

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

---

Mechanical (and Materials) Engineering --  
Dissertations, Theses, and Student Research

Mechanical & Materials Engineering,  
Department of

---

8-2013

## Interface properties of bio-based composites of polylactic acid and bamboo fibers

Quentin Viel

University of Nebraska-Lincoln, [quentin.viel@live.fr](mailto:quentin.viel@live.fr)

Follow this and additional works at: <https://digitalcommons.unl.edu/mechengdiss>



Part of the [Applied Mechanics Commons](#)

---

Viel, Quentin, "Interface properties of bio-based composites of polylactic acid and bamboo fibers" (2013). *Mechanical (and Materials) Engineering -- Dissertations, Theses, and Student Research*. 56.  
<https://digitalcommons.unl.edu/mechengdiss/56>

This Article is brought to you for free and open access by the Mechanical & Materials Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Mechanical (and Materials) Engineering -- Dissertations, Theses, and Student Research by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Interface properties of bio-based composites  
of polylactic acid and bamboo fibers

by

Quentin Viel

A THESIS

Presented to the Faculty of  
The Graduate College at the University of Nebraska  
In Partial Fulfillment of Requirements  
For the Degree of Master of Science

Major: Mechanical Engineering and Applied Mechanics

Under the supervision of Professor Joseph A. Turner

Lincoln, Nebraska

August, 2013

Interface properties of bio-based composites  
of polylactic acid and bamboo fibers

Quentin Viel, M.S.

University of Nebraska, 2013

Advisor: Joseph Turner

Environmental impact plays an ever-increasing role in the industrial production of materials, and because of its importance, the scientific community is examining a wide variety of new materials that are more environmentally friendly. Bioplastics are characterized by the fact that the usual petrochemical resins (polypropylene, polyethylene etc.) are replaced by bio-sourced resins and the reinforcements (glass fibers, carbon fibers etc.) are replaced by natural fibers (bamboo, flax, cotton, etc.). Polylactic acid (PLA) is a biodegradable polymer that is increasingly used in biomedical applications and in packaging. Additionally, bamboo is a promising source of fibers that could be used as reinforcement. In fact, bamboos are grasses with rigid, woody stems, which grow extremely fast and profusely. By virtue of these properties, bamboo is a good candidate as a natural fiber source. Therefore, composites made of a PLA matrix which are reinforced by bamboo fibers may offer many potential advantages as a replacement for less biodegradable alternatives.

The mechanical performance of polymer-based composites is often dominated by the interfacial properties between the fibers and matrix, especially with respect to mechanical

failure. In this thesis, both untreated fibers and those modified with a NaOH treatment were examined. The shear strength at the interface between a bamboo fiber and the surrounding PLA matrix is quantified. A novel method for processing pull-out-test samples and the details of a test procedure are described. Electron and optical microscopy are both used to examine the failure mode and to quantify the geometry of the fiber-matrix interface. The value of the interfacial shear strength is reported, and its statistical variations are discussed. The results provide important information regarding the future design of natural composites.

# ACKNOWLEDGEMENTS

First of all, I would like to thank Dr. Joseph Turner for having been highly concerned of my thesis and for having followed me throughout this year which was very fascinating for me. His patience helped me to realize this thesis in the best possible conditions and for this reason; I could adapted myself at the University of Lincoln quickly. I would like to thank highly Dr. Antonella Esposito, who has helped me many times in the creation of samples, the different presentation that I have made and for the interpretation of the data obtained; and all of these by videoconference (thank you). Prof. Jean-Marc Saiter was very important also in the decision in which way this thesis leads, and that's why I thank him for this reason this time. Now I want to thank especially my wonderful desk neighbors Séverine and Céline for the help that they have brought me and the pleasant moments that we have spent. All the graduate student and PHDs in "Turner's lab" deserve a great thank, I have appreciated to spend time with everybody Andrea, Lucas, Ehsan, Raphael, Chris, Ping... All the structures as BM3 or Machine Shop were very open-minded and sometimes interesting about my work so I thank the people who are working in these structures. I am also thinking of Alicia Harvey who having recently surgical operation. I have appreciated working with her. It's now the time to mention the three "road fellows" : Emilie, Ben and Etienne who are friends for long after these two years spent with them out of France. Finally, I will be eternally grateful for the duo Prof. Jean-Marc Saiter and Prof. Mehrdad Neghaban who are responsible for this incredible year for me. I never thought before that this experience could happen in my life. MERCI

# CONTENTS

List of Figures .....	vii
List of Tables .....	xiii
Chapter 1: Introduction.....	1
1.1 Environmental issues.....	3
1.2 Natural fibers and bio-sourced polymers .....	5
1.3 Polylactic Acid (PLA).....	8
1.4 Bamboo Fibers .....	10
1.5 Composites made with PLA and Bamboo Fiber .....	14
1.6 Treatment of bamboo fibers .....	18
Chapter 2: Single fiber pull-out test.....	25
2.1 Theory .....	25
2.2 Microbond tests .....	29
2.3 Experiments.....	31
2.3.1 Detailed Description of the Bose instrument: .....	31
2.3.2 Sample preparation .....	34
2.4 Methods.....	40
2.4.1 Pull out tests.....	40

2.4.2	Microscope imaging.....	41
2.4.3	Mercerization of fibers.....	42
2.4.4	Infrared measurement .....	44
2.4.5	Profilometer .....	45
2.4.6	Scanning Electron Microscopy .....	47
Chapter 3:	Experimental Results .....	50
3.1	Untreated fibers .....	50
3.2	Mercerized fibers.....	67
3.3	Fourier Transform Infrared (FT-IR) Spectroscopy .....	72
Chapter 4:	Conclusions and perspectives .....	75
Bibliography	.....	79

# LIST OF FIGURES

Figure 1. Production of plastics in world in millions of tons in function of years. The plastics production in 2050 is an estimation from the European Plastics Productions [1].	3
Figure 2: The list of the mechanical properties of the fibers used in composites. The properties of natural fibers are approximately located in the red circle [9].	5
Figure 3: Schematic of the production of the polylactic acid. A is fermentation. B can be dehydrative and condensation + chain coupling agent with $H_2O$ .	8
Figure 4. Surface schematic of polylactic acid. The double bond oxygen is reactive and may interact with the environment.	9
Figure 5. Schematic of the cross-section of bamboo fibers. It is composed of bundles of elementary fibers, itself composed of nano fibril, linked by lignin and hemicellulose [4].	10
Figure 6: Pictures of the G1 and G2 grades of bamboo fiber. The classification is made of short fiber to very short fiber G1 to G6.	11
Figure 7. (A) SEM images of bundle of elementary bamboo fiber after extraction. (B) SEM pictures of the surface of the bamboo after extraction [21].	12
Figure 8: Schematic of bamboo fiber surface where hydroxyl groups are reactive and may interact with environment	14
Figure 9. Bamboo fiber and PLA pellets are mixed in the funnel to be then compressed and heated by the single screw until the spinneret to create composite.	15



Figure 10: (A) Interface is formed by molecular entanglement; (B) Interface made by electrostatic attraction; (C) Both elements interdiffuse with each other; (D) Chemical reaction with A element and B element; (E) New interface phase created by chemical reaction; (F) Interface created by mechanical interlocking [63].....	16
Figure 11: Schematic of the composite interface between bamboo fiber and PLA matrix. .....	17
Figure 12: Mercerization of bamboo fiber, (called also alkali treatment). Sodium hydroxide allows making hydroxyl groups present on the surface of fiber.....	19
Figure 13. Chemical structure of lignin according to Adler (1977) and its reduced writing .....	20
Figure 14. Mercerization allows altering the chemical structure of lignin. (A) Adding of NaOH, (B) Negative charge transfer, (C) Separation of the phenolic group, (D) Lignin hydrolyzed by H <sub>2</sub> O .....	20
Figure 15. The permanganate treatment allows cellulose radical to be created in order to make it chemically active.....	21
Figure 16. Silane treatment on fiber allows a coating with hydroxyl groups to be created, in order to improve the chemical adhesion [30]. .....	22
Figure 17: Characteristic curve of single fiber pull-out test performed in this work. Force of pull is measured as a function of displacement .....	25
Figure 18. Model of single fiber pull out test. The fiber is embedded in the matrix. ( $F + dF$ ) is the force of pull-out, ( $\tau$ ) is the interfacial shear strength, ( $dx$ ) is the embedded length of the fiber in matrix, ( $l$ ) length displaced .....	26

Figure 19. Schematic of a microbond test .....	29
Figure 20: Characteristic curve of a microbond test.....	30
Figure 21: Bose Electroforce 3200 device.....	31
Figure 22: Grips Standard Dynamic Analysis .....	32
Figure 23: Titanium T/C Grips .....	32
Figure 24: Compression platens.....	33
Figure 25: Load cells .....	33
Figure 26: Schematic of the the initial step to create polylactic acid matrix sample by using a heated hydraulic press .....	37
Figure 27: Schematic of the final step to create polylactic acid matrix sample by using a hydraulic press .....	38
Figure 28: Samples obtained after hydraulic press .....	39
Figure 29: A schematic zoom of the single fiber pull-out test performed with the BOSE device .....	41
Figure 30: Hydroxyde de sodium NaOH are in pellet form .....	43
Figure 31: After the treatment with NaOH, the washing of fiber is made by Buchner flask .....	43
Figure 32: Nicolet Avatar 360 FT-IR. Infrared device .....	44
Figure 33: Scantron Proscan 1000 Profilometer .....	45
Figure 34: Schematic of profilometer process [51] .....	46
Figure 35. The Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) .....	49

Figure 36. On the left, a single fiber pull-out test is considered as failed because some elementary fibers were broken during the tensile part, thus data do not quantify the interface of the bio-sourced composite. On the right, a pull-out test considered as successful and therefore interpretable to quantify the interface. ....	52
Figure 37: Tip of a bamboo fiber which is not well preserved, as observed by optical microscopy (x10 magnification) after a pull-out test considered as “non-uniform” (“sample with problem”). Elementary fibers got separated as a consequence of the pull-out test. ....	53
Figure 38: Tip of a well preserved bamboo fiber, as observed by optical microscopy (x10 magnification) after a pull-out test considered as “regular” (“uniform sample”). Elementary fibers remained connected even after the pull-out test. ....	54
Figure 39: Bamboo fiber as observed by optical microscopy (10× magnification). A separation of the elementary fibers is detected after the pull-out test. ....	54
Figure 40: SEM picture, of the hole left in the polylactic acid matrix by bamboo fiber as a consequence of a pull-out test. ....	57
Figure 41: SEM picture, of a PLA/bamboo sample after pull-out test. Evidences of a complex failure mechanism suggest that the result of the test should be carefully interpreted .....	58
Figure 42: SEM picture, bamboo fiber were broken before debonding during the single fiber pull-out fiber. ....	59
Figure 43. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber length embedded into the polymeric matrix. ....	62

Figure 44. Interfacial shear strength as a function of the fiber diameter .....	62
Figure 45. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber diameter (only uniform samples were selected).....	63
Figure 46. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber diameter (only “non-uniform” sample were selected) .....	64
Figure 47: Interfacial shear strength between PLA and bamboo fibers as a function of the fiber length embedded into the polymeric matrix (only “uniform” samples were selected). .....	65
Figure 48. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber length embedded into the polymeric matrix (only “non-uniform” samples were selected).....	65
Figure 49. SEM pictures of the surface of a bamboo fiber before mercerization (untreated fiber).....	67
Figure 50: SEM pictures of the surface of a mercerized bamboo fiber. Residual salts (NaOH) can be seen on the surface of the fiber. ....	68
Figure 51: SEM picture of a mercerized bamboo fiber (technical fiber, i.e. bundle of elementary fibers). ....	69
Figure 52. Interfacial shear strength between PLA and treated bamboo fibers as a function of the diameter of the fibers (only “uniform” samples were selected). ....	70
Figure 53. Interfacial shear strength between PLA and treated bamboo fibers as a function of the fibers length embedded into the polymeric matrix (only “uniform” samples were selected).....	71

Figure 54. Infrared analysis performed on untreated bamboo fibers (blue curve), treated fiber with one washing with filtered water (red curve), and treated fiber with two washing with filtered water (green curve).....	72
Figure 55. Zoom of Figure 54 on 1200-2000 $\text{cm}^{-1}$ wavenumber .....	74

# LIST OF TABLES

Table 1. World production of fibers used as reinforcement, in bio-sourced composites. ..	6
Table 2: Mechanical characterization of some natural fibers listed in the literature .....	6
Table 3: Mechanical properties of bio-sourced polymers used as matrix in composites in the literature [10].....	7
Table 4: Some characteristics of the different grades of bamboo fibers.....	12
Table 5: The mechanical properties of bamboo fibers in the literature .....	13
Table 6: Consequences of pretreatment applied on lignocellulosic plant mass. (++) means strong effect, (+) moderate effect, (-) not available [38] .....	23
Table 7: Dimensions of washers used to create the samples .....	36
Table 8: Two sensors available with the profilometer, and their characteristics.....	47
Table 9: Detectors used in SEM analysis in function of the mode chosen.....	48
Table 10. Summary of the characterization of different categories of bamboo fibers .....	56
Table 11. Interfacial shear strength determined for different polymeric matrix/untreated natural fiber composites through pull-out tests and microbond tests in the literature. ....	60

# CHAPTER 1: INTRODUCTION

This thesis is expected to contribute to eco-design of bio-based composite materials. These eco-materials have a future in several sectors such as automotive, packaging, textiles and building construction among others. The reconciliation of environmental and industrial production plays an increasingly important role in the collective thought about the future of humanity. Because of increased attention to the environmental impact of industrial production, it becomes important to produce economically, environmentally, and socially sustainable materials. Plastics from oil production are increasingly less desirable due to increasing prices and the polluting nature of the raw material. Scientific, environmental, and industrial communities are working to propose new materials which are more environmentally friendly. Plastics from bio-resources are rising sharply in recent decades, with the goal being to replace plastics derived from petrochemicals.

Bioplastics are characterized by the fact that the petrochemical matrix is replaced with plant (or bacterial) resin and traditional reinforcements (fiberglass, carbon fiber) are replaced with natural fibers (bamboo, hemp, flax). The mechanical and thermal properties offered by bioplastics are generally lower than plastics derived from petrochemicals. There are adhesion problems with the reinforcement of natural fibers and adverse effects on the physical properties of bioplastics created by humidity. Data reproducibility is poor due to

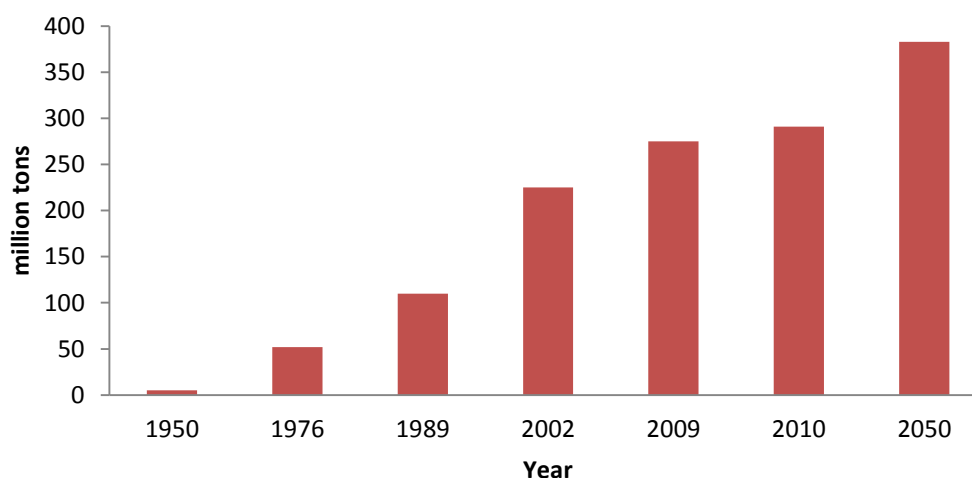
crop quality of agricultural products. Despite these draw backs, bio-sourced composites materials are recyclable and biodegradable.

