culm parts; c) culm wall distribution; d) vascular bundle: (I) metaxylem vessels, (II) protoxylem, (III) phloem, (IV) fiber bundles (fibers), (V) parenchyma tissue; e) elementary fibers or microfibrils

Source: Author

one or two protoxylem elements, the phloem and fiber bundles (Figure 1-1.d). Fiber bundles (fibers) consist of thick and thin layers formed by microfibrils or elementary
fibers, with pentagonal and hexagonal forms (Figure 1-1.e) (Ray et al., 2004; Osorio et al., 2011).

1.2.1 Bamboo fibers

Fibers constitute around 40% of the volume and 70% of the weight of the culm (Londoño et al., 2002) and are the anatomical component that provides the mechanical strength of the plant. They are located at the internodes, forming a protective layer around the conductive vessels in the vascular bundles. Their length is extremely related to their position in the internode and to the internodal length; shortest fibers are always located near to the nodes and longest ones, at the middle part of the internode. Longer fibers are also found in the middle region of the culm, where the internodal length is higher. The fiber diameter varies from 10 \( \mu \text{m} \) to 40 \( \mu \text{m} \) (Liese, 1998).

According to Parameswaran and Liese (1976); Liese (1998); Moreno et al. (2006); Osorio et al. (2011), the internal structure of bamboo microfibers corresponds to a polylamellate structure (Figure 1-2), with alternate internal thick and thin layers. In respect of thick layers (layers with \( T \) affixes on Figure 1-2), the cellulose fibrils are small angle-oriented to the fiber axis (between 85\(^\circ\) and 90\(^\circ\)), while as to thin layers (layers with \( L \) affixes on Figure 1-2), the fibrils show a transversal orientation (between 2\(^\circ\) and 20\(^\circ\)). \( P \) corresponds to the primary wall and \( S0 \) is the secondary wall transition lamella (not always present).

**Figure 1-2:** Model of the polylamellate structure of a thick-walled bamboo fiber

(Adapted from Parameswaran and Liese (1976))
1.2.1.1 Fiber distribution along the wall thickness

In this research the fiber distribution was analyzed along the culm wall using digital image analysis. Measurements were made for guadua culms, and the fiber distribution variation was established in four different sections, as shown in Figure 1-3. Sections were obtained from the culm parts commercially used in Colombia: bottom (cepa), middle (basa), top (sobrebasa) and stick (varillón). Culm division into these four parts was made using the methodology described in a previous research project developed by the Structures and Materials Research Group GIES of the Universidad Nacional de Colombia (Universidad Nacional de Colombia, 2010).

Figure 1-3: *Guadua angustifolia* culm parts used for measuring fiber distribution along the wall thickness

From the central region of each culm part, annular sections were cut having 5cm length (Figure 1-4.a). From each annular section, circular segments were obtained with 1 cm width and the thickness corresponds to the culm wall thickness (Figure 1-4.b and
c). From each circular segment, samples for experimental observations were prepared (Figure 1-4.d). One side of the samples’ cross-section was polished using 80, 120, 240, 320, 400, 600 grain size sandpaper, and finally with a cloth along its surface to improve it. Sample identification was made using the first letter of the culm part from which it was obtained; thus, B, M, T ans S correspond to samples obtained from the bottom, middle, top and stick sections, respectively.

**Figure 1-4:** Sample preparation used for measuring fiber distribution along the wall thickness: a) annular sections; b) and c) circular segments; d) sample used for optical observations

As can be seen in Figure 1-1.c, the hollow clean veins (i.e., metaxylem, protoxylem and phloem) appear as dark points in the image and can be mistaken for fiber bundles on digital image. For distinguishing the veins, they were filled by smearing white toothpaste on the polished surface as advised by Azadeh and Ghavami (2015). Thereby, on digital image the veins appear as white structures, clearly differing from fiber bundles. Figure 1-5 shows a polished cross-section with and without filled veins.

All images of samples’ cross-section were taken using a Motic SMZ168 stereo microscope and a 3X magnification, and the images were acquired using a 3.0MP Moticam attached to the stereo microscope.

Image analysis starts turning the raw image of the curved segments (Figure 1-6.a) into an image with a rectangular shape (Figure 1-6.b). The normalized image was subject to a proper filtration process in order to remove uneven light exposure and to intensify the contrast between fibers and matrix. The image was converted to a binary one (Figure 1-6.c), where the fibers appear in black and the matrix and veins in white. The binary images were transformed into a matrix with $m \times n$ dimensions,
corresponding to $m \times n$ pixels from the binary image. Each pixel value in the $i$ row and $j$ column of the matrix is considered as $v_{ij}$, which can only have two values: 0 for the black ones (i.e. fibers bundles) or 255 for the white ones (i.e. veins or matrix). Therefore, the fiber density $A_i$ of each row of the matrix was calculated by using the Equation 1.1. Finally, it was possible to plot the profile of the normalized image and the percentage of fibers of each row on the matrix (Figure 1-6.d). By modifying the curved segment into a rectangular one, the fiber density is slightly overestimated. The image analysis was made using the ImageJ software.

$$A_i = \frac{\sum_{j=1}^{n} v_{ij}}{n}$$ (1.1)

Figure 1-7 shows the profiles obtained for each culm wall section; on the horizontal axis, 0 and 1 correspond to the inner and outer boundaries, respectively. In general, all the profiles describe the same pattern: the lowest fiber volume at the inner layer which increases toward outer layer. According to Ghavami (2005), bamboo plants evolved according to the stress distribution state in its natural environment; thus, the highest fiber volume is closer to the outer skin, a distribution consistent with the stress distribution state when the culm is subjected to wind forces. The plotted profile for the bottom part is slightly different from those obtained for the middle, top and stick parts. On the bottom part, it could be considered that there is no variation in the fiber volume fraction for the first 20% of the wall thickness; from this point, the fiber volume fraction continuously increases. On the other hand, as for the middle, top and stick parts, it can be seen that from the inner layer to approximately the 60% of the
Figure 1-6: Image analysis: a) initial image; b) normalized image; c) binary image; d) fiber volume distribution at normalized wall thickness

Source: Author

wall thickness, the increment of the fiber volume fraction is very limited. From this point the variation could be considered insignificant.

Table 1-2 shows the equations that describe the fiber distribution along the culm wall for each section, with the corresponding $R^2$. Furthermore, Figure 1-7 shows the fitted equations with continuous lines, while the dashed lines correspond to the 95% confidence bounds of each polynomial. The fitted equations were obtained by interpolation with a second-order polynomial. As can be seen, all $R^2$ are up to 0.90, which is considered statistically acceptable.

Table 1-3 shows the total fiber percentage, $V_f(\%)$, which was determined as $V_f(\%) = \sum A_i$ for each culm section. Results show that there is a variation in the fiber percentage along the culm height; the bottom part exhibits the lowest fiber percentage, while
the stick shows the highest ones. This behavior is explained by the diminishing of the wall thickness with the height, which suggests a higher reduction in the parenchyma tissue than in the vascular bundles. There is a high variation between the fiber percentages calculated for the bottom section and those of the middle part (around 15%), which are the highest differences considering the calculated values for the other culm parts. Fiber percentage of middle, top and stick parts presents low differences. Torres et al. (2014) used a similar procedure to measure the fiber density in sections of guadua bamboo culms. According to their results, the bottom, middle and top parts of the culm have a maximum fiber density of 41%, 52% and 51%, respectively.
Table 1-2: Second-order polynomials for fiber distribution in each culm section

<table>
<thead>
<tr>
<th>Location</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>$V_f(x) = 28.51x^2 + 17.80x + 22.11$</td>
<td>0.9020</td>
</tr>
<tr>
<td>Middle</td>
<td>$V_f(x) = -64.61x^2 + 124.60x + 14.78$</td>
<td>0.9154</td>
</tr>
<tr>
<td>Top</td>
<td>$V_f(x) = -49.73x^2 + 117.70x + 16.07$</td>
<td>0.9201</td>
</tr>
<tr>
<td>Stick</td>
<td>$V_f(x) = -74.05x^2 + 141.70x + 8.94$</td>
<td>0.9123</td>
</tr>
</tbody>
</table>

Table 1-3: Fiber percentage for each culm section

<table>
<thead>
<tr>
<th>Location</th>
<th>Fiber percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>40.52</td>
</tr>
<tr>
<td>Middle</td>
<td>55.54</td>
</tr>
<tr>
<td>Top</td>
<td>57.82</td>
</tr>
<tr>
<td>Stick</td>
<td>58.09</td>
</tr>
</tbody>
</table>

1.2.2 Mechanical properties of *Guadua angustifolia* bamboo culms

Upon considering that bamboo is a natural composite material with longitudinally aligned fibers, it has a better behavior when receiving forces applied in parallel to fiber than in perpendicular direction. Furthermore, this material’s tensile strength is higher than its compressive strength in parallel to fiber. According to Lamus (2008), the tensile and compressive strength of guadua samples are around 145 MPa and 55 MPa, respectively. Similar values have been reported by other researches (Ciro et al., 2005; Takeuchi and González, 2007; Correal and Arbeláez, 2010). Lower compressive strength parallel to fiber can be explained by the absence of fibers in perpendicular direction. When compression forces are applied in longitudinal direction, fibers tend to separate by the action of transversal deformations. This is due to the Poisson ratio, which needs to be withstood by the lignin matrix which, according to some authors (Osorio et al., 2009; Takeuchi, 2014), has deficient mechanical performance.

According to Correal and Arbeláez (2010), the guadua culms’ average bending strength is 95 MPa, featuring an average Young modulus of 17.2 GPa. These values were obtained from 30 tested beams, following the procedure established by NTC5525 (ICONTEC, 2007), in which culms with a total length of 30 times the outer diameter
have to be used (total length is approximately 3 m). A similar value was obtained by González et al. (2007), they reported an average bending strength of 105 MPa, using samples featuring 10x10 mm cross-section and 200 mm length.

Additionally, because of the longitudinally aligned fiber distribution, the shear and tensile strengths perpendicular to fiber are very low. Guadua samples’ shear strength is between 5 and 7 MPa (Ciro et al., 2005; Pantoja and Acuña, 2005). Pacheco (2006) found a tensile strength perpendicular to fiber of 0.71 MPa. As for the compression perpendicular to fiber, Vidal and Gomez (2002) reported an average strength of 3 MPa.

In 2010, the Structures and Materials Research Group GIES from the Universidad Nacional de Colombia carried out a research project in order to mechanically characterize the guadua culms from Colombia (Universidad Nacional de Colombia, 2010; Luna et al., 2011, 2012, 2014a). In this research project, culms from three different locations in Colombia (Cundinamarca, Quindío and Valle del Cauca) were collected for mechanical tests. Compressive and tensile tests parallel to the fiber were performed shear, bending and compression perpendicular to the fiber. All tests were performed following the procedures of the NTC5525. In order to study the influence of the position along the culm height on the mechanical strength, samples were obtained from the bottom, middle and top parts of culms. Table 1-4 shows the obtained results on this research. As in the literature, results show that guadua has a better tensile strength performance in comparison to its compressive strength. Obtained values for the tensile and compressive parallel to fiber, as well as those for the bending strength are lower than those reported in other studies. In the case of shear and compression parallel to fiber, results are similar to those of the literature. Due to the fact that there is a fiber percentage variation along the culm height, load strength varies too, thus being higher for samples taken from the top part than for those obtained from the bottom part. This behavior can be observed by comparing the results from the compressive and tensile strength parallel to fiber and the bending ones.

1.3 Chemical composition and cell structure of natural fibers

Chemically, the main components of natural fibers are cellulose, hemicellulose, and lignin, with several minor non-cellulosic components such as pectin, wax, protein, tannins, ash, and inorganic salts (Hughes, 2012; Faruk et al., 2012; Azwa et al., 2013; Sathishkumar et al., 2013; Ali et al., 2016; Rohit and Dixit, 2016). According to John
Table 1-4: Obtained results on the mechanical characterization of bamboo \textit{Guadua angustifolia} from Colombia (Universidad Nacional de Colombia, 2010)

<table>
<thead>
<tr>
<th>Load type</th>
<th>Bottom</th>
<th>C.V (%)</th>
<th>Middle</th>
<th>C.V (%)</th>
<th>Top</th>
<th>C.V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MPa)</td>
<td></td>
<td>(MPa)</td>
<td></td>
<td>(MPa)</td>
<td></td>
</tr>
<tr>
<td>Compression</td>
<td>29.32</td>
<td>20.20</td>
<td>29.39</td>
<td>22.86</td>
<td>37.61</td>
<td>22.71</td>
</tr>
<tr>
<td>Tensile</td>
<td>59.79</td>
<td>25.21</td>
<td>61.80</td>
<td>24.80</td>
<td>63.16</td>
<td>17.97</td>
</tr>
<tr>
<td>Shear</td>
<td>5.79</td>
<td>24.63</td>
<td>5.75</td>
<td>16.43</td>
<td>6.08</td>
<td>23.26</td>
</tr>
<tr>
<td>Bending</td>
<td>-</td>
<td>-</td>
<td>67.11</td>
<td>34.33</td>
<td>72.18</td>
<td>26.75</td>
</tr>
<tr>
<td>Compression</td>
<td>6.70</td>
<td>33.32</td>
<td>5.71</td>
<td>50.61</td>
<td>7.35</td>
<td>40.10</td>
</tr>
</tbody>
</table>

C.V: Coefficient of Variation

and Anandjiwala (2008), natural fibers can be considered as composites of hollow cellulose fibrils held together by a lignin and hemicellulose matrix. The age, source, extraction process, climatic condition among other factors, determine the percentage of components into the fiber (Bledzki and Gassan, 1999; Fernandes et al., 2015; Fuqua et al., 2012; Jawaid and Abdul, 2011; Ramamoorthy et al., 2015). Table 1-5 shows the chemical composition of some natural fibers.

The cellulose content plays the greater role in governing the properties of natural fibers, and determines their mechanical performance (Hughes, 2012). High proportion of cellulose leads to a high tensile strength and stiffness (Fangueiro and Rana, 2016); lignin content also contributed to the stiffness (Ali et al., 2016). On the other hand, the increment of non-cellulosic components tends to reduce the strength and stiffness (Fuqua et al., 2012).
Table 1-5: Chemical composition of some natural fibers (Adapted from Bledzki et al. (1996)\textsuperscript{a}, John and Anandjiwala (2008)\textsuperscript{b}, Jawaid and Abdul (2011)\textsuperscript{c} and Ali et al. (2016)\textsuperscript{d})

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
<th>Waxes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo\textsuperscript{d}</td>
<td>26-43</td>
<td>30</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>Banana\textsuperscript{d}</td>
<td>64</td>
<td>20</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Cotton\textsuperscript{d}</td>
<td>95</td>
<td>2</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>Flax\textsuperscript{d}</td>
<td>70-73</td>
<td>18-20</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Hardwood\textsuperscript{c}</td>
<td>31-64</td>
<td>25-40</td>
<td>14-34</td>
<td>0.1-7.7</td>
</tr>
<tr>
<td>Hemp\textsuperscript{d}</td>
<td>70</td>
<td>22</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Henequen\textsuperscript{b}</td>
<td>60</td>
<td>28</td>
<td>8</td>
<td>0.5</td>
</tr>
<tr>
<td>Jute\textsuperscript{a}</td>
<td>61</td>
<td>20.4</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>Softwood\textsuperscript{c}</td>
<td>30-60</td>
<td>20-30</td>
<td>21-37</td>
<td>0.2-8.5</td>
</tr>
</tbody>
</table>

1.3.1 Cellulose

Figure 1-8 shows a cellulose macromolecule, in which the elementary unit is anidro-
\textit{d}-glucose and three alcohol hydroxil (-OH) (Bledzki et al., 1996). The OH\textsuperscript{-} groups form inter- and intra-molecular hydrogen bonding making it hydrophilic in nature (Ramamoorthy et al., 2015). A hydrophilic nature is characterized by a high moisture absorption of the fibers (Azwa et al., 2013). Also, OH\textsuperscript{-} groups lead to a large number of hydrogen bonds, which with the Van der Waals forces make that part of the cellulose molecules align together, forming the highly oriented crystalline regions. Meanwhile, molecules with less ordered arrangement constitute an amorphous region (Maya and Sabu, 2008).

Figure 1-8: Macromolecule of cellulose (Bledzki et al., 1996)

The cellulose chemical structure remains similar for all the natural fibers, while their polymerization degree changes thus influencing their mechanical properties. It
has been observed that bast fibers have the highest polymerization degree compared to most of the other plants (Ramamoorthy et al., 2015). According to Fuqua et al. (2012) the cellulose polymerization degree is between 7000 and 15000.

1.3.2 Hemicellulose

This chemical structure designates a group of polysaccharides composed of a combination of various carbon ring sugars. This usually occurs in the interface between cellulose and lignin. According to some authors (Silva et al., 2009; Fuqua et al., 2012), its name is inadequate, because hemicellulose and cellulose are different chemical structures. Hemicellulose contains several different sugar units whereas cellulose contains just one. Hemicellulose is a purely amorphous branched polymer with little strength, compared to crystalline linear cellulose. Moreover, the hemicellulose polymerization degree is between 500 and 3000 (Maya and Sabu, 2008).

1.3.3 Lignin

Lignin is a highly crosslinked molecule with amorphous structure; its chemical structure is not clear until today even though most of the functional groups and units are identified (Maya and Sabu, 2008). It is composed by phenylpropane units in a form of a three-dimensional and amorphous macromolecule (Fernandes et al., 2015). Lignin acts as a binder agent between individual fiber cells and the microfibrils forming the cell wall (Ramamoorthy et al., 2015).

1.3.4 Cell structure

Natural fibers are characterized by highly ordered cells known as crystalline regions, and disordered cells or amorphous regions, interconnected through lignin and hemicellulose fragments (Azwa et al., 2013; Kabir et al., 2013). These regions do not possess well-defined borders and undergo a transition from an ordered arrangement of crystalline chains to an amorphous one (Fernandes et al., 2015).

Figure 1-9 shows a schematic representation of the natural fiber cell structure. As can be seen, there are several distinct layers in a single fiber: the center lumen, the secondary wall (which is composed of three separate layers: S1 (outer layer), S2 (middle layer), and S3 (inner layer)), the primary wall and the middle lamella from inside to outside (Ramamoorthy et al., 2015; Rohit and Dixit, 2016). The secondary
wall, primary wall and middle lamella are composed of microfibrils oriented into space in defined angles according to each layer (Fernandes et al., 2015).

**Figure 1-9:** Schematic representation of natural fiber structure: middle lamella, primary wall, S1 - outer secondary wall, S2 - middle secondary wall and S3 - inner secondary wall, lumen (Silva et al., 2009)

The primary wall consists of a disordered and irregular arrangement of cellulose microfibrils, which are closely packed together and placed in a matrix of pectin, hemicellulose, lignin, and protein (Ali et al., 2016). Primary wall is the first layer deposited, containing hemicelluloses and cellulose during the cell growth encircling the secondary wall (Fuqua et al., 2012).

Secondary wall consists of crystalline cellulose microfibrils organized in a spiral arrangement (Fernandes et al., 2015). These microfibrils are made up of 30 to 100 cellulose molecules, with a diameter between 10-30 nm (Fuqua et al., 2012). Secondary wall is made up of three layers: S1, S2 and S3. The S2 layer is thicker than the S1 and S3 layers and determines the mechanical properties of natural fibers (John and Anandjiwala, 2008). The S1 layer is considered to be important for controlling fiber stability under compression, by limiting excessive lateral cell expansion, whereas the S3 layer is believed to withstand hydrostatic pressure within the cell (Hughes, 2012).

The middle lamella, the outer layer of fiber cell, is composed predominantly by pectin that acts as cement between fibers (Fernandes et al., 2015).
1.4 Physical and mechanical properties of natural fibers

The properties of natural fibers are strongly influenced by their chemical composition, orientation angle of microfibrils, defects, extraction process, surface modifications, degree of crystallinity and moisture content, among others (de Andrade et al., 2008). This could be the reason to find several values of the mechanical properties reported for similar fibers. Table 1-6 shows the properties of some natural fibers that are commonly used for engineering applications. In this table was included the cellulose content of each fiber, which in some cases, corresponds to values showed in Table 1-5.

Table 1-6: Properties of some natural fibers (Adapted from Delvasto et al. (2010)\textsuperscript{a}, Faruk et al. (2012)\textsuperscript{b} and Fernandes et al. (2015)\textsuperscript{c})

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$\sigma_t$ (MPa)</th>
<th>$E$ (GPa)</th>
<th>$\Delta L$ (%)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Cellulose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo\textsuperscript{b}</td>
<td>140-230</td>
<td>11-17</td>
<td>-</td>
<td>0.6-1.1</td>
<td>26-43</td>
</tr>
<tr>
<td>Coconut\textsuperscript{b}</td>
<td>175</td>
<td>4.6</td>
<td>3.0</td>
<td>1.2</td>
<td>30-43</td>
</tr>
<tr>
<td>Cotton\textsuperscript{c}</td>
<td>287-800</td>
<td>5.5-12.6</td>
<td>7-8</td>
<td>34</td>
<td>95</td>
</tr>
<tr>
<td>Fique\textsuperscript{a}</td>
<td>43-571</td>
<td>8.2-9.1</td>
<td>9.8</td>
<td>0.72</td>
<td>70</td>
</tr>
<tr>
<td>Flax\textsuperscript{b}</td>
<td>345-1100</td>
<td>27.6</td>
<td>2.7-3.2</td>
<td>1.5</td>
<td>70-73</td>
</tr>
<tr>
<td>Pineapple\textsuperscript{b}</td>
<td>400-627</td>
<td>1.44</td>
<td>14.5</td>
<td>0.8-1.6</td>
<td>81</td>
</tr>
<tr>
<td>Sugar cane bagasse\textsuperscript{b}</td>
<td>290</td>
<td>17</td>
<td>-</td>
<td>0.6-1.1</td>
<td>55</td>
</tr>
</tbody>
</table>

$\sigma_t$: Tensile strength; $E$: Modulus of elasticity; $\Delta L$: Strain-to-failure; $\rho$: Density

Gassan et al. (2001) proposed two models to calculate the elastic properties of natural fibers. The first model (model A) is based on antisymmetric laminated structure, while the second one (model B) is based on a thick laminated composite tube model. They demonstrate that the elastic modulus decreases as the spiral angle of microfibrers on S2 layer increases. Also, the cellulose content affects the elastic modulus; higher cellulose contents lead to higher elastic modulus values. Even though those conclusions were calculated by the two proposed models, there was a discrepancy close to 30% between calculated values. By comparing the obtained results using the models with the published values for different fibers, they concluded that model B better describes the natural fiber behavior, since it takes into account a cross section closer to a real one of natural fibers.
A review paper made by Hughes (2012) researched the origin and features of natural fiber damage and defects, and how these defects affect their mechanical properties. He remarked that natural fibers’ structure is highly heterogeneous and that possesses certain anatomical features such as pits (openings in the fiber cell wall that facilitate the water flow in the living plant), as well as other defects featuring curls, crimps and kinks which affect its properties. The origin of these defects is not entirely clear, but it is known that when fibers are extracted from plants subjected to loads (wind or drought) they exhibit an increase in the number and severity of defects. Also, the extraction process induced some damage to fibers, even when the process was carried out carefully. In general, the presence of defects in natural fibers decreases their mechanical performance. This behavior would imply that the defects act as a stress concentrator.

The study developed by Alves et al. (2013) was focused on correlating the morphology of natural fibers with their mechanical properties via image analysis. to this end, tensile tests were performed using jute, sisal, curaua, coir and piassava fibers; the cross-sectional areas of the fibers were calculated using images obtained from a scanning electron microscope. As for the jute fiber, tests were performed for several gage lengths in order to analyze their influence on the tensile strength, using gage lengths between 10 and 60 mm. They concluded that the gage length has not influence on the jute fibers’ tensile strength and Young’s modulus. From the morphology analysis, they found that as the lumen inner area decreases and the secondary wall thickness increases, the fiber’s strength and Young’s modulus increase as well.

Wang et al. (2016) studied the relationship among the chemical composition, crystallinity, microfibril orientation angle and tensile strength of kenaf fibers, by using single fibers and fiber bundles. They found that for the different X-ray diffraction patterns and tensile strength test samples, the single fiber showed lower crystallinity and higher orientation angle and tensile strength compared to the fiber bundle. In the case of the single fiber, the cellulose content showed a higher tensile strength correlation degree, followed by the orientation angle, hemicellulose, crystallinity and lignin. In the case of fiber bundles, their tensile strength is more influenced by the orientation angle, followed by the hemicellulose content, crystallinity, lignin and cellulose.

1.4.1 Properties of bamboo fibers

As all-natural fibers, the bamboo fibers’ properties depend on the growing condition, chemical composition, defects, extraction process, surface modifications, degree of crystallinity and moisture content, among others. According to some authors, the
mechanical performance of bamboo fibers is rather brittle (Osorio et al., 2011; Shao et al., 2013).

Osorio et al. (2011) characterized the extracted *Guadua angustifolia* bamboo fibers by using a novel process. They found an average tensile strength of 800 MPa, a Young’s modulus of 43.5 GPa, a strain-to-failure of 1.8% with an average diameter of 149 µm. The typical failure mode was characterized by a clean fracture plane, indicating an adequate bonding between elementary fibers and an effective stress transfer between them. In relation to this work, Trujillo et al. (2014) characterized the fiber strength distribution by using a novel approach to assess the effect of defects introduced by the extraction process as a function of three scale variables: fiber length, fiber surface area and fiber volume. The average fiber strength decreased as the gage length increased from 943 MPa at $L = 1$ mm to 733 MPa at $L = 40$ mm and it was nearly independent of the mean fiber volume.

Shao et al. (2013) mechanically characterized bamboo fibers by using an average diameter of $200 \pm 15$ µm, making use of different gage lengths ranging from 20 to 60 mm. They found that the tensile strength decreases as the test length was increased from 555 MPa to $L = 20$ mm to 442 MPa to $L = 60$ mm. This behavior is attributed to the increasing probability of encountering more severe defects with larger test lengths. Also, they proposed a model based on the weak-link theory, which accurately describes the failure of many brittle materials, and is based on the assumption that the material can be divided into smaller linked elements and that the fracture of a specimen is identified with the unstable propagation of the most “critical” cracks. Results obtained indicate that this model can be used to predict the bamboo fibers tensile strength with high accuracy; the differences between experimental results are around 4%.

The main purpose of a research developed by Wang et al. (2014) was to study the variation of the mechanical behavior of *Dendrocalamus latiflorus* Munro bamboo fibers with respect to the age of and their locations within the culm. To that end, they performed microtests on fibers extracted from 1 and 4-year-old culms. The sample length was between 0.7 and 0.8 mm. Results show that 4-year-old fibers are stiffer and stronger than the equivalent 1-year-old-fibers. The average tensile strength varies from 1.2 GPa for 1-year-old fibers to 1.5 GPa for 4-year-old fibers. In the case of the Young’s modulus, the variation is from 39.5 GPa for 1-year-old fibers to 45.8 GPa for 4-year-old fibers. The in-trunk variation of the mechanical properties is rather small for both radial and longitudinal directions. This behavior could be explained by the rather constant microfibrillar angle in the culms.
A research developed by Wang et al. (2015) was focused on studying the effect of the elementary fiber variability on bamboo fiber strength. They worked with fibers extracted from *Phyllostachys heterocycla var. pubenses* bamboo culms. In order to analyze the effect of the fiber diameter on the fibers’ fracture strength, tests were performed using various diameters and a gage length of $L = 20\text{ mm}$ for all samples. The diameter of each individual fiber was evaluated from observations using an optical microscope, and the cross-sectional area was calculated assuming a circular shape. As expected, the population of elementary fibers increased as the fiber diameter was also increased. Results from mechanical tests showed that the bamboo fiber average strength decreased from 568 to 483 MPa as the mean diameter increased from 196.6 to 584.3 $\mu\text{m}$. Also, it was shown that tensile strength decreases as the number of elementary fibers increases. This behavior could be explained on the fact that larger fibers have larger number of elementary fibers and therefore there is an increased probability of encountering the debonding, which significantly reduces the loading capacity of the fiber bundles.

The study developed by Correia et al. (2016) compared the properties of bamboo (*Bambusa tuldaides*) fibers at macro-, micro- and nanoscale. The average thickness for the fibers at macro-, micro- and nanoscale were 0.26 mm, 19.8 $\mu\text{m}$ and 16.2 nm respectively. Results show that the process made to obtain nanofibers (pulping process) removes the amorphous part and increases the fibers’ crystallinity degree. The reduction of fiber scale decreases its mechanical properties. Tensile strength and Young’s modulus for macrofibers were 373.6 MPa and 13.9 GPa respectively. In the case of nanofibrils, the tensile strength and Young’s modulus were 70.4 MPa and 1.98 GPa respectively.

### 1.5 Natural fiber extraction

In general terms, there are three main methods that can be used for the extraction of natural fibers: mechanical, chemical, and a combination thereof (Luna and Lizarazo-Marriaga, 2016). Other researchers (Estrada, 2010) also included biological methods into the extraction methodologies. The main advantage of mechanical fiber extraction over chemical processes is its lower environmental impacts.

Mechanical methods can be performed using different procedures such as steam explosion or heat steaming, retting, crushing, grinding and rolling in a mill (Subash et al., 2017). Depending on the hardness of the raw material, these processes can be inefficient and generate great damage and defects on extracted fibers (Estrada, 2010).
The purpose of chemical methodologies is to separate the main components of natural fibers (cellulose, hemicellulose and lignin) (Estrada, 2010). It is known that they are effective removing the hemicellulose and lignin (Subash et al., 2017). Removing these components can affect the mechanical performance of obtained fibers because there could be a weak stress transfer between elementary fibers (Kabir et al., 2013). Also, these procedures could attack the crystalline cellulose, thus decreasing the mechanical performance of obtained fibers (Ramirez et al., 2011). The most common procedures are degumming, alkali or acid retting and chemical assisted natural retting (CAN) (Zakikhani et al., 2014). Using heat during the chemical procedure accelerates the separation process (Estrada, 2010; Phong et al., 2012).

Biological methods use the enzymes of different micro-organisms, like bacteria, in order to decompose the lignin. This process usually takes between 2 and 3 weeks at room conditions. Indeed, this is one of the most important difficulties for the industrial application of these methods. Also, some micro-organisms could damage the cellulose structure (Estrada, 2010).

1.5.1 Extraction of bamboo fibers

Table 1-7 shows an overview of the applied extraction methods along with the corresponding physical and mechanical properties of natural fibers. As can be seen, mechanical methods are commonly used, being the steam explosion procedure the most employed one. Even when the range of properties of bamboo fibers extracted using different procedures is wide, comparing the mechanical performance of obtained fibers using different extraction methods, from a general point of view, shows that chemical methods reduce bamboo fibers’ tensile strength of bamboo fibers, while their stiffness seems not to be altered by the used extraction methodology. As explained in the previous section, fiber extraction chemical methods reduce the stress transfer between elementary fibers and also affect the crystalline cellulose, thus decreasing the obtained fibers’ tensile strength. By using an appropriate combination of chemical and mechanical procedures, as can be seen in Table 1-7, it is possible to obtain fiber with an adequate mechanical performance.
### Table 1-7: Properties of bamboo fibers based on the extraction methodology (Adapted from Okubo et al. (2004), Murali and Mohana (2007), Estrada (2010), Phong et al. (2012), Biswas et al. (2013), Kim et al. (2013), Zakikhani et al. (2014), Luna and Lizarazo-Marriaga (2016)). Showed values correspond to average properties.

<table>
<thead>
<tr>
<th>Extraction Procedure</th>
<th>σ&lt;sub&gt;t&lt;/sub&gt; (MPa)</th>
<th>E (GPa)</th>
<th>φ (µm)</th>
<th>L (mm)</th>
<th>ρ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical Grinding</td>
<td>393 ± 125</td>
<td>61-155</td>
<td>90-180</td>
<td>200-350</td>
<td>1.46-1.6</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>419 ± 14</td>
<td>30</td>
<td>-</td>
<td>300-600</td>
<td>0.89-1.3</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>469 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>460 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Steam explosion</td>
<td>400 ± 22</td>
<td>30</td>
<td>-</td>
<td>150-300</td>
<td>0.8-1.2</td>
</tr>
</tbody>
</table>

- σ<sub>t</sub>: Tensile strength; E: Modulus of elasticity; φ: Diameter; L: Length; ρ: Density
Chapter 2

Methodology for the extraction of *Guadua angustifolia* bamboo fibers

This chapter describes the research work carried out for the establishment of a methodology for guadua fiber extraction. From this point forward, the word “fiber(s)” refers to a fiber bundle or a macrofiber, which, as explained in previous chapters, is the union of some micro or elementary fibers.

As mentioned in Chapter 1, there are three main methodologies for extracting natural fibers: mechanical, chemical, and a combination thereof. The proposed methodology is based on a chemical-mechanical procedure similar to the one described by Deshpande et al. (2000). The chemical procedure followed an alkaline process, using sodium hydroxide solutions. The methodology involves the immersion of guadua’ rectangular segments in a sodium hydroxide solution and crushing them by using a machine designed and manufactured for the purpose, as part of this research project. The main purpose of the chemical procedure is to “soften” the guadua’ rectangular segments, to separate the lignin, hemicellulose and cellulose. The mechanical procedure is used to separate the fibers.

2.1 General procedure for the establishment of the extraction methodology

This section describes the general procedure used for the establishment of a methodology for guadua fiber extraction. The studied variables and the description of the crushing machine are presented below.
3 to 6-year old guadua culms were used for obtaining the fibers. For this research, the fibers were obtained from the bottom part of the plant. Initially, culms were divided into longitudinal strips measuring $0.025 \text{ m} \times t \times 0.60 \text{ m}$ (width $\times$ wall thickness of the culm $\times$ length). They were polished in order to remove all protuberances at nodes and to eliminate the outer cover layer. Polished strips were immersed in sodium hydroxide solutions (NaOH) at different concentrations and different immersion times and temperature conditions, as explained below. After that, the strips were washed thoroughly using tap water, and a crushing machine (composed of three steel rollers) was used to crush the strips. Finally, some fibers were separated directly, and in some cases, it was necessary to separate them manually. For strips too thick, it was necessary to repeat the crushing process, decreasing the gap between the rollers until the fibers could be separated manually. All obtained fibers were washed several times using fresh tap water, until the water became clear. Then, the fibers were immersed in clean tap water during 24 h; after this time, some fibers (approximately 2 g), randomly chosen, were immersed in 100 ml of distilled water, and after 3 min they were removed to verify verified the pH of the distilled water, that had to be close to neutral ($\text{pH} \approx 7\%$) to ensure the complete NaOH removal from extracted fibers (Estrada, 2010; Zhang et al., 2015; Cai et al., 2016; Hashim et al., 2017). The measurement of water pH was made using a digital pH tester (Hanna Instruments HI98130). After this verification the fibers were dried at laboratory temperature. This procedure is shown in Figure 2-1.

**Figure 2-1:** General chemical-mechanical procedure for obtaining guadua fibers  
(Luna and Lizarazo-Marriaga, 2016)
2.2 Crushing machine

The mechanical procedure developed in this research was carried out using the roller-machine shown in Figure 2-2 to crush the softened and washed strips, in order to separate the fibers. In the front part of the machine, three corrugated steel rollers crush the strips, and in the back part, a cylinder coupled with straight metallic elements, brushes the crushed strips and separates the fibers. The movement of the front rollers is accomplished by an electric engine rotating at 1740 rpm and a gear-engine rotating at 1290 rpm, which was attached to the first bottom roller. The other two rollers rotate by a sprocket and a metal chain joining them. The upper roller can be adjusted in order to decrease the gap. The back cylinder rotates faster than the rollers, in order to brush more efficiently the crushed strips.

Figure 2-2: Crushing machine used for guadua fiber extraction (Luna and Lizarazo-Marriaga, 2016)
2.3 Experimental procedure

This section explains the experimental program developed to establish the methodology for guadua fiber extraction. As explained below, it was studied the influence of some variables involved in the chemical softening, on the obtained fibers’ mechanical performance, as well as their easily of extraction accomplishment.

2.3.1 Extraction variables

It was studied the influence of the NaOH solution temperature, the solution concentration and immersion time on the extraction process. In the case of the solution temperature, two conditions were used: a) room temperature and b) 80°C. The studied concentrations for solutions at room temperature were 2.5, 5, 7.5 and 10%, using immersion times of 24, 48, 72, 120 and 192 h. For the solution temperature at 80°C, the concentration was settled at 2.5%, using 2, 3 and 4 h immersion times. As explained in chapter 1, heating the solution accelerates the separation process. Accordingly, there was no increment the solution concentration using temperature at 80°C.