In this thesis, mechanical properties of biocomposites are studied using single fiber pull-out tests. The interfacial shear strength is determined with its dispersion. A chemical treatment with sodium hydroxide is used on the bamboo fibers in an attempt to improve the mechanical characteristics of the fiber matrix interface.



## 1.1 Environmental issues

In recent years, the production of plastics from renewable resources has become a new social and economic challenge. The increased attention is related to the awareness of the risk to our planet presented by the growing use of plastics and their polluting nature which is only exacerbated by poor recycling options. Indeed, annual world plastics production is projected to be about 400 million tons in 2050, as shown in Figure 1. For these reasons, production needs to become more environmentally friendly.



**Figure 1.** Production of plastics in world in millions of tons in function of years. The plastics production in 2050 is an estimation from the European Plastics Productions [1]

Biopolymers, which are alternatives to low performance plastics, are produced from natural organisms, and they can also be synthesized from renewable polymers. Therefore, they are biodegradable, and they can be used as a substitute or mixed with other materials to create some other properties for different applications. Indeed, in a more

environmentally-friendly world, biopolymers will surely play an increasingly important role.

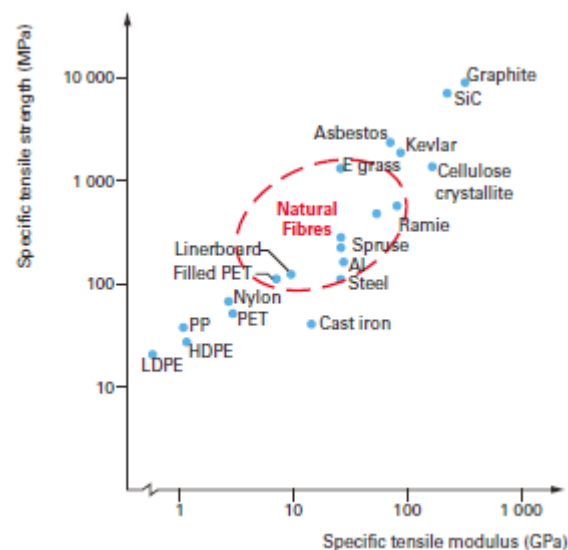
The biodegradability comes from the bacterial origin of the biopolymer. The first biopolymer that scientists considered is cellulose. It belongs to the family of polysaccharides. The mechanical and thermal characteristics of this biopolymer are closest to low performance polymers. These are some reasons that it has been designated by some industrial and scientific research to replace some low-performance thermoplastics such as polypropylene (PP), polyethylene (PE), and polystyrene (PS) [2] [3].

Biopolymers are made with different natural or synthetic processes including microbial processes, where micro-organisms secrete some microbial polymer after fermentation of natural raw materials (glucose for example). There are also plant processes, with cellulose, lignin, hemicellulose which are organized as a natural biopolymer within plants [4]. Polylactic acid (PLA) belongs to a biological process. Its production is made by chemical polymerization of biological molecules. The monomer called lactic acid is mainly produced by fermentation of sugars. It can also be synthesized by different chemical methods [5].

## 1.2 Natural fibers and bio-sourced polymers

Natural composites play an increasingly important role in scientific communities and have for many years. Many research scientists are studying the combination of natural fibers with thermoplastics [6] or conversely, a biopolymer associated with glass fibers to improve the biodegradability of materials [7]. However, the ecological interest is, of course, to reach a 100% natural biocomposite material. Bio-sourced composites utilize natural fibers as reinforcements embedded in a bio-based polymer matrix.

Both elements constituting the biocomposite must be biodegradable. The fibers often need a chemical treatment to increase properties such as adhesion between interfaces [8]. The mechanical properties of fibers are often characterized by their tensile modulus and specific strength as shown in Figure 2.



**Figure 2: The list of the mechanical properties of the fibers used in composites. The properties of natural fibers are approximately located in the red circle [9]**

Recent natural fibers used as reinforcement are listed in Table 1, which also includes their world production [10].

**Table 1. World production of fibers used as reinforcement, in bio-sourced composites.**

Fibers	World production (10 <sup>3</sup> tons)
Hemp	214
Flax	830
Cotton	-
Jute	2300
Ramie	100
Bamboo	30000

Bamboo is the most abundant lignocellulosic plant produced in the world and for this reason it represents a good opportunity for use as reinforcement in natural composites. The mechanical characterization of plant fibers has been studied, and some of these are listed in Table 2.

**Table 2: Mechanical characterization of some natural fibers listed in the literature**

Fibers	Tensile strength (MPa)	Tensile modulus (GPa)	Failure strain (%)	Reference
Hemp	270-900	23.5-90	1-3.5	[11]
Flax	600-2000	12-85	1-4	[9] [11]
Cotton	287-597	5.5-12.6	7-8	[9] [11]
Jute	393-773	24.70-26.5	1.5-1.8	[9] [12]
Ramie	400-1000	24.5-128	1.2-4	[9] [11]
Bamboo	464-907	33.37	1.2-1.9	[12]

In this thesis, the bamboo will be used as reinforcement to study the mechanical behavior of the fiber in the natural composite. Indeed, bamboo fiber is produced in large amounts, and it also presents better mechanical properties than the other fibers, as shown in Table 2. Flax fiber has generally better mechanical characteristics than the other natural fibers

and that is largely studied in the literature [13] [14] [15]. The tensile modulus and the tensile strength of each fiber are both determined in literature and the different data shown are dispersed due to their natural property. This dispersion proves that each fiber may have similar mechanical characteristics. Therefore, research on different varieties of fibers are necessary to find the better candidate to aspire to be the reinforcement in biocomposites. Because of the abundance of bamboo throughout the world, it is chosen as the reinforcement in this thesis.

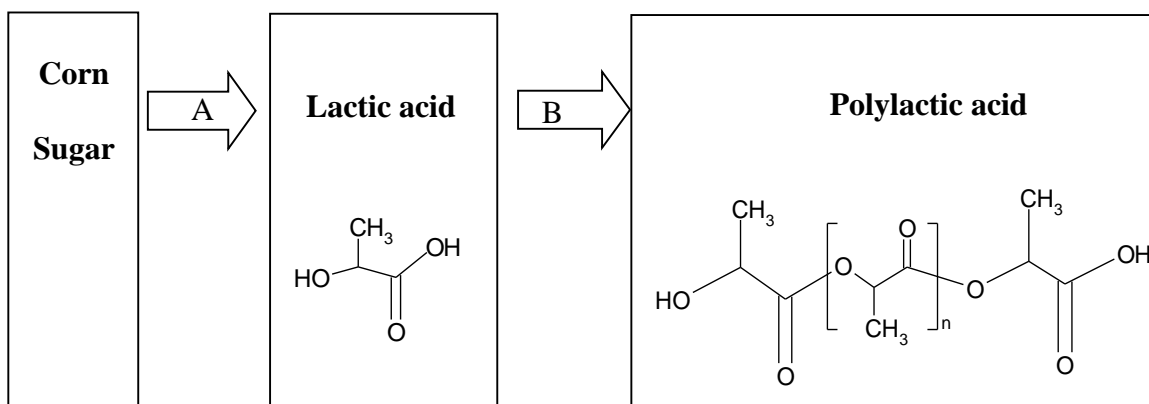
**Table 3: Mechanical properties of bio-sourced polymers used as matrix in composites in the literature [10]**

Matrix	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation at break (%)
PHB	$27.3 \pm 0.3$	$2.14 \pm 0.7$	$7.0 \pm 1.1$
PLA	$63.5 \pm 0.4$	$3.4 \pm 0.23$	$3.3 \pm 0.5$

Recent bio-based polymers used as matrixes include polyhydroxyburate- (PHB) and polylactic acid- (PLA) as listed in Table 3. PLA matrix has higher tensile strength and tensile modulus than PHB. However, its tensile elongation at break is lower. PLA has better mechanical characteristics and this polymer was logically chosen as matrix in the natural composites studied in this thesis.

### 1.3 Polylactic Acid (PLA)

The polymer used for the matrix of the composite materials studied here is polylactic acid (PLA). It belongs to the family of aliphatic polyesters. PLA is a thermoplastic that is semi-crystalline and biodegradable. Polylactic acid has a degradation rate in the range of six months to two years [16]. Its crystallinity is around 1% and can vary as a function of the molecular mass and nature of the lactide isomer [17]. It is also biocompatible and bioabsorbable for different applications such as medical devices or in contact with food. PLA represents a high potential for being produced as a renewable packaging material.

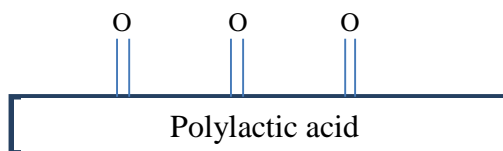


**Figure 3: Schematic of the production of the polylactic acid. A is fermentation. B can be dehydrative and condensation + chain coupling agent with  $\text{H}_2\text{O}$ .**

Figure 3 shows how the fermentation of sugar (for example from corn) can create a lactic acid monomer. Then, two transformations exist to polymerize the lactic acid. The dehydrative process allows for the creation of a polylactic acid with a high molecular weight PLA ( $M_w > 100000$ ). On the other hand, condensation of the monomer leads

instead to a low molecular weight prepolymer ( $M_w = 200$  to  $10000$ ). By adding chain coupling agents, the prepolymer can become a high molecular weight PLA [16]. Polylactic acid has two different molecular structural organizations enantiomeric forms such as L-lactide and D-lactide [5]. The copolymerization between the D and L forms is interesting for the producer because the molecule properties are enhanced for packaging applications. The glass transition also increases [18]. However the monomer lactic acid can be used as a plasticizer and therefore decreases the glass transition of the polymer. The D-polymer is less common. Usually, PLA has L-form with D-form structure (not indicated by the provider).

Surface PLA and its bulk properties are important to take into consideration in order to understand the mechanical behavior of the PLA matrix during a pull-out test. Here the focus is on surface properties, which play an important role for composites. Indeed, interfacial shear strength depends on the properties of bonds at the matrix surface, more specifically the potential interaction that the matrix surface can create with its environment. The surface of the PLA matrix is represented in Figure 4.



**Figure 4. Surface schematic of polylactic acid. The double bond oxygen is reactive and may interact with the environment.**

## 1.4 Bamboo Fibers

Bamboo is a grass, with woody stems, which grows extremely fast. It reproduces mainly through the formation of new rhizomes and culms. Bamboo is characterized by the particular structure of aerial stems or culms. Each culm is divided into segments (as in other grasses) including nodes (solid) and internodes. Nodes give the necessary strength for the culm to remain straight. The internal structure of thatch<sup>1</sup> is very fibrous and is designed to withstand the enormous weight of the branches. Bamboo wood is made up of nearly 90 % of support structures in the form of cellular and tissue structural fibers and 10 % of vascular bundles that carry water and nutrients. This ratio may not be accurate for all different species of bamboo that exist in the world [19].

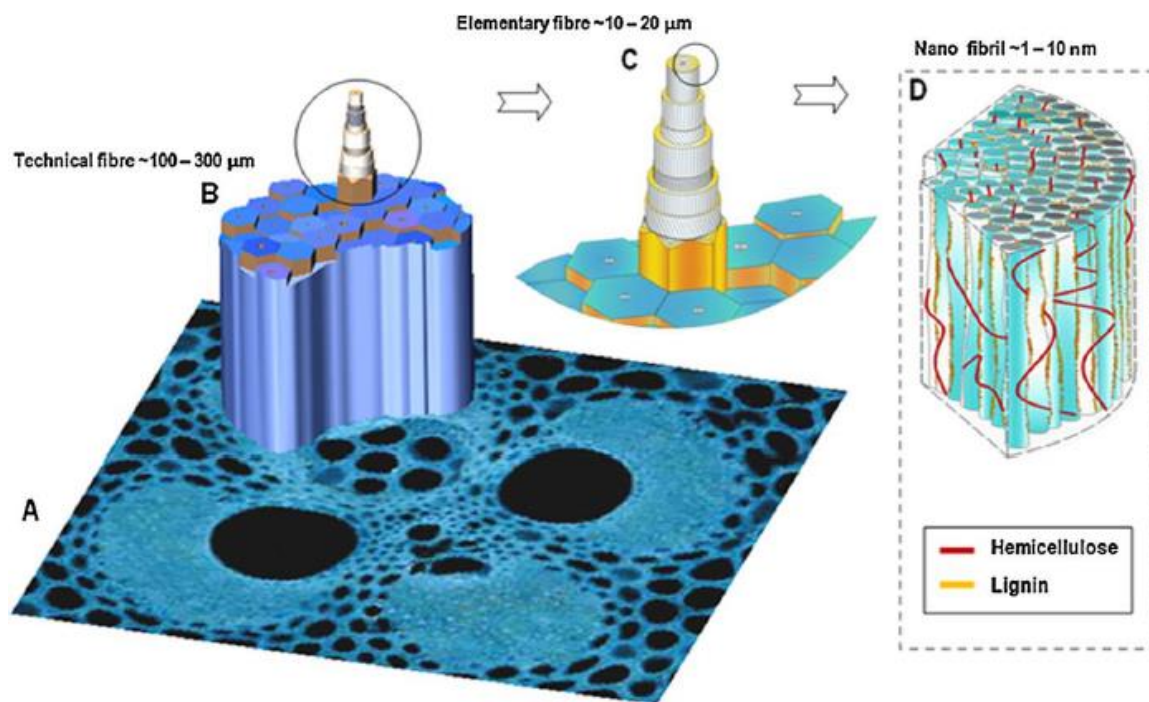


Figure 5. Schematic of the cross-section of bamboo fibers. It is composed of bundles of elementary fibers, itself composed of nano fibril, linked by lignin and hemicellulose [4].

<sup>1</sup> Bamboo trunk



Figure 5 shows a schematic of the cross-section of a bamboo fiber which shows the organization of lignin and hemicellulose in the fiber. In (A) the cross-section of thatched bamboo is represented. In (B) a technical fiber is shown with a corresponding size of 100-300  $\mu\text{m}$ . The technical fiber is precisely a bundle of elementary fibers (C) which have diameters around 10-20  $\mu\text{m}$ . Finally, (D) shows the organization between the nano fibrils with the hemicellulose and the lignin. Hemicellulose and lignin are both organic molecules present in the walls of plants and organized as polymers. They serve as the binder between the nano fibrils assembled into a block.

Table 4 lists the dimensional characteristics of bamboo fibers obtained from the provider “Bamboo Fiber Technology” [20].

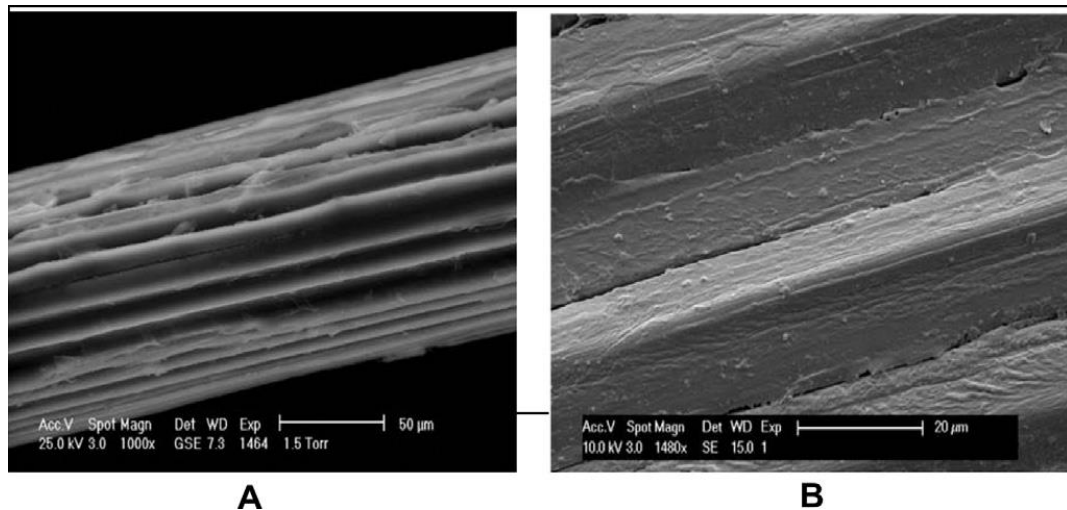


**Figure 6: Pictures of the G1 and G2 grades of bamboo fiber. The classification is made of short fiber to very short fiber G1 to G6**

**Table 4: Some characteristics of the different grades of bamboo fibers.**

	<b>Long fibers (grade 1 and 2)</b>	<b>Short fibers (grade 3 to grade 5)</b>
Length	5 to 150 mm	3 mm to 50 $\mu\text{m}$
Density	90 $\text{kg/m}^3$	215 $\text{kg/m}^3$
Humidity	between 8 and 15%	between 8 and 15%

The lengths of bamboo fiber of grades 5 and 6 are too small to be considered as an effective reinforcement. Fibers from grades 1 and 2 have longer lengths such that these two grades are chosen to be used as potential reinforcement. All the tests described in this thesis are performed with G1 and G2 fibers.



**Figure 7. (A) SEM images of bundle of elementary bamboo fiber after extraction. (B) SEM pictures of the surface of the bamboo after extraction [21]**

The extraction of the bamboo fibers creates bundles composed of elementary fibers. The SEM images shown in Figure 7 (A) highlight that a single bamboo fiber is organized as a bundle of elementary fibers after extraction. Figure 7 (B) represents the surface of the bamboo fiber after extraction. According to these images, the single bamboo fiber does not have a perfect circle diameter, but the fiber is assumed to be perfectly round throughout this thesis. Otherwise, Table 5 lists the mechanical properties of bamboo fibers shown in the literature. The average of tensile strength of bamboo fiber is around 538 MPa and the tensile modulus is around 30.25 GPa. Moreover, failure strain is around 9 %. These mechanical characteristics are necessary to take into account in order to understand the mechanical behavior of the fiber during the single fiber pull-out test.

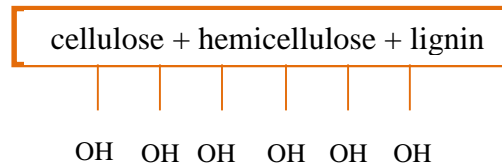
**Table 5: The mechanical properties of bamboo fibers in the literature**

Tensile strength (MPa)	Tensile modulus (GPa)	Failure strain (%)	Reference
500-575	24-40	1.9-3.2	[21]
265-369	8-12	17-27	[22]
464-907	33	1.4-3.6	[12]
610	46	-	[23]

The chemical composition of bamboo fibers is important to consider when characterization results are analyzed. The composition of chemical constituents of bamboo fiber is 73.83 % of cellulose, 12.49 % of hemicellulose, 10.15 % of lignin and 3.53 % of aqueous extracts with pectin [21]. Cellulose is the major constituent of bamboo fibers and is expected to have a high influence on the mechanical behavior of the composite.

The surface properties of bamboo fiber are very important for the adhesion behavior of bio-sourced composites. The surface of bamboo fiber is mainly composed of links of lignin

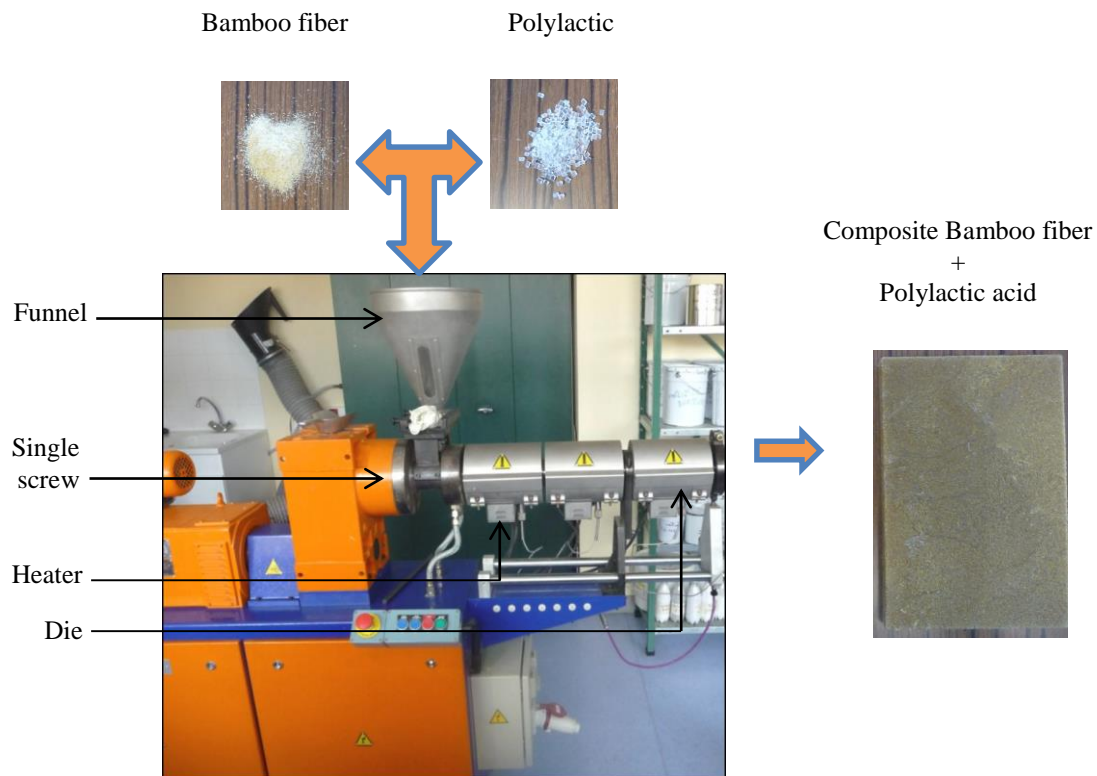
(C-(C,H)) , C-OH, C=O) and also composed of C-OH of cellulose [24]. Hydroxide bonds are dominant and reactive due to the presence of lignin and cellulose [25]. The surface chemical composition can be summarized as schematically shown in Figure 8.



**Figure 8: Schematic of bamboo fiber surface where hydroxyl groups are reactive and may interact with environment**

## 1.5 Composites made with PLA and Bamboo Fiber

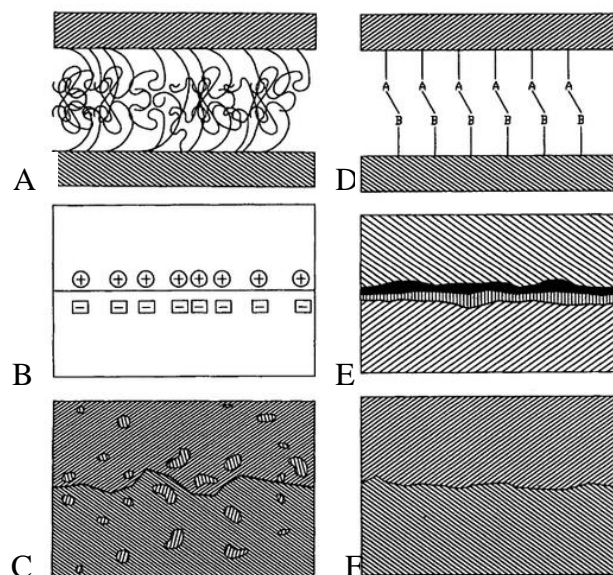
Composites made with PLA and bamboo fibers were studied previously [26], including thermal and mechanical characterization of the bio-sourced composite. First of all, composites were created with a single screw extruder which is a classic device allowing pumping and compressing. Figure 9 shows how that composite was manufactured. The single screw extruder allows mixing elements of bamboo fiber and polylactic acid in a funnel, to then bring the compound through the die by a single screw surrounded by heaters while heating it. Finally, the composite is collected and compressed into a square mold.



**Figure 9. Bamboo fiber and PLA pellets are mixed in the funnel to be then compressed and heated by the single screw until the spinneret to create composite.**

Once the composite is created, thermal and mechanical characterization can be performed by several tests. Indeed, some macroscale characterization tests such as three-point bending, impact, hardness, dynamic mechanical analysis and thermogravimetric analysis were performed. At the micro/nano scale, nanoindentation and scanning electron microscopy were used to characterize the PLA / bamboo fiber composite [26]. Mechanical characterization needs to be studied more precisely, and that is why interfacial shear strength is performed in this work. The interface between the two elements of a composite is critical to the overall performance. As both surfaces of matrix and fibers defined before, the suggestion is that the interface of matrix and fiber will bond to each other with different interactions such as covalent bond, van der Waals force among others. In order to predict

what kind of interface is present, it is necessary to know the possible connections that can be created at the interface, as shown in Figure 10.

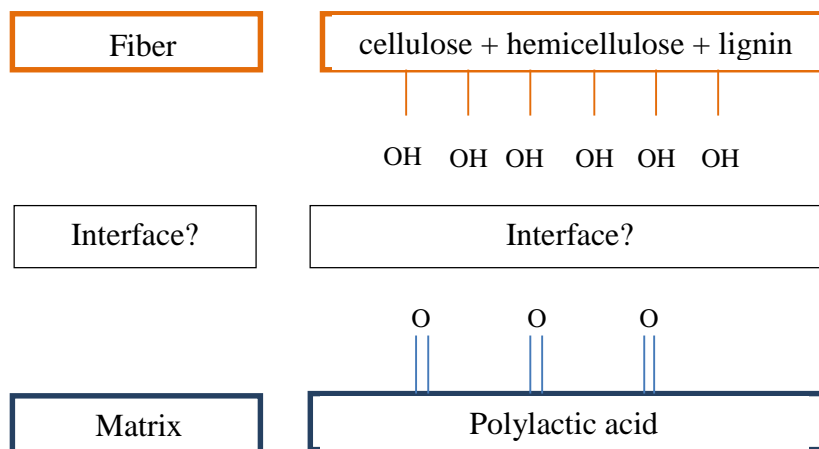


**Figure 10: (A) Interface is formed by molecular entanglement; (B) Interface made by electrostatic attraction; (C) Both elements interdiffuse with each other; (D) Chemical reaction with A element and B element; (E) New interface phase created by chemical reaction; (F) Interface created by mechanical interlocking [63]**

For polylactic acid and bamboo fiber composites, the interface property predicted will be characterized by multiple interfaces at the same time. Indeed, one acceptable prediction is a chemical reaction with surface elements of bamboo fiber and surface elements of polylactic acid (C). Then, concerning mechanical interface, one supposition can be that fibers and matrix are interlocked with each other (F). Bamboo fibers have a hydrophilic nature which is incompatible with the hydrophobicity of matrix [27].

As shown schematically in Figure 11, on the surface of bamboo fibers, hydroxyl groups (polar molecule) are mainly present. On the surface of polylactic acid, a double oxygen bond with a high electronegativity is present and may interact with hydroxyl groups.

However, the bonding between fiber and matrix will be done by insertion of bamboo fiber in a melted PLA matrix. Thus, OH phenolic hydroxyl groups of lignin have a high potential to interact with carbonyl groups of PLA [28]. Finally, it should be noted that the interface is difficult to predict; only hydrogen bonds, van der Waals interactions and capillary forces [13] may interfere with each other.



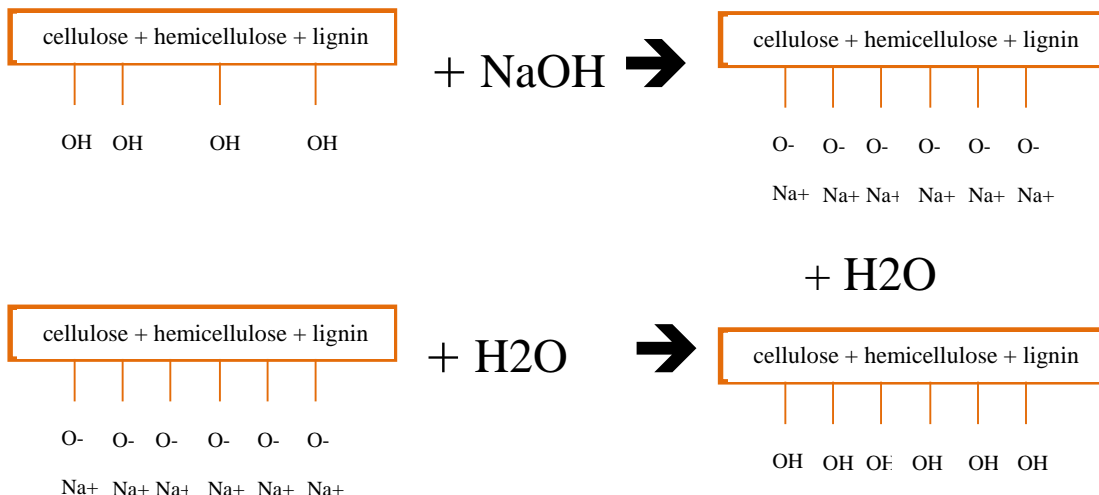
**Figure 11: Schematic of the composite interface between bamboo fiber and PLA matrix.**

## 1.6 Treatment of bamboo fibers

The characterization of the interface between fiber and matrix is largely studied in this thesis during the creation of composites. Hydrophilic natural fibers and hydrophobic polymer matrixes do not bond very well to each other. The aim of scientists is to improve the interface to produce composites with better mechanical properties. Because of this improvement, treatments of fibers are used in order to improve the surface of reinforcement. Mercerization is one common treatment for bamboo fibers. It allows the surface and bulk properties of the bamboo fiber to be modified chemically. Some mercerization, or alkali treatment, consists of treating bamboo fibers with sodium hydroxide (NaOH) in order to break hydrogen bonds and then remove impurities and amorphous cellulose [29] [30]. Moreover, this process cleans the fiber surface, and therefore improves smoothness and promotes a chemical adhesion between the natural fiber and the polylactic acid matrix [25]. In addition, this treatment allows removal of some lignin and hemicellulose present on the surface of the fiber [31] resulting in an improvement of tensile strength of composites reinforced by bamboo fiber [32]. Another contribution of this treatment is the separation of the macro fiber bundle into elementary fibers due to the removing of the lignin and hemicellulose which link the internal organization of the fibers. The alkali pretreatment causes swelling of fibers, resulting in an improvement of internal surface area [33] and therefore separation of structural bonds which link lignin and carbohydrates, finally leading to disorganization of the lignin structure [34].