As explained in Chapter 1, chemical procedures can decrease the tensile strength of natural fibers due to a poor stress transfer between elementary fibers. For this reason, the obtained results for the researched variables were compared with values obtained for fibers extracted without immersions in NaOH solution. In this case, guadua fibers were extracted by immersing the rectangular segments into tap water (NaOH concentration of 0%) at room temperature during 2160 h (90 days) before mechanical procedure. Figure 2-3 shows the studied variables: solution temperature, solution concentration and immersion time. Additionally, Table 2-1 shows the nomenclature used for identifying the fibers extracted using each variable.

Table 2-1: Nomenclature used for extracted fiber identification

<table>
<thead>
<tr>
<th>Solution temperature</th>
<th>NaOH Solution concentration (%)</th>
<th>Immersion time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Room temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heated at 80°C</td>
<td>2.5</td>
<td>B2.52</td>
</tr>
</tbody>
</table>
2.3.2 Methodology for determining the cross-sectional area of guadua fibers

This section shows a brief description of a novel methodology proposed and developed in this research to determine the cross-sectional area of guadua fibers. This methodology was already published in the *Journal of Natural Fibers* (Luna and Lizarazo-Marriaga, 2017), and is showed in Appendix B. The published paper describes in detail the proposed methodology, which is based on optical observations of the cross-sectional area of fibers. Figure 2-4 shows schematically the proposed methodology. In the paper is also made a comparison of area measurements using the proposed and gravimetric methodologies, commonly used to determine the cross-sectional area of natural fibers (Osorio et al., 2009, 2010, 2011).

**Figure 2-4:** Schematic representation of the proposed methodology for determining the cross-sectional area of guadua fibers
The main purpose of the proposed method was to ensure that the area measurements be carried out on a plane perpendicular to the longitudinal axis of the fiber, which can be achieved by arranging the fibers within a (transparent) resin before taking micrographs. This procedure ensures that the perpendicular axis of the cross section of the observed image matches the observer axis, thus avoiding optical distortions of the image. Using this methodology it is possible to measure the fiber cross-sectional area close the fracture plane (normal to fiber axis), as is recommended in ASTM C1557-14 (ASTM, 2014) for the calculation of tensile strength of the fiber. Figure 2-5 shows schematically the obtained sample used to perform the micrograph observations. A captured image is shown in Figure 2-6. The calculation of the cross-sectional area was achieved by using the ImageJ software.

**Figure 2-5:** Schematic representation of the obtained sample to perform the micrograph observations applying the proposed methodology

![Schematic representation of the obtained sample](image)

**Figure 2-6:** Guadua fiber cross-sectional area (Luna and Lizarazo-Marriaga, 2017)

![Guadua fiber cross-sectional area](image)

### 2.3.3 Determination of the system compliance for the testing machine employed

The system compliance for the testing machine used and guadua fibers was determined using the methodology proposed in ASTM C1557-14 (ASTM, 2014). Extracted fibers were used for this calculation employing the variables identified as A10120.
All tests were performed using a Shimadzu universal machine, and employing a 50 N load cell. The tests were carried out working under a 1.5 mm/min load rate, and after around 30 s the fiber failure was achieved, according to the indications of ASTM C1557-14. In order to avoid axial load deviation due to incorrect fiber positioning on testing grips, all samples were placed on paper frames as shown in Figure 2-7, using different gage lengths following the recommendations of the same standard. For this research, the employed gage lengths correspond to 10, 20, 30, 40, 50 and 60 mm, and five samples were used per each length. After positioning the sample in the testing machine, the frame was carefully cut. Figure 2-8 shows the testing machine and the restraint system used in this research.

Figure 2-7: Paper frame used for fiber mechanical tests

According to ASTM C1557-14, the total cross-head displacement during the fiber tests, $\Delta L_f$, was determined using Equation 2.1, where $F_f$ is the applied force, $GL$ the used gage length, $E_f$ the modulus of elasticity, $A$ the cross-sectional area of the fiber, and $C_s$ the system compliance. Hence, by plotting $\Delta L_f/F_f$ versus $GL/A$, a straight line was obtained with a constant slope $(1/E_f)$, and the intercept with the vertical axis corresponds to the system compliance $C_s$. Thereby, the fiber elongation, $\Delta l_f$, can be determined with Equation 2.2.

$$ \frac{\Delta L_f}{F_f} = \frac{GL}{E_f A} + C_s \quad (2.1) $$

$$ \Delta l_f = \Delta L_f - C_s F_f \quad (2.2) $$
The tensile strength of each fiber ($\sigma_{t,f}$) was calculated using Equation 2.3, where $P_{\text{max},f}$ indicates the failure load and $A$ provides the cross-sectional area of each tested fiber. For the determination of the cross-sectional area, the APM procedure explained in section 2.3.2 was used.
\[ \sigma_{t,f} = \frac{P_{\text{max},f}}{A} \] (2.3)

Fiber strain \((\varepsilon_f)\) was calculated using Equation 2.4, where \(GL\) corresponds to the gage length used for each sample. The modulus of elasticity (secant modulus) was calculated as the slope between the 30% and 60% of the maximum \(\sigma_{t,f}\). In general, for the guadua fibers used in this research, between the 30% and 60% of the maximum \(\sigma_{t,f}\) there is a linear behavior of strain-stress curves.

\[ \varepsilon_f = \frac{\Delta l_f}{GL} \] (2.4)

### 2.3.4 Extracted fiber mechanical tests

Tensile tests were carried out to determine the extraction variables on the mechanical behavior of obtained fibers. In order to obtain results that represent the mechanical behavior of guadua fibers, 16 replicas were tested for each studied variable. This sample size was calculated as a function of an expected error of 20 MPa on the fiber strength, with a confidence level of 90% and using the strength data obtained for the determination of the system compliance (see Appendix A).

All tests were performed using the same equipment and methodology employed for the determination of system compliance. In this case, the gage length used on all paper frames was 40 mm, as shown in Figure 2-9.

**Figure 2-9:** Paper frame used for fiber mechanical tests

Equations 2.2, 2.3 and 2.4 were used to calculate the actual elongation, tensile strength and strain of each tested fiber, respectively. In this case, in Equation 2.4,
As in the determination of system compliance, the modulus of elasticity was calculated as the slope between the 30% and 60% of the maximum $\sigma_{t,f}$.

### 2.3.5 Efficiency of fiber-washing process

According to some authors (Mwaikambo and Ansell, 1999; Estrada, 2010; Benyahia et al., 2013; Zhang et al., 2015; Cai et al., 2016; Hashim et al., 2017), it is important to verify the complete removal of NaOH from the fibers surface after their immersions in the chemical solution. Excess of NaOH sticking on the fiber surface continues reacting with fiber constituents, and eventually it could result in lower tensile strength values. Thus, fibers A7.572 and A1072 were used to verify whether the washing procedure explained in section 2.1 ensures the complete removal of NaOH from the extracted fibers. This verification was made through tensile tests on fibers washed using the general procedure, and on fibers washed without the immersion during 24h in tap water after extraction. Tensile tests were made 6, 60 and 120 days after the extraction. Table 2-2 shows the sample group identification used for this verification, where the washing condition 1 refers to fibers washed using the general procedure, and condition 2 refers to fibers washed without the immersion in tap water.

**Table 2-2:** Nomenclature for samples group used to verify the efficiency of fiber-washing process

<table>
<thead>
<tr>
<th>Washing condition</th>
<th>Test time after extraction (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>A7.572</td>
</tr>
<tr>
<td></td>
<td>A1072</td>
</tr>
<tr>
<td>2</td>
<td>A7.572-W0</td>
</tr>
<tr>
<td></td>
<td>A1072-W0</td>
</tr>
</tbody>
</table>

1: Fibers washed using the procedure explained in section 2.1
2: Fibers washed without the immersion during 24h in tap water after extraction

### 2.3.6 Extraction ease score (E.S)

The ease of extraction is an important parameter to take into account to propose the guadua fibers-extraction methodology. This is a qualitative parameter used to measure
the extraction process efficiency, where the mechanical effort and the material obtained volume were taken into account. Therefore, a score between 0 and 1 was assigned for each studied variable in order to represent this parameter. Table 2-3 shows the score assigned depending on the fiber-extraction ease for each studied variable.

Table 2-3: Extraction ease score

<table>
<thead>
<tr>
<th>Assigned score</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>too difficult</td>
</tr>
<tr>
<td>0.25</td>
<td>difficult</td>
</tr>
<tr>
<td>0.5</td>
<td>medium difficulty</td>
</tr>
<tr>
<td>0.75</td>
<td>easy</td>
</tr>
<tr>
<td>1</td>
<td>too easy</td>
</tr>
</tbody>
</table>

2.3.7 Final score for each studied variable

For this research, the most important parameters for the determination of the guadua fiber-extraction methodology are its tensile strength and ease of extraction. The first parameter (tensile strength) is important when fibers are going to be used as reinforcement in composite materials. The second parameter, ease of extraction, is relevant when it is intended that the proposed methodology can be implemented at industrial level.

Thus, a Final Score \( F.S \) was assigned to each studied variable, which was calculated using Equation 2.5, where \( \sigma_{t,f}^N \) is the normalized average tensile strength for a data set of a studied variable and \( E.S \) is the extraction ease score assigned. \( \sigma_{t,f}^N \) is calculated by Equation 2.6, where \( \sigma_{t,f} \) is the average tensile strength for a data set of a studied variable and \( \sigma_{t,f}^{MAX} \) is the maximum average tensile strength of all studied variables. In Equation 2.5 the weight assigned to \( E.S \) is lower than the assigned to \( \sigma_{t,f}^N \) since \( E.S \) is a quantitative measurement.

\[
F.S = 0.8\sigma_{t,f}^N + 0.2E.S
\]  
(2.5)

\[
\sigma_{t,f}^N = \frac{\sigma_{t,f}}{\sigma_{t,f}^{MAX}}
\]  
(2.6)
2.4 Results and discussion

All results presented in this section, do not include the outliers which were identified using boxplots. The boxplots and all statistical analysis presented in this section were performed using MATLAB R2013a (The MathWorks Inc., Natick, Massachusetts, US). All statistical inferences assumed a confidence level of 95% ($\alpha = 0.05$).

2.4.1 System compliance for used testing machine

Figure 2-10 shows the result on the system compliance determination for the universal testing machine and the restraint system used. A linear least-squares regression was made for the points cloud, which was extrapolated to the vertical axis; the cut-off point obtained is the $C_s$ value. The $R^2$ of the linear regression was 0.63.

Figure 2-10: Determination of the system compliance $C_s$

Table 2-4 presents the average results obtained for each gage length in terms of tensile strength, modulus of elasticity and strain-to-failure values. The modulus of elasticity was calculated as-measured, i.e based on the cross-head displacement, and using the determined $C_s$, i.e corrected for compliance. When comparing both methodologies for calculating the modulus (of elasticity), the results clearly show that higher values are achieved when the determined $C_s$ is used. Figure 2-11 shows the “as-measured” (raw data) versus the corrected for compliance typical stress–strain response of guadua fibers. It can be noticed that at a given stress, the system compliance contribution of the testing machine resulted in a larger strain. This behavior is related to higher modulus (of elasticity) values calculated from the corrected curve compared to the
as-measured calculation. Similar observation was reported by Alves et al. (2013). The peaks shown in Figure 2-11 around 20 MPa and 50 MPa are consequence of the rupture of some elementary fibers.

Table 2-4: Average results obtained on the determination of the system compliance of the used testing machine

<table>
<thead>
<tr>
<th>Gage length (mm)</th>
<th>Tensile strength (MPa)</th>
<th>As-measured modulus of elasticity (GPa)</th>
<th>Modulus of elasticity corrected for compliance (MPa)</th>
<th>Strain-to-failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>219.98 ± 39.41</td>
<td>10.02 ± 3.50</td>
<td>16.06 ± 7.79</td>
<td>2.87 ± 0.63</td>
</tr>
<tr>
<td>20</td>
<td>210.97 ± 60.25</td>
<td>16.23 ± 1.84</td>
<td>30.71 ± 5.86</td>
<td>1.32 ± 0.33</td>
</tr>
<tr>
<td>30</td>
<td>183.58 ± 42.65</td>
<td>17.37 ± 6.82</td>
<td>29.37 ± 9.27</td>
<td>1.37 ± 0.44</td>
</tr>
<tr>
<td>40</td>
<td>175.34 ± 48.47</td>
<td>21.04 ± 5.33</td>
<td>36.17 ± 10.95</td>
<td>1.43 ± 0.56</td>
</tr>
<tr>
<td>50</td>
<td>199.46 ± 55.47</td>
<td>19.69 ± 6.12</td>
<td>27.04 ± 10.37</td>
<td>1.03 ± 0.43</td>
</tr>
<tr>
<td>60</td>
<td>188.49 ± 58.64</td>
<td>16.82 ± 5.21</td>
<td>21.26 ± 9.76</td>
<td>1.29 ± 0.37</td>
</tr>
</tbody>
</table>

Figure 2-11: Stress-strain curve for guadua fibers used in the determination of $C_s$, raw and corrected data for system compliance

A statistical analysis was made to identify significant differences among the mechanical properties of the fibers tested by using different gage lengths. In the case of
the modulus of elasticity, the analysis was made for the values corrected for compliance. Initially, by using the Shapiro-Wilk tests, it was verified the normality of each data set; then, the homoscedasticity was verified among the collected data through the Levene’s test. An ANOVA analysis was applied in the cases to fulfill both criteria of normality and homoscedasticity; in the opposing cases, the Kruskal-Wallis test was used.

A random variable \( X \) follows a normal distribution if and only if its Probability Density Function is described by Equation 2.7, where \( \mu_n \) (\( -\infty < \mu_n < \infty \)) and \( \sigma^2_n \) (\( \sigma^2_n > 0 \)) are the mean and variance of the distribution.

\[
f(x) = \frac{1}{\sqrt{2\pi\sigma_n}} e^{-\frac{(x-\mu_n)^2}{2\sigma^2_n}}, \text{ for } -\infty < x < \infty \tag{2.7}
\]

The Shapiro-Wilk test analyzes the normality or non-normality of a distribution based on the \( p \)-values. This test assumes a normal distribution as the null hypothesis and will be accepted if \( p\)-value > 0.05. In contrast, if \( p\)-value < 0.05, the test discards the null hypothesis and identifies the distribution as non-normal.

The Levene’s test evaluates the null hypothesis that \( J \) samples come from populations with the same variance (Glass, 1966). The ANOVA analysis is a parametric test to compare means of more than two levels of a single factor, by evaluating the null hypothesis that the mean of samples is equal (Ross, 2004); this analysis is based on the assumption of normality and homoscedasticity of all data sets. On the other hand, the Kruskal-Wallis test is a non-parametric method to evaluate the null hypothesis that medians of samples are equal (Montgomery and Runger, 2002). In all tests, i.e Levene’s test, ANOVA and Kruskal-Wallis test, the null hypothesis will be attempted when \( p\)-value > 0.05.

Table 2-5 shows the \( p\)-values obtained from each test in the statistical analysis. ANOVA results showed that the tensile strength and modulus (of elasticity) do not seem to be a function of the gage length. The variability in these mechanical properties, for a given gage length, is probably related to the variability in the microstructure of the guadua fiber and some possible damage during the extraction process, as previously reported by Alves et al. (2013). On the other hand, statistical analysis revealed that strain-to-failure results seem to be higher for 10 mm gage length, besides having shown significant variation for 20 mm and higher lengths. According to de Andrade et al. (2008), these phenomena (tensile strength and modulus being independent and strain-to-failure dependent on gage length) could be explained as follows: the mean defect size of all materials controls the mean strength, but the number of defects controls the strain-to-failure results. Thus, while the fibers with lower gage length have a smaller
number of defects, the average defect size is also independent of the gage length. Accordingly, the mean flaw size controls the strength, and said size does not change as the gage length varies. Once a crack is formed at the largest flaw, the speed with which the link between flaws occurs will determine the strain-to-failure results. Thus, if a larger number of flaws exists, the linkage between flaws will be quicker, and the strain-to-failure lower.

Since results revealed that using gage length over 20 mm does not seem to influence the mechanical behavior of guadua fibers, for the characterization of extracted fibers a 40 mm gage length was used. This length facilitates the preparation of samples, and the fiber portion lengths after tensile tests result to be adequate for cross-sectional area measurements.

**Table 2-5:**  $p$ – *values* obtained from statistical analysis on mechanical properties of guadua fibers using different gage lengths

<table>
<thead>
<tr>
<th>Gage length (mm)</th>
<th>Tensile strength</th>
<th>Modulus of elasticity</th>
<th>Strain-to-failure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SW</td>
<td>Levene</td>
<td>ANOVA</td>
</tr>
<tr>
<td>10</td>
<td>0.2150</td>
<td>0.4773</td>
<td>0.9502</td>
</tr>
<tr>
<td>20</td>
<td>0.6399</td>
<td>0.0586</td>
<td>0.0966</td>
</tr>
<tr>
<td>30</td>
<td>0.1471</td>
<td>0.5082</td>
<td>0.0847</td>
</tr>
<tr>
<td>40</td>
<td>0.8989</td>
<td>0.8771</td>
<td>0.9934</td>
</tr>
<tr>
<td>50</td>
<td>0.6027</td>
<td>0.8276</td>
<td>0.1531</td>
</tr>
<tr>
<td>60</td>
<td>0.1109</td>
<td>0.8604</td>
<td>0.8818</td>
</tr>
</tbody>
</table>

SW: Shapiro-Wilk test  
Levene: Levene’s test

**2.4.2 Mechanical behavior of extracted fibers**

All fiber-strain calculations presented and used in this section were corrected by the calculated system compliance.

Figure 2-12 presents a typical stress-strain curve for extracted fibers. It is clear that extracted fibers are rather brittle featuring a strain-to-failure close to 2%. Similar behavior was observed by other researchers regarding the same bamboo fiber species (Osorio et al., 2011). All tested samples show a linear elastic behavior up to fracture.

Table 2-6 shows the results of average tensile strength ($\sigma_{t,f}$), modulus of elasticity ($E_f$) and strain-to-failure ($\varepsilon_f$) for each extraction condition. Table 2-6 includes the
Figure 2-12: Typical stress-strain curve for extracted fibers

maximum ($max$) and minimum ($min$) values, as well as the coefficient of variation (C.V) calculated for each mechanical property. Also, these results are graphically shown in Figures 2-13, 2-14 and 2-15, where results were grouped by immersion times, as well as each solution concentration column are identified using different colors. The Figures also include, as error bars, the standard deviation calculated for each sample group.

Figure 2-13: Tensile strength for each extraction variable: a) solutions at room temperature; b) solutions heated at 80°C

As expected, heating the NaOH solution accelerates the hemicellulose and lignin separation process. Guadua segments that were immersed in 2.5% solutions and heated at 80°C were sufficiently softened after 2 h to start the mechanical separation process using the crushing machine. In contrast, segments that were immersed using the same concentration at room temperature were sufficiently softened after 24 h.
As can be seen in Table 2-6 and Figure 2-13, using NaOH during the guadua fiber extraction process decreases the tensile strength of extracted fibers. Also, the solution concentration and the immersion time increment drastically decrease the obtained fibers' tensile strength. For example, N fibers have an average tensile strength of 437.5 MPa; in contrast, A10192 fibers present an average tensile strength of 109.3 MPa. This behavior could be the result of two phenomena: 1) high hemicellulose and lignin removal which leads to a poor stress transfer between elementary fibers (Kabir et al., 2013) and, 2) NaOH attacks the crystalline cellulose present in fibers (Symington et al., 2009; Estrada, 2010; Ramirez et al., 2011).
When comparing the different immersion times results at the same solution concentration, higher concentrations show a greater tensile-strength decrease after immersion time. For 2.5 and 5% concentrations, a maximum variation of 35% was obtained, after having compared the results obtained for fibers extracted from segments immersed during 24 h and 192 h. On the other hand, the maximum tensile strength variation for fibers extracted using concentrations of 7.5 and 10% was around 50%, after having compared the results obtained from segments immersed during 24 h and 192 h. The maximum tensile strength decrease for the heated solution was around 10%, after having compared the results for segments immersed during 2 h and 4 h.

Results in terms of modulus of elasticity (Table 2-6 and Figure 2-14) show that there is a variation of this property among different extraction conditions, but the variation, unlike tensile strength, does not describe a single trend.
In general, the modulus of elasticity decreases with the increment of NaOH solution concentration and immersion time. However, it is noticed an increment close to 20% of this property for almost all concentrations (2.5, 5 and 7.5%) between 24h and 48h after immersion time at room temperature. In the case of 10% concentration, this increment is around 65%. According to some authors (Symington et al., 2009; Vijaya Ramnath et al., 2016), using NaOH solution in natural fibers could decrease the microfibrillar angle, which could improve load alignment by transferring the load closer to the fiber axis, thus increasing their modulus of elasticity. Similar results were observed by Symington et al. (2009) in flax, kenaf, abaca and sisal fibers treated during 10 min using 3% NaOH solution. As for heated solutions, there is always a decrease in the modulus of elasticity of extracted fibers. When comparing all the results obtained with values calculated for fibers extracted using a 0% concentration, in almost all cases the modulus of elasticity is below of this reference value. This behavior could be a result of the alteration of crystalline cellulose (Symington et al., 2009).

The strain-to-failure of extracted fibers could be considered unaltered by the extraction process, since there are not significant variations of this property among different extraction conditions (Table 2-6 and Figure 2-15). In general, by comparing the reference fibers (0% concentration) with heated and non-heated NaOH solutions, it can be seen that the use of NaOH solutions to extract guadua fibers decreases the fibers’ ability to deform and strain.

There is a high variability in the mechanical properties of all extracted fibers. The calculated C.V are between 11 and 60%. This high variability has been observed in many researches on natural fibers (Symington et al., 2009; Estrada, 2010; Ramirez et al., 2011; Trujillo et al., 2014; Fangueiro and Rana, 2016; Shahinur and Ullah, 2017).

2.4.3 Efficiency of fibers’ washing process

Figure 2-16 shows the tensile strength obtained during the study of the efficiency of the fibers’ washing process. Numerical results are shown in Table 2-7.

As can be seen for both sample groups (A7.572 and A1072), the tensile strength of fibers washed using condition 2 decreases in time. This is an indication of the presence of NaOH in extracted fibers. In contrast, the tensile strength of fibers washed using condition 1 remains unaltered in time. It is clear that the general procedure used to wash the fibers after extraction (explained on section 2.1) ensures the complete NaOH removal.
Figure 2-16: Tensile strength of fibers used to study the efficiency of washing process: a) fibers A7.572; b) fibers A1072

Table 2-7: Tensile strength of fibers used to study the efficiency of washing process

<table>
<thead>
<tr>
<th>Sample group</th>
<th>$\sigma_t$ (MPa)</th>
<th>C.V (%)</th>
<th>Test time after extraction (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A7.572</td>
<td>286.00</td>
<td>23.52</td>
<td>6</td>
</tr>
<tr>
<td>A7.572-1</td>
<td>283.66</td>
<td>46.50</td>
<td>60</td>
</tr>
<tr>
<td>A7.572-2</td>
<td>287.78</td>
<td>40.87</td>
<td>120</td>
</tr>
<tr>
<td>A7.572-W0</td>
<td>285.01</td>
<td>32.85</td>
<td>6</td>
</tr>
<tr>
<td>A7.572-W1</td>
<td>232.15</td>
<td>34.35</td>
<td>60</td>
</tr>
<tr>
<td>A7.572-W2</td>
<td>143.51</td>
<td>33.16</td>
<td>120</td>
</tr>
<tr>
<td>A1072</td>
<td>211.57</td>
<td>35.29</td>
<td>6</td>
</tr>
<tr>
<td>A1072-1</td>
<td>215.05</td>
<td>33.17</td>
<td>60</td>
</tr>
<tr>
<td>A1072-2</td>
<td>212.75</td>
<td>36.92</td>
<td>120</td>
</tr>
<tr>
<td>A1072-W0</td>
<td>214.12</td>
<td>42.85</td>
<td>6</td>
</tr>
<tr>
<td>A1072-W1</td>
<td>142.41</td>
<td>16.27</td>
<td>60</td>
</tr>
<tr>
<td>A1072-W2</td>
<td>95.11</td>
<td>43.42</td>
<td>120</td>
</tr>
</tbody>
</table>

2.4.4 Extraction ease score (E.S)

The extraction ease score assigned to each extraction condition is shown in Figure 2-17. The lowest extraction ease score was assigned to N fibers, since for using this condition the fibers could be extracted after 2160 h, the separation process was difficult and the volume of obtained fibers was low.
As shown in Figure 2-17, the increment of the NaOH solution concentration, immersion time and the use of heated solutions, facilitate the fiber separation process. This behavior is due to NaOH acts as a remover of lignin and hemicellulose, which are the natural binders of all natural fibers. Higher solution concentrations and immersion time could lead to higher removal of binders.

**Figure 2-17:** Extraction ease score for each extraction variable: a) solutions at room temperature; b) solutions heated at 80 °C

![Figure 2-17](image)

### 2.4.5 Final score for each studied variable

Figure 2-18 shows the normalized tensile strength ($\sigma_{t,f}^N$) calculated for each studied extraction variable. The maximum average tensile strength of all studied variables ($\sigma_{t,f}^{MM}$) corresponds to the value calculated for the N fibers. Figure 2-19 shows the calculated final grade for each extraction condition. In general, for solutions at room temperature (Figure 2-19.a), the final score decreases as the solution concentration and immersion time increase as well. This behavior is a result of the sharp tensile strength fall of obtained fibers. In the case of heated solutions, there is an increase of the final score when comparing the values calculated for B2.52 and B2.53. This result is consequence of the increment of the ease of extraction for higher immersion times. On the other hand, there is a slightly decrease between the final scores calculated for B2.53 and B2.54, due to the tensile strength decrease of B2.54 fibers. Although the highest normalized tensile strength was achieved by N fibers, the highest final score corresponds to that of the B2.53 fibers.

![Figure 2-18](image)
2.5 Selected extraction methodology

The proposed guadua fiber extraction methodology corresponds to the extraction variable with the highest final score. Thus, based on the results shown in the previous section, the conditions used for the extraction variable B2.53 will be used in this research to obtain guadua fibers. When applying this extraction conditions, guadua rectangular segments will be softened by immersing them during 3 h in a 2.5% NaOH solution, previously heated at 80°C, before proceeding with the mechanical separation by the crushing machine. By implementing these conditions during the extraction
process, it is possible to obtain guadua fibers with adequate tensile strength, that
could be used as reinforcement of composite materials, taking into account the ease of
extraction, an important parameter for industrial applications. Figure 2-20 shows a
handful of the extracted fibers.

When immersing guadua rectangular segments at room temperature, the extraction
variable for which the highest final score was obtained, was the A2.572 condition,
in which the chemical softening of guadua segments was made using 2.55% NaOH
solution concentration during 72 h. By comparing the final score obtained for the
B2.53 ($F.S = 0.84$) and A2.572 ($F.S = 0.77$) extraction conditions, it can be seen that
there are no great differences between both extraction methodologies. Nevertheless,
using B2.53 conditions, it is possible to obtain guadua fibers in less time that using
A2.572 conditions. However, the A2.572 extraction condition can be used when heating
the NaOH solution becomes difficult. Thereby, the methodology used in this research
for obtaining guadua fibers corresponds to the B2.53 conditions.

**Figure 2-20:** Guadua fibers extracted using the proposed methodology for this
research
P/BG composite
Chapter 3

Characterization of extracted
*Guadua angustifolia* bamboo fibers

Guadua fibers extracted by the methodology described in Section 2.5 were physically and chemically characterized. The physical characterization involves the determination of their length, density, water absorption and morphological analysis by means of scanning electron micrographs. The chemical characterization was focused on the determination of the functional groups present in fibers, through FTIR spectroscopy. The experimental procedures used for the characterization, as well as the obtained results are presented in this chapter. An statistical analysis was carried out for the purpose of fitting the fiber’s length and density properties to a probability distribution model. Also, it was studied the variation of fibers’ mechanical properties with respect to their location in culm. All statistical analysis shown in this chapter were performed using MATLAB R2013a (The MathWorks Inc., Natick, Massachusetts, US), and inferences assumed a confidence level of 95% ($\alpha = 0.05$).

3.1 Experimental program

3.1.1 Length

The extracted fibers’ length was determined by direct measurements from 200 guadua fibers randomly chosen. The measurement was made using a digital caliper featuring a 0.01 cm precision.
3.1.2 Density

Fibers’ density measurement was made according to the international standard ASTM D3800-99 (ASTM, 2010a), following the procedure A, which is based on Archimedes’ principle. The immersion liquid was tap water, with an average temperature of 22°C, using a volume of 1500 ml. All measurements were made at a controlled environment, at an average temperature and humidity of 25°C and 50%, respectively. A total of 80 fiber samples were used to determine the density. Each fiber sample featured a weight of 1 g approximately and was randomly chosen. All weight measurements (immersed and not) were taken using an analytical balance with a 0.001 g precision.

3.1.3 Water absorption

Fiber absorption experiments were carried out as follows. Sample fibers, of approximately 1.5 g, were immersed in 200 ml of tap water during 0, 1, 2, 3, 6, 12 and 24 h. After immersions, the excess of water was removed by centrifugation during 1 min. Then, the wet weight was measured and the sample was introduced into an oven at 50°C. After 24 h, each sample was weighed at regular intervals of not less than 2 h. The drying was considered to be complete when the difference between the successive weight determinations did not exceed 0.010 g. All weight measurements were performed using an analytical balance featuring a 0.001 g precision. The water absorption during each immersion time was calculated as the moisture content ($MC$) using Equation 3.1, where $m_w$ and $m_d$ stand for the wet sample and the dry weight. For each condition, a total of 10 samples were used.

$$MC(\%) = \frac{m_w - m_d}{m_d} \times 100$$ (3.1)

3.1.4 FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the fiber functional groups. All samples were kept at room temperature overnight before being analyzed. FTIR was determined using a FT-IR Nicolete iS 10 spectrometer (Thermo Fisher Scientific). Scans of 40 readings were performed by spectrum; the data was recorded in a range from 4000 to 800 cm$^{-1}$. 
3.1.5 Morphological analysis

The extracted fibers’ surface appearance was observed by a Tescan Vega 3 SB scanning electron microscope, operated at a secondary electron mode.

3.1.6 Variation of fibers’ mechanical properties along the culm height

In order to determine whether there was a variation in the fibers’ mechanical properties along the culm height, guadua fibers were extracted from different parts of the culm: bottom (B), middle (M), top (T) and stick (S). For the purpose of diminishing the variation of fibers’ mechanical properties due to different culm source, one culm, between 3 and 6 years old, was used to obtain the fibers. The division of the culm was made using the methodology described in Luna et al. (2012). From each culm part, 16 replicas were tested (see section 2.3.4). Fiber mechanical tests and calculations were performed following the procedure described in Section 2.3.4.

3.2 Results and discussion

3.2.1 Length and density

Table 3-1 shows the results ning the extracted fibers’ length and density. The average density obtained in this research is within the range reported in the literature. Faruk et al. (2012) reported that bamboo fiber density, in general, ranges from 0.6 g/cm$^3$ to 1.1 g/cm$^3$. The bamboo fiber density reported by Osorio et al. (2011) for the same specie studied in this research (Guadua angustifolia) was 1.4 g/cm$^3$. The bamboo fiber length is influenced by the internode length (Osorio et al., 2009), which is variable between bamboo species. According to Ghavami and Marinho (2005) the internode length for Guadua angustifolia bamboo culms varies from 100 mm to 350 mm. The shortest lengths are found in the bottom part, and the longest ones are located in the upper third part of the culm. Taking into account that the fibers used in this research were extracted from the bottom part of the culm, the average obtained length is within the expected range. The high variability of length measurements (C.V> 60%) is due to the brushing process carried out by the crushing machine, which cuts the fibers randomly.

Figure 3-1 shows the histograms for length and density measurements. In the length case, the histogram is skewed to the left; on the other hand, the density data
Table 3-1: Length and density results of extracted guadua fibers

<table>
<thead>
<tr>
<th>Property</th>
<th>Average</th>
<th>Maximum</th>
<th>Minimum</th>
<th>C.V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.359</td>
<td>1.567</td>
<td>1.185</td>
<td>5.40</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>91.64</td>
<td>205.00</td>
<td>11.00</td>
<td>62.27</td>
</tr>
</tbody>
</table>

set histogram can be considered symmetrical. Accordingly, the Weibull and lognormal distributions were chosen to fit the length data set and a normal distribution for the density. These distributions were explained in Chapter 2.

Figure 3-1: Histograms for: a) length and b) density distributions

The distribution fitted for each data set is shown in Figure 3-1. It can be seen that a normal distribution fits the density data set (Figure 3-1.b). Moreover, it is not clear the distribution that better fits the length data set (Figure 3-1.a). The density dataset normality was verified by the Shapiro-Wilk test, explained in Chapter 2. In this case $p-value = 0.99$, which means these data are normally distributed.

Table 3-2 shows the estimated parameters for each probability distribution, which were determined by the MLE method.

Table 3-2: Summary of distribution fit for density and length data sets

<table>
<thead>
<tr>
<th>Normal distribution</th>
<th>Weibull distribution</th>
<th>Lognormal distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_n$</td>
<td>$\sigma_n$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Maximum log-likelihood</td>
<td>$\mu$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Maximum log-likelihood</td>
<td>$\sigma$</td>
</tr>
</tbody>
</table>

| Density   | 1.359 | 0.073 | - | - | - | - | - | - |
| Length    | -     | -     | 10.271 | 1.655 | -611.251 | 1.977 | 0.747 | -520.351 |
Regarding the length data set, the distribution fit goodness was calculate by using a procedure based on the likelihood ratio test, as explained in Chapter 2.3.2. The Maximum log-likelihood column of Table 3-2 shows calculated values for the logarithm of each distribution’s likelihood function. As can be seen, higher values of this parameter were obtained by Weibull distribution. Thus, it is clear that the Weibull distribution provides a better fit than the lognormal distribution.

### 3.2.2 Water absorption

Figure 3-2 shows the MC values calculated for each immersion time. Average MC values are presented in Table 3-3, where it is also included the C.V of each data set. As expected, MC increases as the immersion time increases as well. The water absorption capacity of the extracted fibers feature two well distinct stages: a first stage showing a rapid increment of absorbed water (between 0 h and 6 h), and a second stage showing a water absorption stabilization (between 6 h and 24 h). Similar MC values have been found by Ramadevi et al. (2012) on non-alkali-treated abaca fibers immersed in different sources of water (pond, river, bore, and sea water) during 24 h. The average MC value (7.25%) obtained for fibers immersed during 0 h is the result of the absorbed atmospheric moisture due to the presence of hydroxyl groups (OH) associated with the components of the cell wall macromolecules (cellulose, hemicellulose and lignin) (Hill et al., 2009). MC values closer to 200% can be explained by two phenomena: 1) swelling and 2) filling of free spaces between microfibrils. Regarding the swelling of all-natural fibers in presence of water, OH groups in the cellulose, hemicellulose, and lignin build a large amount of hydrogen bonds between the macromolecules in the natural fiber cell wall. Subjecting the fiber to humidity causes these bonds to break. The OH groups then form new hydrogen bonds with water molecules, which induce swelling (Mwaikambo and Ansell, 2002). After this, the water occupies the free spaces between the microfibrils (Rocha et al., 2015). According to Biagiotti et al. (2004), the moisture content of natural fibers is also a function of the fraction of non-crystalline regions and the void content.