Treatment with sodium hydroxide allows the creation of active hydroxyl groups present at the fiber surface and therefore enhances the chemical reaction between fiber and matrix, resulting in efficient stress transfer at the interface [35]. The chemical reaction associated with this process is shown in Figure 12. The sodium hydroxide (NaOH) reacts with the hydroxyl groups present on the surface of fibers, resulting in O<sup>-</sup>. The washing allows a reaction of O<sup>-</sup> with H<sub>2</sub>O to create more hydroxyl groups on the surface of the bamboo fiber.



**Figure 12: Mercerization of bamboo fiber, (called also alkali treatment). Sodium hydroxide allows making hydroxyl groups present on the surface of fiber**

The washing by H<sub>2</sub>O allows OH bond to be created and also allows a neutral pH to be attained [36].

One important aspect is the chemical reaction of lignin with sodium hydroxide. The chemical structure of lignin according to Adler (1977) is shown in Figure 13 [37]. Lignin is composed of complex and varied molecules of propylphenol.

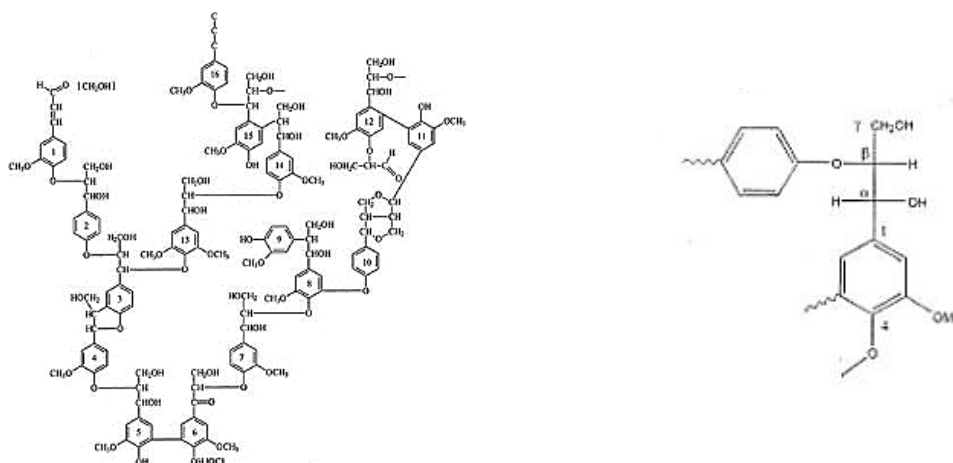


Figure 13. Chemical structure of lignin according to Adler (1977) and its reduced writing

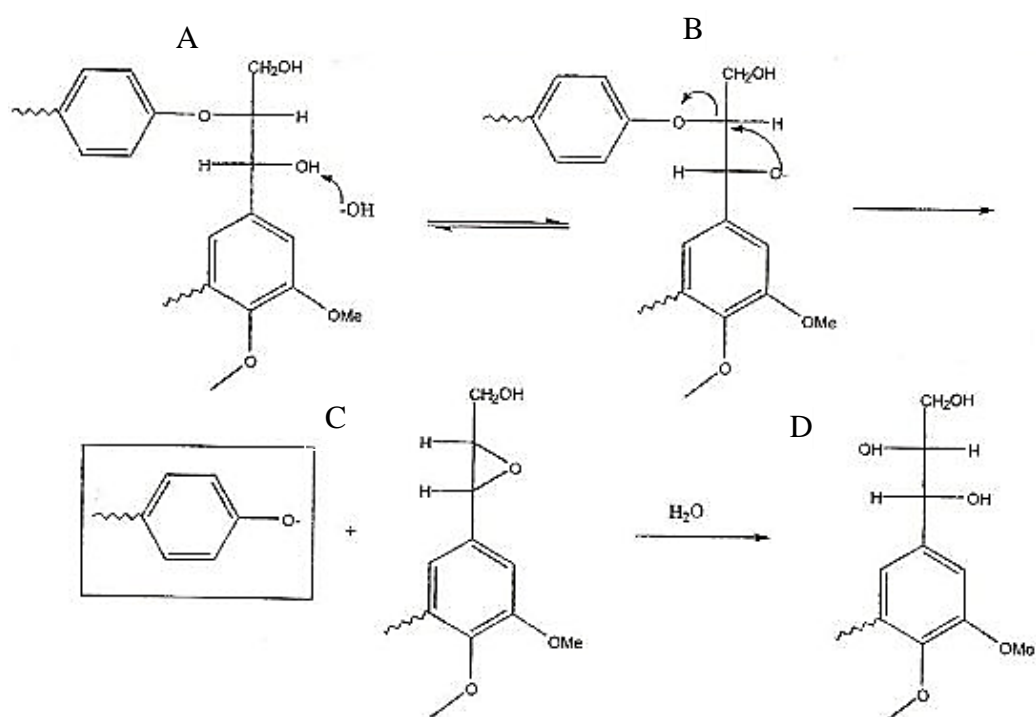
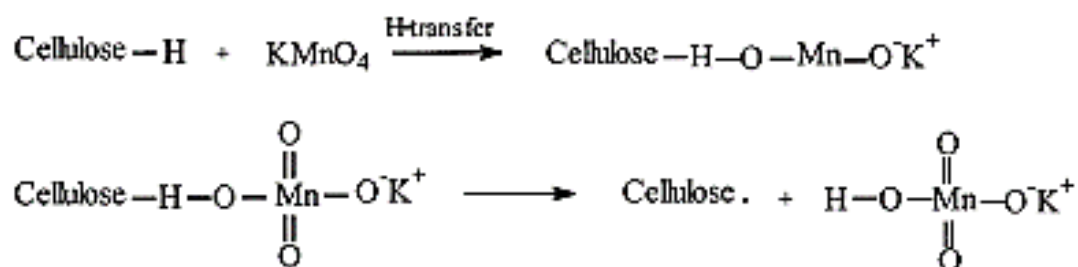


Figure 14. Mercerization allows altering the chemical structure of lignin. (A) Adding of NaOH, (B) Negative charge transfer, (C) Separation of the phenolic group, (D) Lignin hydrolyzed by H<sub>2</sub>O

The chemical reaction with sodium hydroxide allows the lignin to be transformed and altered structurally as shown in Figure 14. The adding of NaOH allows reacting hydroxide

HO- with the group hydroxide OH of the lignin structure, resulting in oxygen with negative charge O<sup>-</sup>. The negative moves until it reaches an oxygen atom which is very electronegative, and therefore the bonding between oxygen and the main structure of lignin is broken. The phenolic group is separated from the lignin and the washing by H<sub>2</sub>O allows creating OH bond on the surface of the lignin and also allows a neutral pH to be attained [36].

Permanganate treatment performed by [30] allows cellulose radical to be formed, and therefore capable to better react chemically as shown in Figure 15.



**Figure 15.** The permanganate treatment allows cellulose radical to be created in order to make it chemically active.

Another treatment, called silane treatment, allows bonds with hydroxyl groups to be formed. The first step is to hydrolyze the alkoxy group to create silanols. Then a hypothetical reaction with the cellulose, hemicellulose and lignin forms a coating. The hydroxyl groups present on the coating should help the formation of bonding with the matrix as shown in Figure 16.

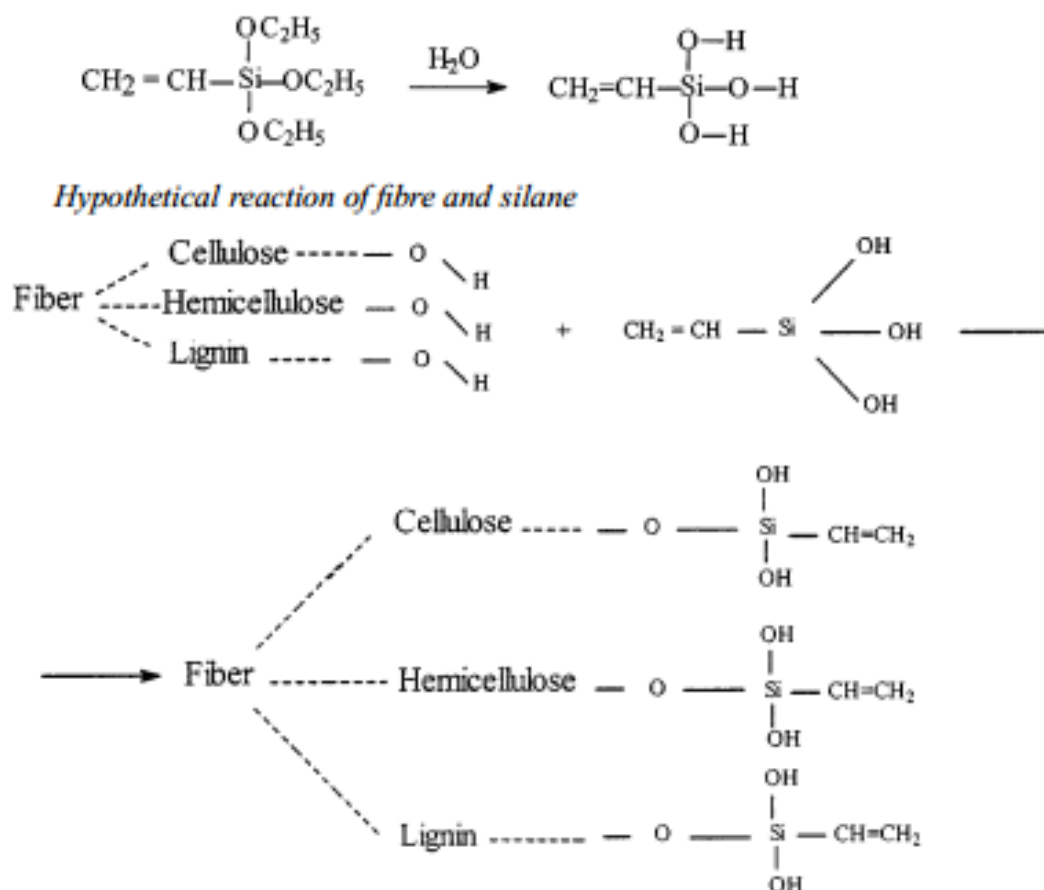


Figure 16. Silane treatment on fiber allows a coating with hydroxyl groups to be created, in order to improve the chemical adhesion [30].

Some pretreatments on structures of lignocellulosic biomass exist in the literature. The effects of these pretreatments are listed in Table 6.

**Table 6: Consequences of pretreatment applied on lignocellulosic plant mass. (++) means strong effect, (+) moderate effect, (-) not available [38]**

	Increases accessible surface area	Decrystallizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure
Uncatalyzed steam explosion	++	-	++	-	+
Liquid hot water	++	-	++	-	+
pH controlled hot water	++	-	++	-	-
Flow through liquid hot water	++	-	++	+	+
Dilute acid	++	-	++	-	++
Flow through acid	++	-	++	+	++
Ammonia fiber expansion	++	++	+	++	++
Ammonia Recycled percolation	++	++	+	++	++
Lime	++	-	+	++	++

Table 6 shows that different treatments exist for lignocellulosic plants including bamboo fibers. The ammonia fiber expansion and recycled percolation may represent a good alternative to alkali treatment to enhance the mechanical properties of the fibers for the single fiber pull-out test. The other treatments are interesting if the fibers require one of the specific tasks described in Table 6.

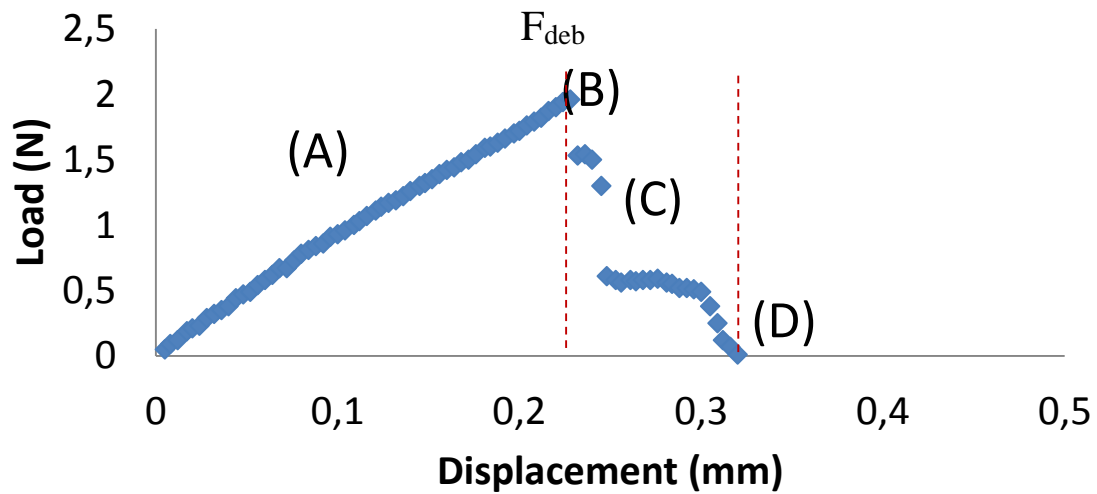
The alkali treatment was performed by [26], and it was concluded that the mercerization of fiber does not always give better mechanical properties such as material strength, however the adhesion was improved between the bamboo fibers and the PLA matrix. So

the pull-out test with treated fiber can be significant as a mechanical test to quantify the adhesion of the biocomposite.