In order to describe the variation of the water absorption capacity of guadua fibers as a function of the immersion time, MC calculated values were fitted to an exponential model. In general terms, an exponential model is represented by Equation 3.2, where \( a \) and \( b \) are constants. These models are often used when the change ratio of a quantity is limited and proportional to the initial amount of said quantity. A negative coefficient associated to \( e \) represents a decay. Equation 3.3 represents a two-term exponential model, which is used when two decay (or growth) modes exist (MathWorks, 2002).
Figure 3-2: Water absorption of guadua fibers

Table 3-3: Water absorption of guadua fibers for different immersion times

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>MC (%)</th>
<th>C.V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.25</td>
<td>4.41</td>
</tr>
<tr>
<td>1</td>
<td>62.27</td>
<td>5.19</td>
</tr>
<tr>
<td>2</td>
<td>84.11</td>
<td>5.71</td>
</tr>
<tr>
<td>3</td>
<td>88.62</td>
<td>5.80</td>
</tr>
<tr>
<td>6</td>
<td>150.94</td>
<td>3.49</td>
</tr>
<tr>
<td>12</td>
<td>182.75</td>
<td>3.82</td>
</tr>
<tr>
<td>24</td>
<td>184.67</td>
<td>2.97</td>
</tr>
</tbody>
</table>

\[ f(x) = ae^{bx} \]  \hspace{1cm} (3.2)

\[ f(x) = ae^{bx} + ce^{dx} \]  \hspace{1cm} (3.3)

Equation 3.4 presents the fitted function for MC data and immersion time. This equation was obtained using a nonlinear least square method, run in MATLAB R2013a. In this case, the \( R^2 = 0.9786 \) indicates an adequate fitting of the selected model. Furthermore, the continuous line included in Figure 3-2 shows the fitted function, and the dashed lines correspond to the 95% of confidence bounds.
\[ f(x) = 210.9e^{-0.0052x} - 196.9e^{-0.2086x} \]  

(3.4)

### 3.2.3 FTIR spectroscopy

The FTIR spectrum of extracted guadua fibers is shown in Figure 3-3. The spectrum shows the vibration modes characteristic of lignocellulosic fibers reported in literature (He et al., 2007; Fang et al., 2013; Kim et al., 2013). The spectrum clearly shows the strong and broad characteristic band at the 3600–3200 cm\(^{-1}\) regions assigned to the hydroxyl group (–OH) stretching (Hossain et al., 2013; Phuong et al., 2010; Pandiyaraj and Selvarajan, 2008). The peak in 2850 cm\(^{-1}\) is associated to the C-H stretching vibration from CH and CH\(_2\) in cellulose and hemicellulose (Bozaci et al., 2013). Peaks between 1660 and 1600 cm\(^{-1}\) are associated to absorbed water in crystalline cellulose (Bozaci et al., 2013). Instead, peaks in the region from 1510 cm\(^{-1}\) to 1450 cm\(^{-1}\) are produced by the bending of aromatic C-H (ring) bond present mostly in lignin (Tserki et al., 2005; Chattopadhyay et al., 2011). The typical absorption peak attributed to the bending of cellulose appears at 1421 cm\(^{-1}\) (Zhang et al., 2015). Finally, the prominent peak between 1100 and 1000 cm\(^{-1}\) is assigned to the C-O stretching and the vibration of the C-H cellulose group (Rocha et al., 2015). Similar results were reported by Lu et al. (2013) and Zhang et al. (2015) for bamboo fibers.

### 3.2.4 Morphological analysis

Figure 3-4 shows the surface morphology of extracted fibers. As pointed by other researchers (Phong et al., 2012; Wang et al., 2015), it can be clearly observed from micrographs that guadua fibers are the union of a large number of elementary fibers which are oriented parallel to fiber axis (Figures 3-4.a, b, d and f). Also, the surface presents some non-homogeneous irregularities attributed to the presence of hemicellulose, lignin, waxes an oils that cover the fiber (Luna et al., 2016a; Espitia-Nery et al., 2018). The pits observed in Figures 3-4.b, c and g correspond to parenchyma cells (Habibi and Lu, 2014; Chou et al., 2015; Zhu et al., 2016). The micrographs at 5\(\mu\)m (Figures 3-4.f, g and h) show a mild surface with some continuous and slight ridges.
3.2.5 Variation of fibers’ mechanical properties along the culm height

Table 3-4 shows the average tensile strength ($\sigma_{t,f}$), modulus of elasticity ($E_f$) and strain-to-failure ($\varepsilon_f$) of fibers extracted from different parts of the culm. Table 3-4 includes the maximum ($^{max}$) and minimum ($^{min}$) values, as well as the C.V for each mechanical property. The results did not include the outliers which were identified using boxplots. These results are graphically shown in Figure 3-5, where the standard deviations calculated for each sample group were included as error bars.

A statistical analysis, similar to that explained in Section 2.4.1, was made to identify significant differences among the mechanical properties of fibers from different parts of the culm. Table 3-5 shows the $p$ – values obtained from the statistical analysis of each tests. The results from all mechanical properties measured (i.e tensile strength, modulus of elasticity and strain-to-failure) show that there are no significant differences among guadua fibers extracted from different parts of the culm. Similar results were
Figure 3-4: Surface morphology of extracted fibers: a) general view at 200 µm; b), c) and d) detail at 20 µm; e), f) and g) detail at 5 µm

found by Wang et al. (2014), who points out that this behavior is due to the relatively constant microfibrillar angle in bamboo culms.
Table 3-4: Mechanical properties of guadua fibers from different parts of the culm

<table>
<thead>
<tr>
<th>Culm part</th>
<th>( \sigma_{t,f} ) (MPa)</th>
<th>( \sigma_{t,f}^{\max} ) (MPa)</th>
<th>C.V</th>
<th>( E_f ) (GPa)</th>
<th>( E_{f}^{\max} ) (GPa)</th>
<th>( E_{f}^{\min} ) (GPa)</th>
<th>C.V</th>
<th>( \varepsilon_f ) (%)</th>
<th>( \varepsilon_f^{\max} ) (%)</th>
<th>( \varepsilon_f^{\min} ) (%)</th>
<th>C.V</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>323.21</td>
<td>694.51</td>
<td>48.47</td>
<td>29.25</td>
<td>58.24</td>
<td>10.90</td>
<td>50.22</td>
<td>1.5070</td>
<td>2.3609</td>
<td>0.8828</td>
<td>29.0200</td>
</tr>
<tr>
<td>M</td>
<td>344.38</td>
<td>539.94</td>
<td>26.03</td>
<td>49.63</td>
<td>13.57</td>
<td>38.00</td>
<td>1.8094</td>
<td>2.5707</td>
<td>0.8094</td>
<td>25.1223</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>336.64</td>
<td>570.73</td>
<td>36.05</td>
<td>23.73</td>
<td>6.24</td>
<td>40.02</td>
<td>2.0302</td>
<td>2.7152</td>
<td>1.1526</td>
<td>24.2301</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>347.59</td>
<td>543.46</td>
<td>29.50</td>
<td>29.10</td>
<td>3.27</td>
<td>53.97</td>
<td>1.5059</td>
<td>2.7489</td>
<td>0.6537</td>
<td>40.2808</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-5: Mechanical properties of fibers from different parts of the culm: a) tensile strength, b) modulus of elasticity and c) strain-to-failure

Table 3-5: \( p \) – values obtained from the statistical analysis of the mechanical properties of guadua fibers from different parts of the culm

<table>
<thead>
<tr>
<th>Culm part</th>
<th>Tensile strength</th>
<th>Modulus of elasticity</th>
<th>Strain-to-failure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SW</td>
<td>Levene</td>
<td>ANOVA</td>
</tr>
<tr>
<td>B</td>
<td>0.3410</td>
<td>0.0577</td>
<td>0.8491</td>
</tr>
<tr>
<td>M</td>
<td>0.3103</td>
<td>0.1098</td>
<td>0.9865</td>
</tr>
<tr>
<td>T</td>
<td>0.8245</td>
<td>0.9862</td>
<td>0.2701</td>
</tr>
<tr>
<td>S</td>
<td>0.4769</td>
<td>0.9187</td>
<td>0.3683</td>
</tr>
</tbody>
</table>

SW: Shapiro-Wilk test
Levene: Levene’s test
Chapter 4

Conclusions part 1

The relevant aspects of the first part of the research are discussed below:

- It was proposed a methodology for determining the cross-sectional area of guadua fibers. This work was already published in the *Journal of Natural Fibers* (Luna and Lizarazo-Marriaga, 2017), and is showed in Appendix B. This methodology can be used when it is desired to take measurements of specific planes perpendicular to the longitudinal axis of the fiber, such as the failure plane, ensuring more precise measurements since the fracture plane will always be perpendicular to the observer’s plane.

- The strain-to-failure of guadua fibers decreased from approximately 2.89% down to 1.29% when the gage length was increased from 10 mm to 40 mm. On the other hand, the tensile strength and modulus of elasticity were found to be independent of the gage length. This can be explained by the fact that the average flaw size is independent of the gage length, but the number of flaws increases as the volume increases as well. Thus, while average flaw size controls the strength, the number of flaws may play a more important role in controlling the strain-to-failure, since the linking of cracks at flaws determines the strain-to-failure. It follows that, at larger gage lengths, the linking of flaws is easier, because of the larger number of flaws.

- It was proposed a guadua-fiber extraction methodology, which combines chemical and mechanical extraction procedures. By using the proposed extraction methodology, it is possible to obtain fibers with an adequate tensile strength, that could be used as reinforcement of composite materials, and with a high ease of extraction, an important parameter for industrial applications.
Based on the results for the different guadua fibers’ extraction variables, various aspects can be pointed out. Heating the sodium hydroxide solution accelerates the hemicellulose and lignin separation process; however, its use decreases the mechanical properties (i.e. tensile strength, modulus of elasticity and strain-to-failure) of the obtained fibers. This behavior could be a consequence of a poor stress transfer between elementary fibers, due to a high removal of hemicellulose and lignin. Also, the sodium hydroxide attacks the crystalline cellulose present in fibers, which, according to literature, determines the natural fibers’ mechanical performance.

Probability distribution models were proposed to describe some of the guadua fiber measured properties. The guadua fiber density follows a normal distribution. In the case of the fiber length, the Weibull distribution provides an adequate fit. These proposed distribution functions can be used to aid the development of larger mathematical models for predicting the mechanical behavior of guadua fibers or composite materials reinforced with these fibers.

The results on the mechanical properties of guadua fibers extracted from different parts of the culm show that there is no variation in the fiber mechanical performance along the culm height. According to literature, this behavior is due to the relatively constant microfibrillar angle in bamboo culms. These results show that the variation in the mechanical properties of bamboo culms are mainly attributable to the fiber density distribution in the culm rather than to the fiber itself.
Part II
Polymers

The second part of this research is focused on the characterization of a polyester resin, which could be used as a matrix in composite materials. In the first chapter of this part of the document, a brief description is made on some relevant engineering aspects and characteristics of polymers that could affect the behavior of composite materials when they are used as matrices. The next chapter shows the experimental characterization of the polyester used in this research. The last chapter summarizes the relevant conclusions of this part of the research.


Chapter 5

Generalities on polymers

The term “polymer” derives from the Greek word polus, meaning “many”, and meros, meaning “units”. Thus, a polymer is a material composed by “many units” (Askeland et al., 2013). In general terms, polymers are giant chainlike molecules (called macromolecules), composed of many repeated units (called monomers), joined by covalent bonds or van der Waals forces, forming long and flexible structures with a back-bone of carbon atoms (Meyers and Chawla, 2009). Typically, the number of monomers in a molecular chain is around $10^3$ to $10^5$, resulting in an overall molecular length of up to a few micrometres. The average number of monomers in the molecular chain of a polymer is called the degree of polymerization (Roesler et al., 2006).

Polymers are the most widely used matrix material for fiber composites. Their main advantages for the composite industry are low cost, easy processability, and low specific gravity. Some disadvantages from their use are low strength and modulus compared with metallic matrices, low operating temperatures (below 260°C) and their degradation as a result of prolonged exposure to ultraviolet light and some chemical solvents (Agarwal et al., 1990).

In this chapter, a brief description of some engineering aspects of polymeric materials is made, emphasizing the relevant characteristics when they are used as matrices in composite materials.

5.1 Polymerization process

The process of forming macromolecules from monomers is called polymerization. There are two processes to make the polymerization: by condensation and by addition (Chawla, 2011). In the condensation polymerization process, a stepwise reaction of molecules occurs to form the polymer and a simple compound as a by-product (usually water).
Conversely, during addition polymerization, the monomers join to form the polymer without producing any by-product (Tuttle, 2004). Addition polymerization is generally carried out in the presence of a catalyst (Chawla, 2011).

5.2 Main characteristics of polymers

The main characteristics of polymers are their molecular structure and configuration, molecular size and weight, and the amount and type of bonds (covalent or van der Waals). These characteristics determine the behavior of polymer materials (Meyers and Chawla, 2009).

5.2.1 Molecular structure

Polymer molecular structure can be grouped into four major types: linear, branched, cross-linked and ladder polymers (Chawla, 2011). The four types of molecular structure are shown schematically in Figure 5-1.

As for linear polymers (Figure 5-1.a), the monomer units join together side-by-side along a single direction, forming the macromolecules (Carrasquero, 2004). In a bulk polymer, these macromolecules become entangled and twisted together. As the molecular weight of the polymer increases, the number of entanglements increases as well (Osswald and Menges, 2012). According to Tuttle (2004), the stiffness of a polymer is directly related to its molecular weight and the number of entanglements. Therefore, a linear polymer with high number of entanglements will be stiffer than one with low number of entanglements.

As shown in Figure 5-1.b, branching polymers have branches (short side chains) attached to the primary back-bone of the macromolecule. This molecular structure can occur with linear, cross-linked, or ladder polymers (Meyers and Chawla, 2009). Because of the branches greatly increase the number of entanglements, a branched polymer will be stiffer than a linear polymer with similar molecular weight (Tuttle, 2004).

Cross-linked polymers form long chains, either branched or linear, that can form crosslinks (i.e covalent bonds) between individual molecular chains (Figure 5-1.c). Hence, when polymerization is complete, a vast three-dimensional network is formed (Tuttle, 2004). This cross-linked three-dimensional molecular structure results in strong and rigid polymers (Meyers and Chawla, 2009).
Ladder polymers have two linear polymers linked in a regular manner (Figure 5-1.d). Consequently, ladder polymers are more rigid than linear polymers (Meyers and Chawla, 2009; Chawla, 2011).

**Figure 5-1:** Molecular structure of polymers: a) linear; b) branched; c) cross-linked; d) ladder (Chawla, 2011)

### 5.2.2 Molecule configuration

The configuration provides information about the distribution and spatial organization of the macromolecule. During polymerization, it is possible to place monomers on the carbon back-bone in different directions. The order in which they are arranged is called the *tacticity*. The polymers with side groups that are placed in a random manner are called *atactic*. The polymers whose monomers are all on the same side are called *isotactic*, and those molecules with regularly alternating monomers are called *syndiotactic* (Sperling, 2006). The tacticity determines the degree of crystallinity that the polymer can reach. Polymers with high isotactic content will reach a high degree of crystallinity and consequently will be stiffer and stronger than the same polymer with low isotactic content (Osswald and Menges, 2012).

### 5.2.3 Degree on crystallinity

In general terms, the degree of crystallinity of a material can be defined as the fraction of the material that is fully crystalline (Meyers and Chawla, 2009). Polymers cannot be fully crystalline, unlike metals and ceramic materials (Askeland et al., 2013). This
feature is a consequence of the long length of molecular chains, reason why it is highly improbable that they are linear or regularly folded up when cooling the polymer from a liquid state. Moreover and statistically speaking, it is more likely that a chain molecule be highly twisted and entangled with other molecules (Roesler et al., 2006). Thus, the molecular structure of polymers may be amorphous or semi-crystalline (Tuttle, 2004). Amorphous polymers are those whose the molecules solidify in a random arrangement, whereas some of the molecules in semi-crystalline polymers align with their neighbors, thus forming regions with a three-dimensional order (Osswald and Menges, 2012). In practice, depending on the polymer type, molecular weight, and polymerization temperature, the amount of crystallinity in a polymer can vary from 30 to 90% (Chawla, 2011).

Some polymer properties are influenced by the degree of crystallinity. According to Meyers and Chawla (2009) and Chawla (2011), the stiffness and strength of a polymer increase as the degree of crystallinity increases as well. Also, their density and resistance to chemical attack increase with the degree of crystallinity (Askeland et al., 2013).

5.2.4 Molecular weight

The polymer molecular weight is given by the product of the molecular weight of the repeat unit and the number of repeat units (Meyers and Chawla, 2009). By comparing with other materials, the polymer molecular weight is very high, ranging from about 25000 to 1000000 g/mol or higher (Sperling, 2006).

As shown schematically in Figure 5-2, the properties of polymeric materials are strongly influenced by their molecular weight. In general, polymers with high molecular weight are stiffer and stronger than polymers with low molecular weight (Sperling, 2006; Osswald and Menges, 2012). Figure 5-3 shows the effect of molecular weight on the polymer’s tensile strength. At very low molecular weights the tensile strength is near to zero.

5.3 Thermoplastic and thermostetting polymers

Based on their behavior upon heating, polymers can be classified into two categories: thermoplastic and thermostetting polymers. Thermoplastic polymers have the ability to remelt after they have solidified. Thermosets polymers are those that solidify
via a chemical reaction that causes cross-linked molecules, which cannot remelt after solidification (Osswald and Menges, 2012).

Solidified thermoplastic polymer can take two different structures: amorphous or semi-crystalline. The molecules in an amorphous thermoplastic polymer are randomly oriented and entangled, with no discernible pattern. In contrast, in a semi-crystalline thermoplastic polymer there are regions of highly oriented molecular arrays. Typically, a semi-crystalline thermoplastic polymer features higher strength, stiffness and density than an otherwise comparable amorphous thermoplastic polymer (Tuttle, 2004). Depending on the solidification conditions, amorphous or semi-crystalline thermoplastic polymers can exhibit anisotropic properties (Hull, 1987). In general, thermoplastic polymer’s mechanical properties depend on the inherent properties of monomers and
their molecular weight, exhibit high deformation rates before failure and, under constant load show an increasing of deformation (Hull, 1987; Meyers and Chawla, 2009).

Thermoset polymer’s molecular structure presents highly cross-linked patterns, and as a consequence they are amorphous (Meyers and Chawla, 2009). Thermoset polymer’s mechanical properties depends on the inherent properties of monomers and on the length and density of the cross-linked structure. In general, thermoset polymers feature an isotropic and brittle behavior (Hull, 1987).

Table 5-1 shows some properties of common thermoplastic and thermoset polymers. By comparing thermoset polymer’s properties, epoxies feature higher strength and elastic properties, with low curing contraction and coefficient of thermal expansion. Epoxies show high viscosity before curing, thus making the fiber inclusion difficult. Also, epoxies are expensive compared to polyester.

Table 5-1: Properties of common thermoplastic and thermoset polymers (Hull, 1987; Agarwal et al., 1990; Chawla, 2011)

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Thermosets</th>
<th>Thermoplastics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Epoxy</td>
<td>Polyester</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>1.2 - 1.3</td>
<td>1.1 - 1.4</td>
</tr>
<tr>
<td>Modulus of elasticity (in bending)</td>
<td>GPA</td>
<td>2.75 - 4.10</td>
<td>4 - 6.4</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td></td>
<td>0.38 - 0.4</td>
<td>0.37 - 0.39</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>55 - 130</td>
<td>40 - 90</td>
</tr>
<tr>
<td>Compression strength</td>
<td>MPa</td>
<td>100 - 200</td>
<td>90 - 250</td>
</tr>
<tr>
<td>Strain-to-failure (tensile)</td>
<td>%</td>
<td>1 - 6</td>
<td>2</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>$10^{-6}/\degree C$</td>
<td>45 - 65</td>
<td>55 - 100</td>
</tr>
<tr>
<td>Water absorption (24h a 20°C)</td>
<td>%</td>
<td>0.1 - 0.4</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>Curing contraction</td>
<td>%</td>
<td>1 - 2</td>
<td>4 - 8</td>
</tr>
<tr>
<td>Use temperature</td>
<td>°C</td>
<td>150</td>
<td>80</td>
</tr>
</tbody>
</table>

5.4 Polymers in building construction

The polymer industry evolution during the 20th century, enabled that nowadays polymers have become an important engineering material. Because of their wide range of
properties, they can be used in many applications, and their ease of fabrication makes it possible to produce very economical finished items. Accordingly, many industries such as fibers, composites, rubber, sealant, paints, adhesives, among others are based on polymers (Halliwell, 2015).

In building construction, they are frequently used for both structural and non-structural applications (Akovali, 2005). According to Grand View Research (2019), this industry is the second largest user of polymers, with around 30% of the worldwide production in 2017. The main advantages from using polymers in building construction are their lightweight, lower cost, resistant to corrosion and moisture and shape readiness. However, there are some disadvantages from using them, which can be highlighted as follows: their lower fire-resistance over traditional materials, degradation on the presence of UV radiation and, depending on the polymer used, the mechanical behavior can be brittle (Kasapoglu, 2008).

For structural applications, where it is required proper mechanical performance (mainly adequate strength and stiffness) in the material, polymers are frequently used in the fabrication of FRP (Fiber Reinforcement Polymer) bars used to reinforce concrete structural elements such as load-bearing walls, columns and beams (Akovali, 2005). FRP bars consist of a reinforcing phase (fibers) embedded into a matrix (polymer) (Nanni et al., 2014), and are used as a replacement of conventional steel bars in applications where high corrosion resistance is needed. Another important structural application of polymers in building construction is in the conformation of SWP (Sandwich) panels. SWP panels are layered structures featuring two thin, high modulus (metallic, concrete or polymeric) facings adhered to a lightweight foam or honeycomb core (Halliwell, 2015). Also, polymers are widely used to strengthen and/or repair load-bearing structural parts in retrofitting applications (Bank, 2006a). Finally, in minor proportion than last examples, since 1990’s buildings have been completely constructed from polymeric composite materials (Akovali, 2005; Bank, 2006a). The use of polymers in building construction is preferably intended for non-structural applications, which can be divided into four main areas: piping and conduit, cladding and profiles, insulation materials, and sealants and gaskets (Akovali, 2005).

5.4.1 Polyester

Unsaturated polyester is a material of easy fabrication technique, light weight, good resistance to corrosive environment, low cost, adequate thermal stability, excellent dimensional steadiness and good creep resistance (Ciupagea et al., 2013). Because of the high content of aromatic vinyl groups, the crosslinked polyester is easily susceptible to
thermo-oxidative decomposition, which reduces the long-term use temperature (Akovali, 2005; Daniel and Ishai, 2006). The term *unsaturated* means that there are reactive spots in the molecule. Frequently, a catalyst such as an organic peroxide is added to initiate the curing process. Curing can be accelerated by raising the temperature; this increases the decomposition rate of the catalyst (Chawla, 2011). Since the beginning of the composite industry, this resin has been the most commonly used matrix in polymeric composite materials (Avella et al., 1985); according to Agarwal et al. (1990), its uses represent approximately 75% of the total resin used in this industry.

Most polyester resins are viscous, pale coloured liquids consisting of a solution of a polyester in a monomer which is usually styrene (Avella et al., 1985; Vilas et al., 2001). The curing reaction of unsaturated polyester resins is a free radical chain growth polymerization (Yang and Lee, 1988). Before the reaction, the system contains styrene monomer, unsaturated polyester molecules, and curing agents. When the reaction starts, the initiator decomposes, forming free radicals to trigger the polymerization. Free radicals link adjacent unsaturated polyester units and form primary polymer chains through connecting styrene monomers and by both inter- and intramolecular reactions (Vilas et al., 2001).
Chapter 6

Polyester resin characterization

It is well known that the mechanical properties of composite materials depend on the properties of their constituents, i.e. fibers and matrix (Hull, 1987; Daniel and Ishai, 1994; Agarwal et al., 1990; Chawla, 2011). This chapter presents the experimental program and the obtained results on the characterization of the polyester resin used as matrix in this research, which corresponds to an unsaturated polyester with commercial reference 555 and methyl ethyl ketone peroxide (MEKP) as the catalyst.

The resin characterization was focused on the establishment of the influence of the catalyst proportion on temperature evolution, specific heat, needle penetration hardening during the solidification process and mechanical resistance to tension and compression. Resin manufacturers recommend a 2%. Therefore, another two proportions were chosen below and above this value. Thus, the catalyst proportions used to begin the resin solidification (i.e. polymerization) process were 1%, 2% and 2.5%. Using catalyst proportions above 2.5% induces failure planes and discontinuities in the hardened resin, as shown in Figure 6-1. The most convenient catalyst proportion corresponds to the percentage for which the highest properties can be obtained, and that has an adequate hardening time, taking into account the next step of the research which consists of the inclusion of guadua fibers into the polyester resin. Once the most convenient catalyst proportion was determined, bending and tensile tests were carried out. Also, it was determined whether catalyst proportion influences the density of polyester resin.
Figure 6-1: Failure planes and discontinuities on the polyester resin hardened by using catalyst added at 3%

6.1 Experimental program

6.1.1 Temperature evolution and specific heat during solidification process

The thermosets polymer’s solidification process is dominated by an exothermic chemical reaction called curing reaction. The curing reaction is an irreversible process that results in the cross-linked structures typical of this polymer family (Pusatcioglu et al., 1979; Avella et al., 1985; Kenny et al., 1990; Sperling, 2006; Osswald and Menges, 2012). The thermoset polymer’s curing reaction that cures at room temperature starts immediately after mixing two components, usually resin and catalyst; the reaction is accelerated by the exotherm process or heat released during chemical reaction (Osswald and Menges, 2012).

Temperature evolution and specific heat during solidification process were measured in this research for different catalyst proportions during 4800 s (80 min). For this, freshly made samples were introduced into a semi-adiabatic chamber in order to measure the heat emitted from temperature evolution. The heat developed during the curing reaction was equal to the heat accumulated in the calorimeter and the heat lost through the semi-adiabatic chamber.

Figure 6-2 shows the semi-adiabatic chamber used in this research, which was designed in a previous research carried out by the structures and materials research group GIES from the Universidad Nacional de Colombia (Pena, 2011) for the purpose of measuring the hydration heat of cement and mortar mixtures. The semi-adiabatic chamber was made using expanded polystyrene, which is a material with a low thermal
conductivity coefficient. For this research, two replicates were used for each catalyst proportion.

Figure 6-2: Semi-adiabatic chamber used in this research

6.1.2 Needle penetration hardening

The polymer curing progress was measured through a needle penetration, which could be used as an index to follow the evolution of the resin hardening during the solidification process. The measurement was carried out using the same standardized Vicat apparatus employed to determine the setting time in Portland cement (Figure 6-3.a). The average weight of tested samples was 25 g, and three replicas were tested for each catalyst proportion. The experiment setup is shown in Figure 6-3.b. All tests were carried out in a controlled temperature room using 21 °C and 60% RH.

6.1.3 Mechanical tests

All mechanical tests explained in this section were carried out using a Shimadzu universal machine (reference AG-X plus), and employing a 300 kN load cell. The load rate and testing conditions used in each test are explained in below sections.

6.1.3.1 Influence of catalyst proportion

In order to establish the influence of catalyst proportion on the polymer mechanical response, tensile and compression tests were carried out following the guidelines set out in ASTM D3039/D3039M-08 (ASTM, 2008) and ASTM D695-10 (ASTM, 2010b) respectively. Ten tension samples and fourteen compression samples from each catalyst proportion were tested. The average dimensions of samples and the setup of the test
are shown in Figure 6-4. The used load rate in tensile and compression tests were 2 mm/min and 1.3 mm/min, respectively. As shown in Figure 6-4.a, during tensile tests it was necessary to insert sheets of expanded polyethylene foam between grips and sample, to keep the sample attached during loading. In order to ensure an axial load during compression tests, all samples were placed over an external ball joint, as shown in Figure 6-4.b.

The polyester’s tensile ($\sigma_{t,p}$) and compression ($\sigma_{c,p}$) strengths were calculated using Equations 6.1 and 6.2, respectively. In Equation 6.1, $P_{t,p}$ indicates the tension failure load and $A_{t,p}$ the failure area, which were measured with a digital caliper (Redline mechanics, range: 0 – 200 mm) after each test, assuming a rectangular cross-sectional failure plane. In Equation 6.2, $P_{c,p}$ indicates the compression failure load and $A_{c,p}$ is the cross-sectional area of each sample, calculated as the average of three diameters measured along the sample length before mechanical tests.

$$\sigma_{t,p} = \frac{P_{t,p}}{A_{t,p}} \quad (6.1)$$

$$\sigma_{c,p} = \frac{P_{c,p}}{A_{c,p}} \quad (6.2)$$
6.1.3.2 Bending and tensile test for the most convenient catalyst proportion

Once determined the most convenient catalyst proportion, bending tests were performed following the procedure established on ASTM D790-10 (ASTM, 2010c). A total of eight samples were tested, and the average dimensions are shown in Figure 6-5.a. According to the standard, all samples were tested in flatwise position. As shown in Figure 6-5.b, this test consists of a three-point bending test; the support span for all samples was 80 mm. All samples’ deflection was measured in the middle of the span, using an Epsilon deflectometer (model 3540-012M-ST). The deflection was recorded until reaching a value close to 1 mm. At this moment, the deflectometer was removed and
the load application continued until the sample failed. The load rate was 0.5 mm/min during the deflection measurement and then was increased to 0.61 mm/min. The last load rate was calculated following the recommendation of ASTM D790-10.

**Figure 6-5:** Bending tests: a) sample average dimensions; b) test execution

![Bending test setup](image)

The bending strength for each sample, $\sigma_{b,p}$, was calculated using Equation 6.3 where $P_{b,p}$ is the failure load, $L_{b,p}$ is the support span, $b_{b,p}$ and $d_{b,p}$ are the width and depth of each beam tested, respectively.

$$\sigma_{b,p} = \frac{3P_{b,p}L_{b,p}}{2b_{b,p}d_{b,p}^2}$$

(6.3)

The modulus of elasticity for bending strength, $E_{b,p}$, was calculated using Equation 6.4 where $m_p$ is the slope of the tangent to the initial straight-line portion of the load-deflection curve for each tested sample.

$$E_{b,p} = \frac{L_{b,p}^3 m_p}{4b_{b,p}d_{b,p}^3}$$

(6.4)

Also, for the same catalyst proportion, three samples in tension were tested in order to measure the modulus of elasticity of the resin for this solicitation. In order to facilitate the samples assembly and to prevent their sliding from testing grips, the samples were prepared for these tests with a narrowed middle section, as shown in Figure 6-6. In order to measure the samples’ strain, electrical strain-gauges were attached on one side of samples, at their middle length (Figure 6-6). The strains were recorded from the beginning of the tests until the sample failed, using a strain recorder Electro Measurements (reference P3). For these tests, the used load rate was 0.5 mm/min, which is lower than the one recommended by the ASTM D3039/D3039M-08. The followed standard indicates that the load rate for tensile tests is 2 mm/min, but
when using this load rate, the sample failure tends to be prompt, making it difficult to record the samples’ strains. According to the ASTM D3039/D3039M-08, the modulus of elasticity (secant modulus) in tension was calculated as the slope between the 25% and 50% of the maximum $\sigma_{t,p}$.

**Figure 6-6:** Sample tensile test for experimental measurement of resin’s modulus of elasticity

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### 6.1.4 Density

Samples prepared for tensile tests carried out to determine the most convenient catalyst proportion were used to measure resin’s density. All measurements were performed before mechanical tests. The experimental procedure and calculation were made following the guidelines of ASTM D792-13 (ASTM, 2013). This procedure is based on Archimedes’ principle, and calculates the plastic’s density as the ratio between the sample’s weight in the air and that immersed in a liquid. All measurements were made using tap water, with an average temperature of 19.3°C, and a volume of 5000 ml. All weight measurements (immersed and not) were performed using an analytical balance with a 0.1 g precision.
6.2 Results

6.2.1 Temperature evolution and specific heat during solidification process

Temperature evolution measured in the semi-adiabatic chamber during the solidification process for the different catalyst proportions is shown in Figure 6-7. Although the temperature rate increased and the maximum temperatures were different for each catalyst proportion, all samples had a similar profile: a continuous increase of temperature until a maximum value was reached, followed by a continuous temperature decrease. The measured profiles of samples using 2.5% and 2% of catalyst proportions are quite similar. Samples with 2.5% catalyst proportion had temperature increases during 570 s and reached a maximum peak of 80°C. Samples with 2% had temperature increases during 630 s and showed a maximum peak of 82°C. Furthermore, samples with 1% catalyst proportion had a maximum peak of 70°C, reached at 990 s after mixing the components.

Figure 6-7: Temperature evolution during polyester curing reaction

Figure 6-8 shows the heat released during the solidification process for the different catalyst proportions. Heat was calculated as the specific heat, defined as the heat per mass unit (Joules/gram). The heat released from the three catalyst proportions showed the same behavior: a first stage showing a slow heat release and a second stage featuring a high-speed heat release. The end of the first stage matches the time when the maximum temperature is reached.
Table 6-1 shows the total specific heat accumulated 4800 s after the initial resin-catalyst mixing. The lower exothermic reaction of samples was measured using 1% of catalyst proportion. The heat released was expected to be a function of the catalyst proportion; however, the specific heat of samples with 2% catalyst was higher than that of the samples with 2.5%, showing an optimum concentration in terms of polymer chemical reactions.

Compared to common construction building materials, polymers present higher specific heat. This behavior is mainly a consequence of its cross-linked chemical struc-
Table 6-1: Specific heat accumulated during 4800 s for the different catalyst proportions

<table>
<thead>
<tr>
<th>Catalyst proportion</th>
<th>Specific heat after 4800 s (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>1580</td>
</tr>
<tr>
<td>2%</td>
<td>1787</td>
</tr>
<tr>
<td>2.5%</td>
<td>1610</td>
</tr>
</tbody>
</table>

ture (Osswald and Menges, 2012). According to Schmid et al. (2014) the specific heat of an ordinary concrete is around 880 (J/g), while an ordinary clay brick features 840 (J/g), and steel 450 (J/g). The bigger the specific heat, the better the stability of the indoor temperature (Zhang, 2010).

6.2.2 Needle penetration hardening

The resin curing progress during the solidification process is shown in Figure 6-9. The needle penetration measured for the three catalyst proportions showed a similar behavior, featuring two well distinct stages: a first stage without changing the resin hardening (horizontal zone in the curve), and a second stage characterized by a rapid increase in the resin hardening. The increment in the catalyst proportion decreased the time when the second stage was reached. Also, the variation of catalyst proportion changed the hardening velocity; samples with 2.5% catalyst proportion had a quick needle penetration shift showing a flash set, while samples with 1% catalyst proportion took longer to start curing.

The time when the needle does not penetrate into the sample was assumed as the final needle penetration time, in which the resin is completely solidified. Table 6-2 shows the final penetration time for each catalyst proportion. As can be seen, using higher catalyst proportion decreases the time in which the resin is considered to be completely solidified, also remembering that the curing reaction is an exothermic process, which is accelerated by the heat released during the chemical reaction Osswald and Menges (2012). Thus, it was expected that by using 1% of catalyst proportion, the curing reaction took longer time because, as shown in Figure 6-7, the maximum $\Delta$Temperature peak is the lower one when compared to the other two catalyst proportions used.
**Figure 6-9**: Needle penetration for polyester resin

![Image of needle penetration graph]

**Table 6-2**: Final penetration time for each catalyst proportion

<table>
<thead>
<tr>
<th>Catalyst proportion</th>
<th>Final penetration times</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>2430</td>
</tr>
<tr>
<td>2%</td>
<td>1680</td>
</tr>
<tr>
<td>2.5%</td>
<td>1206</td>
</tr>
</tbody>
</table>

**6.2.3 Mechanical tests**

All results shown in this section, do not include the outliers which were identified using boxplots. The boxplots and all statistical analysis presented in this section were performed using MATLAB R2013a.

**6.2.3.1 Influence of catalyst proportion**

Figure 6-10 shows the average values calculated from tensile and compression strength for each catalyst proportion. The standard deviation calculated for each sample group was included in this figure as error bars. It is clear that polyester resin features a better performance regarding compression than tension. The catalyst proportion affects the resin strength, a behavior which was shown for both loads applied. Higher strength values were determined for samples with a 2% catalyst proportion; lower strength values were determined for samples holding 2.5% catalyst. For this reason, a 2%
catalyst addition is the most convenient catalyst proportion. This proportion meets the recommendation by resin manufacturers.

**Figure 6-10:** Tensile and compression strength for each catalyst proportion

From Figure 6-10 it can be seen that the standard deviation of each catalyst proportion test is different. These differences could be explained by the typical failures observed at the end of mechanical tests. In the case of tensile tests, the standard deviations for samples fabricated using catalyst proportions of 1% and 2.5% are higher than the ones obtained for 2% samples. During tensile tests of the first groups of samples (using catalyst proportions of 1% and 2.5%), it was observed that some samples had more than one cracking plane, as shown in Figure 6-11.a. In contrast, regarding tensile tests of samples fabricated using 2% catalyst proportion, just one cracking plane was observed, thus matching the sample’s failure plane, as shown in Figure 6-11.b. Consequently, the highest standard deviations were calculated for sample groups in which it was observed more than one cracking plane during the mechanical test. Similarly, for compression tests, the highest standard deviation was calculated for samples fabricated using a 1% catalyst proportion, and the values calculated for 2% and 2.5% samples are similar. During compression tests, it was not observed a typical failure mode for samples holding 1% additions. Some samples failed suddenly, thus presenting an “explosive” failure (Figure 6-12.a). In other cases, one portion of the samples failed, decaying the sample’s capacity to withstand the applied load (Figure 6-12.b). Conversely, samples holding 2% and 2.5% additions showed a typical compression failure, in which only a portion of the samples failed (Figure 6-12.c and d). Therefore, the
higher standard deviation was calculated for the sample group that did not present a typical compression failure mode.