# CHAPTER 2: SINGLE FIBER PULL-OUT TEST

## 2.1 Theory

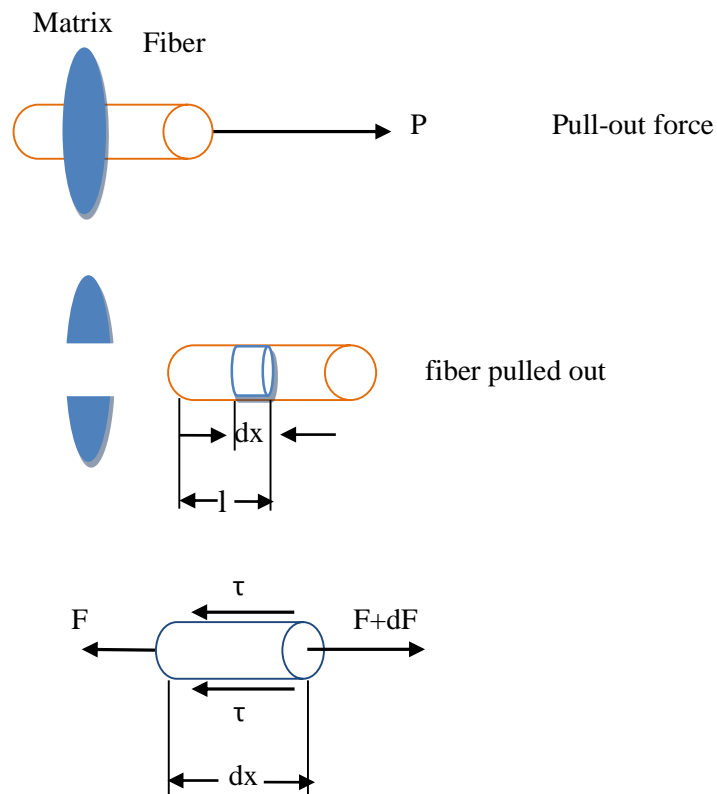
Single fiber pull out tests are largely used for studying and characterizing composites [39], [40]. This test consists of embedding a fiber in a matrix, and then performing a tensile test on the fiber. The goal of the test is to pull out the fiber until it debonds from the matrix, thus failing the interface. The force and the displacement are measured during the test. The aim is to determine interfacial shear strength  $\tau$  of the interface between the fiber and matrix.



**Figure 17: Characteristic curve of single fiber pull-out test performed in this work. Force of pull is measured as a function of displacement**

An example load-displacement curve is shown in Figure 17. It includes (A) the linear part corresponding to the tensile stress of the bamboo fiber until complete debonding.

(B) Complete debonding occurs when the interface bonds between the fiber and matrix are broken. Moreover, maximum force, called force of debonding ( $F_{\text{deb}}$ ) is measured at this stage. Then, (C) frictional sliding of the bamboo fiber appears with respect to the surrounding matrix until extraction of the fiber. (D) The end of the pull-out test occurs after the fiber is completely extracted. The interfacial shear strength between the fiber and the matrix can be determined by the model of Greszczuk [41], as shown in Figure 18. The results of the pull out test associated with the equations of shear-lag theory are used on embedded fibers in matrices with various thicknesses.



**Figure 18. Model of single fiber pull out test. The fiber is embedded in the matrix. ( $F + dF$ ) is the force of pull-out, ( $\tau$ ) is the interfacial shear strength, ( $dx$ ) is the embedded length of the fiber in matrix, ( $l$ ) length displaced**



All applied force,  $F$ , acts on a small portion of fiber  $dx$  at equilibrium. The force balance is given by

$$F - (F + dF) + (\pi D)dx\tau = 0, \quad (1)$$

where  $dF$  is the incremental charge in the force. Rearranging Eq.(1) gives,

$$\frac{dF}{dx} = \pi D\tau. \quad (2)$$

The strain,  $\varepsilon$ , in the fiber is given by

$$\varepsilon = \frac{dl}{dx} = \frac{E}{\pi \times D^2/4 \times E_f}, \quad (3)$$

where  $l$  is unstretched length and  $E$  is the modulus of elasticity. The shear strain in the matrix is given by

$$\varphi = \frac{l}{b}, \quad (4)$$

where  $b$  is the effective width of the fiber/matrix interface. The relationship between stress and strain gives

$$\varphi = \frac{\tau}{G}. \quad (5)$$

By combining Eqs. (4) and (5), the shear strength is given by

$$\tau = l \frac{G}{b}. \quad (6)$$

Substitution of Eq. (7) into (3) and (4) gives

$$F'' - \alpha F = 0, \quad (7)$$

with  $\alpha = \left[ \frac{2G}{brE_f} \right]^{1/2}$ .

The solutions of Eq. (7) are

$$F = A \sinh \alpha x + B \cosh \alpha x \quad , \quad (8)$$

where  $A$  and  $B$  are two constants which are determined by boundary conditions. As shown in Figure 18, these conditions are

$$\begin{aligned} F &= P, \text{ at } x = 0 \\ F &= 0 \text{ at } x = l. \end{aligned} \quad (9)$$

The final solution for all  $x$  is then

$$\tau = \frac{P\alpha}{\pi D} (\sinh \alpha x - \coth \alpha l \cosh \alpha x). \quad (10)$$

The average shear stress is found by integrating Eq. (10) from 0 to  $l$  such that

$$\tau_{ave} = \frac{P}{\pi D l}. \quad (11)$$

In this case, Eq. (10) can be written as

$$\frac{\tau}{\tau_{ave}} = \alpha l (\sinh \alpha x - \coth \alpha l \cosh \alpha x). \quad (12)$$

At  $x = 0$ , the shear stress is maximum:

$$\frac{\tau_{max}}{\tau_{ave}} = \alpha l \coth \alpha l. \quad (13)$$

When  $\alpha l \rightarrow 0$ ,  $\lim_{\alpha l \rightarrow 0} \frac{\tau_{max}}{\tau_{ave}} \rightarrow 1$ , that is to say

$$\tau_{max} \rightarrow \tau_{ave}.$$

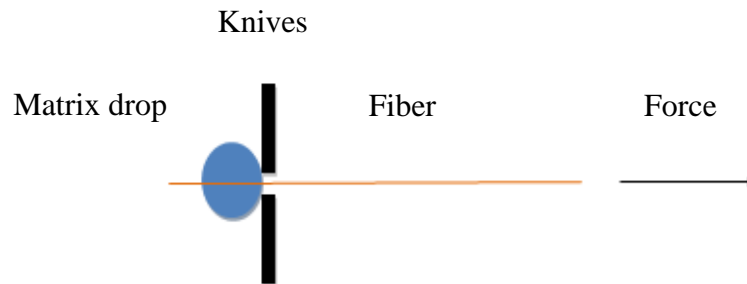
This model allows the interfacial shear strength  $\tau$  to be calculated as :

$$\tau = \frac{F_{deb}}{\pi D_f L_{emb}}, \quad (14)$$

where  $\tau$  (MPa) is the interfacial shear strength and  $F_{deb}$  (N) is the force required to break interface bonds. Concerning the morphological parameters,  $D_f$  (mm) is the diameter of fiber and  $L_{emb}$  (mm) is the embedded length of the fiber in the matrix.

## 2.2 Microbond tests

The microbond test is another method to characterize the interface between fiber and matrix. It is used largely in research in composites as the pull-out test described previously [42]. However, sample preparation is slightly different than for a pull-out test. Indeed, microbond tests consist of depositing a melted matrix drop onto a fiber. Then, using a restraint system that includes sharp edges, the fiber is debonded from the drop of matrix.



**Figure 19. Schematic of a microbond test**

Force and displacement are also measured during this test, in order to calculate the interfacial shear strength  $\tau$ . The advantage of this process is control of the embedded length.

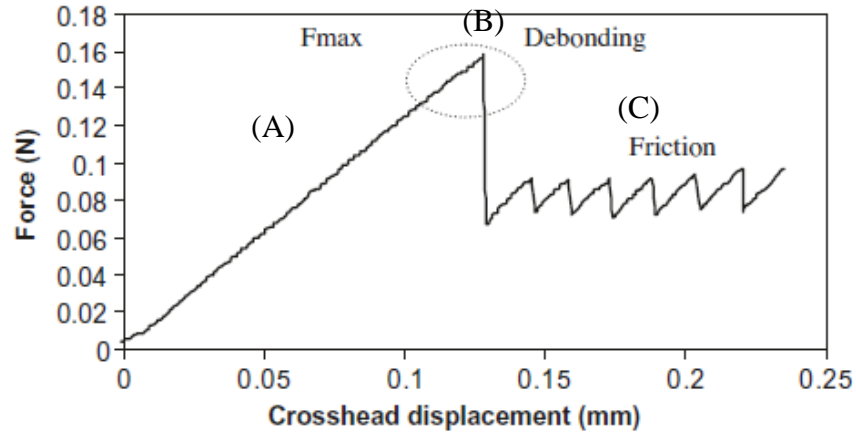


Figure 20: Characteristic curve of a microbond test

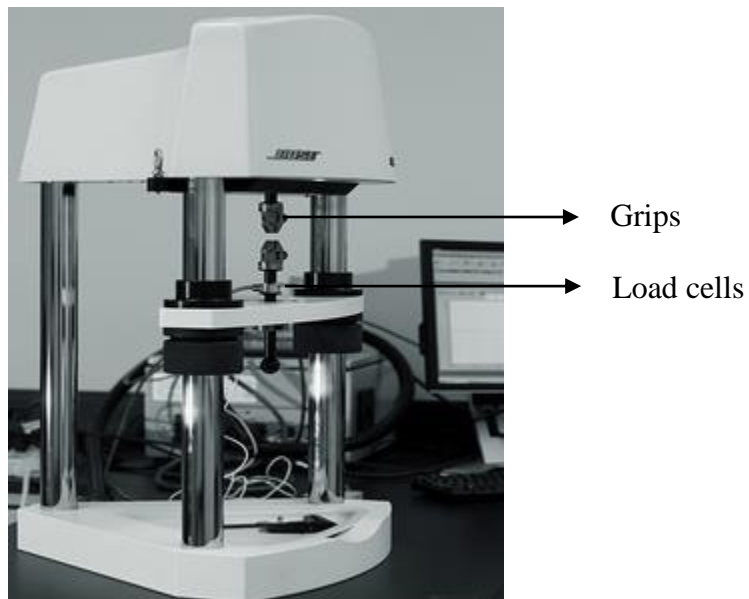
An example result from a force-displacement measurement is shown in Figure 20. (A) The linear part corresponds to the tensile part of the fiber until the (B) complete debonding of interface between fiber and matrix. (C) The frictional part is logically more important than for the pull-out test because the drop of matrix is still connected with the fiber after debonding.

Interfacial shear strength is determined by the same equation as the pull-out test, Eq. (14).

## 2.3 Experiments

### 2.3.1 Detailed Description of the Bose instrument:

For this work, the pull out test is realized with a Bose ElectroForce 3200. It allows measurement of the load and the displacement with a high level of precision during an advanced mechanical test. The maximum applied force is 225 N for the instrument shown in Figure 21. It has a static mode and can perform dynamic tests up to 200 Hz. The device is designed in order to accept several engineered materials test applications. Torsion tests, tensile tests and creep (dynamic) can be performed.



**Figure 21: Bose Electroforce 3200 device**

The BOSE Company has three different grips adapted for the tests. The standard grip, shown in Figure 22, is used essentially for dynamic mechanical analysis. It could be useful to perform the pull out test. However, the design of the sample needs to be thought of in relation to the characteristics of the grip. Firstly, the grip allows samples with a maximum width of 12.5 mm (0.50 inch) to be tested. Secondly, the maximum length provided by the clamp is 8.4 mm (0.33 inch). The polylactic acid matrix sample has to be designed to be held by this grip, that is to say the width of the sample must not exceed 12.5 mm and the length must be less than 8.4 mm. Moreover, the force capacity of this grip is 450 N (100 lb). The maximum applied force being 225 N, the capacity of this grip is large enough to support the force applied by the test. Furthermore, the clamp design works with a knurled screw for locking the sample into the grip tightly.



**Figure 22: Grips  
Standard Dynamic  
Analysis**

Titanium T/C Grips as shown in Figure 23, are for flat specimens. The technical name of these grips is GRP-TC-Ti450N-F. The “Ti450N” means that the grips are made of titanium and they have a 450 N force capacity. The design of future samples must be considered also directly



**Figure 23:  
Titanium T/C  
Grips**

in relation to the characteristic of this grip. The maximum specific width reaches 25 mm (1.00 inch) and the maximum length is 8 mm (0.37 inch). These dimensions mean that the sample will have a lower width and a lower length in order to be held by these grips. Similarly to the previous grip, the force capacity reaches 450 N (100 lb). However, the

system of locking is ensured by hex drive nuts on each side. Finally, the clamp is lightweight (79 grams) which contributes to the precision of the measurement.

Platens, shown in Figure 24 are used for other advanced mechanical tests such as compression tests. They are not useful for tensile tests on single fibers embedded in a PLA matrix, but the sample can be designed in order to “push out” the fiber instead of pull out [43]. In this case, the platens can be an option to measure the load and displacement to push out the fiber incorporated in the matrix.



**Figure 24:**  
**Compression platens**

One important and necessary electronic component used to perform the analysis is the load cell. The two load cells shown in Figure 25 allow the low force in tensile/compression tests to be measured with a high level of precision. The force capacity of the two sensors is 220 N for the bigger cell and 22 N for the smaller one. The tests here were performed initially with the 220 N load cell, but subsequent tests and those shown in this thesis were performed with the 22 N load cell because it is more precise for the load range necessary for these tests.



**Figure 25: Load cells**  
**220N      22N**

### 2.3.2 Sample preparation

Selecting fibers and arranging them according to their surface uniformity along the fiber is the first step to prepare the sample. Fibers of grade 1 and grade 2 have average lengths around 6 to 160 mm. Their densities are around  $90 \text{ kg/m}^3$ . The first step is to select the best candidates to create a sample for the test. One of the particularities of bamboo fibers is that the surface is not uniform along the fiber. Sometimes, the elementary fibers are still connected with lignin and hemicellulose. Therefore, the different fibers form a bundle which is not meaningful for a single pull-out test. The interest of the study is to understand what connections there are between the surface of the fiber and the surface of the PLA. The fibers can also have different thicknesses along the fiber. The smaller part of one fiber creates a weak point for a mechanical test because it may break before the interfacial debonding and that disturbs the measurement of the pull out test. Thus, it is clear that the fibers should be as uniform as possible.

Once the fibers are arranged, the aim is to observe and measure the diameters with a microscope to determine the size distribution of the fibers. This information is needed to calculate the interfacial strength. As the diameter varies along the fiber, an average value of all measurements is then calculated. A representative average is, at minimum, 5 measurements. The next step consists of creating a PLA matrix with the hydraulic press press manual SPECAC 25T with PLA pellets PLI003

The creation of the PLA matrix is very important for the debonding of fiber of the interface during the pull-out test. First of all, the PLA pellets must be totally dried for this experiment to avoid the formation of air bubbles at the interface between the fiber and the PLA.



Another important parameter is the thickness of the matrix. It must be large enough to keep the fiber incorporated and thin enough that the fiber does not break during tensile test. For that, a washer with a thickness of 840  $\mu\text{m}$  is used to get the specific matrix for the test.

The first step is to know how many pellets are required to fill the hole of the washer. The thickness  $e$  is 840  $\mu\text{m}$  and the inside diameter  $D_i$  of the washer is 34 mm. Polylactic acid has a density  $\mu$  of 1.25kg/m<sup>3</sup> (provided by the manufacturer). The mass  $m$  of pellets required can be determined approximately as

$$m = \pi(D_i/2)^2 e \mu.$$

In this experiment, the total mass  $m$  required of pellets is around 3.81g. Furthermore, one pellet has an average mass  $m_1$  around 0.15-0.16 g. Thus, the total number of pellets needed is given by

$$n = m/m_1.$$

Therefore, the number of the pellets required to obtain a matrix with a thickness of 840  $\mu\text{m}$  is around 23-25. Then, the creation of the thin matrix can be initiated. First of all, aluminum foil should be cut precisely to the size of the diameter inside the washer. On one side of the aluminum foil, holes are created with a hole punch to design the sample. The other side provides support for the sample. The aim is to coat the matrix of PLA with aluminum foil. Not only does the foil allow for cutting the matrix very easily, but also it allows the PLA to be distinguished better under the microscope. Then, 23-25 pellets are placed in the washer with a thickness of 840  $\mu\text{m}$ . Furthermore, adding of Teflon paper above and below the hole of the washer is useful to ensure non-adhesion between the melted plastic and the

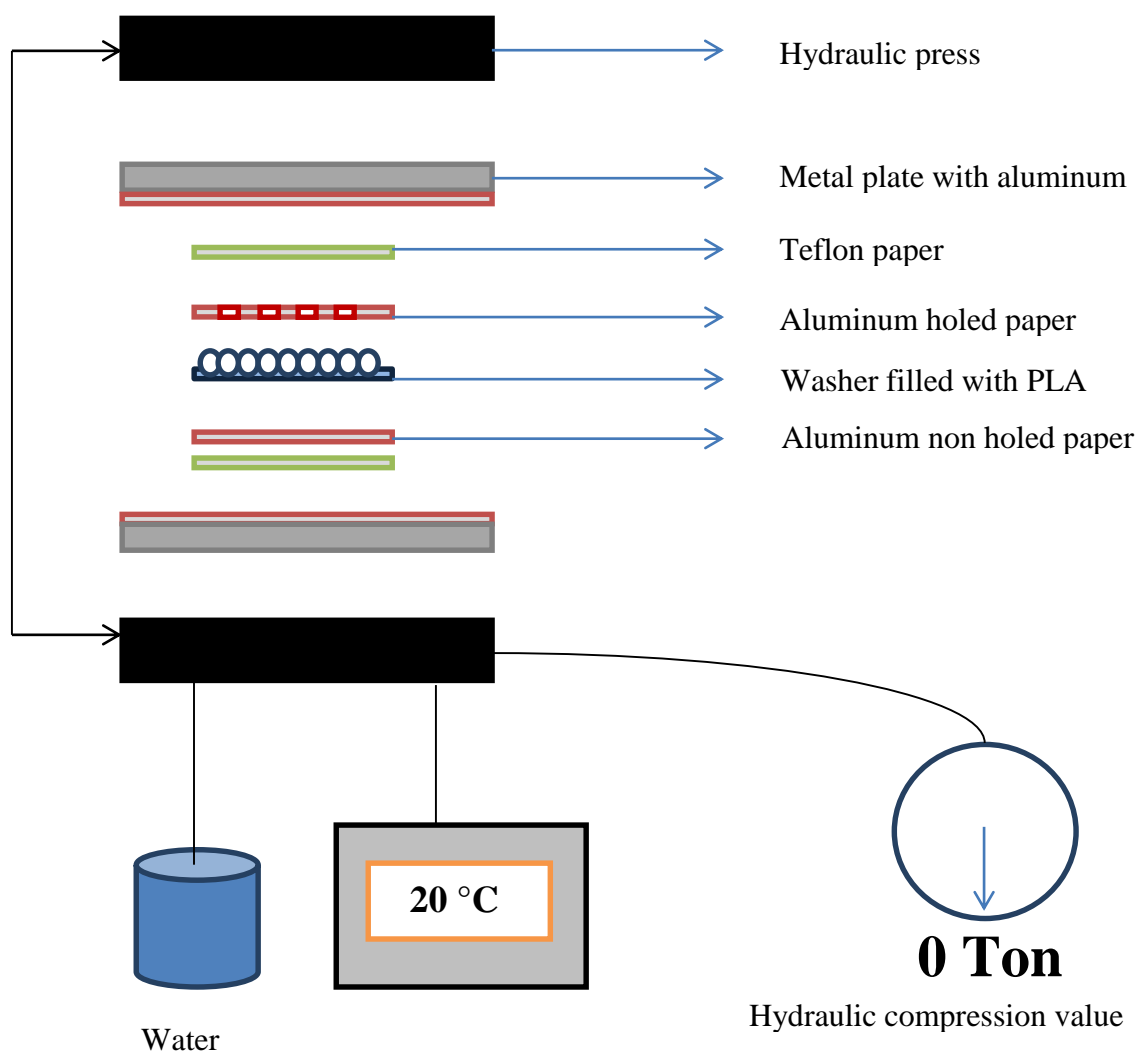
metal plates. Finally, two metal plates (themselves coated with aluminum) are used to support the compression to obtain the finest possible matrix.

Four washers of different thickness were used and Table 7 summarizes their dimensions.

**Table 7: Dimensions of washers used to create the samples**

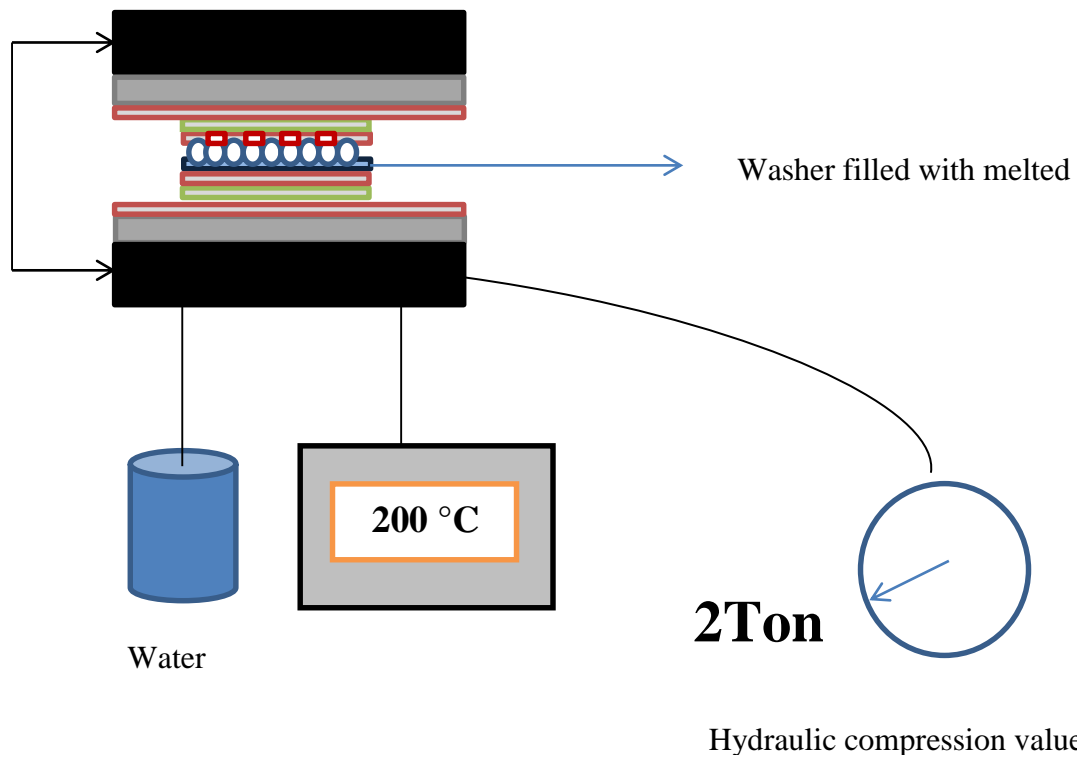
	Washer 1	Washer 2	Washer 3	Washer 4
Diameter inside (mm)	34	38.16	44.56	44.40
Thickness (mm)	0.84	0.15	0.65	0.55
Number of pellets	23-25	5-6	8-9	6-7

The hydraulic press is used in order to create the sample. Two metal plates coated with aluminum allow the PLA placed inside the washer to be compressed. Some Teflon paper is used in order to prevent the adhesion of the melted PLA with metal plate coated with aluminum. Aluminum holed paper is placed to make the PLA matrix appear in the designing of the sample. The order of the materials within the press is shown schematically in Figure 26.



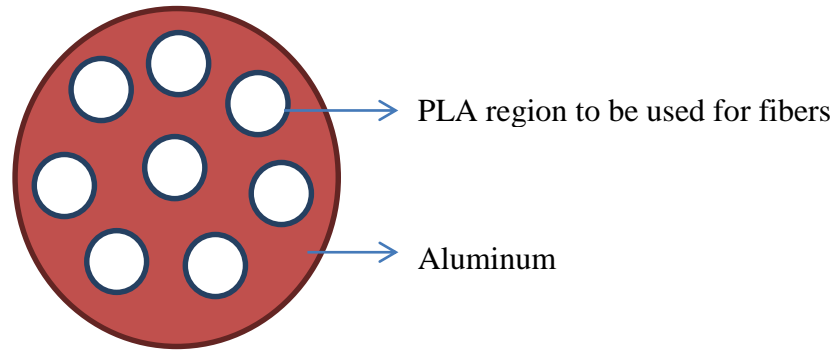
**Figure 26: Schematic of the the initial step to create poly(lactic acid) matrix sample by using a heated hydraulic press**

After all materials are inside the press, it is heated to 200°C. The melting temperature of the pellets of PLA is 145-155°C (manufacturer data). The pellets need to be melted before the compression. After that, the plates are pressed at 2 tons for 2 minutes.



**Figure 27: Schematic of the final step to create polylactic acid matrix sample by using a hydraulic press**

After that the sample is removed and allowed to cool for 1 minute. Then the Teflon paper is removed from the matrix with similar holes. A schematic of the top view of the sample is shown in Figure 28.



**Figure 28: Samples obtained after hydraulic press**

The cutting of the different samples needs to be made after the drying (easy to do with aluminum). The thickness of the matrix obtained is measured with a caliper and then listed in an Excel table. Another technique can be used to measure more precisely the thickness of the different samples (see the profilometer description).

First of all, the bamboo fibers need to be completely dried in order to avoid weakening the interface [44]. The test consists of incorporating single fibers into the melted thin surface of polylactic acid. The goal is to get the fiber as perpendicular as possible in relation to the surface. Therefore, the fiber is embedded in the polylactic acid when the sample is dried.

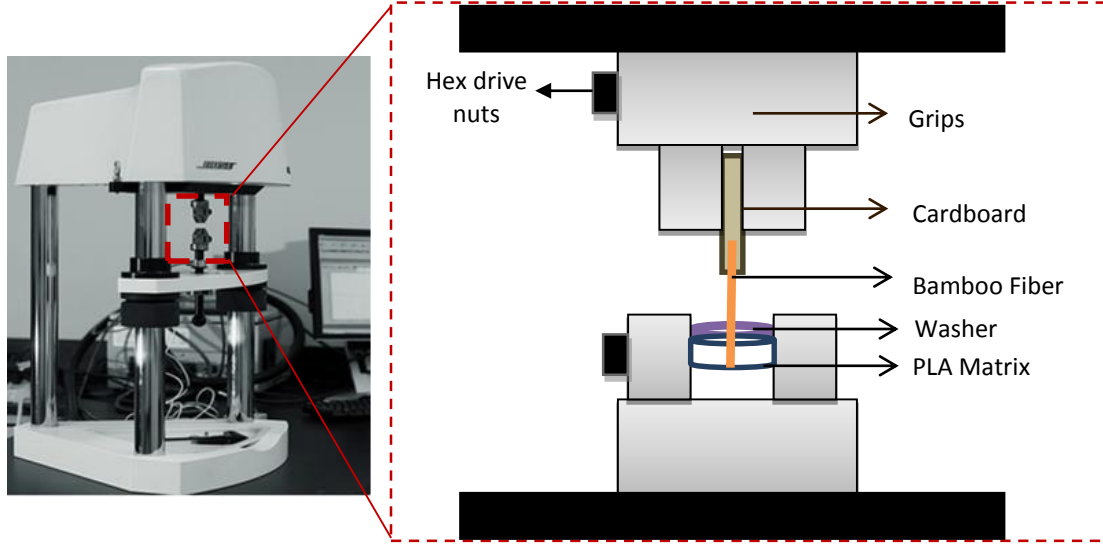
## **2.4 Methods**

### **2.4.1 Pull out tests**

The pull out tests are performed with the Bose ElectroForce 3200 described previously. The samples need to be designed in relation to the shape and the size of the different grips of the Bose device. The two potentially adapted grips used are standard dynamic analysis and titanium T/C grip. They are sized similarly but their shapes vary. Indeed the titanium T/C grip is more adapted for flat specimens than the standard grip. Moreover, the system of locking is ensured by hex drive nuts, thus facilitating placement of the sample in the clamps.

The software used to treat all the data is “WinTest”. It allows the load and displacement measurements to be recorded into numerical data.

The most important step is the preparation of the samples in order to adapt them to the titanium T/C grip. The sample obtained previously is in the form of a small cylinder of low thickness (a function of the thickness of the washer). As shown in Figure 29, the single bamboo fiber is glued with MultiTemp<sup>®</sup> [45], on a cardboard tab more easily clampable than the bamboo fiber alone. A washer is also placed to avoid the sliding of the PLA matrix in the grips. 74 tests with untreated fibers and 17 tests with untreated fiber were performed and with a rate of 0.005 mm per second and a load cell of 22.5N



**Figure 29: A schematic zoom of the single fiber pull-out test performed with the BOSE device**

### 2.4.2 Microscope imaging

Once the pull-out test is completed, the interface between the fiber and the matrix is observed with a microscope. Such observations are needed to interpret the results obtained. The interface is essentially observed in order to determine whether the fiber slides over the interface, or if a portion of the fiber remains.

The qualitative analysis of the tip of fibers after the test can be used to provide another interpretation of the data measured. Usually, the embedded length should be obvious under the microscope. The embedded lengths of all samples vary from 230-1137  $\mu\text{m}$  according to the thickness of all matrices. The microscope lens is used at a  $10\times$  magnification, so that images are made from which geometric measurements can be taken. The microscope used is an Olympus BX51 / BX52 [46].

Microscope images require appropriate parameters such as brightness and focus in order to precisely observe the fibers and the tip of fibers. The PLA matrix is also observed by scanning electron microscopy (SEM) because of the transparent properties of polylactic acid. With this approach, the hole in the matrix can be observed in greater detail.

### **2.4.3 Mercerization of fibers**

This part of the project consists of performing a treatment on the bamboo fibers with a solution of sodium hydroxide (NaOH) in order to remove lignin from the surface and to give better interfacial properties. Some treatments given in the literature have been shown to improve mechanical characteristics of natural fibers [31] [4]. Indeed, interfacial shear strength of bamboo fiber/PLA composites is supposed to increase with a smoother surface of fiber and therefore a better interface between the fiber and matrix. The treatment here consists of immersing the bamboo fibers in a beaker filled with a solution of 5% NaOH. This concentration is expected to be efficient and not destructive [32].

The treatment consists of using a solution of sodium hydroxide NaOH of  $97 \pm 1.5\%$  purity. Bamboo fibers are from Bamboo Fibers Technology [47]. The solution of sodium hydroxide (NaOH) used is in the form of pellets as shown in Figure 30.

The first step consists of weighing 50 grams of sodium hydroxide pellets (221465-500G from SIGMA-ALDRICH, ACS reagent  $\geq 97.0\%$ ), with a classic balance (Shiferscientific A250) and to put it in a 1 liter beaker. Then, the beaker is completely filled with water.