**Figure 6-11:** Failure modes for tensile-tested samples fabricated using catalyst proportions of: a) 1% and 2.5%; b) 2%

Table 6-3 shows the tensile and compressive strength obtained for the different catalyst proportions used. This table also includes the maximum ΔTemperature for each sample group. It can be seen that the highest strengths were obtained for samples fabricated using the 2% catalyst proportion, which match with the sample group for which the highest maximum ΔTemperature was measured. This behavior could be attributed to the higher cross-linked structures of solidified polyester. In contrast, the lower strengths were obtained for samples fabricated using 2.5% catalyst proportion, but the lowest ΔTemperature was measured for 1% catalyst sample group. The
**Figure 6-12:** Failure modes for compression-tested samples fabricated using catalyst proportions of: a) and b) 1%; c) 2% and c) 2.5%

Strength decreasing in 2.5% catalyst proportion samples could be attributed to some micro failure planes and discontinuities that were not identified before mechanical tests, more than a lower cross-linked structure of solidified polyester.

**Table 6-3:** Polyester’s tensile and compressive strengths, and maximum ΔTemperature for each catalyst proportion

<table>
<thead>
<tr>
<th>Catalyst proportion</th>
<th>Tensile strength</th>
<th>Compressive strength</th>
<th>Maximum ΔTemperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>18.73</td>
<td>73.89</td>
<td>71.17</td>
</tr>
<tr>
<td>2%</td>
<td>23.01</td>
<td>95.63</td>
<td>82.11</td>
</tr>
<tr>
<td>2.5%</td>
<td>17.01</td>
<td>69.81</td>
<td>79.84</td>
</tr>
</tbody>
</table>
6.2.3.2 Bending and tensile test for the most convenient catalyst proportion

Figure 6-13 shows a typical load-deflection curve for bending-tested samples. Continuous line in Figure 6-13 shows the load-deflection behavior during the measurements with the deflectometer, and the dashed line represents the observed typical behavior until sample failure, which is an extrapolation of measured behavior and not a direct measurement. As can be seen, the relation between the applied load and deflection remains unaltered during the measurements with the deflectometer, and all samples exhibit a brittle failure.

Figure 6-13: Typical load-deflection curve from bending polyester resin samples

![Load-Deflection Curve](image)

Table 6-4 shows the results obtained from the mechanical characterization of polyester resin using the most convenient catalyst proportion (2%), including the results obtained from tensile and compression tests for this sample group. This table includes the maximum and minimum values, as well as the coefficient of variation (C.V) calculated for each mechanical property. As mentioned in previous sections, it is evident that the polyester resin used in this research showed a better compression behavior in comparison to tension and bending behavior. The bending strength is close to tensile strength. The obtained tensile strength and strain-to-failure are lower than the values showed
in Table 5-1. In the first case, the obtained tensile strength is close to 50\% below from the value reported in the literature. The obtained strain-to-failure corresponds to the 6.5\% of literature reported value. On the other hand, the compression strength and modulus of elasticity from bending are within the range shown in Table 5-1. The modulus of elasticity from bending is close to 40\% of the modulus of elasticity from tension. In literature, there is a broad range of polyester resin mechanical properties. Deshpande et al. (2000) reported a bending strength of 20 MPa. In the research made by Cuellar and Muñoz (2010) compression and bending strengths of 104.87 MPa and 0.57 MPa were obtained respectively, as well as a modulus of elasticity from bending of 0.18 MPa. Mustapha et al. (2016) reported a tensile strength of 30 MPa with a modulus of elasticity from bending of 500 MPa, while the modulus from bending reported by Ganeshan and Raja (2016) is 6270 MPa.

Table 6-4: Polyester resin mechanical properties at 2\% catalyst proportion

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{b,p}$</th>
<th>$\sigma_{t,p}$</th>
<th>$\sigma_{c,p}$</th>
<th>$E_{b,p}$</th>
<th>$E_{t,p}$</th>
<th>$\varepsilon_{t,p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(GPa)</td>
<td>(GPa)</td>
<td>(%)</td>
</tr>
<tr>
<td>Average</td>
<td>27.49</td>
<td>23.01</td>
<td>95.63</td>
<td>6.54</td>
<td>15.12</td>
<td>0.13</td>
</tr>
<tr>
<td>Maximum</td>
<td>32.92</td>
<td>27.63</td>
<td>103.14</td>
<td>7.04</td>
<td>17.87</td>
<td>0.16</td>
</tr>
<tr>
<td>Minimum</td>
<td>24.24</td>
<td>18.83</td>
<td>86.23</td>
<td>5.99</td>
<td>13.34</td>
<td>0.12</td>
</tr>
<tr>
<td>C.V</td>
<td>11.05</td>
<td>15.81</td>
<td>5.59</td>
<td>6.19</td>
<td>15.98</td>
<td>16.15</td>
</tr>
</tbody>
</table>
6.2.4 Density

Figure 6-15 shows the histogram for polyester density measurement. The density data distribution can be considered almost symmetrical. Therefore, a normal distribution was chosen to fit the data set. The normality of this data set was verified using the Shapiro-Wilk test. Both, normal distribution and Shapiro-Wilk test were explained in Section 2.4.1. The obtained \( p-value = 0.3392 \) verifies that the data set follows a normal distribution. Table 6-5 shows the estimated parameters for this probability distribution, which were determined using the MLE method. Figure 6-15 also shows the average density measured, \( \rho_p = 1.2 \text{ g/cm}^3 \). Mustapha et al. (2016) reported a polyester resin density value of 1.2 g/cm\(^3\), while Ganeshan and Raja (2016) a 1.12 g/cm\(^3\) value.

**Figure 6-15:** Histogram of polyester density distribution

![Histogram of polyester density distribution](image)

**Table 6-5:** Summary of distribution fitting for polyester density distribution

<table>
<thead>
<tr>
<th>Normal distribution</th>
<th>( \mu )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester density</td>
<td>1.2</td>
<td>0.041</td>
</tr>
</tbody>
</table>
P/BG composite
Chapter 7

Conclusions part 2

The relevant aspects of the second part of the research are discussed below:

• The results obtained during matrix characterization showed that polyester behavior is strongly influenced by catalyst proportion. In terms of mechanical strength, 2% is the most convenient catalyst proportion corresponding to the manufacturer’s recommendation. This behavior could be a consequence of a higher cross-linked structure of solidified polyester, reflected on a higher specific heat released during the solidification process.

• The results obtained during the mechanical characterization of polyester resin showed that this polymer has a better compression behavior when compared to tension and bending behavior. Tensile and bending strengths are close to 20% and 2.5% of the compression strength, respectively. These results are within the broad range of polyester resin properties reported in literature.

• An average density of $1.2 \pm 0.041 \text{g/cm}^3$ was obtained for the solidified polyester resin considering the most convenient catalyst proportion. This value is similar to densities reported in literature for the same resin. It was proposed a normal probability distribution model to describe this property, which could be used to aid the development of larger mathematical models for predicting the mechanical behavior of composite materials using this resin as a matrix.
Part III
Polymer composite materials

The third part of this research was focused on the characterization of the polymer composite material developed in this study (P/BG composite material). The matrix used was the unsaturated polyester resin (polyester) described in Chapter 6, which was reinforced using the *Guadua angustifolia* bamboo fibers (guadua fibers) defined in Chapter 2. In the first chapter of this part of the document (Chapter 8 of this thesis), a brief description of the most important aspects related to the mechanical performance of composite materials is made. Additionally, it was included a section for natural fiber-reinforced composites, where a discussion about the compatibilization treatments that could be used to modify the physico-chemical properties of natural fibers is presented, remarking on the treatments employed in this research. Chapter 9 explains the experimental procedure used for treating guadua fibers and the manufacturing process employed for the fabrication of the P/BG composite material. Also, this chapter describes the experimental methodology used for the characterization of treated fibers and the P/BG composite material. Chapter 10 shows the obtained results from the experimental characterization of treated fibers and the P/BG composite. Chapter 11 presents the proposed analytical models for the calculation of treated guadua fiber’s tensile strength (using the treatments and whiting the ranges used in this research) and P/BG composite material’s tensile strength. Finally, the last chapter provides the main conclusions of this part of the research.
Chapter 8

State of the art for natural fiber composites

Engineering materials can be classified into six broad categories: metals, polymers, elastomers, ceramic, glasses and composites (Ashby, 1992). Composite materials consist of two or more physically and/or chemically distinct phases, suitably distributed, which usually have features that are not present in any of their components individually (Meyers and Chawla, 2009).

This chapter describes the most important issues involved in the mechanical performance and analysis of composite materials. Also, a brief introduction to natural fiber-reinforced composites is made, remarking on the critical concern to reinforce polymers using these fibers. Additionally, the two treatment techniques used in this research to cover the purposes of this thesis are explained in detail.

According to the reinforcement used, a composite material can be classified as particle or fiber-reinforced composites. Due to this research is aimed to develop and characterize a natural fiber-reinforced material, the review on the state of the art made in this chapter is focused on these types of composite materials.

8.1 Composite materials

At the macroscopic scale, composite materials are formed by two or more phases which are immiscible. Broadly, one of the constituent phases is discontinuous and called reinforcement, and the other one is a continuous phase called matrix. An additional phase, called interfacial region or interface, occurs between reinforcement and matrix due to physico-chemical interactions (Daniel and Ishai, 1994); the phases present in a composite material are shown in Figure 8-1.
Figure 8-1: Phases of a composite material (Daniel and Ishai, 1994)

Composite properties depend on the properties of its constituents, their geometry, the distribution between phases and the interfacial region properties. Reinforcement distribution determines the composite homogeneity, and its geometry and orientation determine the anisotropy of the system (Daniel and Ishai, 1994; Bank, 2006a). Based on the reinforcement’s size, geometry and distribution along the matrix, composite materials can be classified into three categories (Harris, 1999): short fiber composites (discontinuous fibers), long fiber composites (continuous fibers) and particle composites.

Particle composites consist of particles of different sizes and shapes, distributed randomly into the matrix materials, resulting in a material with a quasi-isotropic behavior. In short fiber composites, the reinforcement material can be aligned or randomly distributed along the matrix; in the case of aligned reinforcement, the mechanical behavior is orthotropic, and regarding a random distribution, the composite behavior tends to be quasi-isotropic. Long fiber composites are reinforced with long and continuous fibers, that could have unidirectional orientation (orthotropic behavior), bidirectional orientation (anisotropic behavior) or multiple orientations (quasi-isotropic behavior) (Agarwal et al., 1990).

8.1.1 Fibers

As mentioned in Chapter 1, fibers are anisotropic materials with high aspect ratio (i.e. high length in relation to their diameter). In composites, they provide the stiffness and strength to the material (Daniel and Ishai, 1994; Chawla, 2011). According to
Mazumdar (2002), in structural composites, between 70 and 90% of the load is carried by fibers.

A large variety of fibers can be used as composite reinforcements. Conventionally, industrial fibers such as glass, carbon and aramid have been used as reinforcement (Liu et al., 2013). Also, natural fibers can be used as an alternative to man-made fibers. Table 8-1 shows some properties of fibers used as reinforcement in the composite industry. It can be seen that conventional fibers have higher mechanical properties (i.e. tensile strength and modulus of elasticity) than natural fibers. Due to this fact, they are frequently used in aviation and aerospace, transportation and military defense industries, when it is necessary to use fibers with an exceptional performance (i.e. high modulus, tenacity and thermal resistance) to produce high-performance structural composites. On the other hand, natural fibers are mainly used in automotive and building construction industries, to produce composites with low and medium performance, that can be used in applications in which it is no necessary a material with an exceptional performance of the material (Yang et al., 2017).

**Table 8-1**: Properties of fibers used as reinforcement in the composite industry

(Adapted from Li et al. (2007)\(^a\) and Faruk et al. (2012)\(^b\))

<table>
<thead>
<tr>
<th>Fiber</th>
<th>(\sigma_t) (MPa)</th>
<th>(E) (GPa)</th>
<th>(\Delta L) (%)</th>
<th>(\rho) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo(^b)</td>
<td>140-230</td>
<td>11-17</td>
<td>-</td>
<td>0.6-1.1</td>
</tr>
<tr>
<td>Coconut(^b)</td>
<td>175</td>
<td>4.6</td>
<td>3.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Flax(^d)</td>
<td>345-1100</td>
<td>27.6</td>
<td>2.7-3.2</td>
<td>1.5</td>
</tr>
<tr>
<td>E-glass(^a)</td>
<td>2000-3500</td>
<td>70</td>
<td>2.5-3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>S-glass(^a)</td>
<td>4570</td>
<td>86</td>
<td>2.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbon(^a)</td>
<td>4000</td>
<td>230-240</td>
<td>1.4-1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Aramid(^a)</td>
<td>3000-3150</td>
<td>63-67</td>
<td>3.3-3.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\(\sigma_t\): Tensile strength; \(E\): Modulus of elasticity; \(\Delta L\): Strain-to-failure; \(\rho\): Density

8.1.2 Matrix materials

In composites, the matrix is required to fulfill several functions, most of which are important for the material’s performance. Bundles of fibers, by themselves, have limited uses in engineering, and it is only the presence of a matrix or binder that enables the practical use of fibers in many engineering applications. The most important function of matrices in composites is that they keep the fibers together. Also, matrices permit
the load transfer among fibers. The efficiency of this load transfer is directly related to the quality of the fiber/matrix bond. Moreover, matrix materials should protect the reinforcement material from mechanical damage (i.e. abrasion) and from environmental attack (Harris, 1999; Chawla, 2011; Pickering et al., 2015).

The materials commonly used as composite matrices are polymers, metals and ceramics. Polymers are used for applications where composite materials will be exposed to temperature below 260°C. In the case of metal matrices, the service temperature is limited by the softening temperature of the used metal. When composite materials are exposed to high temperatures (above 650°C), ceramic and glasses matrices are employed. Figure 8-2 shows the service temperature ranges for common matrices used in the composite industry.

**Figure 8-2:** Service temperature ranges for common matrices (Adapted from Agarwal et al. (1990))

Even polymer has the lowest temperature range among other types of matrices, they are the most frequently used matrices in the composite industry (Askeland et al., 2013). That is due to their versatility, ease of fabrication and low cost. Considering the polymer family, thermosets are the most widely used polymeric resins used for composites (Vison and Sierakowski, 2004). Metal and ceramic matrix materials are only used for special applications, especially in the aerospace industry.

### 8.1.3 Composite interface

The properties and structure of the fiber/matrix interface play an important role in the physical and mechanical properties of a composite material. Composite interface acts as the linkage between the elastic properties of the matrix and the fibers, thus performing the stress transfer from matrix to fibers (Meyers and Chawla, 2009). According to Hull (1987), the properties of the interfacial region are a consequence of the bonding between fibers and matrix, which can be attributed to five mechanisms: wettability, interdiffusion, electrostatic attraction, chemical bonding and mechanical
bonding. These mechanisms, acting separately or in combination, produce the adhesion between composite constituents. Wettability can be understood as the ability of a liquid to spread onto a solid surface. Bonding between two surfaces may be formed by the interdiffusion of atoms or molecules across the interface. The electrostatic attraction of two surfaces is produced by the difference of electrostatic charge between them. The adhesion through chemical bonding is produced by an atomic or molecular transport which involves a diffusional process. Finally, the mechanical bonding solely involves mechanical interlocking between composite phases, due to large number of pits and corrugations on the fiber surface (Jang-Kyo and Yiu-Wing, 1998). These mechanisms are shown schematically in Figure 8-3.

**Figure 8-3:** Interface bonds: a) by molecular entanglement; b) by electrostatic attraction; c) by interdiffusion of constituents; d) by chemical bonding; e) by mechanical interlocking (Adapted from Hull (1987) and Jang-Kyo and Yiu-Wing (1998))

### 8.2 Analytical models for composite materials

The mechanical behavior of composite materials can be determined through three approaches: models based on material mechanics, analytical models, and empirical formulations. In the first approach, the constitutive fibers, matrix and fiber/matrix relations are established to describe the mechanical behavior of a composite. The analytical models are theoretical equations formulated to simulate, in a simplified way, the geometrical and mechanical response and interaction into a composite material. The
empirical formulations are based on experimental measurements, in which the experimental response of a composite material is described through a statistical distribution.

In the literature, it can be found several analytical models proposed by different authors, which introduce different parameters in order to describe geometrical, mechanical properties, and the interactions between composite constituents. In this section only two models are described for being, considered the most relevant ones for this research.

8.2.1 General considerations

The volume of a composite material $v_c$ can be determined by using Equation 8.1, where $v_f$ and $v_m$ are the fiber and matrix volume, respectively. Similarly, the weight of a composite $w_c$ can be determined by adding the fiber $w_f$ and matrix $w_m$ weight, as indicated in Equation 8.2. Equations 8.3, 8.4, 8.5 and 8.6 represent the fiber volume fraction $V_f$, fiber weight fraction $W_f$, matrix volume fraction $V_m$ and matrix weight fraction $W_m$, respectively.

\begin{align*}
v_c &= v_f + v_m \quad (8.1) \\
w_c &= w_f + w_m \quad (8.2) \\
V_f &= \frac{v_f}{v_c} \quad (8.3) \\
W_f &= \frac{w_f}{w_c} \quad (8.4) \\
V_m &= \frac{v_m}{v_c} \quad (8.5) \\
W_m &= \frac{w_m}{w_c} \quad (8.6)
\end{align*}

Hence, $V_f + V_m = 1$.

From this point, the subscripts $f$, $m$ y $c$ refer to fibers, matrix and composites, respectively.
8.2.2 Rule of mixtures (ROM)

The simplest way to model a material composed of two phases is by assuming fibers to be uniform in properties and diameter, continuous, and parallel throughout the composite, as shown in Figure 8-4.

**Figure 8-4:** Parallel model of a composite material (Adapted from Agarwal et al. (1990))

Considering a perfect bonding between fibers and matrix in which no slippage can occur at the interface, the strains exhibited by fibers ($\varepsilon_f$), matrix ($\varepsilon_m$) and composite ($\varepsilon_c$) can be expressed by Equation 8.7. Also, the load applied to the composite, $P_c$, will be withstood by the fibers, $P_f$, and the matrix, $P_m$, as shown in Equation 8.8.

$$\varepsilon_f = \varepsilon_m = \varepsilon_c \quad (8.7)$$

$$P_c = P_f + P_m \quad (8.8)$$

Assuming $A_c$, $A_f$ and $A_m$ as the cross-sectional area for the composite, the fiber and the matrix, respectively, and rewriting the Equation (8.8) in terms of the applied stresses to each composite constituent, results:

$$\sigma_c A_c = \sigma_f A_f + \sigma_m A_m \quad (8.9)$$

Assuming $l$ as the length of the composite material shown in Figure 8-4, it is possible to represent the cross-sectional area of the constituents in terms of their volume fractions:

$$\sigma_c A_c = \sigma_f (V_f A_c) + \sigma_m (V_m A_c) \quad (8.10)$$
or,

\[ \sigma_c = \sigma_f V_f + \sigma_m V_m \]  

(8.11)

Equation 8.11, known as Rule of Mixtures (ROM), can be used to estimate the strength of a composite, and indicates that the contributions of the fibers and the matrix to the average composite properties are proportional to their volume fractions.

According to some authors (Zweben and Rosen, 1970; Agarwal et al., 1990; Madsen et al., 2009; Venkateshwaran and ElayaPerumal, 2011; Takahashi et al., 2011), predictions of Equation (8.11) are quite accurate for synthetic aligned long-fiber composites when tensile loads are applied parallel to fiber, and the results obtained agree with experimental results. Other authors (Venkateshwaran and ElayaPerumal, 2011; Nayak et al., 2013; Tham et al., 2018), pointed out that ROM fail to show reasonable agreement with experimental tensile properties of natural fiber composites, due to some factors that affect the tensile properties of these composites, related to the variability of natural fibers (fiber content, length and diameter), fiber orientation into the matrix and voids.

### 8.2.3 Bowyer and Bader model

In the case of misaligned fibers, or when the direction of the applied load is not coincident with the fiber axis, the fiber contribution to the composite strength (first term of Equation 8.11) must be reduced (Agarwal et al., 1990).

Moreover, there is a minimum fiber length, commonly called the critical fiber length, \( l_c \) (see Equation 8.12), that ensures, regardless of the applied stress to the composite, that the ultimate fiber strength can be achieved (Agarwal et al., 1990). Therefore, the interfacial shear stress \( (\tau_y) \) and the fiber stress in the composite \( (\sigma_f) \) depend on the fibers length, as shown in Figure 8-5. In Equation 8.12, \( \sigma_{fu} \) is the fiber strength, \( d \) the fiber diameter and \( \tau_y \) the interfacial shear strength at the composite interface. In some cases, when the interfacial shear strength is unknown, and it is not possible to determine it experimentally, \( \tau_y \) is usually taken as the matrix shear strength (Chawla, 2011).

\[ l_c = \frac{\sigma_{fu} d}{2\tau_y} \]  

(8.12)

The Bowyer and Bader model (Bowyer and Bader, 1972) introduces two parameters, \( K_1 \) and \( K_2 \), to the first factor of ROM in order to take into account the fiber
Figure 8-5: Fiber stress and interfacial shear on fibers of different lengths when subjected to the same composite stress: a) schematic representation; b) interfacial shear strength; c) fiber stress (Adapted from Santhanam and Chandrasekaran (2014))

orientation ($K_1$) and their length ($K_2$), as shown in Equation 8.13. According to the authors, $K_1$ may be between 1 and 0.167; the upper limit corresponds to load-aligned fibers and the lower one to random distribution. On the other hand, $K_2$ can take two values depending on fiber length, as shown in Equation 8.14, where $L$ is the fiber length and $l_c$, the critical fiber length.

$$\sigma_c = K_1 K_2 \sigma_f V_f + \sigma_m V_m$$  \hspace{1cm} (8.13)

$$K_2 = \begin{cases} \frac{L-l_c}{2L}, & \text{for} \quad L > l_c \\ \frac{l_c}{2L}, & \text{for} \quad L < l_c \end{cases}$$  \hspace{1cm} (8.14)

According to Beckermann and Pickering (2009) the assumptions of this model are: no fiber–matrix debonding occurs, the factor $K_1$ is independent of the strain and the same for all fiber lengths, the interfacial shear stress is independent of the loading angle, and the composite voids are negligible. However, this model has shown good agreement with the experimental observations of natural fiber-reinforced composites (Kalaprasad et al., 1997; Venkateshwaran and ElayaPerumal, 2011; Santhanam and Chandrasekaran, 2014; Tham et al., 2018).
8.3 Natural fiber-reinforced composites

Since the 1990s, composite materials reinforced by using natural fibers (NFC) have been used in various industrial applications, as an alternative to those reinforced with synthetic-origin fibers (SFC) (Faruk et al., 2012). NFC have been manufactured for their use in automotive, furniture, packing and construction applications, where a high load carrying capacity is not required (Alsaeed et al., 2013a; Sanjay et al., 2016, 2018). According to Grand View Research (2018), the global market of NFC was valued at USD 4.46 billion in 2016, and a 12% growth is expected from 2016 to 2024.

The main advantage from using natural fibers as reinforcement of different matrices is that they are renewable resources, whose production requires little energy and involves CO$_2$ absorption, in addition to other technical issues such as low density, high specific strength and stiffness, abundant availability, corrosion resistance, low cost and non/abrasive processing features (Pickering et al., 2015; Sanjay et al., 2018; Halip et al., 2019). In addition, according to Joshi et al. (2004), NFC are environmentally superior than SFC due to three basic aspects: (1) natural fiber production causes lower environmental impacts compared to those from the synthetic fiber production; (2) NFC bear a higher fiber content for an equivalent performance, thus reducing the amount of matrix needed, which in most cases is highly polluting; and (3) the end-of-life incineration of natural fibers generates energy and carbon credits. However, there are some disadvantages from using natural fibers, from which it’s worth highlighting their high variability of properties and moisture absorption, low strength and durability, processing temperatures lower than those of synthetic fibers limiting matrix options, and poor fiber/matrix bonding (Pickering et al., 2015; Sanjay et al., 2018).

As mentioned in a previous section for industrial composites, polymers are also the most common matrix used in NFC (Pickering et al., 2015). Commonly, the polymer selection is limited by the temperature at which natural fibers degrade. Most of the natural fibers used as reinforcement in NFC are thermally unstable above 200°C (Summerscales et al., 2010). Due to this limitation, only polymers that softened or cured below this temperature are used in the NFC industry. Regarding thermoplastics, the most commonly used matrices are those made from polyethylene and polypropene, and as for thermosets, unsaturated polyester (Aziz and Ansell, 2004), epoxy resin and phenol formaldehyde are included (Pickering et al., 2015).

Some authors argue that the main disadvantage from using natural fibers as reinforcement for polymeric matrices, is the incompatibility between hydrophilic natural fibers and the hydrophobic behavior of polymer matrices (John and Anandjiwala, 2008;
Alsaeed et al., 2013a; Rohit and Dixit, 2016; Hashim et al., 2017; Sanjay et al., 2018; Peças, P.; Carvalho, H.; Salman, H.; Marco, 2018; Halip et al., 2019), leading to a poor bonding between composite phases. In order to overcome this limitation, there are two main procedures that can be used to improve the adherence at the composite interface. The first procedure is focused on the modification of the physico-chemical properties of polymer matrices, and the second one on the modification of the physico-chemical properties of fibers (Valadez-Gonzalez et al., 1999). The second procedure is commonly used for industrial applications (Summerscales et al., 2010; Luna et al., 2016a).

Fiber modification methods can be classified into two main groups, namely, chemical and physical methods (Bledzki et al., 1996; Faruk et al., 2012; Islam et al., 2013; Fernandes et al., 2015). The purpose of chemical methods is to reduce the hydrophilic features of natural fibers by using chemical compounds that react with some hydroxyl groups present in fibers, thus inducing more compatibility with polymer matrices (George et al., 2001; Sanjay et al., 2018). Chemical methods involve alkali, silane, benzoylation, acetylation, isocyanate, peroxide, and permanganate treatments among others (Halip et al., 2019). Alkali treatments are the most used ones for natural fibers (Li et al., 2007; Fernandes et al., 2015). Instead of altering the fiber chemical composition, physical methods only change the fiber’s structural and surface properties, thus mainly affecting its mechanical (frictionally) bonding with polymers (Bledzki et al., 1996; Halip et al., 2019). The most common physical methods include plasma, vacuum ultraviolet irradiation, ozone, corona, γ-ray and laser treatments (Sanjay et al., 2018). According to Pickering et al. (2015), literature is more focused on chemical approaches than on physical approaches.

The following sections explain the chemical and physical methods used in this research for the modification of the physico-chemical properties of guadua fibers.

8.3.1 Alkali treatment

As discussed in the first part of the document, the main components of natural fibers are cellulose, hemicellulose, and lignin, shown in Figure 8-6. Among these fiber constituents, cellulose is the primary load carrying component, while hemicellulose and lignin act as binders to hold the cellulose. In fibers, cellulose structure appears as crystalline and amorphous. In the crystalline region, cellulose is compacted and regularly oriented compared to the amorphous region (Maya and Sabu, 2008; Nishiyama, 2009; Ramamoorthy et al., 2015). Hemicellulose and lignin are always present in amorphous structures. The hydroxyl groups present in the cellulose amorphous region and
in the hemicellulose and lignin, can easily combine with water molecules from the atmosphere. Initially, the hydroxyl groups present in the hemicellulose and lignin give access to water molecules to penetrate the fiber surface. Then, water molecules combine with hydroxyl groups in the amorphous region of the cellulose, and stay in the fiber structure conferring the hydrophilic features of natural fibers (Kabir et al., 2013). Figure 8-7 schematically shows the natural fiber components which are able to combine with water molecules from the atmosphere.

**Figure 8-6:** Natural fiber components (Adapted from Kabir et al. (2013))

Alkali treatments, also called mercerization (Kalia et al., 2009; Ali et al., 2016), can use sodium hydroxide (NaOH) solutions to increase the natural fiber compatibility with polymeric matrices. These treatments are focused on removing the hemicellulose and lignin, thus reducing the fiber hydrophylic behavior. Also, NaOH reacts with hydroxyl groups in the amorphous cellulose region, exposing the crystalline cellulose to reaction with binder materials (John and Anandjiwala, 2008; Ilomäki, 2011; Lui et al., 2012). According to some authors (Li et al., 2007; Kabir et al., 2012; Ramadevi et al., 2012; Luna et al., 2016a), if the alkali treatment is too aggressive (high concentration of alkali solution or longer exposure time), an excessive fiber delignification can take place, thus resulting in a fiber strength deterioration.

In literature, there is a wide range of alkali treatment conditions used to improve the natural fiber compatibility with polymer matrices. The conditions used by different
researchers can be grouped into four categories: 1) a constant concentration of NaOH for a constant period of time, 2) using different NaOH concentration for a constant time period, 3) keeping a constant NaOH concentration for different time periods, and 4) using different NaOH concentrations for different time periods. The second and third categories are the most common treatment conditions used by researchers (Sanjay et al., 2018), especially the NaOH solution concentration ranging from 0.5% to 10% (Halip et al., 2019).

A research made by Osorio et al. (2011) studied the effect from treating Guadua angustifolia bamboo fibers with 1, 3 and 5% NaOH solution concentration for 20 min, on the fiber’s tensile behavior and on the fiber-epoxy composite’s flexural behavior. Fiber results showed that the strength and modulus of elasticity increased between 1 and 3% NaOH concentration, and a slight decrease for 5%. According to the authors, the increment could be attributed specifically to the removal of waxes and some amount of lignin from the fiber surface, resulting in a slight reduction of the fiber diameter, but more importantly in a diminution of weak non-cellulosic (hemicellulose and lignin) materials. As for composites, it was observed a general decreasing trend on the bending strength as the alkali concentration was increased. In contrast, the bending stiffness increased with the increment of alkali concentration. The explanation for this behavior
according to the authors, is that the mechanical bonding is the mechanism that controls the interfacial behavior of the composite, and alkali treatments lead to a smoothening of the fiber surface and hence to a less efficient stress transfer at high loads where fiber failure starts to occur.

Kabir et al. (2013) treated hemp fibers with 4, 6, 8 and 10% alkali solutions during 3 h, in order to study the influence of these treatments on the fiber’s tensile behavior. Results showed that alkali treatments reduce the tensile strength of hemp fibers. This behavior was explained by the removing of hemicellulose and lignin coverings from treated fibers, causing that cellulose microfibrils receive less support against tensile loading. In the case of the modulus of elasticity, results do not exhibit a single trend.

Cai et al. (2016) studied the effect from treating abaca fibers with NaOH, on the mechanical features and interfacial adhesion of fibers to an epoxy resin. For this, abaca fibers were immersed in 5, 10 or 15% NaOH solution concentration for 2 h. Results showed that treating abaca fibers in 5% NaOH increased fiber’s crystallinity, strength, and stiffness. On the other hand, higher treatment conditions decrease the fiber’s crystallinity and mechanical properties. Furthermore, all treatments improved the interfacial adhesion of fibers to the epoxy resin; although, the highest interfacial shear stress was obtained for fibers treated in 5% NaOH.

The main purpose of the research made by Manikandan et al. (2017), was to study the effect from treating jute fabrics in 5% NaOH solution concentration during 3, 5 and 7 h, on the tensile and flexural mechanical properties of unsaturated polyester resin hybrid epoxy composites. Results showed an overall improvement in the mechanical properties of composites using treated jute fabrics, attributed to the bonding enhancement between fabric and matrix. The maximum tensile and flexural strengths were obtained for composites fabricated using fibers treated during 3 h.

### 8.3.2 Plasma treatments

The application of plasma has been successfully used since the 1960s in a broad number of purposes in material science (Li et al., 1997). Plasma is considered the fourth state of matter, and consists of the ionization (partial or total) of a gas or gasses (Albella, 2003; Costa et al., 2006; Sparavigna, 2008; Morshed et al., 2010). As shown in Figure 8-8, when matter in the solid state is heated, it melts to become liquid state; if more heat is added to the system, it becomes gaseous state. On further heating, the atoms and molecules of the gas get ionized and start conducting electricity. This final state of the matter is known as plasma (Nema and Jhala, 2015).
Figure 8-8: Schematic representation of states of matter (Adapted from Nema and Jhala (2015))

Plasmas are generated in highly energetic processes, such as applying electric discharges to a gas, or heating a gas at high temperatures. However, in materials processing, plasmas are commonly generated by electric discharges (Albella, 2003). Figure 8-9 shows the simplest plasma reactor, consisting of two opposite parallel plate electrodes. When a sufficiently high frequency voltage (in the range between 300 and 1500 V, but for certain applications it can be increased to several kV (Bogaerts et al., 2002)) is applied between the two electrodes placed in a gas, the latter will break down into positive ions and electrons, which are able to conduct electricity, thus causing the gas discharge. The discharge process occurs when the electric field between the electrodes is sufficiently high to ionize the gas. This gas ionization process is called breakdown, and the particles (positive ions and electrons) present in the conducting media are known as plasma (Flamm and Herb, 1989; Bogaerts et al., 2002).

Figure 8-9: Plasma generation using a direct current (DC) reactor (Adapted from Albella (2003))
Plasmas can be classified into two categories: hot plasmas (thermal plasmas) and cold plasmas (non-thermal plasmas) (Konuma, 1992; Tendero et al., 2006; Morent et al., 2011). Hot plasmas are characterized by very high temperature species into the ionized gas (from 4000 K to 20000 K) and a thermal equilibrium among them. Cold plasmas are characterized by electrons with much higher temperatures than positive ions (Shenton and Stevens, 2001; Bogaerts et al., 2002), and in consequence, there is non-thermal equilibrium (Denes and Manolache, 2004). Due to most materials present changes in their microstructural composition, and degradation at high temperatures, cold plasmas are frequently employed in material science (Nema and Jhala, 2015). Cold plasmas can be generated by using low ($10^{-4}$ to $10^{-2}$ kPa (Tendero et al., 2006)) or atmospheric pressure (Albella, 2003); in both cases, the ionization is started and maintained by using direct current (DC), radio frequency (RF) or microwave (MW) power, with or without an additional electric (bias) or magnetic field (Denes and Manolache, 2004; Tendero et al., 2006). DC discharges are commonly used, due to their facility of implementation (Bogaerts et al., 2002). Nevertheless, RF and MW discharges are more efficient for atom ionization than DC discharges (Albella, 2003).

In general, cold low-pressure plasmas fulfill three main purposes: surface functionalization, thin film deposition, and etching (Li et al., 1997; Albella, 2003; Denes and Manolache, 2004). Although surface alterations are complex when using cold plasma, it has been reported that in general these alterations have no effect on bulk properties (Carlsson and Stroem, 1991; Costa et al., 2008; de Oliveira et al., 2010; Barra et al., 2015; Halip et al., 2019), which represents its main advantage. According to Hua and co-workers (Hua et al., 1997), plasma species do not penetrate deeper than $100 \times 10^{-10}$ m (100 Å) from the material surface. Those surface alterations are achieved after a few minutes of plasma treatment (Barra et al., 2015).

Etching processes are focused on removing some material from the material surface (Bogaerts et al., 2002), and there are two main alternatives to be attained: using a purely chemical process, called wet etching; or using a physical or chemical-physical process, called dry etching. Dry processes have several advantages over wet processes because they are direct methods (Flamm and Herb, 1989), which can be developed in a wide range of pressures (Denes and Manolache, 2004). Dry etching treatments could be carried out by physical sputtering, chemical reaction or ion-assisted mechanism. On the physical sputtering procedure, the material is removed by purely physical processes. When an ion present in the plasma approaches a solid surface (called target), the phenomena shown in Figure 8-10 may occur, independently or in combination: the ion may be reflected, the impact of the ion may cause the target to eject an electron (called
secondary electron), the ion may become buried in the target (called ion implantation),
the ion impact may also be responsible for some structural rearrangements in the target
material (called radiation damage), or the ion impact may set up a series of collisions
among atoms of the target, possibly leading to the ejection of one of these atoms. This
ejection process is known as sputtering (Chapman, 1980). The phenomenon produced
depends on the surface properties (material, structure, density, etc), and the energy
and type of incoming particles (Benedikt, 2010).

Figure 8-10: Interaction of ions with targets (Adapted from: Benedikt (2010);
Wang and Chung (2013))

Figure 8-11 shows the SEM micrographs obtained in the research made by Potluri
et al. (2018), in which bamboo rice was treated by using etching plasma with a 25 W
power during 10 min. According to the authors, as can be seen in Figure 8-11.a, the
untreated rice surface is relatively homogeneous. In contrast, the plasma-treated grain
surface (Figure 8-11.b) showed the formation of deeper cracks, cavities, and fissures,
attributed to the etching effect of the plasma treatment. Also, Figure 8-12 shows
the SEM images obtained by Wohlfart et al. (2010) of different PET films treated
using etching plasma, where it can be seen that the sputtered atoms from the material
surface due to plasma treatment modify the superficial roughness of PET films. Also,
etching effect is increased as the treatment time increases as well.

Gases commonly used for plasma generation include oxygen ($O_2$), nitrogen ($N_2$),
argon ($Ar$) and hydrogen ($H_2$). However, the used gas must respond to the intentions
of the applied treatment (Meichsner et al., 2013). When it is not desirable that ions react
with target, noble gases must be used. Additionally, for gas selection it is important
to take into account the sputtering yield, which is the number of target atoms ejected
per incident ion. According to Wang and Chung (2013), higher atomic number ($Z$)
generates higher sputtering yield. Accordingly, radon ($Z = 86$) is the heaviest noble gas, but it is also radioactive. Xenon ($Z = 54$) and krypton ($Z = 36$) are in the next level, but argon ($Z = 18$) is typically used because it is easily available and cheaper than other noble gases (Chapman, 1980).

The research made by Kafi et al. (2011) studied the effect of helium, helium/nitrogen, and helium/acetylene gases mixtures under atmospheric plasma glow discharge using 970 W power, on some physical and mechanical properties of jute fabrics and jute/polyester composites. They found that, for all used gases, 10 s of treatment was enough to significantly improve the wetting behavior of the fabrics. In the case of jute/polyester composites, different levels of improvement up to 55%, 62% and 40% in flexural strength, flexural modulus, and interlaminar shear stress respectively were observed, and these highest increments were observed for helium/acetylene-treated fabrics.

The main purpose of the research made by Bozaci et al. (2013) was to improve the interfacial adhesion between flax fibers and high-density polyethylene (HDPE) and unsaturated polyester, by using argon and air atmospheric plasma treatments. Even though results showed that plasma treatments reduce fiber’s strength, both treatments improve the interfacial adhesion between fibers and polymers. They attributed the improvement of the interfacial adhesion to the increment of the flax surface roughness with applied treatments.
Scalici et al. (2016) studied the effect from treating *Arundo Donax* L. leaf fibers with plasma, on some properties of fibers and fiber/epoxy composites. Composite results showed a remarkable enhancement of mechanical properties, indicating that plasma treatment improves fiber/matrix adhesion. SEM micrographs taken from the composite’s failure areas, showed that the epoxy resin better adheres around treated fibers than to untreated ones. In the case of fibers, the tensile properties of treated samples slightly decrease from the untreated ones. Also, Fourier Transform Infrared spectroscopy show significant changes in the superficial composition of treated fibers, mainly in the ranges of 800 - 1100 cm\(^{-1}\), attributed to cellulose components.
A preliminary study on this research was made in order to evaluate alkali and plasma treatments *Guadua angustifolia* bamboo fiber’s tensile strength. For alkali treatments 2 and 10% NaOH solution concentrations were used, and the fibers were immersed during 10 and 60 min. The plasma treatment corresponded to a dry etching (physical sputtering), which was carried out by using a DC etching system with Ar gas. The fibers were exposed to ion bombardment during 300 s using a 50 mA current at a working pressure of $5 \times 10^{-2}$ mbar. Results showed that the NaOH concentration notably decreased the treated fibers’ tensile strength. Conversely, applied dry etching plasma treatment does not affect the guadua fiber’s strength. SEM images revealed that NaOH acts as a cleaner, by removing the non-cellulosic materials from the cracks and pits on the fiber surface, but when considering the higher concentration during the higher treatment time, the fiber was divided into microfibers. On the other hand, plasma treatment drastically increased the fiber’s superficial roughness. These results were already published in the journal *Construction and Building Materials* (Luna et al., 2016a), and is showed in Appendix B.

### 8.4 Fabrication methods of natural fiber-reinforced composites

Natural fiber composites (NFC) can be fabricated by using traditional manufacturing techniques developed for synthetic fiber composites (SFC) (Ansell and Sapuan, 2014). The most important criteria to be considered when choosing the appropriate composite-manufacturing technique are size, shape and desired properties of the final material; the production speed and the manufacturing cost are also important issues for industrial applications (Salit et al., 2015). According to Ho et al. (2012), the success in the NFC production by using traditional techniques requires proper understanding of the structure and properties of the natural fibers to be used, emphasizing on the low chemical compatibility with conventional polymer matrices. Several manufacturing techniques have been used to produce NFC, within which the most common are hand lay-up (Kushwaha and Kumar, 2010; Sever et al., 2011; Sharma et al., 2015b; Rassiah et al., 2015; Djamil et al., 2015; Song et al., 2015; Prasanna et al., 2015; Khan et al., 2017), injection moulding (Thwe and Liao, 2003; Krishnaprasad et al., 2009; Okubo et al., 2009; Huang et al., 2012; Kwon et al., 2013; Sathishkumar, 2015) and compression moulding (Kang and Kim, 2011; Fang et al., 2013; Gupta, 2014; Sharma
et al., 2015a; Bahari and Krause, 2015; Chunhong et al., 2016; Faiizin et al., 2016; Constante and Pillay, 2016; Gopi et al., 2016).

An important parameter to verify the quality of composite manufacturing is the void volume fraction. It is well known that polymer composites have voids after fabrication (Daniel and Ishai, 2006). A well-fabricated composite may have a void volume fraction around 1% or less; higher void contents indicate poor fabrication process (Agarwal et al., 1990). The void content of a composite can drastically affect the mechanical properties and performance of the obtained material (Salit et al., 2015).

8.4.1 Hand lay-up

The hand lay-up technique is the simplest way for composite manufacturing (Chawla, 2011). Nevertheless, the quality of the fabricated composite depends on the manufacturer skills (Salit et al., 2015), thus making it difficult to standardize the process. This is an open-mold technique in which the fibers are laid onto a mold by hand and then the resin is brushed (or by roller) on them (Chawla, 2011). This composite fabrication method is commonly used with thermosetting resins, i.e polyester and epoxies (Agarwal et al., 1990). Usually, the fibers are used in the form of chopped strand mats, cloth, or woven roving (Hull, 1987). The final composite thickness is controlled by the layers of materials placed against the mold. In most cases, the first step in the fabrication process using this technique is the application of a specially formulated resin layer, commonly called gel coat, which ensures a smooth surface and protects the fibers (Agarwal et al., 1990). According to Akovali (2005) the main advantages from using this manufacturing method are the economy and the design flexibility (i.e large and complex items can be produced easily). However, the process is labour intensive and the formed parts only have one finished surface. Figure 8-13 shows schematically the fabrication process using this technique.

![Figure 8-13: Schematic representation of the hand lay-up technique manufacturing process (Adapted from Chawla (2011))](image)
8.4.2 Injection moulding

In the injection moulding technique, a measured amount of a mixture of molten polymer and short fiber is forced to pass through a mould cavity, which has the desired shape of the composite item (Ho et al., 2012). According to Salit et al. (2015), this technique is one of the most widely used manufacturing processes to produce polymer composites. By using this manufacturing process, composites holding thermoplastic polymers matrices can be formed. As pointed out before, the raw material used in this process consists of a mixture of a thermoplastic polymer and short fibers, in a pelletized form. The pelletized process is carried out as a separate process prior to the injection moulding (Agarwal et al., 1990). The manufacturing process using this technique is shown schematically in Figure 8-14. The pellets are individually fed through a hopper into a heated compression barrel, in which the material softens due to the heating. The barrel bears a screw to mix the fibers and polymer and to push the blend towards the converging section of the barrel, where it is injected through nozzle into the mould cavity with the desire shape, by using high pressure (Ho et al., 2012). The main disadvantage from using this technique is that the process could limit the fiber length below its critical length, thus affecting negatively the composite’s mechanical performance. Also, Agarwal et al. (1990) pointed out that the fiber orientation into the matrix experienced variation with respect to the thickness direction and the in-plane direction. Therefore, the mechanical properties of the composite may vary in respect to the thickness direction according to the corresponding fiber orientation.

![Schematic representation of injection moulding technique](image)

**Figure 8-14:** Schematic representation of the injection moulding technique manufacturing process (Adapted from Akovali (2005))

8.4.3 Compression moulding

The compression moulding is the oldest transformation method used in the polymer industry, that was adapted to the polymer composites manufacturing. It is commonly
used with thermosetting matrices (Salit et al., 2015). This manufacturing technique is frequently used in the automotive industry, where it is used to mould large automotive panels, because of its high-volume capabilities (Mazumdar, 2002). The compression moulding process can be made using heat or not. The heating manufacturing processes are commonly used with thermoplastic matrices. In this case, the raw material consist of pellets made out of the mixture of the polymer with the fibers. When using thermosetting matrices, the process can be made without heat (Ho et al., 2012). It is necessary to design and fabricate a male-female mold, with the desire size and shape, prior the composite manufacturing. In the case of using thermoset matrices, the fibers can used in the form of chopped strand mats, cloth, or woven roving, and as fibers themselves (short or long) aligned or randomly oriented. Also, it is necessary to cover the contact walls of the male-female mold by using a release agent, in order to facilitate the extraction of the formed composite. Initially, the fibers are placed into the mold, then the resin (liquid) previously mixed with the catalyst is poured. Subsequently, the mold is closed by bringing down the upper half, until the male-female parts fit. As the mold closes, the resin is scattered to all parts of the moulding cavity. According to (Mazumdar, 2002), it is advantageous to perform the moulding by firstly closing the mold almost completely and then opening it for a few seconds before applying the final pressure. This procedure allows the evacuation of trapped air between fibers, and the gases produced during the resin curing reaction. Once the mold is completely closed, the maximum pressure is applied, and the fibers-resin are forced to occupy completely the moulding cavity. This pressure in maintained until the complete resin solidification. The manufacturing process is schematically shown in Figure 8-15.

![Figure 8-15: Schematic representation of the compression moulding technique manufacturing process (Adapted from Mazumdar (2002))](image)

The main disadvantage from using this method is that it is not easily adapted to fabricate items with complex shapes. Also, it is not recommended to mold thick-
walled items (more than 1 cm) (Mazumdar, 2002). According to Salit et al. (2015), this composite manufacturing technique can be easily adapted to laboratory scale.
Chapter 9

Experimental program on the characterization of treated *Guadua angustifolia* bamboo fibers and the P/BG composite material

This chapter describes the methodologies used for treating guadua fibers, and for the fabrication of P/BG composite. Also, it is explained the experimental program used to characterize treated guadua fibers and P/BG composite.

It is important to clarify that the P/BG composite is made using guadua fibers, embedded into a polyester resin. As mentioned previously, guadua fibers were extracted following the methodology proposed in Chapter 2. The polyester resin used as a matrix corresponds to the unsaturated polyester resin (polyester) characterized in Chapter 6, which consists of an unsaturated polyester with commercial reference 555 and methyl ethyl ketone peroxide (MEKP) acting as the catalyst at 2%.

In order to clarify the methodology explained in this Chapter, Figure 9-1 graphically shows the main stages used for fiber treatment and characterization, and for the manufacturing and characterization of the P/BG composite. In the figure are indicated the number of the section in which the used methodology is described.
**Figure 9-1:** Main stages used in the experimental program on the characterization of treated *Guadua angustifolia* bamboo fibers and the P/BG composite material.
9.1 Compatibilization treatments applied to guadua fibers

As explained in Chapter 8, the main disadvantage from using natural fibers as reinforcement of polymer matrices is the low compatibility between hydrophilic fibers and hydrophobic polymers, leading to a poor bonding between composite phases. Therefore, it is necessary to modify the physical-chemical properties of polymers or fibers in order to increase the bonding properties at the interfacial region. Since the physico-chemical properties of natural fibers are commonly modified for industrial applications (Summerscales et al., 2010; Luna et al., 2016a), the physico-chemical properties of guadua fibers were modified in this research. This modification was made using chemical and physical methodologies. The chemical modification was made using alkali solutions, while the physical modification involve dry etching plasma treatments, through a physical sputtering procedure.

9.1.1 Alkali treatment

Alkali solutions were used to reduce the hydrophilic behavior of guadua fibers. Thus, guadua fibers were immersed in 1%, 2.5%, 5% and 10% sodium hydroxide (NaOH) concentrations during 1 h. After immersions, treated fibers were washed using the same procedure described on Chapter 2. Following this procedure, all treated fibers were washed several times using fresh tap water, until the water became clear; then, the fibers were immersed in clean tap water during 24 h. As explained in Chapter 2, this washing procedure ensures the complete removal of NaOH from fibers. Nevertheless, the pH of the distilled water in which some treated fibers were immersed was also verified. For all cases, the pH was close to 7%, thus ensuring the complete removal of NaOH from treated fibers (Estrada, 2010; Zhang et al., 2015; Cai et al., 2016; Hashim et al., 2017).

9.1.2 Dry etching plasma treatment (physical sputtering)

As explained in Chapter 8, the main purpose of dry etching plasma treatments is to remove some material from the surface, by purely physical bombardment processes. These treatments were performed using the DC etching equipment showed in Figure 9-2 (Bal-tec SCD 050) and the plasma was generated using argon gas. Guadua fibers were exposed to ion bombardment during different times using the same energy. In
a previous research (Luna et al., 2017a), it was concluded that treating guadua fibers below 1000 s does not increase the mechanical strength of polyester/guadua composites. Thus, in this research the exposure times were 400, 1000, 1500 and 2000 s (0.11, 0.28, 0.42, 0.56 h). All treatments were carried out using an average current of 30 ± 3 mA, a voltage of 500 ± 10 V and a working pressure of 10^{-2} kPa.

**Figure 9-2:** DC etching system, Bal-tec SCD 050, used for dry etching (physical sputtering) plasma treatments

In order to prevent the vacuum pump from absorbing the guadua fibers due to their low weight, before the treatment, the fibers were placed between two aluminum rings, as shown in Figure 9-3. The diameters of internal ($d_1$) and external ($d_2$) rings were 8 and 8.6 cm, respectively (Figure 9-3.a). The inner ring was covered with an aluminum film, in order to ensure the efficiency of the treatment (Figure 9-3.b). The goal of the external ring was the fixation of the fibers during the ion bombardment (Figure 9-3.c).

### 9.1.3 Characterization of treated fibers

Treated guadua fibers were characterized in order to establish the influence of applied treatments on some fibers’ properties. This characterization was focused on the establishment of tensile properties, water absorption, chemical composition and morphological analysis. All the equipments and methodologies used for the characterization of treated fibers, were described in previous chapters.

#### 9.1.3.1 Tensile tests

Tensile tests were carried out in order to establish the influence of applied treatments on fibers’ tensile strength. To this purpose, 16 replicas were tested for each treatment
Figure 9-3: Aluminum rings used for plasma treatments: a) rings diameter; b) aluminum film used to cover the internal ring and put over it the fibers to treat; c) setting with external ring; d) assembly used for dry etching (physical sputtering) plasma treatment.

condition. This sample size, as explained in Chapter 2, statistically represents the fibers’ tensile strength, which was calculated as a function of an expected error of 20 MPa with a confidence level of 90% (see Appendix A).

All fibers’ tensile tests were performed in a Shimadzu universal machine, employing a load cell of 50 N, following the procedure established under ASTM C1557-14 (ASTM, 2014), using a load rate of 1.5 mm/min. Before mechanical tests, all samples were placed on paper frames as shown in Figure 9-4, in order to avoid axial load deviation; after positioning the frames on testing grips, they were carefully cut. This equipment and methodology correspond to those used for the mechanical characterization of extracted guadua fibers (see Chapter 2).

Equation 9.1 was used to calculate the tensile strength ($\sigma_{t,f}$) of each tested fiber. In this equation, $P_{\text{max},f}$ and $A$ correspond to failure load and cross-sectional area of each fiber, respectively. The cross-sectional area of each fiber was determined at its fracture plane, using the methodology described in Chapter 2, which allows to determine more accurate measurements.
Fiber’s strain ($\varepsilon_f$) was calculated using Equation 9.2, where $\Delta l_f$ is the fiber elongation, which was calculated based on the cross-head displacement, the applied force and the system compliance determined in Chapter 2 (see Equation 2.2). The number 40 in Equation 9.2, corresponds to the gage length used on the paper frame (see Figure 9-4).

$$\varepsilon_f = \frac{\Delta l_f}{40} \quad (9.2)$$

Following the same procedure used for the characterization of extracted fibers, the modulus of elasticity (secant modulus) of treated fibers were determined as the slope between the 30% and 60% of the maximum $\sigma_{t,f}$.

### 9.1.3.2 Water absorption

The water absorption of treated guadua fibers was measured following the same procedure used for the characterization of extracted fibers (Chapter 3). Approximately 1.5 g of treated fibers, were immersed in 200 ml of tap water during 0, 1, 2, 3, 6, 12 and 24 h. After immersions, the wet weight of each sample was measured prior to removing the excess of water by centrifugation during 1 min. Then, the wet samples were introduced into an oven at 50°C. After 24 h, each sample was weighed at regular intervals of not less than 2 h. The drying was considered to be complete when the
difference between the successive determinations of the weight did not exceed 0.010 g. All weight measurements were performed using an analytical balance with a precision of 0.001 g. The water absorption was calculated using Equation 9.3, in which \( MC \) corresponds to the moisture content after each immersion time. In Equation 9.3, \( m_w \) and \( m_d \) indicate the sample’s wet and dry weight. For each immersion time, a total of 10 samples were used.

\[
MC(\%) = \frac{m_w - m_d}{m_d} \times 100
\]

(9.3)

9.1.3.3 FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional groups of treated fibers. All samples were kept at room temperature overnight before being analyzed. FTIR was determined using a FT-IR Nicolette iS 10 spectrometer (Thermo Fisher Scientific). Scans of 40 readings were performed by spectrum; the data were recorded in a range from 4000 to 800 cm\(^{-1}\).

9.1.3.4 Morphological analysis

The surface appearance of treated fibers was observed using a Tescan Vega 3 SB scanning electron microscope, working in the secondary electron mode.

9.2 Manufacturing of P/BG composite

The composite manufacturing was made using the compression moulding technique. Composite components, i.e. guadua fibers and polyester resin in liquid state were inserted into a closed cubic metallic mold which was able to apply a compression load, in order to spread the liquid resin throughout the mold and evacuate the trapped air. The compression load was maintained constant until the resin was completely cured.

Figure 9-5 shows the metallic mold used in this research. It is composed of six metallic plates, forming a closed cubic box of 0.2 × 0.2 × 0.05 m (side×side×height). In order to apply compression forces during composite manufacturing, a bolt was attached to the cover plate, which was allowed to move up and down supported by an external metallic frame linked to the mold lateral plates. The force applied during composite manufacturing was controlled by the strain of two strain-gauges attached to the vertical external supports of the cover plate.
Prior to the composite manufacturing, the strain-gauges deformations were calibrated by using an external load cell (Controls, model 82-E0100/AS with 30 kN of maximum load capacity), in order to convert the strain measurements into applied load during composite manufacturing. Figure 9-6 schematically shows the experimental assembly used for this strain-load calibration. 6 load cycles were made, from which load and strain (for both strain gauges) measurements were registered for each load increment. The load increment and the maximum applied load in each calibration cycle were approximately 0.2 kN and 3.6 kN, respectively.

The calibration curves for each strain-gauge are shown in Figure 9-7, where dots/triangles indicate each load-strain measurements, and continuous lines represent the linear fitted curve for each strain-gauge. In the case of the fitted line for load-strain measurements using strain-gauge 1, the coefficient of determination $R^2$ is close to 0.90. On the other hand, the $R^2$ obtained for the fitted line using strain-gauge 2 is close to 1.00. These $R^2$ values indicate that the variation of the applied load can be represented by the linear equations proposed for each strain-gauge.

Figure 9-8 shows the P/BG composite manufacturing process. Initially, guadua fibers were placed randomly into the mold (Figure 9-8.a). Then, the polyester resin, previously mixed with the catalyst (added at 2%) was poured (Figure 9-8.b). The cover plate was adjusted to make contact with the surface of the resin, and the com-
**Figure 9-6:** Schematic experimental assembly used for the strain-load calibration in the metallic mold used for P/BG composite manufacturing

![Schematic experimental assembly](image)

**Figure 9-7:** Calibration curves for strain measurements on the mold used for the P/BG composite manufacturing

![Calibration curves](image)

Compression force was progressively increased until the beginning of the resin curing process. The force achieved at this stage was maintained until the resin was completely toughed. Figure 9-8.c and d show the P/BG composite square plates featuring 0.2 m of length and 0.01 m of thickness (200 × 10 mm), which were obtained using the described methodology. The applied compression stress at the manufacturing stage ($\sigma_{cm}$) was

\[
y = -0.0587x \\
R^2 = 0.9759
\]

\[
y = -0.2589x \\
R^2 = 0.8964
\]
calculated by using Equation 9.4, where $P_{cm}$ corresponds to the applied compression force (in kN) and 0.04 is the cross-sectional area of the cover plate in $m^2$.

Figure 9-8: P/BG composite manufacturing process: a) guadua fibers randomly placed; b) polyester resin pouring; c) and d) obtained composite square plate
9.2.1 Tuning of the composite manufacturing process

In order to establish whether the applied compression stress during composite’s moulding influenced the mechanical response and quality (void volume fraction) of the obtained material, the P/BG composite manufacturing process was tuned. Thus, it was analysed the influence of the compression stress applied during composite moulding on the tensile strength and void content of the obtained composite material. Therefore, composite’s square plates were prepared by using compression stresses of 40, 50 and 60 kPa. After the fabrication of the composite’s square plate, 10 samples to be tension-tested were prepared for each composite.

Tensile tests were carried out following the guideline of ASTM D3039/D3039M-08 (ASTM, 2008), which corresponds to the same standard used for polyester characterization. Due to the dimension of the metallic mold used for composite preparation, the total length of samples was 0.2 m (200 mm); it was also necessary to reduce the cross-sectional area of all samples at the middle of the length, in order to prevent them from sliding off the testing grips and to ensure the failure at this plane. Figure 9-9 shows the average dimensions of composite samples and the test set-up.

Figure 9-9: Calibration of composite manufacturing process tests: a) sample average dimensions; b) test execution
The tensile strength of P/BG composite samples ($\sigma_{t,c}$) was calculated using Equation 9.5, where $P_{t,c}$ and $A_{t,c}$ are the applied load and failure area, respectively. As in the characterization of the polyester resin, the composite failure area was measured with a digital calliper (Redline mechanics, range: 0 – 200 mm) after each test, assuming a rectangular cross-sectional failure plane.

$$\sigma_{t,c} = \frac{P_{t,c}}{A_{t,c}}$$ (9.5)

After mechanical tests, the void content of each tested sample was measured, following the procedure established under the ASTM D2734-16 - Test method A (ASTM, 2016). According to the standard, the void content ($V_v$) was calculated as the difference between the theoretical composite’s density ($\rho_{tc}$) and the actual (measured) composite’s density ($\rho_{ec}$), as shown in Equation 9.6. $\rho_{tc}$ was calculated using Equation 9.7, where $W_f$ and $W_m$ represent the fiber and matrix weight fraction, respectively, and $\rho_f$ and $\rho_m$ the fiber and matrix density, respectively. The used values for the fiber and matrix density correspond to average values calculated in Chapters 3 and 6, respectively ($\rho_f = 1.359$ g/cm$^3$ and $\rho_p = 1.2$ g/cm$^3$). All composites were reinforced using 2% guadua fiber ($W_f = 2\%$) and a matrix weight fraction of 98% ($W_m = 98\%$). The actual density of composite samples was measured according to ASTM D792-13 (ASTM, 2013), following the same procedure used for the measurement of polyester density, described in Chapter 6.

$$V_v = \frac{100(\rho_{tc} - \rho_{ec})}{\rho_{tc}}$$ (9.6)

$$\rho_{tc} = \frac{100}{\frac{W_m}{\rho_p} + \frac{W_f}{\rho_f}}$$ (9.7)

Figure 9-10 shows the average tensile strength and void content for samples fabricated using the different compression stresses during composite manufacturing. The values 40, 50 and 60 in the figure correspond to samples prepared from composites fabricated using 40, 50 and 60 kPa, respectively. Also, the standard deviation of each sample group’s tensile strength was included as error bars. Results show that increasing the compression stress during material preparation has a favorable response on the composite’s tensile strength and void content. Higher void content leads to composites with more internal defects that in turn could affect their mechanical performance (Salit et al., 2015). Sample S60 is deemed a material bearing an adequate manufacturing process according to Agarwal et al. (1990), since the samples’ average void content
was $\nu = 0.46\%$. The error bars shown in Figure 9-10 are similar, thus indicating that the variation on the composite’s tensile strength is strongly influenced by the variation on the properties of the composite’s constituents, rather than for the manufacturing process.

**Figure 9-10:** P/BG composite’s tensile strength and void content for the different compression stresses applied during composite manufacturing

![Graph showing tensile strength and void content](image)

### 9.3 Characterization of P/BG composite

This section describes the tests made in order to establish the influence of the applied treatments on fibers, on some physical and mechanical properties of the P/BG composite. In the case of mechanical characterization, tensile, bending and pull-out tests were carried out. The physical characterization corresponds to the morphological analysis of the fracture surface of composite samples after mechanical tests. In order to make comparisons, samples bearing non-treated fibers were fabricated for all tests.

#### 9.3.1 Mechanical characterization

**9.3.1.1 Tensile and bending tests**

Tensile and bending tests were carried out on composite samples fabricated using non-treated and treated fibers. These tests were performed on the same equipment used
for the mechanical characterization of polyester resin (Shimadzu universal machine reference AG-X plus, employing a load cell of 300 kN). Tested samples were prepared from composite square plates similar to those shown in Figure 9-8.d. The composite manufacturing process corresponds to the compression moulding technique explained in the preceding section, applying a compression stress during composite moulding of 60 kPa. In order to obtain results that represent the mechanical behavior of the P/BG composite, 8 samples were tested. This sample size was calculated as a function of an expected error of 2 MPa on the composite strength, with a confidence level of 90% and using the tensile strength data obtained from the calibration of the composite manufacturing process (see Appendix A).

All composites were reinforced using a fiber weight fraction of around 6% ($W_f \approx 6\%$) and a matrix weight fraction of around 94% ($W_m \approx 94\%$). Using fiber weight fractions higher than 6% make it difficult to spread the liquid resin throughout the entire mold, thus causing fiber portions not to be embedded into the polyester matrix (Figure 9-11). Also, using higher weight fractions generates fiber agglomerations, as shown in Figure 9-11. Both described effects reduce the quality of the fabricated composite’s square plate.

**Figure 9-11:** P/BG composite square plate fabricated using a fiber weight fraction of 9% ($W_f = 9\%$). Fiber agglomeration and portions without polyester matrix can be observed

Based on the average density of guadua fibers ($\rho_f = 1.359 \text{ g/cm}^3$) and polyester resin ($\rho_p = 1.2 \text{ g/cm}^3$) shown in Chapters 3 and 6, it was possible to calculate the fiber volume fraction, $V_f$, using Equation 9.8 (Daniel and Ishai, 2006). Thus, during the
fabrication of composite samples a $V_f = 5.3\%$ was used. This value is similar to $W_f$, since the densities of guadua fibers and polyester resin are quite similar.

$$V_f = \frac{1}{1 + \frac{\rho_f}{\rho_m} \left( \frac{1}{W_f} - 1 \right)} \quad (9.8)$$

The ASTM D3039/D3039M-08 (ASTM, 2008) procedure was followed for tensile testing. As with the tensile characterization of the polyester resin, in order to prevent the sliding of samples off testing grips, the samples used for composite tensile tests were prepared with a narrowed middle section, as shown in Figure 9-12.b. In order to measure the composite strain, electrical strain-gauges were attached on one side of 3 samples, at their middle length (Figure 9-12). For these instrumented samples, the strains were recorded from the beginning of the tests until the sample failure by using a strain recorder Electro Measurements (reference P3). Different load rates were used for instrumented and non-instrumented samples, since when using the load rate indicated in the ASTM D3039/D3039M-08 (2 mm/min), the sample fail promptly, thus making it difficult to record the sample’s strains. Thus, for instrumented and non-instrumented samples the load rate was 0.5 mm/min and 2 mm/min, respectively. The tensile strength of each tested sample, $\sigma_{t,c}$, was calculated by using Equation 9.5, the same one used for the calibration of composite manufacturing. According to the ASTM D3039/D3039M-08, the modulus of elasticity (secant modulus) from tension was calculated as the slope between the 25% and 50% of the maximum $\sigma_{t,c}$.

The flexural behavior was measured through three-point bending tests, based on the ASTM D790-10 (ASTM, 2010c), following the same procedure used for the bending characterization of the polyester resin. As shown in Figure 9-13, all samples were placed in flatwise position, using a support span of 80 mm. All samples’ deflection was recorded at the middle of the span, by using an Epsilon deflectometer (model 3540-012M-ST). The deflection was recorded until a value close to 1 mm was reached. At this moment, the deflectometer was removed and the load application continued until the sample failed. The load rate was 0.5 mm/min during the measurement of the deflection and then it was increased to 0.61 mm/min. The final load rate was calculated following the guidelines of ASTM D790-10.

The bending strength for each sample, $\sigma_{b,c}$, was calculated using Equation 9.9 where $P_{b,c}$ is the failure load, $L_{b,c}$ is the support span, $b_{b,c}$ and $d_{b,c}$ are the width and depth of each tested beam, respectively.

$$\sigma_{b,c} = \frac{3P_{b,c}L_{b,c}}{2b_{b,c}d_{b,c}^2} \quad (9.9)$$
The composite’s modulus of elasticity from bending, $E_{b,c}$, was calculated using Equation 9.10 where $m_c$ is the slope of the tangent to the initial straight-line portion of the load-deflection curve for each tested sample.

$$E_{b,c} = \frac{L_{b,c}^3 m_c}{4b_{b,c}d_{b,c}^3}$$ (9.10)
9.3.1.2 Pull-out tests

These tests were made in order to comprehend and explain most of the obtained results from the tensile characterization of the P/BG composite. Thus, these tests were performed on samples using treated fibers, for which the highest tensile strengths were obtained for each compatibilization treatment applied, i.e. for alkali and plasma treatments. In order to make comparisons, a third sample group was tested, in which non-treated fibers were used.

The main purpose of pull-out tests is to measure the interfacial shear strength (IFSS) between a single fiber and the bulk matrix material that surrounds the fiber (Sydenstricker et al., 2003; Fu et al., 2006). For this, a single guadua fiber was embedded into a polyester matrix block, as shown in Figure 9-14, and a force was applied to the free end to pull it out of the matrix. The interfacial shear stress between fiber and matrix (τ) was calculated using Equation 9.11 (Cai et al., 2016; Huang and Young, 2019), where \( F \) is the pull-out load (peak force recorded in tests), \( d \) the fiber diameter, and \( l_e \) the fiber length embedded into the matrix. Thus, the IFSS corresponds to the slope of \( F \) vs. \( \pi d l_e \) (embedded surface area) graphs (Chawla, 2011; Cai et al., 2016).

The fiber diameter, \( d \), and the embedded length, \( l_e \), of each sample were measured before the tests, by using a Motic SMZ168 stereo microscope and a 3X magnification, and the images were acquired using a 3.0MP Moticam attached to the stereo microscope. Figure 9-15 shows the measured dimension for one sample.

\[
\tau = \frac{F}{\pi d l_e} \tag{9.11}
\]

All pull-out tests were performed in the same equipment used for fibers’ tensile tests, employing a load cell of 50 N and using a load rate of 2 mm/min. These tests were performed following and adapting the procedures used in similar researches (Cai et al., 2016; Valadez-Gonzalez et al., 1999). The used load rate was established from preliminary tests, in which it was observed that when using lower load rates, the failure takes a longer time, but if the load rate is incremented above the adopted value, the sample suddenly fails making it difficult to record the sample’s behavior during the tests. The test execution is shown in Figure 9-14.b.

For the fabrication of samples cubic plastic molds were used to form the bulk polyester matrix material. On one side of the cubic plastic molds holes were opened, with a needle, in order to introduce the single guadua fiber used in each sample. After positioning the fibers into the hole, and adjusting the embedded length, the polyester resin, previously mixed with the catalyst was poured. In all sample series,
**Figure 9-14:** Pull-out tests: a) schematic representation of used sample; b) test execution

![Figure 9-14](image)

**Figure 9-15:** Dimensions of the embedded length and diameter of the fibers used for pull-out tests

![Figure 9-15](image)

the embedded length varies randomly from 0.2 mm to 2.7 mm, and 50 samples were prepared for each series. After the resin was completely tough, the samples were carefully demolded from the molds. Figure 9-16 shows some samples fabricated for these tests.
9.3.2 Morphological analysis

A morphological characterization of the composite was conducted by scanning electron microscopy (SEM). These images were taken from the fracture surface of the samples used for tensile tests. Observations were carried out by using a Tescan Vega 3 SB microscope, the same one used for the morphological analysis of treated fibers, working in the secondary electron mode.
P/BG composite
Chapter 10

Results on the experimental characterization of treated *Guadua angustifolia* bamboo fibers and the P/BG composite material

This chapter presents the obtained results from the characterization of treated guadua fibers and the P/BG composite material. The methodology used for the experimental characterization was shown in Chapter 9.

All results showed in this chapter do not include the outliers, which were identified using boxplots. The boxplots and statistical analysis were performed using MATLAB R2013a (The MathWorks Inc., Natick, Massachusetts, US). All statistical inferences assumed a confidence level of 95% ($\alpha = 0.05$).

10.1 Results from the characterization of treated fibers

This section shows the obtained results from the experimental characterization of treated fibers. The obtained results were identified as follows: H1, H2.5, H5 and H10 correspond to results of alkali-treated fibers for each solution concentration, respectively. In the same way, P400, P1000, P1500 and P2000 correspond to results of plasma-treated fibers for each exposure time, respectively. All determined properties were compared with the obtained values for non-treated guadua fibers, which correspond to those shown in the first part of the research.
10.1.1 Tensile tests

Figure 10-1 shows the typical strain-stress curves for alkali and plasma treated fibers. Also, the figure includes the typical stress-strain curve for extracted fibers, shown in Chapter 2. As observed for extracted fibers, treated fibers exhibit a linear elastic brittle behavior until failure. Therefore, applied treatments do not modify the mechanical behavior of fibers. The small peaks shown on some curves, remarked with dashed lines in Figure 10-1, are a consequence of the rupture of some elementary fibers.

Figure 10-1: Typical stress-strain curves for treated fibers: a) alkali treated; b) plasma treated
Table 10-1 shows the results on average tensile strength ($\sigma_{t,f}$), modulus of elasticity ($E_f$) and strain-to-failure ($\varepsilon_f$) for each applied treatment. Table 10-1 includes maximum ($\sigma_{\text{max}}^t$) and minimum ($\sigma_{\text{min}}^t$) values, and the coefficient of variation (C.V) calculated for each mechanical property. Also, these results are graphically shown in Figures 10-2, 10-3 and 10-4. These figures also show the standard deviations calculated for each sample group as error bars.