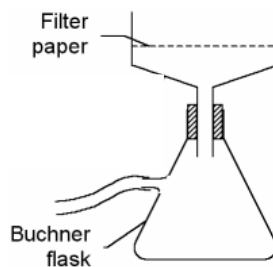


Thus, the weight concentration is 5 wt% and the grade 1 and grade 2 bamboo fiber can be added in the beaker to be mercerized by sodium hydroxide.



**Figure 30: Hydroxyde de sodium NaOH are in pellet form**

Then, a plastic tray with a filter paper allows the bamboo fibers to be retained and washed with filtered water.



**Figure 31: After the treatment with NaOH, the washing of fiber is made by Buchner flask**

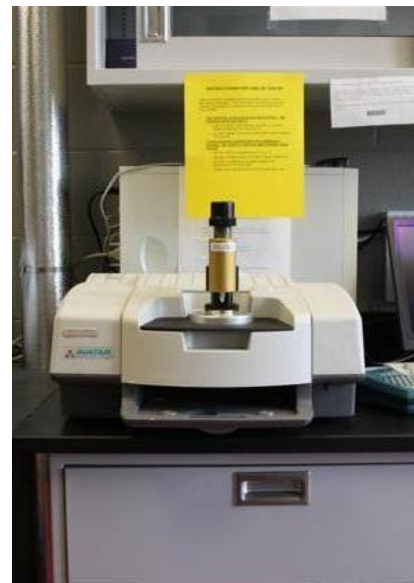
The fibers are cleaned in filtered water with a Buchner flask, as illustrated in Figure 31. Cleaned bamboo fibers are placed on a plate coated with an aluminum foil in an oven at

80 °C. The fibers are dried for 24 hours and then they are ready to be selected as a potential candidate for a single fiber pull-out test.

#### 2.4.4 Infrared measurement

Once the mercerization was performed on the bamboo fiber, infrared measurements were made in order to compare the surface and internal composition before and after the treatment. Two films of bamboo fibers before and after treatment have been created with the hydraulic press described previously.

The device shown in Figure 32 is a Nicolet Avatar 360 FT-IR with a maximum resolution of 0.5 wavenumber.

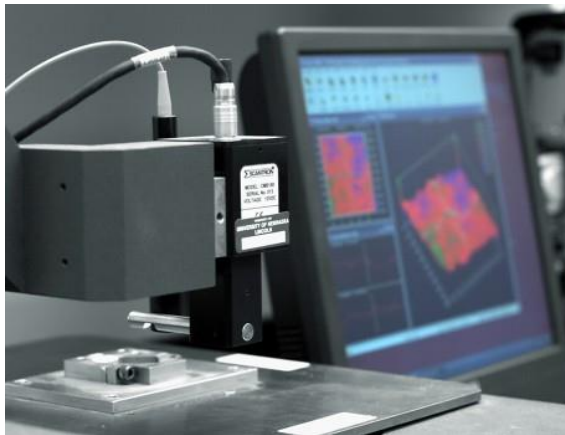


**Figure 32: Nicolet Avatar 360 FT-IR. Infrared device**

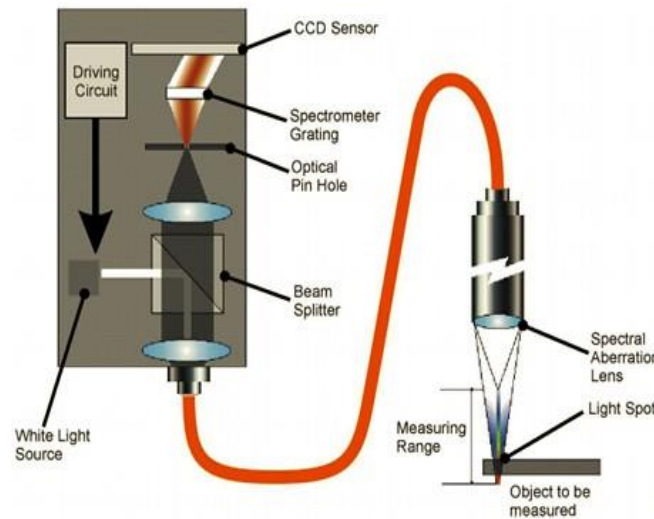
The range of analysis is around 400 to 4000 wavenumber [48], meaning that the device is mid-IR and rather common. The attenuated total reflectance (ATR) technique is used with this device [49]. In particular the sample can be placed directly on the stage, compressed by a crystal support, which allows the sample position to be maintained during the measurement.

### 2.4.5 Profilometer

The profilometer allows the surface to be measured in three dimensions for many applications. The aim is to determine the profile of the samples here with high precision. Once the pull-out test has been completed, the samples are divided in two parts: the removed fiber and the matrix with hole. One scan of the profilometer consists of measuring the ratio of the visible rays sent and reflected with a light sensor. The software calculates the surface area to standard ISO roughness with normalized peak count. Therefore, it plots the surface profile of the sample with a 3D profile. The height resolution of the probe sensor is 5 nm with 1,000 points per second.



**Figure 33: Scantron Proscan 1000 Profilometer**



**Figure 34: Schematic of profilometer process [51]**

The (S-Type) chromatic technique is the principle of this system as shown in Figure 34. It consists of reflecting a white light with a beam splitter in order to send the light in the measurement head. The white light is focused in the spectral aberration lens which allows for different wavelengths to be used at various positions in the measurement range. One specific position of the object corresponds to one wavelength of light. The returning light passes through the lens and the optic cable. It is then brought through the optical pin hole and deflected by a spectrometer grating into a CCD sensor. The position of the object is determined with the wavelength of the sensor and the position of the light on the CCD sensor.

The device includes two different types of sensors, S 5/03 and S 38/3, for different applications. Table 8 lists the features of the different sensors [50].

**Table 8: Two sensors available with the profilometer, and their characteristics**

Sensor	Resolution (μm)	Measuring range (mm)	Spot size (μm)	Technology
S5/03	0.01	0.3	4	Chromatic
S38/3	0.1	3.0	10	Chromatic

The geometry of the polylactic acid matrix requires a high resolution and a high measuring range. Indeed the embedded lengths of fibers in the matrix studied here are around 230-1137 μm. This characteristic requires the S38/3 sensor in order to measure the depth of the hole matrix after the pull-out test.

A profilometer analysis corresponds to a scanning of the measurement head on the surface. Indeed, the holes performed by the pull-out test have a rough surface and an unusually large diameter for the device. The S38/3 sensor is inconvenient with its resolution. The scanning seems to be insufficient to see the entire hole.

The idea is to focus the light of the measurement head in the middle of the hole as deep as possible. Then, the scanning will allow for a more precise measurement of the height of the hole.

The total surface area will be calculated with the function  $A = 2\pi rL$ , where  $A$  is the surface area (mm<sup>2</sup>),  $r$  is the radius of hole (mm), and  $L$  is the depth of the hole (mm).

#### **2.4.6 Scanning Electron Microscopy**

After testing single fiber pull-out test samples, a scanning electron microscope (SEM) shown in Figure 35, is used in order to visualize precisely, the interfaces at the microscale. SEM images are obtained by bombarding electrons on to the surface of a specimen. The

interactions between the electron beam and the surface will create secondary and backscattered electrons which are detected by sensors described in Table 9. Then, images of the precise topography of the surfaces of the specimen are obtained which allows the tests in this study to be interpreted. Because of this high precision, pictures give more information about the composite characteristics such as rupture profile bond/debonding between fiber and matrix, as well as surface aspects before/after treatment. The device used is the Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) which includes a field emission gun electron source (FEG) placed inside a high pressure chamber. A low vacuum mode is available to observe nonconductive objects such as plastics and fibers, papers. Indeed three modes of vacuum can be chosen: ESEM (10-2600 Pa), low-vacuum (10-200 Pa) and high-vacuum ( $6.10^4$  Pa). Seven samples can be placed on a motorized stage. Concerning detectors systems, there are many for each mode as shown in Table 9. Finally, images were taken at several different magnifications (100× to 2500×).

**Table 9: Detectors used in SEM analysis in function of the mode chosen**

high vacuum mode	low vacuum mode	high and low mode	ESEM mode
Everhart- Thornley detector	Large field, gaseous secondary electron dectector	Solid state backscattered electron detector optimized for low kV (until 3kV)	Gaseous secondary electron detector



**Figure 35. The Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM)**

## CHAPTER 3: EXPERIMENTAL RESULTS

### 3.1 Untreated fibers

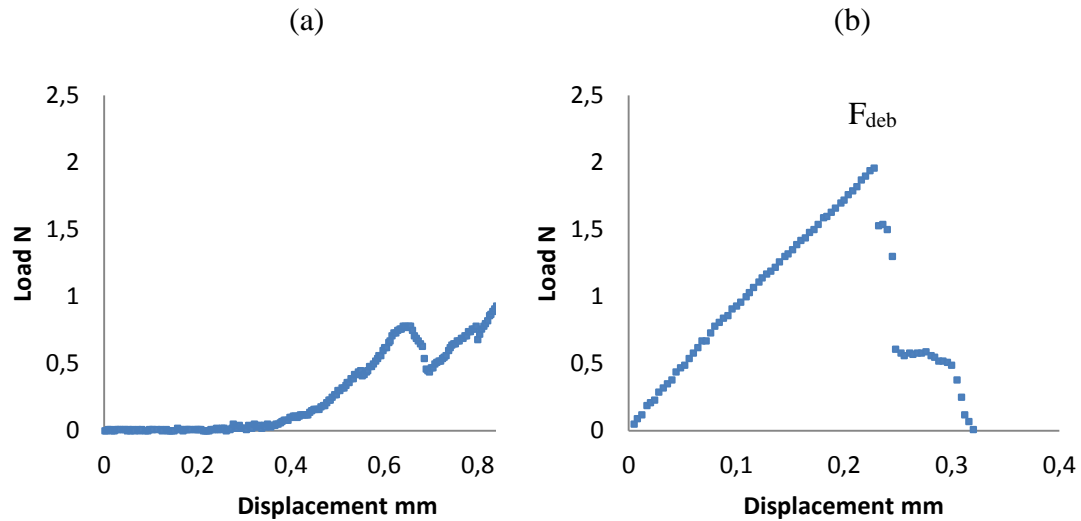
The aim of this study is to evaluate the interfacial shear strength  $\tau$  between PLA and bamboo fibers by performing single fiber pull-out tests. The first pull-out tests were performed on untreated fibers (without mercerization). 74 tests were performed; 38 were successful and could be interpreted to find the interfacial shear strength, whereas 36 tests failed. A test was considered as failed when the load applied on the sample did not allow the fiber to debond from the matrix. Indeed, some bamboo fibers broke before the interface was stressed, and occasionally the fiber and/or the matrix slid between the grips. Otherwise, the interfacial shear strength was interpreted as the fiber loaded until debonding and complete extraction from the matrix.

For every successful pull-out test, images of the whole length of each fiber were taken using a microscope to measure the diameter. This parameter has to be quantified in order to determine the interfacial shear strength as described by Eq. (14) in Chapter 2. The maximum force  $F_{deb}$  has also to be evaluated for each test, while the embedded length was found by measuring the thickness of the matrix (the embedded length is assumed to be equivalent to the thickness of the PLA matrix). The value of interfacial shear strength obtained was  $\tau = 4.1 \pm 3.3$  MPa. First of all, the standard deviation (3.3 MPa) is quite high as compared to the average value of  $\tau$ . The following interpretations aim to explain and understanding how and why the measurements are dispersed as the experimental results



have shown. The natural properties of the bamboo fibers and of the bio-sourced PLA matrix are the first reason for such a wide data dispersion. Some mechanical tests, including pull-out and microbond tests performed, were reported in the literature explaining that data dispersion is due to the non-homogeneity of the surface and to the size of the bamboo fibers [51]; thus a morphological study on the bamboo fibers employed in this work may be useful to explain the results obtained. For future interpretations, it is necessary to understand that every bamboo fiber is actually a bundle of elementary fibers, as shown in Figure 5. Figure 36 shows two examples of characteristic curves as obtained during the pull-out tests considered as successful. Figure 36 (a) reveals that some steps may occur during the tensile part of the test, meaning that the elementary fibers forming the bundle break before the interface starts to get stressed as the tensile test proceeds. When phenomena like this occur (cohesive failure as single bamboo fibers are pulled out from within the bundle of fibers), the pull-out test cannot be considered as efficient as expected to determinate the interfacial shear strength (in this case, the interface being stressed is the one connecting two elementary fibers within the same bundle). On the other hand, Figure 36 (b) refers to the ideal pull-out test, in which the tensile portion of the recorded curve is linear until the fiber completely debonds from the polymer matrix; this kind of result is the one potentially suitable to find the load ( $F_{deb}$ ) to be used to determine the interfacial shear strength  $\tau$ . None of the fibers in the bundle broke during the test, therefore the maximum force measured by the Bose corresponds to the force required to debond the fiber from the surrounding matrix and to pull it out. After debonding, the fiber is probably still connected to the matrix by friction or interlocking connections, which is the reason why the extraction

of the fiber does not correspond to a linear curve and a simple (linear) reduction of the load. The end of the pull-out test occurs when the fiber is totally extracted from the matrix and the measured load goes back to 0 N.



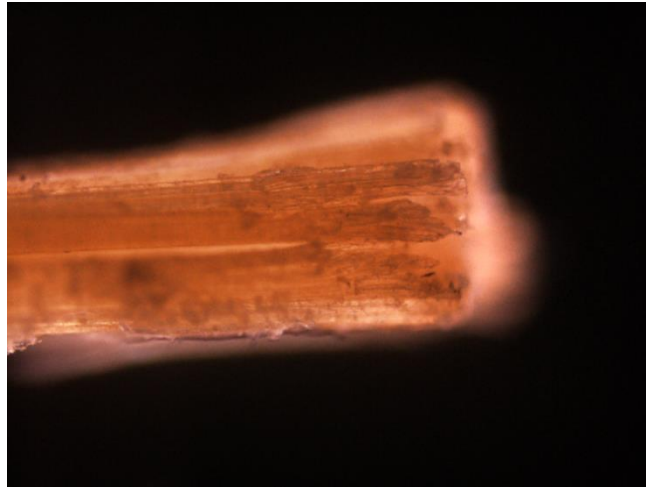
**Figure 36.** On the left, a single fiber pull-out test is considered as failed because some elementary fibers were broken during the tensile part, thus data do not quantify the interface of the bio-sourced composite. On the right, a pull-out test considered as successful and therefore interpretable to quantify the interface.