**Table 10-1: Results on the mechanical characterization of treated guadua fibers**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$\sigma_{t,f}$ (MPa)</th>
<th>$\sigma_{\text{max}}^t$ (MPa)</th>
<th>$\sigma_{\text{min}}^t$ (MPa)</th>
<th>C.V (%)</th>
<th>$E_f$ (GPa)</th>
<th>$E_{\text{max}}^f$ (GPa)</th>
<th>$E_{\text{min}}^f$ (GPa)</th>
<th>C.V (%)</th>
<th>$\varepsilon_f$ (%)</th>
<th>$\varepsilon_{\text{max}}^f$ (%)</th>
<th>$\varepsilon_{\text{min}}^f$ (%)</th>
<th>C.V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-treated</td>
<td>347.88</td>
<td>414.76</td>
<td>261.72</td>
<td>13.48</td>
<td>40.75</td>
<td>26.10</td>
<td>13.48</td>
<td>6.43</td>
<td>33.75</td>
<td>1.6588</td>
<td>2.5950</td>
<td>0.9183</td>
</tr>
<tr>
<td>Alkali-treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>334.19</td>
<td>511.38</td>
<td>169.24</td>
<td>28.69</td>
<td>39.15</td>
<td>21.83</td>
<td>13.04</td>
<td>7.10</td>
<td>45.50</td>
<td>1.9412</td>
<td>1.9174</td>
<td>0.3771</td>
</tr>
<tr>
<td>H2.5</td>
<td>313.58</td>
<td>483.78</td>
<td>138.39</td>
<td>30.89</td>
<td>35.02</td>
<td>22.44</td>
<td>13.04</td>
<td>13.04</td>
<td>29.12</td>
<td>1.6813</td>
<td>2.2381</td>
<td>1.2311</td>
</tr>
<tr>
<td>H5</td>
<td>269.30</td>
<td>451.36</td>
<td>156.46</td>
<td>33.78</td>
<td>54.70</td>
<td>27.15</td>
<td>11.97</td>
<td>11.97</td>
<td>45.17</td>
<td>1.4250</td>
<td>2.0819</td>
<td>0.6914</td>
</tr>
<tr>
<td>H10</td>
<td>200.44</td>
<td>296.23</td>
<td>133.25</td>
<td>23.89</td>
<td>19.90</td>
<td>12.06</td>
<td>10.85</td>
<td>12.06</td>
<td>24.18</td>
<td>1.3381</td>
<td>1.9385</td>
<td>0.7992</td>
</tr>
<tr>
<td>Plasma-treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P400</td>
<td>344.10</td>
<td>480.84</td>
<td>231.25</td>
<td>25.13</td>
<td>38.40</td>
<td>29.45</td>
<td>18.08</td>
<td>18.08</td>
<td>20.92</td>
<td>1.4038</td>
<td>3.5643</td>
<td>0.5004</td>
</tr>
<tr>
<td>P1000</td>
<td>345.56</td>
<td>513.39</td>
<td>226.81</td>
<td>21.08</td>
<td>45.31</td>
<td>27.51</td>
<td>16.02</td>
<td>16.02</td>
<td>31.35</td>
<td>1.7552</td>
<td>3.0984</td>
<td>0.7433</td>
</tr>
<tr>
<td>P1500</td>
<td>318.20</td>
<td>446.15</td>
<td>136.78</td>
<td>32.34</td>
<td>36.75</td>
<td>27.89</td>
<td>9.83</td>
<td>9.83</td>
<td>31.02</td>
<td>1.4820</td>
<td>3.1098</td>
<td>0.5374</td>
</tr>
<tr>
<td>P2000</td>
<td>276.20</td>
<td>432.35</td>
<td>162.54</td>
<td>27.53</td>
<td>26.64</td>
<td>18.06</td>
<td>8.80</td>
<td>8.80</td>
<td>33.65</td>
<td>1.9014</td>
<td>3.0079</td>
<td>0.7069</td>
</tr>
<tr>
<td>C.V: Coefficient of Variation (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 10-2: Tensile strength of treated fibers**

As mentioned for extracted fibers, when separately analyzing each column of Figures 10-2, 10-3 and 10-4, guadua fibers show high mechanical properties variability,
which is quite characteristic of natural fibers. According to de Andrade et al. (2008), this variation is the result of three main factors: test parameters/conditions, plant characteristics, and area measurements. Because in this part of the research similar extraction parameters and conditions were used during all tests, as well as a methodology to measure the cross-sectional area with high accuracy, the variation could be mainly attributed to differences in the raw material (guadua culms), fiber’s microstructure, and to the errors inherent in the experimental procedure. In the case of tensile
strength (Figure 10-2), the non-treated fibers’ standard deviation was lower as compared to that from applied treatments. This difference may be result of anisotropic changes induced by the applied treatments on the fiber’s microstructure. In general, in the case of modulus of elasticity and strain-to-failure (Figures 10-3 and 10-4), there is no high variation among standard deviations of treatments.

Results show that treating guadua fibers using alkali solutions or dry etching plasma, modifies the mechanical properties thereof. As shown in Figure 10-2, both treatments applied to guadua fibers decrease their tensile strength; the decrease was more significant for alkali treatments as compared to the decrease from plasma treatments. Moreover, the changes in the modulus of elasticity and strain-to-failure do not show a single trend (Figures 10-3 and 10-4). In general, alkali treatments decrease the stiffness and strain-to failure of fibers. On the other hand, plasma treatments do not modify drastically these mechanical properties of fibers.

However, in order to identify significant differences in the obtained mechanical properties of treated fibers respect to extracted fibers, a statistical analysis similar to the one explained in Section 2.4.1 was performed. Initially, through the Shapiro-Wilk tests, it was verified whether each data set distribution followed a normal distribution. The homoscedasticity was verified among the data collected through the Levene’s test. An ANOVA analysis was applied to the cases to fulfill both criteria, that is, normality criteria and homoscedasticity. As for the opposing cases, the Kruskal-Wallis test was used. In all cases, the significance level used was 0.05. Table 10-2 shows the p-values obtained from each test, on the statistical analysis for each applied treatment. As can be seen in the table, an ANOVA analysis was performed for all mechanical properties.

In the case of the fiber’s tensile strength, the statistical analysis pointed out variations among some of the values obtained. However, there are no differences between the average fiber’s strength of the non-treated fibers, H1, H2.5 and all cases using plasma. In contrast, the tensile strengths obtained for H5 and H10 cases are substantially lower as compared to other cases. A previous research revealed similar results for the same treatment techniques (Luna et al., 2016a,b). On the other hand, there is no significant variations among the modulus of elasticity and the strain-to-failure of treated and non-treated fibers. Treating natural fibers with alkali solutions could cause a degradation of their crystalline cellulose, which is the constituent that governs the tensile strength thereof (Hughes, 2012; Fangueiro and Rana, 2016). According to the obtained results, this degradation starts to be significant at values equal to 5% solution concentration and higher. Plasma results corroborated that the applied treat-
Table 10-2: \( p \) – values obtained from statistical analysis on the mechanical properties of alkali and plasma-treated fibers

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Tensile strength</th>
<th>Modulus of elasticity</th>
<th>Strain-to-failure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SW</td>
<td>Levene</td>
<td>ANOVA</td>
</tr>
<tr>
<td>Non-treated</td>
<td>0.8155</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>0.2231</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2.5</td>
<td>0.7355</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H5</td>
<td>0.3912</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H10</td>
<td>0.9455</td>
<td>0.2070</td>
<td>6.57 \times 10^{-6}</td>
</tr>
<tr>
<td>P400</td>
<td>0.1699</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1000</td>
<td>0.7520</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1500</td>
<td>0.3107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2000</td>
<td>0.3278</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SW: Shapiro-Wilk test
Levene: Levene’s test

...does not affect the bulk properties of treated material (Carlsson and Stroem, 1991; Costa et al., 2008; de Oliveira et al., 2010; Barra et al., 2015; Halip et al., 2019).

10.1.2 Water absorption

Tables 10-3 and 10-4 show the average moisture content after each immersion time, \( MC \), calculated for alkali and plasma-treated fibers, respectively. The tables also include the C.V for each data set. In order to compare obtained values, Tables 10-3 and 10-4 show the \( MC \) values calculated for non-treated fibers, which correspond to those shown in Chapter 3. These results are shown graphically in Figure 10-5.

In general, the water absorption behavior is similar for non-treated and treated fibers. \( MC \) increases as the immersion time is increased as well. Furthermore, two stages can be distinguished for all cases: the first stage, between 0 h and 6 h when fibers absorb high quantities of water, and the second stage, between 6 h and 24 h, when water absorption tends to stabilize.

Obtained results for alkali-treated fibers (Table 10-3 and Figure 10-5.a), show that these treatments diminish the \( MC \) after each immersion time, and the diminishing increases as the NaOH solution concentration is also increased. Ramadevi et al. (2012) found similar results, for abaca-alkali treated fibers using 5%, 10%, 15% and 20% NaOH solution concentrations. In that study, treated fibers using 20% solution con-
centration showed around 50% less water absorption compared to non-treated fibers. Also, Sathishkumar (2015) found during 24 h a reduction around 10% on the water absorption of Sansevieria ehrenbergii-alkali treated fibers, using 5% solution concentration. As explained in Chapter 8, the main purpose of chemical treatments is to reduce the hydrophilic features of natural fibers, by removing lignin and hemicellulose of treated fibers. Therefore, treating natural fibers using alkali solutions results in treated fibers showing less hydrophilic features. When compared to non-treated fibers, the reduction in the final $MC$ (for an immersion time of 24 h) was around 15%, 18% and 30% for H2.5, H5 and H10 fibers, respectively. As for H1 fibers, $MC$ values are lower than those of non-treated fibers for immersion times of 1, 2, 3, 6 and 12 h, but there is an increment in the final $MC$. This result could be attributed to a higher and unusual relative humidity at the moment of measuring sample’s dry weights.

Table 10-3: Water absorption after each immersion time for alkali-treated fibers

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Non-treated</th>
<th>H1</th>
<th>H2.5</th>
<th>H5</th>
<th>H10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$MC$ (%)</td>
<td>C.V(%)</td>
<td>$MC$ (%)</td>
<td>C.V(%)</td>
<td>$MC$ (%)</td>
</tr>
<tr>
<td>0</td>
<td>7.25</td>
<td>4.41</td>
<td>7.40</td>
<td>1.92</td>
<td>7.31</td>
</tr>
<tr>
<td>1</td>
<td>62.27</td>
<td>5.19</td>
<td>57.99</td>
<td>5.61</td>
<td>43.39</td>
</tr>
<tr>
<td>2</td>
<td>84.11</td>
<td>5.71</td>
<td>75.75</td>
<td>5.85</td>
<td>62.25</td>
</tr>
<tr>
<td>3</td>
<td>88.62</td>
<td>5.80</td>
<td>81.16</td>
<td>9.04</td>
<td>65.17</td>
</tr>
<tr>
<td>6</td>
<td>150.94</td>
<td>3.49</td>
<td>146.80</td>
<td>8.42</td>
<td>111.75</td>
</tr>
<tr>
<td>12</td>
<td>182.75</td>
<td>3.82</td>
<td>179.14</td>
<td>8.45</td>
<td>149.42</td>
</tr>
<tr>
<td>24</td>
<td>184.67</td>
<td>2.97</td>
<td>192.12</td>
<td>8.21</td>
<td>156.20</td>
</tr>
</tbody>
</table>

C.V: Coefficient of Variation (%)

Table 10-4: Water absorption after each immersion time for plasma-treated fibers

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Non-treated</th>
<th>P400</th>
<th>P1000</th>
<th>P1500</th>
<th>P2000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$MC$ (%)</td>
<td>C.V(%)</td>
<td>$MC$ (%)</td>
<td>C.V(%)</td>
<td>$MC$ (%)</td>
</tr>
<tr>
<td>0</td>
<td>7.25</td>
<td>4.41</td>
<td>7.46</td>
<td>13.57</td>
<td>7.59</td>
</tr>
<tr>
<td>1</td>
<td>62.27</td>
<td>5.19</td>
<td>63.41</td>
<td>9.96</td>
<td>65.00</td>
</tr>
<tr>
<td>2</td>
<td>84.11</td>
<td>5.71</td>
<td>79.98</td>
<td>6.53</td>
<td>83.64</td>
</tr>
<tr>
<td>3</td>
<td>88.62</td>
<td>5.80</td>
<td>83.25</td>
<td>8.19</td>
<td>97.35</td>
</tr>
<tr>
<td>6</td>
<td>150.94</td>
<td>3.49</td>
<td>155.71</td>
<td>7.29</td>
<td>161.76</td>
</tr>
<tr>
<td>12</td>
<td>182.75</td>
<td>3.82</td>
<td>179.75</td>
<td>6.95</td>
<td>185.74</td>
</tr>
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<td>24</td>
<td>184.67</td>
<td>2.97</td>
<td>189.06</td>
<td>6.86</td>
<td>186.89</td>
</tr>
</tbody>
</table>

C.V: Coefficient of Variation (%)
Figure 10-5: Water absorption of treated guadua fibers: a) alkali treated; b) plasma treated

On the other hand, measured $MC$ values for plasma-treated fibers are similar compared to non-treated fibers (Table 10-4 and Figure 10-5.b). The small variations for each plasma treatment condition in each immersion time, could be attributed to differences on the relative humidity at the moment of measuring the samples’ weights. As explained in Chapter 8, modifications induced by plasma treatments are superficial
and do not alter the bulk properties of treated materials. Therefore, dry etching plasma treatments used in this research do not change the hydrophilic features of guadua fibers.

10.1.3 FTIR spectroscopy

Figures 10-6 and 10-7 show the FTIR spectra of alkali-treated and plasma-treated fibers, respectively. Spectrums shown were normalized in order to make comparison among them, and for better understanding the spectra were displaced. Figures 10-6 and 10-7 include the spectra obtained for extracted fibers (marked as non-treated).

**Figure 10-6:** FTIR spectroscopy for alkali-treated guadua fibers

![FTIR spectroscopy for alkali-treated guadua fibers](image)

The transmittance \( T \) is defined as the ratio between the intensity of the light transmitted \( (I) \) and the intensity of the light entering the sample \( (I_o) \), by using Equation 10.1 (Stuart, 2004). Therefore, the “amount” of a functional group observed on a FTIR spectra showing transmittance, is inversely proportional to the intensity of the peak.

\[
T = \frac{I}{I_o} \quad (10.1)
\]
Figure 10-7: FTIR spectroscopy for plasma-treated guadua fibers

Figure 10-6 indicates that alkali treatments change the chemical composition of guadua fibers. The strong and broad band between 3600 cm\(^{-1}\) and 3200 cm\(^{-1}\), assigned to the stretching of the hydroxyl group, changes due to the alkali solution. This behavior is attributed to the removal of hemicellulose and lignin from the treated fibers (Phuong et al., 2010; Ramadevi et al., 2012; Benyahia et al., 2013). The bands that appear between the region of 2919 cm\(^{-1}\) and 2850 cm\(^{-1}\) for H2.5, H5 and H10 fibers, strongly reveal the reduction of the hemicellulose content by the chemical treatment (Zhou et al., 2013). The peaks attributed to the lignin bending of the aromatic C-H bond, between 1510 cm\(^{-1}\) and 1450 cm\(^{-1}\) change for H5 and H10 fibers, thus evidencing a partial lignin reduction from these fibers (Chattopadhyay et al., 2011). Finally, the characteristic peak at 1421 cm\(^{-1}\) attributed to the cellulose bending, and the prominent peak between 1100 cm\(^{-1}\) and 1000 cm\(^{-1}\) attributed to the stretching of the C-O and the vibration of the C-H cellulose group, change in all alkali-treated fibers, which is produced by the exposition of cellulose to alkali treatments (Rocha et al., 2015). From these results, can be concluded that treating guadua fibers with alkali solutions reduces the hemicellulose and lignin content, and also exposes the cellulose. These results explain the observed water absorption behavior: the removal of hemicellulose
and lignin by alkali treatments, reduces the hydrophilic features of treated fibers. High concentrations of alkali solutions, produce higher removal of hemicellulose and lignin, thus affecting negatively the stress transfer between elementary fibers (Oushabi et al., 2017), and reducing the tensile strength of H5 and H10 fibers as observed from fiber’s tensile tests.

In contrast to alkali treatments, the spectrums for plasma-treated fibers are quite similar (Figure 10-7), which indicates that applied plasma treatments do not significantly change the chemical composition of guadua fibers. Similar results were found by other researches (Pandiyaraj and Selvarajan, 2008; Amirou et al., 2013; Rodríguez et al., 2015). The changes observed in $3395 \text{ cm}^{-1}$ and $1240 \text{ cm}^{-1}$ are associated to the removal of hemicellulose and lignin possibly from the fiber surface, due to the ion bombardment. Also, it can be seen that the prominent peak between $1100 \text{ cm}^{-1}$ and $1000 \text{ cm}^{-1}$ changes with the increment of the exposure time of fibers to ion bombardment. This change could be attributed to the cellulose exposure due to the effect of material removal from the surface caused by etching. The intensity band $900 \text{ cm}^{-1}$ tends to disappear in P1000, P1500 and P2000. This band is attributed to the linkage between the sugar units of hemicelluloses (Fan et al., 2012). This change could be attributed to the removing effect of applied plasma treatments on the fiber surface (Bozaci et al., 2013; Scalici et al., 2016). From these results it can be concluded that applied dry etching plasma treatments do not affect greatly the chemical composition of guadua fibers, which explains the similar behavior observed in the water absorption and mechanical properties of non-treated and plasma-treated fibers.

### 10.1.4 Morphological analysis

Figure 10-8 shows the surface morphology of alkali-treated fibers. As pointed out in Chapter 3, from the micrographs it is clear that a guadua fiber is formed by a large number of elementary fibers (Phong et al., 2012; Wang et al., 2015). The irregularities shown on the surface of non-treated fibers are attributed to the hemicellulose, lignin, waxes and oils (Figure 10-8.a) (Luna et al., 2016a; Espitia-Nery et al., 2018). In general, the fiber surface of treated fibers become clean and with less irregularities after alkali treatments (Figures 10-8.b, c, d and e). This cleaning effect is attributed to the removing of hemicellulose and lignin from treated fibers, as evidenced by the FTIR analysis. The pits observed in Figures 10-8.c and d correspond to parenchyma cells (Habibi and Lu, 2014; Chou et al., 2015; Zhu et al., 2016). From Figures 10-8.d and e, it can be seen that fibers treated using 5% and 10% NaOH solution concentration, got divided into some elementary fibers. As explained in Chapter 1, the hemicellulose and
lignin hold together the cellulose elementary fibers; removing these sticky constituents reduces the stress transfer capacity between elementary fibers. As pointed out in previous sections, less amounts of hemicellulose and lignin negatively affect the tensile strength of H5 and H10 guadua fibers as observed from fiber’s tensile tests.

Figures 10-9, 10-10, 10-11 and 10-12 show the surface morphology of plasma-treated fibers during 400, 1000, 1500 and 2000 s, respectively. As can be seen from all figures, plasma-treated fibers exhibit a rough and coarser surface, even with the formation of some cracks. Also, some of the irregularities observed on the surface on non-treated fibers (Figure 10-8.a) disappear from plasma-treated fibers. These behaviors are attributed to the removing effect caused by ion bombardment on the fiber’s surface. Similar results were found in other research works (Amirou et al., 2013; Bozaci et al., 2013; Luna et al., 2016a, 2017b; Potluri et al., 2018).

In P400 fibers (Figure 10-9) it is evident the formation of cracks, which are deeper and more continuous in P1000 fibers (Figure 10-10). In P1500 fibers (Figure 10-11), cracks are still evident but apparently less deep than in P1000 fibers. As for P2000 fibers (Figure 10-12), it can be seen that cracks tend to disappear, and some parts of the surface tends to become smooth again. According to Bogaerts et al. (2002), the sputter-etching mechanism begins with the removal of atoms from the material surface, thus giving rise to small isolated microcracks, which increase with the increment of ion bombardment time, forming “island” of cracks which grow as the treatment time increases as well. For long treatment times, those crack island “coalesce” or merge together and the surface tends to become continuous.

10.2 Results on the characterization of the P/BG composite material

This section are shows the obtained results from the experimental characterization of the P/BG composite material, which is made using guadua fibers, embedded into a polyester resin. The obtained results were identified as follows: CH1, CH2.5, CH5 and CH10 correspond to the results of the composites fabricated using alkali-treated fibers for each solution concentration, respectively. In the same way, CP400, CP1000, CP1500 and CP2000 correspond to the results of the composites fabricated using plasma-treated fibers for each exposure time, respectively. The obtained results for composite samples fabricated using non-treated fibers were identified as CNT.
**Figure 10-8:** Surface morphology of alkali-treated guadua fibers: a) non-treated; b) H1; c) H2.5; d) H5 and d) H10

### 10.2.1 Mechanical characterization

#### 10.2.1.1 Tensile and bending tests

Tables 10-5 and 10-6 present the results obtained on the tensile and bending characterization of the P/BG composite, respectively. These tables include maximum and
Figure 10-9: Surface morphology of plasma-treated guadua fibers during 400 s: a) general view at 50\(\mu m\); b) details at 5\(\mu m\) in different sites of the fiber surface

minimum values, and the coefficient of variation (C.V) calculated for each mechanical property. Also, these results are graphically shown in Figures 10-13 and 10-14, which include the standard deviation calculated for each sample group as error bars.

From Tables 10-5 and 10-6, and Figures 10-13 and 10-14 it is clear that both compatibilization treatments applied to fibers (alkali and plasma treatments) increase, in all cases, the tensile and bending strengths and modulus of elasticity of polyester/guadua composite. The increment of these mechanical properties could be mainly attributed to the improvement of the adherence between polyester and treated-guadua fibers.

In general, when comparing tensile \((\sigma_{t,c})\) and bending \((\sigma_{b,c})\) strengths (Tables 10-5 and 10-6, and Figures 10-13.a and 10-14.a), it can be seen that the bending strength
Figure 10-10: Surface morphology of plasma-treated guadua fibers during 1000 s:

a) general view at 50µm; b) details at 5µm in different sites of the fiber surface

is slightly higher than the tensile strength. Conversely, the modulus of elasticity from tension \( (E_{t,c}) \) is higher than that from bending \( (E_{b,c}) \). Both tensile and bending tests apply tensile stresses to the sample to induce its failure. However, the nature of the stress state from tension and bending is not the same. Regarding tensile testing, away from the load application point, it is assumed that stresses are applied throughout the entire volume. In respect to bending testing, the tension stresses are concentrated on a small region below the neutral axis, and the maximum tension is exerted on the extreme bottom surface. Accordingly, for similar-size test specimens, the tensile sample will experience the maximum tension stress throughout its entire gauge length, i.e over a much larger volume than the corresponding bending sample. Thus, upon knowing
that the material bears defects that act as local stress concentrators, there is a higher probability to find a larger number of defects in tensile samples than in bend samples. In contrast, the differences regarding modulus of elasticity could be associated to the contribution of fibers to the material stiffness. Since during tensile testing the entire volume is under tensile stresses, there is a higher probability to find fibers aligned to the applied load, thus making the composite material more prone to withstand the tension. In bending testing, the probability to find fibers aligned to tensile stresses is lower, so it is expected that the contribution of fibers to the composite’s stiffness be reduced. A similar behavior between tensile and bending strength was found by Mohanty et al.
Figure 10-12: Surface morphology of plasma-treated guadua fibers during 2000 s:
a) general view at 50µm; b) detail at 10µm; c) detail at 5µm in
different sites of the fiber surface

(2013) and Venkatesh Prasanna et al. (2016) in their mechanical characterization of
natural fiber-reinforced materials.

For tensile characterization, regarding alkali treatments, the maximum tensile strength
and modulus of elasticity values were obtained for composites reinforced with fibers
treated using 2.5% NaOH solution concentration (CH2.5), thus showing an increment
of around 80% and 35% in the strength and modulus (of elasticity), respectively. Ac-
cording to Chunhong et al. (2016), using NaOH to treat bamboo fibers increased the
length-to-diameter ratio by removing impurities (hemicellulose, lignin, waxes and oils)
from the fibers’ surface, which led to an increment of the composite’s tensile properties.
However, as explained before, we consider that the increment in the P/BG compos-
Table 10-5: Results on the tensile characterization of the P/BG composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{t,c}$ (MPa)</th>
<th>$\sigma_{t,c}^{\text{max}}$ (MPa)</th>
<th>$\sigma_{t,c}^{\text{min}}$ (MPa)</th>
<th>C.V (%)</th>
<th>$E_{t,c}$ (GPa)</th>
<th>$E_{t,c}^{\text{max}}$ (GPa)</th>
<th>$E_{t,c}^{\text{min}}$ (GPa)</th>
<th>C.V (%)</th>
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<tbody>
<tr>
<td>CNT</td>
<td>44.94</td>
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<td>30.58</td>
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<td>23.59</td>
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<td></td>
</tr>
<tr>
<td>CH1</td>
<td>58.66</td>
<td>115.54</td>
<td>25.80</td>
<td>39.85</td>
<td>28.75</td>
<td>34.57</td>
<td>25.00</td>
<td>17.77</td>
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<td>CH2.5</td>
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<td>62.28</td>
<td>17.53</td>
<td>32.04</td>
<td>36.95</td>
<td>28.58</td>
<td>13.65</td>
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<tr>
<td>CH5</td>
<td>77.64</td>
<td>115.21</td>
<td>48.97</td>
<td>29.37</td>
<td>29.09</td>
<td>36.00</td>
<td>22.64</td>
<td>23.00</td>
</tr>
<tr>
<td>CH10</td>
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<td>42.99</td>
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<td>31.75</td>
<td>23.43</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP400</td>
<td>77.38</td>
<td>93.69</td>
<td>56.76</td>
<td>19.82</td>
<td>51.60</td>
<td>58.33</td>
<td>43.33</td>
<td>14.63</td>
</tr>
<tr>
<td>CP1000</td>
<td>90.28</td>
<td>106.60</td>
<td>69.92</td>
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<td>52.02</td>
<td>58.55</td>
<td>46.82</td>
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<tr>
<td>CP1500</td>
<td>83.92</td>
<td>103.58</td>
<td>63.52</td>
<td>16.51</td>
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<td>53.46</td>
<td>39.97</td>
<td>14.72</td>
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<tr>
<td>CP2000</td>
<td>70.28</td>
<td>86.28</td>
<td>55.15</td>
<td>17.15</td>
<td>43.57</td>
<td>48.09</td>
<td>35.83</td>
<td>15.44</td>
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C.V: Coefficient of Variation (%)

Table 10-6: Results on the bending characterization of the P/BG composite

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<tr>
<th>Sample</th>
<th>$\sigma_{b,c}$ (MPa)</th>
<th>$\sigma_{b,c}^{\text{max}}$ (MPa)</th>
<th>$\sigma_{b,c}^{\text{min}}$ (MPa)</th>
<th>C.V (%)</th>
<th>$E_{b,c}$ (GPa)</th>
<th>$E_{b,c}^{\text{max}}$ (GPa)</th>
<th>$E_{b,c}^{\text{min}}$ (GPa)</th>
<th>C.V (%)</th>
</tr>
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<tbody>
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<td>CNT</td>
<td>46.48</td>
<td>60.01</td>
<td>33.30</td>
<td>17.68</td>
<td>9.23</td>
<td>12.21</td>
<td>6.49</td>
<td>21.74</td>
</tr>
<tr>
<td>Alkali-treated</td>
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<td></td>
</tr>
<tr>
<td>CH1</td>
<td>61.24</td>
<td>82.53</td>
<td>49.20</td>
<td>18.93</td>
<td>28.28</td>
<td>40.30</td>
<td>21.63</td>
<td>21.20</td>
</tr>
<tr>
<td>CH2.5</td>
<td>87.38</td>
<td>104.44</td>
<td>60.11</td>
<td>18.60</td>
<td>25.52</td>
<td>33.34</td>
<td>15.64</td>
<td>22.09</td>
</tr>
<tr>
<td>CH5</td>
<td>65.36</td>
<td>84.81</td>
<td>57.15</td>
<td>14.28</td>
<td>23.11</td>
<td>27.53</td>
<td>20.00</td>
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</tr>
<tr>
<td>CH10</td>
<td>53.54</td>
<td>77.35</td>
<td>26.55</td>
<td>29.64</td>
<td>16.95</td>
<td>21.00</td>
<td>11.29</td>
<td>18.67</td>
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<tr>
<td>Plasma-treated</td>
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</tr>
<tr>
<td>CP400</td>
<td>80.91</td>
<td>103.62</td>
<td>58.67</td>
<td>23.98</td>
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<td>70.87</td>
<td>27.60</td>
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<td>CP1000</td>
<td>96.61</td>
<td>143.70</td>
<td>79.52</td>
<td>24.30</td>
<td>54.11</td>
<td>74.42</td>
<td>39.14</td>
<td>21.72</td>
</tr>
<tr>
<td>CP1500</td>
<td>86.24</td>
<td>118.29</td>
<td>60.06</td>
<td>24.10</td>
<td>62.89</td>
<td>76.93</td>
<td>51.60</td>
<td>14.49</td>
</tr>
<tr>
<td>CP2000</td>
<td>73.61</td>
<td>94.08</td>
<td>52.41</td>
<td>22.65</td>
<td>40.77</td>
<td>52.33</td>
<td>28.96</td>
<td>19.53</td>
</tr>
</tbody>
</table>

C.V: Coefficient of Variation (%)

ite’s mechanical properties is mainly attributed to the improvement of the bonding between composite phases. When the alkali solution exceeds 2.5%, guadua fibers get damaged and divided into some elementary fibers (as was shown in Figures 10-8.d and .e), thus leading to a decrease in their tensile strength (as shown in Figure 10-2), and in turn resulting in a lower tensile-strength composite. Regarding dry etching plasma
Figure 10-13: Results on the tensile characterization of the P/BG composite: a) tensile strength, b) modulus of elasticity in tension

treatments, the maximum tensile properties were obtained for composites reinforced with fibers treated during 1000 s (CP1000). In this case, the increment was close to twice the composite’s strength and modulus. These results are in accordance with the morphological analysis of plasma-treated fibers (Figure 10-10): the composite P1000 reinforced with the roughest fibers, presents the highest tensile properties. This behavior is attributed to the increment of the mechanical interlocking between polyester
**Figure 10-14:** Results on the bending characterization of the P/BG composite: a) bending strength, b) modulus of elasticity in bending

Resin and guadua fibers, as a result of the increment of the superficial roughness of treated fibers, produced by ion bombardment. Similar results were found by de Farias et al. (2017), who uses oxygen and air plasma to etch the surface of coir fibers that were used to reinforce thermoplastic starch matrices. The reduction of the tensile properties of CP1500 and CP2000 samples could be explained by the “coalesce” effect observed in the morphological analysis for these fibers (Figures 10-11 and 10-12) in which the fiber’s surface tends to become continuous and smooth. Obtained results suggest that
treating guadua fibers during 1000 s using dry etching plasma improves in a higher proportion the bonding between composite phases than treating guadua fibers with 2.5% NaOH solution concentration.

When comparing the values shown in Figures 10-2 and 10-13, it can be noticed that the P/BG composite’s tensile strength is more than 50% lower than the guadua fibers’ tensile strength. As explained in Chapter 9, the composite material’s reinforcement was randomly distributed, thus reducing the fibers’ effectiveness to withstand loads. On the other hand, when comparing the modulus of elasticity of treated fibers with the composites’ modulus (Figures 10-13 and 10-3), it can be seen that the composites’ modulus is close to twice higher. This behavior could be explained by the contribution of polyester resin to the composite’s stiffness. The higher increment in the composite’s modulus using plasma-treated fibers compared to using alkali-treated fibers, could be also a consequence of a better improvement of the bonding between polyester and guadua fibers. Also, it can be seen that the composites’ standard deviation is lower than the one obtained for fibers. Since the reinforcement percentage is low, the variation in mechanical properties is controlled by the polyester resin, which is produced in an industrialized process that could ensure more standardized properties.

In order to compare the influence of the applied treatments on the tensile strength of guadua fibers and P/BG composites, the obtained average strengths for fibers and composite samples during each treatment condition were normalized. Figure 10-15 shows the normalized strengths. As can be seen in Figure 10-15.a, alkali treatments decrease the fibers’ strength around 50%, for a 10% solution concentration (H10 samples). However, alkali treatments increase the tensile strength of the P/BG composite, associated to the improvement of the bonding between composite phases, as explained before. On the other hand, as can be seen in Figure 10-15.b, plasma treatments do not alter significantly the fibers’ strengths. Thus, these treatments increment the P/BG composite’s tensile strength twice its value (for 1000 s of treatment time). In this case the increment in the composite’s tensile strength is attributed to the increment in the mechanical interlocking between composite phases.

Figure 10-16 shows a comparison on the average tensile behavior among treated guadua fibers, polyester resin, and P/BG composite. In the case of P/BG composite, the showed average tensile behavior corresponds to that obtained from alkali and plasma treatments, with the highest tensile strength, i.e samples CH2.5 and CP1000. Accordingly, the showed average behavior of the treated fibers correspond to the same treatments. It can be seen that there is a coherence among the obtained average behaviors: the highest composite’s tensile properties (i.e tensile strength and modulus of
Figure 10-15: Normalized tensile strength for treated guadua fibers and the P/BG composite: a) alkali-treated; b) plasma-treated

Upon analyzing the effect from treatments on the bending behavior of P/BG composites (Figure 10-14), it is clear to observe that plasma treatments increase in higher proportions the composite’s bending properties, which is more notorious in the mod-
Figure 10-16: Average tensile behavior of treated guadua fibers, polyester resin, and the P/BG composite

ulus of elasticity. As in tensile characterization, this behavior indicates that plasma treatments improve in higher proportions the bonding between composite phases. The highest bending strength for each group, was obtained for the samples CH2.5 in the case of alkali treatments, and CP1000 in the case of plasma, following the same behavior observed for tensile strength. On the other hand, the highest modulus of elasticity from bending was obtained for CH1 and CP1500 according to alkali and plasma treatments, respectively.

In order to identify significant differences among the obtained composite’s mechanical properties, a statistical analysis similar to that explained in Section 10.1.1 was performed. In the case of tensile strength, ANOVA analysis revealed significant differences among some obtained values. The lowest tensile strength was obtained for CNT and CH1 samples, while the highest values were obtained for CP1000 samples. Statistically, the average strengths for CH2.5, CH5, CP400 and CP1500 samples are similar, which also happens for the samples using CH10 and CP2000 fibers. Similarly, from the ANOVA analysis performed for the modulus of elasticity from tension, it can be concluded that the obtained values for CNT and all samples fabricated using alkali-treated fibers have similar tensile stiffness. Also, the modulus for all samples fabricated using plasma-treated fibers are similar but higher than the obtained values for CNT samples. As for the bending strength, the Kruskal-Wallis test shows that the
lowest strength was obtained for CNT, CH1, CH5, CH10 and CP2000, and there are no statistical differences among these values. The highest bending strength was obtained for CP1000 samples. The average bending strength obtained for CH2.5, CP400 and CP1500 is statistically similar and corresponds to an intermediate value. Likewise, in the case of the modulus of elasticity from bending, the Kruskal-Wallis test concluded that this mechanical property can be grouped into four classes, with statistically similar values under each class. The lowest modulus was obtained for CNT and CH10 samples. The next class groups the obtained values for CH1, CH2.5, and CH5 samples. The third class is composed of CP2000 samples. The highest modulus was obtained for CP400, CP1000, and CP1500 samples. Tables 10-7 and 10-8 show the \textit{p-values} obtained from each statistical test for tensile and bending properties, respectively.

\textbf{Table 10-7:} \textit{p-values} obtained from the statistical analysis on the P/BG composite’s tensile properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength</th>
<th>Tensile modulus of elasticity</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>SW</td>
<td>Levene</td>
</tr>
<tr>
<td>CNT</td>
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</tr>
<tr>
<td>CH1</td>
<td>0.2862</td>
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<tr>
<td>CH2.5</td>
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<td>CH5</td>
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<td>CH10</td>
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<td>CP400</td>
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<td>CP1000</td>
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<td>CP1500</td>
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<tr>
<td>CP2000</td>
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</tr>
</tbody>
</table>

SW: Shapiro-Wilk test
Levene: Levene’s test

10.2.1.2 Pull-out tests

The typical \textit{interfacial shear stress vs. displacement} curves for the CNT, CH2.5 and CP1000 pull-out samples are shown in Figure 10-17. As explained in Section 9.3.1.2, the pull-out tests were made on samples fabricated with non-treated and treated fibers, for which the highest tensile strength for each compatibilization treatment applied was
Table 10-8: $p$ – values obtained from the statistical analysis on the P/BG composite’s bending properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bending strength</th>
<th>Bending modulus of elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SW Kruskal-Wallis</td>
<td>SW Levene Kruskal-Wallis</td>
</tr>
<tr>
<td>CNT</td>
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<td>CH1</td>
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<td>CH2.5</td>
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<td>Alkali-treated</td>
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<td>CP400</td>
<td>0.4455</td>
<td>0.3620</td>
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<td>CP1000</td>
<td>0.0245</td>
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<td>CP1500</td>
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<td>CP2000</td>
<td>0.6466</td>
<td>0.4716</td>
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SW: Shapiro-Wilk test
Levene: Levene’s test

obtained. The calculation of the interfacial shear stress was explained in the same section.

Two different types of stress–displacement curves have been observed. The stress vs. displacement curves for CNT and CP1000 samples are typical of a “stable” debond process, which indicates a mainly mechanically (frictionally) bonded interface, as described by Jang-Kyo and Yiu-Wing (1998) and Li et al. (2008). In these cases, the rising portion of the stress-displacement curves there is no apparent “stick-slips”, and there is no appreciable load drop after the complete fiber debonding (points A and B on Figure 10-17). At these points, the fiber pull-out process starts, in which the interfacial stress decreases until the fiber is fully pulled out from the matrix. The complete fiber debonding in the case of non-treated samples occurs rapidly, due to the smooth and mild fiber surface shown in Figure 10-8.a. Also, according to (Valadez-Gonzalez et al., 1999) and Alsaed et al. (2013b), the rapid decrease of the interfacial shear stress after fiber debonding, agrees well with the behavior of a poor interface that results because of the incompatibility between the hydrophilic fiber and the hydrophobic matrix. Due to the increment of the surface roughness of CP1000 fibers, shown in Figure 10-10, in these samples the complete fiber debonding arises at higher stresses and also the pull-out process of treated fibers occurs slowly. In contrast, the interfacial shear stress vs. displacement curves for CH2.5 samples are typical of a “partially stable” debond
Figure 10-17: Typical interfacial shear stress-displacement curves for CNT, HC2.5 and CP1000 pull-out composite samples

process (Jang-Kyo and Yiu-Wing, 1998). In this case, the curve shows an initial linear relationship that ends at point C, where initial debonding at the P/BG interface occurs. At this point, the interfacial shear stress presents a slight decrease as a consequence of the initial fiber debonding. Then, the stress increases again until reaching a maximum at point D, where the complete debonding occurs along the full embedded fiber length. At this point, the stress suddenly drops and the fiber pull-out starts (point E on Figure 10-17). Then, the stress continuously decreases, tending to zero, until the fiber is fully pulled out from the matrix (Hsueh, 1990). This behavior was described by many authors for different chemically-treated (natural) fiber-reinforced composites (Stamboulis et al., 1999; Valadez-Gonzalez et al., 1999; Li et al., 2008; Cai et al., 2016).

Figure 10-18 shows the relationship between the pull-out load and the embedded area. After applying a linear regression to the data collected for each pull-out composite sample (passing through the origin (Cai et al., 2016)), the average IFSS was calculated from the slopes of the plots. The obtained equations are shown in Figure 10-18. The coefficient of determination $R^2$ for CNT, CH2.5 and CP1000 sample groups were 0.66, 0.64, and 0.65, respectively. According to (Ross, 2004), a value of $R^2$ near 1 indicates that the regression model is able to explain most of the variation in the response data,
thus indicating a good fit. Conversely, $R^2$ values near to 0 indicates a poor fit. The $R^2$ for all sample groups are within the same range, but are far from 1.00. This indicates that a lineal model could be not appropriate to describe the relation between pull-out load and embedded area. However, the obtained $R^2$ are considered satisfactory and according to that obtained in similar researches (Valadez-Gonzalez et al., 1999; Cai et al., 2016). Table 10-9 shows the $IFSS$ obtained for each sample group. CP1000 fibers demonstrated higher interfacial shear strength as a function of the bonding area compared to the CNT or CH2.5 fibers. This reflects that the mechanical bonding between guadua fibers and the polyester matrix as a result of the increment of the fiber surface roughness is stronger than the chemical bonding due to the alkali treatment.

**Figure 10-18:** Interfacial shear strength ($IFSS$) of CNT, CH2.5 and CP1000 pull-out composite samples

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### 10.2.2 Morphological analysis

Figures 10-19, 10-20, 10-21, 10-22, and 10-23 show the fracture surface of P/BG composite tensile samples. In order to enlarge the images of the samples fabricated using alkali or plasma-treated fibers, the figures were divided in two parts, to show the details clearly.
Table 10-9: Interfacial shear strength (IFSS) of CNT, CH2.5 and CP1000 pull-out composite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>IFSS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>12.60</td>
</tr>
<tr>
<td>CH2.5</td>
<td>25.15</td>
</tr>
<tr>
<td>CP1000</td>
<td>34.46</td>
</tr>
</tbody>
</table>

The “river line” patterns that appear on the fracture surface of the matrix are quite characteristic of the brittle polymer failure (Meyers and Chawla, 2009; Wood et al., 2009). Voids are only observed on CH1 and CP1000 composite samples, which indicates that the composite manufacturing process was adequate.

Figure 10-19: SEM images of the fracture surface of tensile composite samples using non-treated fibers (CNT samples)

On the fracture surface of composites fabricated using non-treated fibers, shown in Figure 10-19, it is clear that there is a fiber-matrix debonding, and in some cases, the fibers were pulled out of the matrix. Also, the non-treated fiber surface clearly shows the irregularities attributed to the presence of lignin, hemicellulose and waxes, which confer the hydrophilic behavior. These observations are in concordance with
**Figure 10-20:** SEM images of the fracture surface of tensile composite samples using alkali-treated fibers - part 1: a) and b) CH1; c) and d) CH2.5

The behavior observed from pull-out tests for these samples: there is a mechanically bonded weak interface, due to the incompatibility between polyester and guadua fibers.

Figures 10-20 and 10-21 show the fracture surface of tensile composite samples fabricated using alkali-treated fibers. For these samples the micrographs were taken using magnifications of 500µm and 100µm. As for composites using non-treated fibers, in the case of CH1 composites (Figure 10-20.a and b), it is observed a fiber-matrix debonding with some fibers pulled out of the matrix, consistent with a weak interface. Conversely, for the CH2.5 composite (Figure 10-20.c and d) it is observed a better adhered interface, in which broken fibers can be noticed, indicating the high interfacial
adhesion of the fiber to the matrix at this treatment condition. However, it is also observed a partial debonding at a little portion of one fiber-matrix interface. Although there is evidence of fibers that were pulled out of the matrix, this mechanism occurs for fibers with lower diameter, which suggest that in these cases the embedded area is low. As shown in Figure 10-18, the pull-out load is directly proportional to the embedded area; thus, in tensile tests, the pull-out load could be reached for some fibers, and since the interface was not sufficiently strong by the low embedded area, the pulled out mechanism could occur. The micrographs taken for CH5 and CH10 composite samples (Figures 10-21) indicate a very strong bonding between guadua fiber and the

Figure 10-21: SEM images of the fracture surface of tensile composite samples using alkali-treated fibers - part 2: a) and b) CH5; c) and d) H10
polyester matrix. Even in the micrograph of the CH5 sample at 500µm (Figure 10-21.a), it can be observed a broken fiber, and for the same fiber but in the micrograph at 100µm (Figure 10-21.b) it is possible to observe that part of the polyester matrix was adhered to the fiber surface during the pull out. However, it is clear that these fibers were divided into some elementary fibers due to the high alkali solution used for their treatment, thus reducing their capacity to stress transfer between elementary

**Figure 10-22:** SEM images of the fracture surface of tensile composite samples using plasma-treated fibers - part 1: a) and b) CP400; c) and d) CP1000
fibers, causing weakening. The fiber weakening brings as a consequence the low values obtained from composite mechanical characterization.

Figures 10-22 and 10-23 show the fracture surface of tensile composite samples, fabricated using plasma-treated fibers. Recalling CP1000 pull-out tests, the interface is mechanically bonded for these treatments. This behavior can be extrapolated to the other composite samples fabricated using plasma-treated fibers, due to the effect observed in the SEM images of plasma-treated fibers (Figures 10-9, 10-10, 10-11 and

**Figure 10-23:** SEM images of the fracture surface of tensile composite samples using plasma-treated fibers - part 2: a) and b) CP1500; c) and d) CP2000
In general, all samples present a well-adhered interface, with some partial debonding observed. The fibers’ surface on the fracture planes of CP400, CP1500 and CP2000 composite samples (Figure 10-22.a and b, and Figure 10-23) is free from polymer, which suggests that during the pull-out process of the fiber no polyester is torn in the process. Conversely, for the P1000 (Figure 10-22.c and d), it is evident that during the pull-out process, part of the polyester matrix is torn, suggesting a very strong link between fiber and matrix. These observations are in concordance with the observed surface roughness of plasma-treated fibers: P1000 surface is rougher than P400, P1500 and P2000 fibers’ surface.

These observations are in high agree with the results obtained from the mechanical characterization of fibers and the P/BG composite, and thus confirm some of the assumptions made in the previous sections. Treating guadua fibers with alkali solutions or plasma, increases the adherence between composite’s phases. In the case of alkali treatments, the highest mechanical properties of the P/BG composite were observed for CH2.5 samples, thus indicating a well-adhered interface, with a strong fiber. In the case of plasma treatments, the highest surface roughness of P1000 fibers greatly increases the mechanical grip between composite’s phases, thus increasing the mechanical strength of the P/BG composite.
Chapter 11

Proposed analytical model

In order to theoretically calculate the tensile strength of the P/BG composite material fabricated in this research, an analytical model is proposed based on the Bowyer and Bader model described in Section 8.2.3. This model was chosen because, in its simple way, it takes into account different fiber orientations in respect to the applied load and includes the fiber length.

As described in Section 8.2.3, the Bowyer and Bader model (Bowyer and Bader, 1972) introduces two parameters, $K_1$ and $K_2$, to the first factor of ROM in order to take into account the fiber orientation ($K_1$) and its length ($K_2$), as shown in Equation 11.1. According to the authors, $K_1$ may be lain between 1 and 0.167; the upper limit corresponds to load-aligned fibers and the lower one to the random distribution. On the other hand, $K_2$ can take two values depending on the fiber’s length, as shown in Equation 11.2, where $L$ is the fiber length and $l_c$, the critical fiber length, which is the length that ensures that the ultimate fiber strength can be achieved independent of the stress applied to the composite (see Equation 11.3).

$$\sigma_{c,t} = K_1 K_2 \sigma_{f,t} V_f + \sigma_{m,t}(1 - V_f) \quad (11.1)$$

$$K_2 = \begin{cases} 
\frac{L-l_c}{2L}, & \text{for } L > l_c \\
\frac{L}{2L}, & \text{for } L < l_c 
\end{cases} \quad (11.2)$$

$$l_c = \frac{\sigma_{f,t} d}{2\tau_g} \quad (11.3)$$
11.1 Proposed equations for the calculation of guadua fiber’s tensile strength

From the obtained results shown in the previous chapter (Chapter 10), it is clear that the treatments applied to guadua fibers affect its tensile strength. Due to this fact, equations were initially proposed to calculate the tensile strength of guadua fibers treated using alkali solutions or dry etching plasma, within the range of solution concentration or exposure time, respectively, used in this research. These equations were proposed through a curve fitting on the average strength values obtained from each treatment (see Table 10-1). Proposed equations correspond to the model type through which the highest $R^2$ was obtained. This fitting was made using the curve fitting app of MATLAB R2013a.

Thus, Equation 11.4 was proposed to calculate the strength of guadua fibers treated using alkali solutions, in which $c$ corresponds to the solution concentration (in percentage) used in each treatment. In this case, the fitting for the strength of alkali-treated fibers was obtained by interpolation with a first order polynomial, which was obtained using the linear least square method. Figure 11-1 shows with dots the average strength experimentally obtained for alkali-treated fibers, and with continuous line the fitted (proposed) function. As can be seen in Figure 11-1, the $R^2 = 0.9980$ indicates an adequate fitting of the selected model.

$$\sigma_{t,f}(c) = -14.94c + 348.30 \quad (11.4)$$

The average tensile strength of plasma-treated fibers was fitted to the model described by Equation 11.5, where $a$ is a constant, and $k(t) = bt^c$ is the plasma strength reduction function. The $k(t)$ function reduces the plasma-treated fiber strength as a function of treatment time $t$ (in seconds). Thus, $a = 2.88 \times 10^{-3}$, $b = 1.36 \times 10^{-15}$ and $c = 3.55$. In this case, the fitting was obtained using the nonlinear least square method. The fitted model proposed for the calculation of the tensile strength of plasma-treated fibers is shown in Figure 11-2, where the continuous line corresponds to the proposed equation. This figure also includes with points the experimentally obtained average strength for plasma-treated fibers. As can be seen in Figure 11-2, the $R^2 = 0.9948$ indicates an adequate fitting of the selected model.

$$\sigma_{t,f}(t) = \frac{1}{a + k(t)} \quad (11.5)$$
Figure 11-1: Fitted model for the strength of alkali-treated guadua fibers

![Figure 11-1](image)

Figure 11-2: Fitted model for the strength of plasma-treated guadua fibers

![Figure 11-2](image)

Table 11-1 shows the fibers’ strength calculated using each proposed model. The table includes the average strengths experimentally obtained for each treatment condition. Also, the sample groups were identified as explained in Section 10.1: H1, H2.5, H5 and H10 correspond to the results of alkali-treated fibers for each solution concentration, respectively. In the same way, P400, P1000, P1500 and P2000 correspond to the results of plasma-treated fibers for each exposure time, respectively. The results for non-treated guadua fibers were identified as non-treated.
The calculated strengths are graphically shown in Figure 11-3, where a continuous line at 45° was added as a reference to clearly see how distant the experimental and calculated strengths are. As can be seen, it is clear that fitted equations are in good agreement with the experimental results, which was expected to the high coefficient of determination $R^2$ obtained in the fitting process.

Table 11-1: Tensile strength of treated guadua fibers calculated using the proposed models

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Fiber strength, $\sigma_{t,f}(MPa)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
</tr>
<tr>
<td>Non-treated</td>
<td>348.30</td>
</tr>
<tr>
<td>Alkali-treated</td>
<td>H1</td>
</tr>
<tr>
<td></td>
<td>H2.5</td>
</tr>
<tr>
<td></td>
<td>H5</td>
</tr>
<tr>
<td></td>
<td>H10</td>
</tr>
<tr>
<td>Plasma-treated</td>
<td>P400</td>
</tr>
<tr>
<td></td>
<td>P1000</td>
</tr>
<tr>
<td></td>
<td>P1500</td>
</tr>
<tr>
<td></td>
<td>P2000</td>
</tr>
</tbody>
</table>

Figure 11-3: Experimental and calculated tensile strength of treated guadua fibers
11.2 P/BG composite’s tensile strength using the Bowyer and Bader’s model

The composite’s tensile strength was theoretically calculated by the Bowyer and Bader’s model shown in Equation 11.1, using the fiber volume fraction $V_f$ actually employed for the fabrication of composites samples, i.e $V_f = 5.3\%$ (see Section 9.3.1.1).

To take into account the random distribution of the fibers used in this research, the coefficient $K_1 = 0.167$ (Bowyer and Bader, 1972).

For the calculation of the coefficient $K_2$, it was previously calculated the critical fiber’s length, $l_c$, by using Equation 11.3. In this case, $\sigma_{f,t}$ was calculated using Equations 11.4 or 11.5, as appropriate. The fiber’s diameter was calculated assuming a circular cross-section and based on the fiber average area (Average area = 0.082 mm$^2$, thus $d = 0.32$ mm). The interfacial shear strength at composite interfaces, $\tau_y$, was assumed as the shear strength of the polyester resin, which was calculated as the half of its tensile strength ($\sigma_{t,p} = 23.01$ MPa, thus $\tau_y = 11.51$ MPa). Since the pull-out tests were only performed for the H2.5, P1000 and non-treated composite samples, in these cases the experimentally obtained interfacial shear strength was used, i.e for these composites $\tau_y = IFSS$. Once $l_c$ was calculated, $K_2$ was also calculated for each composite using Equation 11.2, where $L$ corresponds to the fiber length. In this research, the fiber length was assumed as the average fiber length shown in Section 3.2.1 (Average fiber length = 91.64 mm).

Table 11-2 shows the calculated values for the critical fiber length, $l_c$, and the coefficient $K_2$ for each composite. This table also includes the corresponding interfacial shear strength, $\tau_y$. In this table each composite sample group was identified as explained in Section 10.2: CH1, CH2.5, CH5 and CH10 correspond to composites fabricated using alkali-treated fibers for each solution concentration, respectively. In the same way, CP400, CP1000, CP1500 and CP2000 correspond to composites fabricated using plasma-treated fibers for each exposure time, respectively. Finally, the CNT sample group corresponds to composite samples fabricated using non-treated fibers.

It can be seen that when assuming the interfacial shear strength as the half of the matrix’s tensile strength, a weak adherence between composite phases is also assumed, because the value for the non-treated composite and the assumed one are similar. Also, the increment in the interfacial shear strength reduces drastically the critical fiber length. As explained before, $l_c$ is the minimum fiber length that ensures that the ultimate fiber strength can be achieved regardless of the applied stress to the composite; this value is expected to be reduced by an increment in the adherence at composite
phases. In all cases the fiber length \( L = 91.64 \text{ mm} \), is higher than \( l_c \). Although \( l_c \) is different for each composite, the calculated \( K_2 \) values are similar. This suggests that the proposed Bowyer and Bader model assumes that composite phases are perfectly bonded.

**Table 11-2:** Critical fiber length, coefficient \( K_2 \) and interfacial shear strength used in the Bowyer and Bader model

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interfacial shear strength, ( \tau_y ) (MPa)</th>
<th>Critical length, ( l_c ) (mm)</th>
<th>( K_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>12.60</td>
<td>4.47</td>
<td>0.48</td>
</tr>
<tr>
<td>Alkali-treated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH1</td>
<td>11.51</td>
<td>4.68</td>
<td>0.47</td>
</tr>
<tr>
<td>CH2.5</td>
<td>25.15</td>
<td>2.00</td>
<td>0.49</td>
</tr>
<tr>
<td>CH5</td>
<td>11.51</td>
<td>3.84</td>
<td>0.48</td>
</tr>
<tr>
<td>CH10</td>
<td>11.51</td>
<td>2.79</td>
<td>0.48</td>
</tr>
<tr>
<td>Plasma-treated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP400</td>
<td>11.51</td>
<td>4.89</td>
<td>0.47</td>
</tr>
<tr>
<td>CP1000</td>
<td>34.46</td>
<td>1.60</td>
<td>0.49</td>
</tr>
<tr>
<td>CP1500</td>
<td>11.51</td>
<td>4.50</td>
<td>0.48</td>
</tr>
<tr>
<td>CP2000</td>
<td>11.51</td>
<td>3.87</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 11-3 shows the tensile strength of the P/BG composite calculated using the Bowyer and Bader model. The table includes the average strengths experimentally obtained for each composite sample. These values are graphically shown in Figure 11-4, in which a continuous line at 45° was added as a reference in order to clearly see how distant the experimental and calculated composite’s strengths are. It is clear that the Bowyer and Bader’s model does not provide a good agreement with the experimental results. The experimental results show that composite phases are not perfectly bonded as assumes in the Bowyer and Bader model.

### 11.3 Modified Bowyer and Bader’s model

In this research, a new model is proposed based on the Bowyer and Bader’s equation, where a new coefficient is introduced to take into account the adherence between fibers and matrix. The proposed model follows the form described by Equation 11.6, where \( C \) is an adjustment constant and \( \eta \) is the coefficient that represents the adherence between composite phases. Numerical values of \( C \) and \( \eta \) were calculated from the experimental
Table 11-3: P/BG composite’s tensile strength calculated using the Bowyer and Bader model

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composite tensile strength, $\sigma_{t,c}(MPa)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BB Model</td>
</tr>
<tr>
<td>CNT</td>
<td>23.25</td>
</tr>
<tr>
<td>CH1</td>
<td>23.18</td>
</tr>
<tr>
<td>CH2.5</td>
<td>23.14</td>
</tr>
<tr>
<td>CH5</td>
<td>22.92</td>
</tr>
<tr>
<td>CH10</td>
<td>22.64</td>
</tr>
<tr>
<td>Alkali-treated</td>
<td></td>
</tr>
<tr>
<td>CP400</td>
<td>23.22</td>
</tr>
<tr>
<td>CP1000</td>
<td>23.28</td>
</tr>
<tr>
<td>CP1500</td>
<td>23.12</td>
</tr>
<tr>
<td>CP2000</td>
<td>22.95</td>
</tr>
</tbody>
</table>

BB model: Bowyer and Bader model

Figure 11-4: P/BG composite experimental and calculated (using the Bowyer and Bader model) tensile strength

results obtained for fibers, the polyester matrix and P/BG composite samples. In the case of $\eta$, the calculation was made by the normalization of the measured tensile strength of composite samples. The numerical $C$ value was calculated by interpolation,
using a nonlinear regression of 4 independent variables and 1 dependent variable, using the CurveExpert Basic software. The independent variables were the fibers’ strength ($\sigma_{t,f}$), the polyester matrix tensile strength ($\sigma_{t,p}$), the fiber’s volume fraction ($V_f$) and the adherence coefficient ($\eta$). The dependent variable was the P/BG composite tensile strength ($\sigma_{t,c}$).

$$\sigma_{c,t} = C\eta(K_1K_2\sigma_{f,t}V_f + \sigma_{m,t}(1-V_f))$$ (11.6)

Equation 11.7 shows the model proposed in this research. In the calculation of the adjustment constant $C = 4.34$, the coefficient of determination was $R^2 = 0.9949$, which indicates an adequate variable fit. The adherence coefficient $\eta$ can take the values shown in Equation 11.8, depending on the adherence between fibers and matrix.

$$\sigma_{c,t} = 4.34\eta(K_1K_2\sigma_{f,t}V_f + \sigma_{m,t}(1-V_f))$$ (11.7)

$$\eta = \begin{cases} 
0.45 & \text{for poor adherence} \\
0.70 & \text{for intermediate adherence} \\
0.85 & \text{for strong adherence}
\end{cases}$$ (11.8)

By using Equation 11.7 the tensile strength of composite samples was calculated with the appropriate $\eta$ (Equation 11.8). Obtained results are shown in Table 11-4, which includes the experimental average measurement and the values calculated using the Bowyer and Bader’s model (the same shown in Table 11-3). It is to clarify, that the same table includes the $\eta$ assumed for each composite sample. For these calculations, it was used the fibers’ tensile strength calculated with the proposed equations (Equation 11.4 or 11.5 as appropriate), $K_1 = 0.167$ for a random fiber distribution, $K_2$ corresponds to the values shown in Table 11-2 and $V_f = 5.3\%$. These results are graphically shown in Figure 11-5, in which a continuous line at 45° was added as a reference to clearly observe how distant the composite’s experimental and calculated strengths are.

It can be seen that the obtained composite’s tensile strengths obtained by using the proposed model are in good agreement with the experimental results. In general, the difference between the measured and calculated strength is $\pm 3\%$. For CH1 samples, when using the proposed model, the strength is 20% higher than the experimental measurement, due to its was assumed an intermediate adherence between fibers and the matrix ($\eta = 0.70$). If a poor adherence ($\eta = 0.45$) is considered, a lower strength
Table 11-4: P/BG composite’s tensile strength calculated using the proposed model

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \eta )</th>
<th>Composite tensile strength, ( \sigma_{t,c}(MPa) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BB Model</td>
</tr>
<tr>
<td>CNT</td>
<td>0.45</td>
<td>23.25</td>
</tr>
<tr>
<td>CH1</td>
<td>0.70</td>
<td>23.18</td>
</tr>
<tr>
<td>CH2.5</td>
<td>0.85</td>
<td>23.14</td>
</tr>
<tr>
<td>CH5</td>
<td>0.70</td>
<td>22.92</td>
</tr>
<tr>
<td>CH10</td>
<td>0.70</td>
<td>22.64</td>
</tr>
<tr>
<td>CH1</td>
<td>0.70</td>
<td>23.22</td>
</tr>
<tr>
<td>CP400</td>
<td>0.70</td>
<td>23.28</td>
</tr>
<tr>
<td>CP1000</td>
<td>0.85</td>
<td>23.12</td>
</tr>
<tr>
<td>CP1500</td>
<td>0.85</td>
<td>22.95</td>
</tr>
</tbody>
</table>

BB model: Bowyer and Bader model

Figure 11-5: P/BG composite’s experimental and calculated (using proposed model) tensile strength

occurs, but with approximately the same difference in respect to the experimental value. However, the proposed model can be used to describe the macroscopic behavior under tensile loads of the P/BG composite material.
Chapter 12

Conclusions part 3

The relevant aspects of the third part of the research are presented below:

- Based on the results obtained for alkali-treated guadua fibers, various aspects can be pointed out. Alkali solutions decrease the fiber’s tensile strength, without variation in its modulus of elasticity and strain-to-failure. Also, these treatments affect the water absorption behavior of treated fibers, thus decreasing their moisture content as the solution concentration used for the fiber treatment is increased. The FTIR spectra from alkali-treated fibers explain some of these findings: alkali solutions remove the hemicellulose and lignin of treated fibers, thus diminishing their hydrophilic features. However, removing these components negatively affect the treated fibers’ strength, due to the diminishing of the stress transfer among elementary fibers. Additionally, the morphological analysis of alkali-treated fibers corroborates that these treatments act as a “cleaner”, by removing the hemicellulose, lignin and waxes from treated fibers. Also, fibers treated using 5% and 10% NaOH solution concentration were divided into some elementary fibers.

- The results obtained for dry etching plasma treated fibers indicate that these treatments do not affect the mechanical properties (i.e. tensile strength, modulus of elasticity and strain-to-failure) of treated fibers. Furthermore, the water absorption behavior of fibers does not change after plasma treatments. The FTIR spectra obtained for these fibers confirm that plasma treatments do not significantly change the chemical composition of treated fibers, which explains that results remain unaltered after the dry etching process. The morphological analysis of these fibers pointed out that, as expected, these treatments increase the fiber’s superficial roughness, forming crack “islands” that grow as the treatment
time increases as well. For long treatment times, those crack islands “coalesce” or merge together and the surface tends to become continuous. However, this coalesces effect does not affect the behavior of treated fibers.

- It was proposed a methodology for the fabrication of the P/BG composite material, based on the compression moulding technique. Using this manufacturing methodology, it is possible to obtain composites with a void volume fraction less than 1%, which, according to literature, is considered not to have a negative influence on the mechanical performance of the material.

- From the obtained results on the mechanical properties of P/BG composite samples, it can be concluded that treating guadua fibers with alkali solutions or dry etching plasma, increases the bonding between the fibers and the polyester matrix. Based on the results of alkali-treated fibers, it can be concluded that by using these treatments, the increment on the bonding between the composite’s constituents is made by a chemical compatibilization, due to the diminishing of the hydrophilic features of treated fibers. In contrast, when using plasma treatments, the increment in the adherence is made by the improvement of the mechanical bonding between the treated fibers and the matrix. Typical curves obtained on pull-out tests confirm these asseverations: the “partially stable” debond process observed for CH2.5 samples is typical of chemically bonded interfaces; conversely, the “stable” debond process observed for CP1000 samples mainly indicates a mechanically (frictionally) bonded interface.

- Despite increasing the alkali solution used to treat guadua fibers decreases their mechanical strength, it also improves the P/BG composite’s strength. Furthermore, from the morphological analysis of the fracture surface of tensile-tested composite samples, for higher NaOH solution concentrations stronger interfaces were observed, because the chemical adherence between guadua fibers and the polyester matrix is well-adhered. However, since higher NaOH solution concentrations weaken the treated fibers, a diminishing in the mechanical properties of these composites results as a consequence.

- The highest experimental values of the mechanical strength of composite samples were obtained for P/BG composite samples fabricated using fibers treated with dry etching plasma during 1000 s (CP1000 samples). From this, it can be concluded that the improvement on the mechanical interlocking between composite’s
phases, increases in a higher proportion the bonding properties at the interface, when compared to chemical compatibilization made using alkali treatments.

- These observations are in high agreement with the results obtained from the mechanical characterization of fibers and P/BG composites, and confirm some of the assumptions made in the previous sections. Treating guadua fibers with alkali solutions or plasma, increases the adherence between composite’s phases. In the case of alkali treatments, the higher mechanical properties observed for CH2.5 samples indicate a well-adhered interface, with a strong fiber. In the case of plasma treatments, the highest surface roughness of P1000 fibers greatly increases the mechanical grip between composite’s phases, thus increasing the mechanical strength of the P/BG composite CP1000.

- Equations were proposed to predict the tensile strength of alkali and plasma-treated guadua fibers. These equations were proposed using a curve fitting on the average strength values obtained from each treatment. In the case of alkali-treated fibers, the proposed equation follows the form of a first order polynomial. For plasma-treated fibers, it was used inverse function in which the plasma strength reduction function \( k(t) \) was incorporated to reduce the plasma-treated fiber strength as a function of treatment time \( t \). Using these equations, it is possible to obtain fibers’ tensile strengths in good agreement with experimental measurements.

- In spite of using the actual (measured experimentally) interfacial shear strength on the calculation of the \( K_2 \) coefficient of the Bowyer and Bader’s model, the composite’s tensile strength was not obtained in accordance with the experimental observations. This indicates that the Bowyer and Bader’s model does not take into account the bonding properties at the composite’s interface.

- Based on the Bowyer and Bader’s model, it was proposed an analytical model to predict the tensile strength of P/BG composites. The proposed equation takes into account the bonding properties at the composite’s interface. For this, the \( \eta \) coefficient was incorporated in the Bowyer and Bader’s equation. This coefficient can take three different values, depending on the adherence between the fibers and the matrix (poor, intermediate or strong adherence). Using this analytical model the composite’s tensile strength was obtained in accordance with the experimental observations.
Chapter 13

Final remarks

The main purpose of this thesis was to research the influence of treating natural fibers using chemical or physical methodologies, in order to improve their adherence to polymers. This purpose was fulfilled through the experimental characterization of *Guadua angustifolia* bamboo fibers and the P/BG composite material, constituted by *Guadua angustifolia* bamboo fibers embedded into a polyester matrix. During the progress of the research, all the proposed objectives described in the introduction of this document were achieved, and several findings emerged bringing new and innovative contributions to the natural fiber composites’ science.

This final chapter is divided into three sections. In the initial part of this last chapter, the main thesis contributions are summarized. Most of the key conclusions have been presented at the end of each part of the document. In the second part the principal limitations and constrains of the research are explained and identified in order to clarify the scope of the research. Finally, and taking into account the main contributions and limitations of the research, suggestions are given for possible further studies.

### 13.1 Scientific contribution of the thesis

As explained at the introduction of this document, the principal aim of this research project was to establish the mechanical behavior of the P/BG composite material made using *Guadua angustifolia* bamboo fibers, embedded into a polyester matrix. To this end, three objectives were proposed, being the first one related to the extraction and characterization of *Guadua angustifolia* bamboo fibers. The second one to the evaluation of the effect of treating *Guadua angustifolia* bamboo fibers using alkali or argon plasma, on the properties of fibers and the P/BG composite material. The last
objective was related to the establishment of an analytical model to describe the tensile behavior of the P/BG composite material. Each part of the research, and of this document, was related to one of these goals: the objectives of the thesis were fulfilled with the first and third parts of the research. However, the second part was important to understand some findings obtained in the last part of the thesis.

The key findings and scientific contribution of the thesis are presented below.

1. During the first part of the research, it was proposed an extraction methodology to obtain *Guadua angustifolia* bamboo fibers. The proposed methodology combines a chemical and mechanical procedure. By using this methodology, it is possible to obtain fibers with adequate physical (density and length) and mechanical (tensile behavior) properties for being used as composite reinforcement.

2. In the first part of the research, it was also proposed a methodology for determining the cross-sectional area of *Guadua angustifolia* bamboo fibers, which ensures precise measurements since the fibers’ fracture plane will always be perpendicular to the observer’s plane. This work was published in the *Journal of Natural Fibers* (Luna and Lizarazo-Marriaga, 2017), and is showed in Appendix B. Even though this methodology was designed for the fibers employed in this research, it can be adapted for being used with other natural or synthetic fibers, when it is desired to take measurements at specific planes perpendicular to the longitudinal axis of the fiber.

3. Based on the obtained results on the establishment of the *Guadua angustifolia* bamboo fibers extraction methodology, and on the results of alkali treated fibers, it can be concluded that the sodium hydroxide negatively affects the guadua fibers’ tensile behavior. In both cases, when using higher NaOH concentrations, the decreasing in the fiber’s tensile properties was higher. This behavior is a consequence of the poor stress transfer between the elementary fibers that composed the macrofiber, because of the removing of the hemicellulose and lignin. This assumption was confirmed by the FTIR spectra and the morphological analysis of alkali-treated fibers.

4. On the other hand, the argon plasma treatment (dry etching) employed in this research does not affect the tensile properties of *Guadua angustifolia* bamboo fibers. Even more, the FTIR spectra obtained from plasma-treated fibers revealed that applied treatments do not significantly change the chemical composition of treated fibers, which explains that the mechanical properties remain
unaltered after the dry etching process. Conversely, the morphological analysis showed that these treatments increase the fiber’s superficial roughness. Based on these findings, it can be concluded that plasma treatments do not affect the bulk properties of treated materials.

5. Alkali or argon plasma treatments improve the strength (tensile and bending) of the P/BG composite material. This improvement is attributed to the increment in the adherence between the Guadua angustifolia bamboo fibers and the polyester matrix. In the case of alkali treatments, the increment in the adherence is a consequence of the chemical compatibilization between composite phases, due to the reduction of the hydrophilic features of treated fibers. The reduction of hydrophilic features was confirmed by the measurements of water absorption of alkali-treated fibers. Conversely, by using argon plasma (dry etching) treatments, an improvement is made in the mechanical interlocking between composite phases, due to the increment in the superficial roughness of plasma-treated fibers. Pull-out tests confirm these asseverations: the typical “partially stable” debond process observed for alkali-treated samples is typical for chemically bonded interfaces; on the other hand, the “stable” debond process observed for plasma-treated samples indicates a mainly mechanically (frictionally) bonded interface.

6. By comparing the obtained results for the P/BG composite fabricated using alkali or plasma-treated fibers, it can be concluded that from the treatment conditions employed in this research, the bonding between composite phases produced by a mechanical interlocking, is stronger than the chemical bonding induced by the compatibilization between constituents.

7. Based on the obtained results, it can be concluded that the properties of composite materials depend on the properties of the constituents, but the properties at the interface play a vital role in the mechanical performance of the final material. Also, it is necessary to take into account the geometry and distribution of fibers into the matrix. The analytical model established to describe the macroscopical behavior of the P/BG composite material under tensile loads, involves all these parameters, geometry and distribution of fibers, and the adherence between composite’s phases. The proposed equation is based on the Bowyer and Bader’s model, which in its simple form takes into account the fiber’s geometry and distribution. However, in this research the parameter $\eta$ was included into the Bowyer and Bader’s original equation, in order to quantify the properties at
the composite’s interface. By using this analytical model the composites’ tensile strength was obtained in good agreement with experimental observations.

13.2 Thesis constrains

The work carried out in this research needs to be circumscribed within a context in which its limitations be clearly identified. These limitations make reference to specific features of the materials and of the experimental process, as presented below.

1. *Guadua angustifolia* bamboo fibers used in this research were extracted from the bottom part of culms originating from bamboo plantations at the northwestern region of the department of Cundinamarca - Colombia. This raw material was used due to its availability at the campus of the Universidad Nacional where the research was developed. Since natural materials show a higher variation in their properties than the synthetic ones, it is believed that the origin of the plant could affect the performance of the fibers obtained. Thus, it is important to clarify that the results obtained in the research related to fibers, only represent the population of *Guadua angustifolia* bamboo fibers from the northwestern region of the department of Cundinamarca - Colombia.

2. The experimental work carried out in the research was developed at the laboratory scale, but the methodology used can be reproduced at a large scale. However, in the case of plasma treatments, it is important to clarify that it is necessary to design, manufacture or adapt available equipment, for the modification of the fiber’s superficial roughness at the industrial scale.

3. Although the composites’ void content measurement indicate an acceptable manufacturing process, it is important to clarify that the methodology used for the fabrication of the P/BG composite material could be used at the laboratory scale. For industrial applications, it is necessary to change or modify the manufacturing process, taking into account the technical and design issues for the desired element.

13.3 Future work

Based on the main contributions and constraints of the thesis, the following suggestions were identified in relation to the possible work in the research field addressed in this investigation.
1. It is important to extend the characterization of *Guadua angustifolia* bamboo fibers population. Thus, it is recommended to use the extraction methodology proposed in this thesis, to obtain fibers from culms of bamboo plantations of different climatic conditions (height above sea level, average precipitation level, humidity, and wind velocity), in order to establish the influence of culm growing conditions on the fiber’s performance.

2. Upon considering material manufacturing processes less aggressive with the environment, it is proposed to use methodologies similar to the ones employed in this thesis, in order to fabricate composite materials in which all elements, i.e. fibers and matrix, be from renewable resources. Similarly, it is proposed to extract fibers from other plants or even from agricultural wastes, and develop new researches intended to use them as reinforcement for polymeric matrices.

3. Although the results obtained in terms of the mechanical performance of the P/BG composite material are adequate for use in engineering applications, it is important to evaluate the durability of the material. Thus, it is proposed to make an experimental programme intended to evaluate the durability of the material, taking into account the mechanical performance under permanent load (creep), and also under aggressive environmental conditions like water and UV radiation.

4. Due to the encouraging result obtained for the P/BG composite fabricated using plasma-treated fibers, it is important to work with an interdisciplinary group to design or adapt existing equipment for the implementation at the industrial scale of the dry etching plasma treatment performed in this research. In the same way, it is important to adapt a manufacturing process to produce the composite material at a large scale.

5. The results obtained in this research for the mechanical performance of *Guadua angustifolia* bamboo fibers, the polyester matrix and the fibers-matrix interfacial region, could be the basis to formulate models based on the constitutive relations of the P/BG composite material.
Appendices
Appendix A

Sample size for guadua fiber and polyester/guadua composite tests

According to Montgomery and Runger (2002) and Dally (2008), knowing that the fiber strength data set has a normal distribution, the sample size $n$ can be calculated in function of an expected error, with a particular confidence level of $(100(1 - \alpha))$, by using Equation A.1, where $(Z_{\alpha/2})$ is the area under the curve of a normal distribution for a particular confidence level (tabulated value), $E$ is the expected error and $S$ is the standard deviation of preliminary tests.

$$n = \frac{Z_{\alpha/2}S}{E} \quad (A.1)$$

For guadua fibers, the assumption of normality was verified on the determination of the system compliance of used testing machine (see Section 2.4.1), and assuming an error of 20 MPa in the determination of the fiber tensile strength, with a confidence level of 90% ($\alpha/2 = 0.05$) and a standard deviation $S = 47.54$ MPa (calculated on the determination of the system compliance of used testing machine), the sample size $n_f$ corresponds to:

$$n = \frac{1.645 \times 47.54}{20}n = 15.29 \approx 16 \quad (A.2)$$

The required sample size of P/BG composite was calculated based on the strength results obtained during the calibration of composite manufacturing process, using the S60 data set (see Section 9.2.1). In this case, was assumed an error of 2 MPa in the determination of the composite strength, with a confidence level of 90% ($\alpha/2 = 0.05$) and a standard deviation $S = 3.51$ MPa. Thus, the sample size for the P/BG composite $n_c$ is:
\[ n = \frac{1.645 \times 3.51}{2} n = 7.73 \approx 8 \] (A.3)
Appendix B

Papers published
Guadua angustifolia bamboo fibers as reinforcement of polymeric matrices: An exploratory study

P. Luna a,⇑, J. Lizarazo-Marriaga a, A. Mariño b

a Departamento de Ingeniería Civil y Agrícola, Universidad Nacional, Bogotá, Colombia
b Departamento de Física, Universidad Nacional, Bogotá, Colombia

Highlights

• Effect on surface appearance of bamboo fibers treated using sodium hydroxide baths.
• Effect on tensile strength of bamboo fibers treated using sodium hydroxide baths.
• Effect on surface appearance of bamboo fibers using a dry plasma etching technique.
• Effect on tensile strength of bamboo fibers using a dry plasma etching technique.

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Abstract

Mechanical behavior of composites depends on the individual properties of each component; however, bonding between fibers and matrix plays a predominant role in the material performance. The interfacial region, which is considered as a zone of property gradients, determines the stress transfer between the bonded fibers and the matrix. A well establish interface linkage assures an adequate mechanical behavior of composite materials.

The main disadvantage for using natural fibers as reinforcement of polymeric matrices is the physico-chemical incompatibility between fibers and matrix. Because of the hydrophilic nature of fibers and the hydrophobic character of resins, it is necessary to treat both materials in order to improve the final properties of composites, avoiding premature and delamination failures.

This paper describes an exploratory research intended to use Guadua angustifolia bamboo fibers as reinforcement of polymeric matrices. Two different techniques of compatibilization were employed: first, standard baths of sodium hydroxide as coupling agent were applied to fibers, and second, a novel plasma treatment was implemented for natural fibers. The influence of both compatibilization methods on tensile strength and surface appearance of fibers were evaluated. Results confirm that sodium hydroxide baths decrease the mechanical strength of fibers and clean its surface. In contrast, plasma treatments showed very encouraging results, without changes on mechanical strength and improving the fiber surface.

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1. Introduction

Automotive, aerospace and construction industries have shown special interest in developing new polymeric composites due to its versatility of manufacture, and especially to the high cost of production of traditional materials. Developed countries use around 50% of polymers produced on the manufacture of composite materials [1].

Synthetic fibers such as carbon, aramid, glass and nylon are commonly used as reinforcement in composite polymeric materials. However, in the last two decades natural fibers have become an important resource in composite industry [2–6]. The average annual growth rate of global market for polymeric composites reinforced with natural fibers was 38% from 2003 to 2007 [7]. In the future, it is expected that the application of this kind of materials increases.

The use of natural fibers as reinforcement of polymeric matrices gives multiple benefits such as lower abrasion during production, possibility of recycling, higher mechanical properties per weight unit, and lower manufacturing cost per volume unit [8]. Nevertheless, the potential of natural fibers has not been completely profit in the polymeric composite industry due to its
physicochemical incompatibility with commonly used hydrophobic matrices (polystyrene, polyester, polyethylene, among others). Natural fibers are composed by a high content of cellulose that confers its hydrophilic properties, resulting in a low compatibility between the reinforcement and the matrix, which are the composite phases. Low compatibility may bring poor stress transfer between phases and thus affect the mechanical properties of the final composite material, and in consequence, its use may be limited [2,9–12].

The literature reviewed presents the two commonly used ways to improve the compatibility between polymer matrices and natural fibers: the first is the modification of the physicochemical properties of the matrix, using reactive extrusion processes [13–15]. The second alternative is the modification of the physicochemical properties of natural fibers. This modification can be performed in three different manners: by using coupling agents [2,9,11,16–20]; by a graft polymerization of monomers compatible with the polymer matrix [1]; and subjecting fibers to plasma treatments [21–28].

At industrial level, modification of the physicochemical properties of natural fibers is the most used alternative to increase the compatibility between composite phases. The traditional method to improve the bonding between fiber and matrix employs coupling agents that react with the hydroxyl groups present in the amorphous region of fibers, leaving the cellulose structure exposed in order to bond the polymer matrix. The main disadvantage of using treatments of this type is that they generate a reconfiguration of proportions of the constituents (cellulose, hemicellulose and lignin), reducing the mechanical strength of fibers [29]. However, several studies [2,9,11,16–20], suggest that the mechanical performance of the composite improves when the natural fibers employed have been previously treated with coupling agents.

The modification of surface properties of fiber using plasma is an innovative technique; the aim of this treatment is to increase the mechanical grip on fiber–matrix interface by modifying the surface properties of fibers without major changes in its molecular structure [28]. Some research has been made using natural fibers aiming to evaluate the efficiency of this technique, where different gases have been used, among which the most common were He and Ar. Different exposure times and electrical currents have also been used [21,22,24,23,25,27,26]. In order to establish the effectiveness of the treatment, various polymer matrices have been reinforced using untreated and plasma treated natural fibers [21,22,25,27,26]. The main conclusion of these researches is that the composite tends to be more resistant as a result of the increased bonding between fibers and the polymer matrix. Such resistance was attributed to the increasing surface roughness of the reinforcing material.

This paper presents the results obtained during an exploratory study of some techniques employed to modify the surface properties of Guadua angustifolia bamboo fibers. In order to do this, a common coupling agent such as sodium hydroxide (NaOH) and a novel plasma technique were used. The surface appearance was assessed using a scanning electron microscope, while the influence of each treatment on the mechanical properties was evaluated using tensile tests. These treatments were made in order to, in second stage, develop a polymeric composite material using as reinforcement Guadua angustifolia bamboo fibers, that could be used as non-structural material in buildings.

2. Material and methods

2.1. Fiber extraction

Guadua angustifolia bamboo fibers were extracted from the bottom part of culms, using a compression load similar to that described by [30]. Initially, bamboo raw samples were cut into segments of rectangular cross section with 10 cm of length, which were immersed in a solution containing sodium hydroxide (NaOH) at 10% during 96 h. After immersion, segments were carefully washed using tap water. The rectangular segments were crushed, applying compression loads of about 100 kN. Finally, the fibers were separated using a brush. Using this procedure, fibers with around 10 cm length were obtained.

2.2. Coupling agent treatment

After extraction, fibers were divided into two groups corresponding to the concentration of the solutions (2 and 10%) of NaOH employed in this treatment as coupling agent. The immersion times for both solutions were 10 and 60 min. All the immersions were performed at atmospheric pressure and room temperature.

After this, fibers were carefully washed using tap water and dried at room temperature for two days before the mechanical tests.

2.3. Plasma treatment

In this study, a dry etching plasma treatment (physical sputtering) was carried out. It works at low pressure and high energy. Using this treatment, it is expected that the fiber surface roughness could be increased due to ions bombardment. The treatment was carried out by using a D.C etching system with Ar gas. The fibers were exposed to ion bombardment for 300 s with a current of 50 mA at a working pressure of 50 × 10⁻³ mbar (0.37 Torr). The objective of this treatment is to increase the fiber surface roughness by an ion bombardment from the plasma. Before being treated, fibers were placed on a carbon conductive film in order to ensure the efficiency of the treatment and achieve fixation of the samples during the processing.

2.4. Fiber mechanical testing

In order to study the influence of treatments on mechanical properties of fibers, tensile tests were carried out on specimens without treatment and treated using the coupling agent proposed or plasma technique. Tensile tests were performed following the guidelines established on ASTM C1557-14: Standard Test Method for Tensile Strength and Young’s Modulus of Fibers. The rate of load application was 2 mm/min, in which the failure of fiber was achieved in 30 s, according to the indications of ASTM C1557-14. Before the tests, single bamboo fibers were glued to paper frames as shown in Fig. 1. This setup was implemented in order to avoid deviations of axial load due to incorrect positioning of the specimen in the testing grips. After adjusting the fiber specimen, this frame was carefully cut.

Due to the fact that Guadua angustifolia bamboo fibers have an irregular cross section [31], the average cross section (A) was calculated using Eq. 1, where m and l are the fiber mass and length respectively, and ρ is the apparent density, which according to [32] is 1.44 g/cm³:

\[ A = \frac{m}{\rho l} \]  

(1)

The average tensile strength was calculated using Eq. 2, where Pmax is the maximum load resisted on each mechanical tests, and A is the average cross section.

\[ \sigma = \frac{P_{\text{max}}}{A} \]  

(2)

2.5. Morphological analysis

A scanning electron microscope (SEM) was used to take images of Guadua angustifolia bamboo fibers surface, in order to evaluate the changes in its surface by sodium hydroxide baths or plasma treatment.

Fig. 2 shows the experimental procedure used on this research schematically.
3. Results and discussion

3.1. Fiber mechanical testing

Table 1 presents the results of the average tensile strength for *Guadua angustifolia* bamboo fibers. N values correspond to fibers without treatment; P to fibers with plasma treatment; H210 and H260 to fibers immersed in sodium hydroxide with a concentration of 2% for 10 and 60 min respectively; and H1010 and H1060 to the same treatment with a concentration of 10% for 10 and 60 min respectively.

![Diagram](image)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$\sigma_t$ (MPa)</th>
<th>S.D. (MPa)</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>179.37</td>
<td>78.36</td>
<td>44</td>
</tr>
<tr>
<td>P</td>
<td>173.65</td>
<td>52.87</td>
<td>30</td>
</tr>
<tr>
<td>H210</td>
<td>167.37</td>
<td>65.73</td>
<td>39</td>
</tr>
<tr>
<td>H260</td>
<td>148.30</td>
<td>82.57</td>
<td>56</td>
</tr>
<tr>
<td>H1010</td>
<td>127.08</td>
<td>67.12</td>
<td>53</td>
</tr>
<tr>
<td>H1060</td>
<td>60.01</td>
<td>28.10</td>
<td>47</td>
</tr>
</tbody>
</table>

$\sigma_t$: tensile strength; S.D: standard deviation; C.V.: coefficient of variation.

Results showed that plasma treatment does not reduce the tensile resistance; similar results were found by [27] for jute fibers treated by oxygen plasma. On the other hand, treatments using sodium hydroxide reduce the resistance, and the decrease was more significant when the immersion was done using a higher concentration and during a long time. According to [29], coupling agent treatments can result in a reconfiguration of hemicellulose and lignin constituents, which has a direct effect on fiber strength.

3.2. Morphological analysis

Fig. 3 shows SEM micrographs of the fiber surface for untreated and plasma treated fibers. Before plasma treatment (Fig. 3a), the fiber surface presented some irregularities generated by the presence of non-cellulosic materials (hemicellulose and lignin constituents). After plasma treatment (Fig. 3b), the roughness of fiber surface increases, as a result of the ion bombardment.

It is believed that in immersions using sodium hydroxide it works as a cleaner, removing the non-cellulosic materials from the cracks and pits on the fiber surface (Fig. 4). Fig. 4a) shows the fiber surface before the treatment. The irregularities observed are produced by hemicellulose and lignin constituents. Fig. 4b) and c) shows the surface of fibers treated with a solution of 2% during 10 and 60 min respectively. In Fig. 4b) the cleaning of the surface is not completely efficient and some irregularities are observed; and in 4c) it is evident that the surface is regular, which suggests that the content of non-cellulosic materials is lower. Fig. 4d) and e) shows the surface of fibers treated with a solution

![Fig. 3](image)

(a) (b)

Fig. 3. SEM micrographs for: (a) untreated, and (b) plasma treated *Guadua angustifolia* bamboo fibers.
of 10% during 10 and 60 min; in Fig. 4d) some non-cellulosic materials are visible; in Fig. 4e) the fiber surface is cleaner and it can be observed that the bamboo fiber was divided into microfibers.

Bamboo fibers are composed by microfibers, which from the mechanical point of view work together to resist loads. Baths using NaOH remove hemicellulose and lignin constituents which work as glue-like materials, decreasing mechanical strength (Table 1). Plasma treatment affects the fiber surface, and the results in terms of tensile resistance suggest that the ion bombardment could have no implications on fibers mechanical behavior.

All analysis carried out using SEM micrographs are qualitative observations, which are preliminar results. These should be complemented through other experimental measurements, which are out of the scope of this paper.

4. Conclusions

It can be concluded that the treatment with the coupling agent (sodium hydroxide solutions) used in this research notably affects the tensile strength of *Guadua angustifolia* bamboo fibers. Although the coupling agent works as surface cleaner, it also affects the tensile strength because it removes the hemicellulose and lignin constituents. SEM images suggest that this treatment works as a surface cleaner, but for higher concentrations and prolonged times it results on the division of macrofiber.

Results showed that the use of plasma for treatment of *Guadua angustifolia* bamboo fibers, could increase the adherence between the reinforcement and different polymer matrices. Fibers that were treated with plasma did not show changes in its mechanical strength.

The treatment applied as well as the results obtained stimulate us to propose further exploration on these techniques. Thus, a working second stage of this research seeks to employ this treatments in the development of a polymeric composite material for non-structural elements in buildings.

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References


Proposed Method for Determining Cross-Sectional Area of *Guadua angustifolia* Bamboo Fibers

P. Luna and J. Lizarazo-Marriaga

Department of Civil and Agricultural Engineering, Universidad Nacional de Colombia, Bogotá, Colombia

**ABSTRACT**

This paper summarizes a research aimed to develop a methodology for determining the cross-sectional area of *Guadua angustifolia* bamboo fibers. The method includes the immersion of fibers into a resin, surface preparation, acquisition, and analysis of optical micrographs using commercial software. Measured areas were compared with other values obtained for thereof, from a standard gravimetric methodology commonly used on natural fibers, which showed substantial differences among calculated areas. Random samples were subjected to both methods using data distribution functions, and the analysis was carried out to determine their statistical goodness. Analysis of fibers diameter distributions reveals they are very well described by a lognormal distribution function. Furthermore, standard gravimetric methods tend to overestimate the fibers’ cross-sectional area in an average value of 15%, which could result in similar magnitude differences on the determination of some mechanical properties such as the tensile strength and the modulus of elasticity.

**INTRODUCTION**

Determining the cross-sectional area of fibers is essential to assess their mechanical properties in terms of the modulus of elasticity and tensile strength. According to Parthasarathy (Parthasarathy 2001) and ASTM C1557 (ASTM 2014), their assessment should be made from readings made in cross sections matching the fracture planes of fibers. In literature, there are several methods to determine fibers’ cross-sectional areas, among which the most commonly used is the diameter measurement from optical observations (obtained by optical or scanning electron microscopes) and the subsequent calculation of the area assuming a cross section with circular or elliptical shape (Gassan, Chate, and Bledzki 2001; Liu et al. 2013; Nitta et al. 2013; Ray, Das, and Mondal 2004; Tan, Ng, and Lim 2005; Torres and Cubillas 2005; Wang et al. 2015; Wei, Cao, and Song 2010; Yong and Yi-Qiang 2008; Yu et al. 2011). In another study, Morimoto et al. (Morimoto, Goering,...
and Schneider 1998) proposed a methodology for determining the diameter of the cross section of ceramic fibers by using optical interference techniques. Likewise, the Fresnel diffraction method has been used to measure the diameter of natural or synthetic fibers (Glass 1996; Glass, Dabbs, and Chudleigh 1995; Murali and Mohana 2007).

The mechanical properties of natural fibers are highly variable (Bledzki and Gassan 1999; Faruk et al. 2012; Kabir et al. 2013; Yu et al. 2011), mainly due to differences in the organization of their anatomical structure, growth conditions, the stem position, the maturity of the plant, and the harvest time, among others (Hughes 2011; Summerscales, Hall, and Virk 2011). Considering these variations, Osorio et al. (Osorio et al. 2010), Moreno et al. (Osorio, Espinosa, and García 2009), and Osorio et al. (Osorio et al. 2011) suggest determining the cross-sectional area (A) from a gravimetric indirect measurement in terms of the fiber density (ρ), mass (m), and length (L), by using Equation (1). Moreover, Alves et al. (Alves et al. 2013) and Ramirez et al. (Ramirez et al. 2011) obtained the cross-sectional area from image analysis carried out on SEM micrographs taken from the failure plane of the fibers, without considering the slope thereof with respect to the image plane.

\[ A = \frac{m}{\rho \times L} \]  

Lara-Cuzio and Garcia (Lara-Curzio and Garcia 2009) employed Monte Carlo simulations to estimate the error magnitude in determining fiber resistance when the area used for the calculation does not match to the fracture plane. The obtained results showed that the error magnitude grows when increasing the variability of the fiber diameter along its length, which for some cases may be ± 10%.

This paper describes a methodology to determine the cross-sectional area of Guadua angustifolia bamboo fibers. This proposed new method allows estimating more accurately the cross-sectional area of fibers at the failure plane, and ensures that the perpendicular axis of the image cross-section matches the observer’s eyes axis, thus avoiding optical distortions. It is intended to overcome the issues related to the traditional procedures where large errors in the determination of cross-sectional areas can be expected. Although the fibers’ cross-sectional area estimation seems to be a simple issue, it has a high impact in the calculation of some mechanical properties of fibers such as the tensile strength or the modulus of elasticity.

**Methodology**

**Description of the new proposed methodology Area Proposed Method (APM)**

The purpose of this method, (APM) is to ensure that the area measurements be carried out on a plane perpendicular to the longitudinal axis of the fiber, which can be achieved by arranging the fibers within a (transparent) resin before taking micrographs. This procedure ensures that the perpendicular axis of the cross section of the observed image matches the observer axis, thus avoiding optical distortions of the image.

Initially, the fibers must be fixed perpendicularly to the length of a straight and rigid element; the length of this element must match the size of the mold used during the resin curing. Subsequently, the straight element (with the attached fibers) is inserted into the mold to dump the resin, which must be translucent to allow clear observation of the cross section of the fibers. It is recommended to apply mechanical vacuum or vibrations during the initial resin curing, in order to prevent a large number of air bubbles from getting trapped, thus making the observations difficult. Once the resin has been hardened, the straight element is removed, and the surface must be polished by using sandpaper of different grain sizes (starting with coarse grains and finishing with a fine grain). Finally, the micrographs were obtained using a conventional optical microscope (working at the necessary...
resolution in agreement with the dimensions of the cross section of the fiber), in order to perform
digital analysis of the images obtained.

Figure 1 shows the performed procedure: 1 cm-long fibers were fixed to a rigid timber element,
which was previously cut so that its length could match the diameter of the mold used during the
resin curing. The fibers attachment to the timber element was made using an instant adhesive
composition ethyl-2-cyanoacrylate 80–95% and poly-methyl methacrylate 5–10%). The resin
employed corresponds to an epoxy with reference Twins A, with catalyst reference Twins B,
which was used in equal volumetric ratios. Once the wood element was inserted into the mold,
the dumping of the resin (resin + catalyst) was conducted. To decrease the amount of trapped air,
the set was introduced into a vacuum chamber, which was adjusted to work at a pressure of
−50kPa for 60 min. Subsequently, the set was left on a flat, horizontal surface for 24 h, time after
which the full curing of the resin was achieved.

The polish of the surface was performed using different grain-size sandpaper: 80, 120, 240, 320,
400, and 600 along with a cloth to improve its finish. The micrographs were taken using a

Figure 1. Proposed methodology for determining the cross-sectional area of Guadua angustifolia bamboo fibers.
metallographic microscope Leco500, working at 100× magnification. A captured image is shown in Figure 2. The calculation of the cross-sectional area was achieved by using the ImageJ software.

**Gravimetric method (AGM)**

The indirect gravimetric method was used to calculate the cross-sectional area of *Guadua angustifolia* bamboo fibers using Equation (1), where the used density was 1.4 g/cm$^3$ reported by Osorio et al. (Osorio et al. 2011). These results were compared with the cross-sectional area measurements performed using the aforementioned procedure explained. For this, a total of 120 fibers were used to calculate and measure the cross-sectional areas. As shown in Figure 3, each single fiber area was calculated by using the gravimetric method (AGM), and their measurement was accomplished following the optical methodology proposed in this paper (APM).

**Results and discussion**

Figure 4 shows the linear correlation between the areas obtained from both methodologies by using the least squares regression analysis. It is to be noted that the coefficient of determination $R^2$ obtained (0.688) is considered acceptable in the field of natural materials. However, it shows that there are some deviations of the area due to the experimental methods used. The figure also shows that the values significantly differ, as in most cases, the measurement taken from gravimetric calculations (AGM method) overestimates the fibers’ cross-sectional area. The foregoing is attributed to some aspects of the method applied, which requires a prior determination of the density of the material. It is believed that the experimental method to determine density is a very important source of uncertainties, for example, natural fibers are highly hygroscopic (Fernandes et al. 2015; Kushwaha and Kumar 2010; Li, Tabil, and Panigrahi 2007; Sapuan 2014), and their density is highly moisture-dependent.

![Figure 2. *Guadua angustifolia* bamboo fiber cross-sectional area.](image-url)
Statistical analysis

This section shows the statistical analysis performed from the cross-sectional area data measured using the two methodologies assessed. The main purpose of this analysis was to fit each data set to a probability distribution model. This analysis was performed using MATLAB R2013a (The MathWorks Inc., Natick, Massachusetts, US). All statistical inferences assumed a confidence level of 95% ($\alpha = 0.05$).

The histograms of all experimental data are shown in Figure 5. It is clear that for both data sets, the histograms are skewed to the left. Because of the skewness of the histograms, the lognormal and Weibull distributions were chosen to fit the data sets. The Weibull distribution is a continuous probability distribution. A random variable $X$ follows a Weibull distribution if and only if its probability density function (PDF) is described for Equation 2.

$$f(x) = \frac{\beta}{\delta} \left( \frac{x}{\delta} \right)^{\beta-1} \exp \left[ - \left( \frac{x}{\delta} \right)^{\beta} \right], \text{ for } x > 0$$

Figure 3. Guadua angustifolia bamboo fiber portions used for calculation (AGM) and measurement (APM) of cross-sectional areas.

Figure 4. Linear correlation between gravimetric calculations (AGM) and proposed methodology (APM).

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(2)
where $\beta > 0$ is the shape parameter and $\delta > 0$ is the scale parameter of the distribution. Otherwise, a random variable $X$ follows a log-normal distribution if and only if $Y = \exp X$ has a normal distribution. In this case, the PDF is shown in Equation 3.

$$f(x) = \frac{1}{x \sqrt{2\pi \sigma^2}} \exp \left[ -\frac{(\ln x - \mu)^2}{2\sigma^2} \right], \text{ for } 0 < x < \infty$$

where $\mu$ is the location parameter ($-\infty < x < \infty$) and $\sigma > 0$ is the scale parameter of the distribution. Figure 5 also shows the distribution fitted on each data set. From a qualitative visual inspection, the lognormal distribution (dashed lines) is the one that better fits the data sets for both methodologies.

For each data set, shape and scale parameters for the Weibull distribution, and location and scale parameters for the lognormal distribution were estimated by the method of maximum likelihood (MLE). MLE is one of the best method for obtaining a point estimator of a parameter, and as its name implies, the estimator will be the value of the parameter that maximizes the likelihood function (Montgomery and Runger 2002). Numeric values of estimated parameters for each distribution for both data sets are presented in Table 1.

Two approaches were used to compare the goodness of fitted distributions: (1) a quantitative approach using a procedure based on the likelihood ratio test; and (2) by visual assessment of cumulative probability plots.

According to Lu et al. (Lu et al. 2007), if the (natural) logarithm of the likelihood function for lognormal (or Weibull) distribution is higher than the logarithm of the likelihood function for Weibull (or lognormal) distribution, it is then concluded that the lognormal (or Weibull) fit is preferable over the Weibull (or lognormal) fit. For detailed discussion of this issue, the reader is referred to the quoted work. Column Maximum log-likelihood of Table 1 shows the calculated values

![Figure 5. Histograms of cross-sectional area distributions for methodologies: (a) AGM and (b) APM.](image)

<table>
<thead>
<tr>
<th>Applied methodology</th>
<th>$\beta$</th>
<th>$\delta$</th>
<th>Maximum log-likelihood</th>
<th>$\mu$</th>
<th>$\sigma$</th>
<th>Maximum log-likelihood</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGM</td>
<td>2.457</td>
<td>0.103</td>
<td>217.568</td>
<td>-2.493</td>
<td>0.464</td>
<td>217.801</td>
</tr>
<tr>
<td>APM</td>
<td>2.332</td>
<td>0.093</td>
<td>226.111</td>
<td>-2.600</td>
<td>0.472</td>
<td>228.33</td>
</tr>
</tbody>
</table>
for the logarithm of the likelihood function for each distribution. Higher values of this parameter were obtained for the lognormal distribution for both data sets.

Cumulative probability plots for both data sets are shown in Figure 6; continuous lines show the fitted distribution, and the confidence bounds used for the analysis (95%) are presented in dashed lines. It is clear that both distributions provide an adequate fit to each cross-sectional fiber data set. However, the Weibull distribution does not provide suitable results for low values of cross-sectional areas.

For all data collected, Equation 4 was applied to determine the relative differences in the area (error) according to the APM and AGM methods employed. Figure 7a shows the representative error term distribution, in which it is assumed that the data are symmetrically distributed around the mean while the frequency of occurrence of data farther away from the mean decreases. Statistically, the error data tend to approach a normal distribution, which is supported in the Central Limit Theorem. Although the random error term should have a theoretical mean close to zero, the
calculated mean was −15.4%. Figure 7b shows the probability plot of the data analyzed, which confirms graphically that the data set adjust well to the normal distribution given. Furthermore, it is confirmed that the data obtained from the gravimetric method (AGM) overestimates the fibers' cross-sectional in an average value of 15%.

\[
Error(\%) = \frac{\text{Area}_{(APM)} - \text{Area}_{(AGM)}}{\text{Area}_{(APM)}} \times 100
\]

Conclusions

Based on aforementioned results and commentaries, the following conclusions can be drawn:

- The proposed methodology for determining cross-sectional area of Guadua angustifolia bamboo fibers can be used when it is desired to take measurements of specific planes perpendicular to the longitudinal axis of the fiber, such as the failure plane.
- Gravimetric indirect methods, commonly used for the determination of the cross-sectional area of natural fibers, can lead to errors up to 15% because they use the fiber mass, which is believed to depend mainly on the moisture content of the fiber at the moment of its measurement.
- Some of the methods proposed by the ASTM C1557 standard for determining the diameter of fibers do not specify that the micrograph should be taken ensuring that the fracture plane of the fiber matches the image plane. The proposed methodology ensures more precise measurements since the fracture plane will always be perpendicular to the plane of the observer.
- The lognormal distribution fits each data set of this study. The distribution functions calculated on this work can be used to aid the development of larger mathematical models for predicting the mechanical behavior of Guadua angustifolia bamboo fibers.

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Dry etching plasma applied to fique fibers: influence on their mechanical properties and surface appearance

P. Luna\textsuperscript{a*}, A. Mariño\textsuperscript{b}, J. Lizarazo-Marriaga\textsuperscript{a}, O. Beltrán\textsuperscript{a}

\textsuperscript{a}Department of Civil and Agricultural Engineering, Universidad Nacional de Colombia, Bogotá 11001, Colombia
\textsuperscript{b}Department of Physics, Universidad Nacional de Colombia, Bogotá 11001, Colombia

Abstract

Plasma is a novel technique used in order to modify the surface properties of fibers used as a reinforced of polymeric composites. In this way, this paper shows the results of a research aimed to understand the effect of the dry etching plasma on natural fique fibers. Using different exposure times, the influence of plasma treatments on the tensile strength and surface appearance were investigated. Results showed that natural fibers could be effectively plasma treated without decreasing the strength and with significant modification of their surface appearance.

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Keywords: fique fiber; dry etching plasma; physical sputtering; tensile resistance; surface appearance

1. Introduction

Nowadays, the increasing environmental awareness has prompted searching sustainable materials to reduce the daily use of fossil raw materials. In consequence, natural resources have become important for industrial applications [1]. In composite industry, fibers such as hemp, flax, and sisal, are frequently used as reinforcement materials of different matrices, mainly polymers [2], [3].

The use of natural fibers as reinforcement material of polymeric matrices provides some significant advantages to composites such as high mechanical properties per unit weight, low density and small manufacturing cost per unit volume [4]. However, their potential has not been profitable enough due to the poor compatibility between the

* Corresponding author. Tel.: +57-1-300 344 3797
E-mail address: plunat@unal.edu.co
composite phases. The main component of natural fibers is cellulose, which is a basic unit formed of anhydro-β-glucose. This molecule contains three alcohol hydroxyl groups that can form intra and inter molecular hydrogen bonds, as well as react with hydroxyl present in the air [5], leading to a hydrophilic character [6]. This hydrophilic behavior makes the fibers incompatible with the hydrophobic polymer matrices commonly used [7], [8]. Low chemical compatibility adversely affects the bonding among phases, resulting in a poor stress transfer from matrix to fibers, thus affecting the mechanical overall performance of the composite material [9], [10].

In literature, there are two main alternatives focused on the modification of physicochemical properties of matrices or fibers to improve the compatibility among composite phases. The most common alternative for industrial applications is modifying the physicochemical properties of fibers [11]. Three different procedures can be used for this purpose: using coupling agents [12]–[14]; through a graft polymerization of monomers compatible with the polymer matrix [11], [15]; and by exposing fibers to plasma treatments [16]–[18].

The application of scientific knowledge about plasma has been successfully used since the 60s in a broad number of purposes in material science [15]. Plasma is considered the fourth state of matter and consists in the ionization (partial or total) of a gas or gasses, which can be achieved by applying an electric field to the gas [19]–[22]. Plasmas are composed of positive ions and electrons [23], [24], and can be classified into two categories: hot plasmas (thermal plasmas) and cold plasmas (non-thermal plasmas) [25], [26]. Hot plasmas are characterized by very high temperature species into the ionized gas (from 4000 K to 20000 K) and a thermal equilibrium among them. Cold plasmas are characterized by electrons with much higher temperatures than those of positive ions, and in consequence, there is non-thermal equilibrium. Cold plasmas are frequently employed in material science, due to most materials exhibited changes on their microstructural composition and degradation at high temperatures. Cold plasmas can be generated using low (10^{-4} to 10^{-2} kPa [26]) or atmospheric pressure; in both cases, the ionization is started and maintained by using direct current (DC), radio frequency (RF) or microwave (MW) power, with or without an additional electric (bias) or magnetic field.

As a general point of view, cold low-pressure plasmas fulfill three main purposes: functionalization of surfaces, deposition of thin films, and etching [15], [19], [25]. Although surface alterations are complex when cold plasma is used, it is reported that this has no effect on bulk properties [27]–[30], which represents its main advantage. According to Hua and co-workers [31], plasma species do not penetrate deeper than 100x10^{-10} m (100 Å) from the material surface. Those surface alterations are achieved after a few minutes of plasma treatment [30].

Etching processes are focused on removing some material from the surface [23], and there are two main alternatives to be attained: using a purely chemical process (wet etching), or using a physical or chemical-physical process (dry etching). Dry processes have several advantages over wet processes because they are direct methods [32], which can be developed in a wide range of pressure [25]. Dry etching treatments could be carried out by physical sputtering, chemical reaction or ion-assisted mechanism. On the physical sputtering procedure, the material is removed by purely physical processes. Ions in the plasma transfer significant amounts of energy and momentum to the substrate, causing the atoms removal. On chemical reaction and ion-assisted mechanisms, the surface material is converted into high vapor pressure products to facilitate the removal [32].

This paper shows the results of a research aimed to use dry etching plasma for treating fique fibers, in which the exposure time to the same energy was variable. The influence of the physical sputtering on the mechanical properties was determined through tensile tests, and the changes on the surface appearance were assessed using a Scanning Electron Microscope (SEM). This research explores this plasma technique as improver of interfacial properties of polymeric composite materials.

2. Experimental details

2.1. Fiber obtention

Fique fibers were obtained from the local market. Individual fique fibers were obtained from fabrics. All fibers were cut to an average length of 10 cm because of the space available in the plasma equipment.
2.2. Dry etching plasma treatment

Fibers were exposed to a physical sputtering treatment. In a previous research [18], it was found as a preliminary result, that the employed technique increased the superficial roughness of Guadua angustifolia bamboo fibers; similar conclusions using different dry plasma etching treatments on natural fibers were obtained by other researchers [16], [17], [33]–[36].

In this research the treatment was performed using a DC sputtering (etching) system and employing Argon (Ar) gas. Fibers were exposed to ion bombardment for different times and to the same energy; the exposure times were 200, 400, 600, 800 and 1000 s. All treatments were carried out using an average current of \(30 \pm 3\) mA and a working pressure of \(10^{-3}\) kPa.

2.3. Tensile tests

The aim of tensile tests was to study the influence of treatments applied on the fibers tensile strength. The mechanical tests followed the guidelines established on ASTM 1557-14 [37]. The load application rate was 1.5 mm/min, in order to get a fiber failure in maximum 30s, complying with the recommendation of ASTM 1557-14. Before mechanical tests, all fibers were placed on paper frames, as shown in Fig. 1, to avoid deviation of axial load due to incorrect positioning of the fiber on testing grips. After setting the testing grips, the paper frame was carefully cut.

![Paper frames used on tensile tests.](image)

The ultimate tensile resistance, \(\sigma_t\), was calculated using Eq. 1, where \(P_{\text{max}}\) indicates the failure load of each fiber and \(A\) gives the cross-sectional area. Due to the fact that natural fibers have irregular cross-sections [38]–[40], the cross-sectional area was measured using micrographs obtained at fracture planes of individual fibers after mechanical tests. Micrographs were obtained using a stereo microscope Nikon SMZ 800.

\[
\sigma_t = \frac{P_{\text{max}}}{A}
\]

(1)

Statistical analysis was performed to identify significant differences among tensile resistances for different treatment times. Initially, using a Shapiro-Wilk test, it was verified whether each data set fulfilled a normal distribution. The homoscedasticity among data sets was verified using a Levene test. An ANOVA analysis was applied in the cases to satisfy both criteria of normality and homoscedasticity. In the case where normality and/or homoscedasticity were not satisfied, the Kruskal-Wallis test was used [41]. The significance level for every case was 0.05.
2.4. Scanning electron microscope

In order to assess the influence of etching treatment on surface appearance of fibers, treated and nontreated specimens were observed using a scanning electron microscope Tescan Vega 3 SB, working in secondary electron mode.

3. Results and discussion

3.1. Tensile tests

Fig. 2 shows the tensile resistance results. For each treatment time, the tensile resistance was calculated as an average of at least five specimens tested for each treatment time.

The ANOVA analysis made for the tensile resistance of fique fibers indicates that there are no significant differences among treatment times applied. Researchers who have evaluated the influence of dry etching plasma on tensile strength of different fibers have also concluded that there are no alterations on the mechanical property [17]. Seki et al. [42] found that the tensile strength of jute fibers treated using an oxygen plasma, slightly decreased as a consequence of micro pits and cracks caused by ion bombardment. Ceria et al. [43] and Cheng et al. [44] used oxygen and nitrogen atmospheric plasmas to treat wool fabrics; they found that the tensile strength is positively affected by applied treatment. They attributed this behavior to an increment of inter-fiber frictional force leads on a stronger cohesion inside the fabric structure.

![Tensile strength for fique fibers.](image)

3.2. SEM analysis

Fig. 3 shows the SEM micrographs for fique fibers. Treated fibers exhibit a rough and coarser surface, even with the formation of some cracks. This behavior is attributed to etching effect caused by ion bombardment on the fibers surface. Similar results were found in other research works [36], [44]–[47].

Untreated fique fiber shows a mild surface with some continuous and slight ridges (Fig. 3a). According to Bogaerts et al. [23], the sputter-etching mechanism begins with the removal of material surface atoms, forming little and isolated microcracks (Fig. 3b), which increase with higher treatment times (Fig. 3c and 3d). For treatment times above 800s, those little-isolated microcracks coalesce together and the surface tends to become continuous (Fig. 3e and 3f).
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Fig. 3. SEM micrographs for fique fibers.

4. Conclusions

The statistical analysis made on the mechanical tests concluded that the tensile resistance has no alteration produced by ion bombardment. Although these results are promising, need to be correlated with other experimental results.

SEM images suggest that using plasma dry etching for treating fibers could increase the bonding among phases of composite materials because the treatment causes rough and coarser fiber surfaces.

From mechanical results and SEM images it can be concluded that the coalesce effect does not affect the tensile resistance of treated fibers.

The encouraging results obtained suggest to propose a new research in this field. This compatibilization technique could be used to increase the adherence between polymer composite phases.

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