As suggested before, a morphological study of the bamboo fibers considered for testing may be important to characterize their surface and to interpret the results obtained for the interfacial shear strength and the corresponding data dispersion. A first macroscopic naked-eye inspection of the fibers can be made during sample preparation, as some fibers have “uniform” size along their whole length whereas other fibers appear macroscopically distorted due to their natural properties. In the literature, the diameter along the length of bamboo fibers was subjected to a systematic study as most of the natural fibers have intrinsically dispersed properties [14]. For this reason, each fiber candidate to be pull-out

tested was analyzed by optical microscopy (Olympus BX51 / BX52 system). The diameter was estimated over 5 measurements and the pull-out test was considered as inefficient whenever the data dispersion was too high. The tips of every fiber were also observed before and after the pull-out test to determine what kind of constraints the tip of the fiber embedded in the polymer matrix experienced. Figure 37 shows an example of a fiber tip which is not well preserved after the pull-out test, whereas sometimes the fiber tip is well preserved even after the test, as shown in Figure 38. The fact that elementary fibers break and separate during the pull-out test, as shown by some features of the recorded curves, proves that the corresponding tests do not allow the interface of the fiber and the matrix to be actually stressed and interpreted. In order to distinguish “regular” from “irregular” pull-out tests, the fibers were classed as “uniform” or “non-uniform” on the basis of the results obtained during (curves) and after (tips) the pull-out.

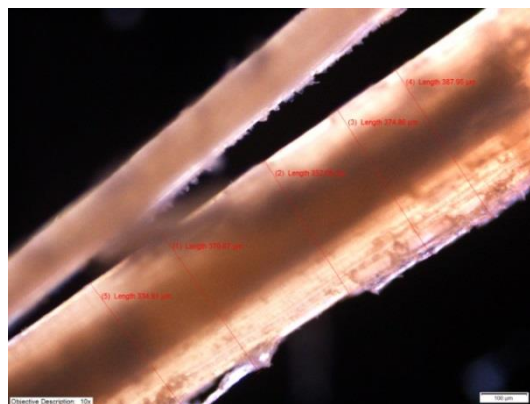


**Figure 37: Tip of a bamboo fiber which is not well preserved, as observed by optical microscopy (10 x magnification) after a pull-out test considered as “non-uniform” (“sample with problem”). Elementary fibers got separated as a consequence of the pull-out test.**



**Figure 38: Tip of a well preserved bamboo fiber, as observed by optical microscopy (10x magnification) after a pull-out test considered as “regular” (“uniform sample”). Elementary fibers remained connected even after the pull-out test.**

The microscope also provided information about whether the fiber underwent a separation of its elementary fibers during the pull-out test, as proved by the example shown in Figure 39. In this case, the diameter of the fiber is nevertheless measured, but the fiber is considered as “non-uniform” and the interface cannot be precisely characterized. Scanning electron microscopy is also used to provide a better picture with higher resolution.

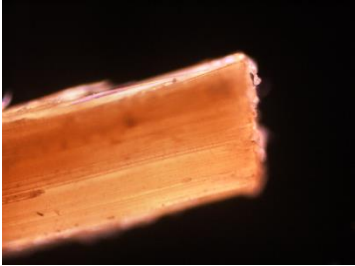


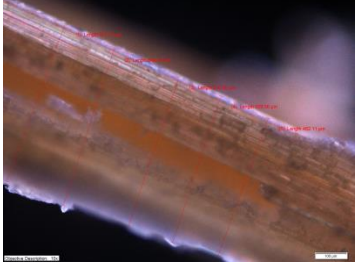
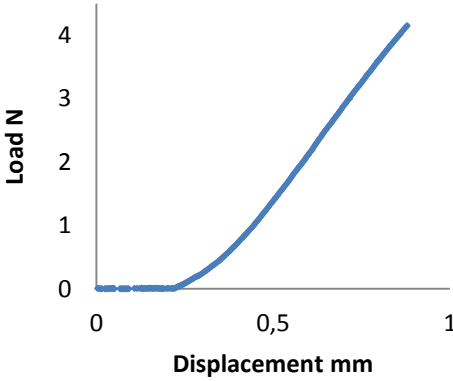
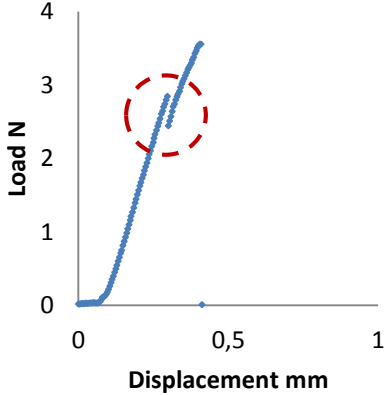


**Figure 39: Bamboo fiber as observed by optical microscopy (10× magnification). A separation of the elementary fibers is detected after the pull-out test.**

The results obtained from the pull-out test measurements are summarized in Table 10.

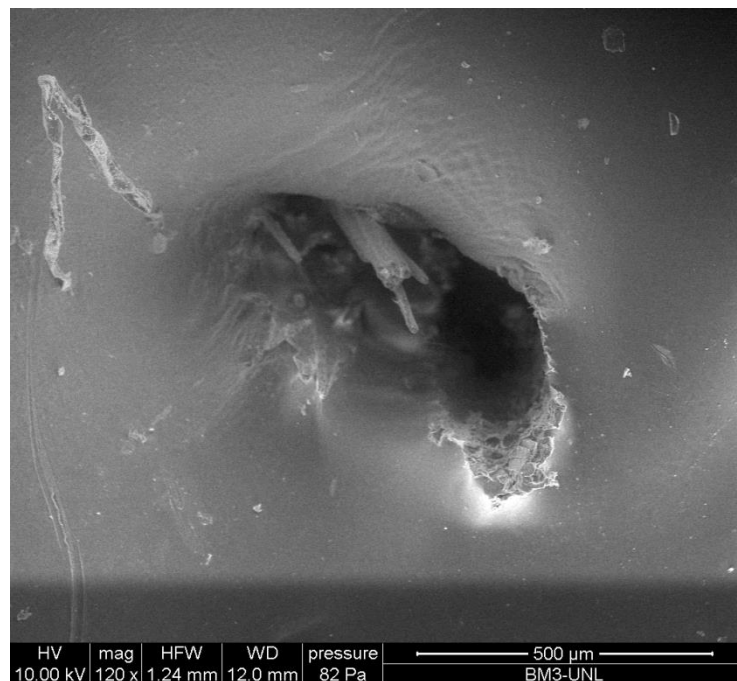
They are classed in two “groups” to take into account the quality of the tests.

Table 10. Summary of the characterization of different categories of bamboo fibers

Uniform fiber	Non-uniform fiber
Fiber tip well preserved after the pull-out test (optical microscope)	Tip showing a separation or breaking of elementary fibers (optical microscope)
	
Low standard deviation of the diameter values measured along the fiber (optical microscope)	High standard deviation of the diameter values measured along the fiber (optical microscope)
	
The tensile portion of the curves recorded during the test is linear and regular	Steps appear on the tensile portion of the curves recorded during the test
	

The scanning electron microscopy (SEM) has been used by scientists since its inception in order to see and understand the behavior of materials studied at the microscale or nanoscale. Because of the precision of SEM pictures, polylactic acid matrices and the bamboo fibers were systematically observed by the Quanta 200 FEG right after the fiber pull-out test, to characterize the bio-sourced composite studied in this thesis better.

Different parts of the tested sample were studied, such as the impact, hole left in the matrix after the test and the surface of the bamboo fiber right after being pulled out.

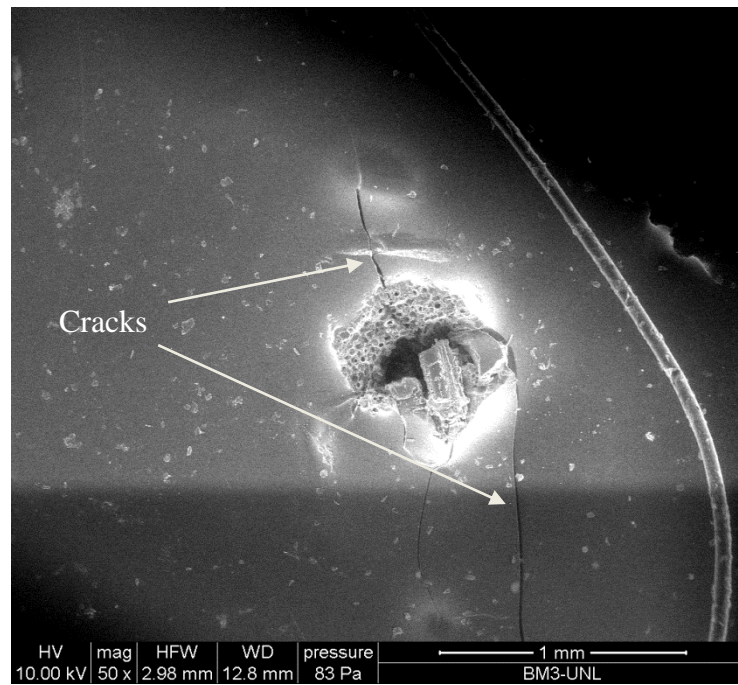


**Figure 40: SEM picture, of the hole left in the polylactic acid matrix by bamboo fiber as a consequence of a pull-out test**

As shown in Figure 40, the PLA matrix typically has a hole as a consequence of the debonding and pulling out of the bamboo fiber. However, sometimes in the hole there are

still a few elementary fibers stuck in the matrix. The interfacial shear strength determined for this sample was  $\tau = 5.0$  MPa.

The interfacial shear strength for the sample shown in Figure 41 was  $\tau = 13.6$  MPa. This interface is more than two times stronger than the previous sample. The impact on interface and the cracks may justify the greater bonding between fiber and matrix.



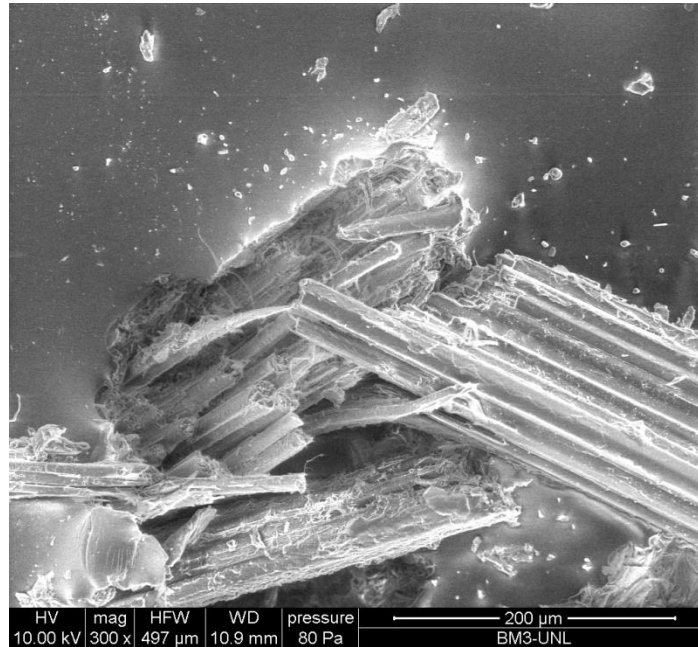
**Figure 41: SEM picture, of a PLA/bamboo sample after pull-out test. Evidences of a complex failure mechanism suggest that the result of the test should be carefully interpreted**

Another situation encountered in the fiber pull-out test was the breaking of elementary fibers from the bamboo technical fiber during the tensile test before the debonding as shown in Figure 42.

The interface can not be determined because the load recorded as a function of the displacement characterizes, in this case, the cohesive failure of the elementary fibers



composing the technical fiber and not the interfacial debonding of the fiber from the matrix.



**Figure 42: SEM picture, bamboo fiber were broken before debonding during the single fiber pull-out fiber**

Once the morphological study on the fiber pull-out test samples was done, the results of interfacial shear strength were divided in two categories depending on the aspect of the sample after the test, namely “uniform” samples and “non-uniform” samples.

The rank gives an interfacial shear strength of  $\tau = 7.0 \pm 3.1$  MPa for the uniform samples while the non-uniform samples has  $\tau = 2.8 \pm 2.5$  MPa. The uniform samples are supposed to represent the interfacial shear strength of the biocomposite PLA and untreated bamboo fiber, whereas the value of the non-uniform samples are unnecessary to quantify the interface. In order to compare the results obtained in this work with the results reported in

the literature, Table 11. lists different kinds of composites reinforced with untreated bamboo fibers and flax fibers and/or PLA and other synthetic polymer as the matrix.

**Table 11. Interfacial shear strength determined for different polymeric matrix/untreated natural fiber composites through pull-out tests and microbond tests in the literature.**

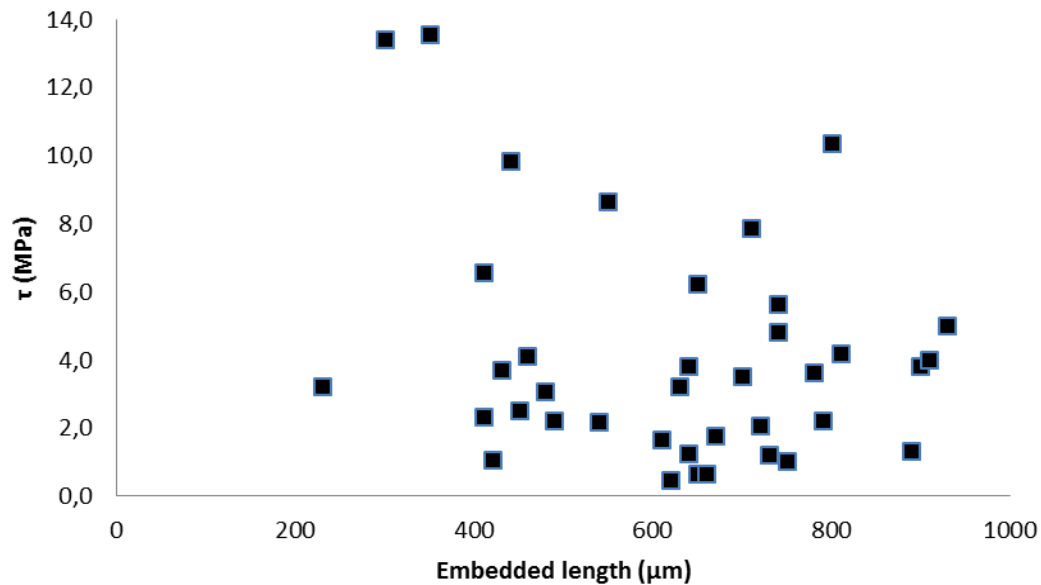
Matrix/Fiber	Interfacial shear strength (MPa)	Test method	Reference
PLA/Flax	6-12	Microbond tests	[52]
PLA/Flax	8-17	Microbond tests	[53]
PVDF/Bamboo	3-7.5	Pull-out tests	[24]
PP/Bamboo	2.1-.3.4	Pull-out tests	[24]
PLA/ Bamboo	4.3	Microbond tests	[54]
<b>PLA/ Bamboo</b>	<b>3.9-10.1</b>	<b>Pull-out test</b>	<b>This work</b>

The results reported in the literature concern only untreated fibers. Essentially, two mechanical tests such as pull-out tests and microbond tests were used in order to evaluate interfacial shear strength. The first biocomposite studied is made of PLA and bundles of flax fibers with an interfacial shear strength of  $\tau = 6-12$  MPa [52]. This paper asserts that the separation of the bundle in elementary fibers results in a higher interfacial shear strength. The fibers were dew-retted and then stripped and combed [52]. Reducing the bundle of fibers as much as possible to elementary fibers seems to be a good solution to improve the interfacial shear strength with polymers in composites. Knowing that bamboo elementary fibers have a diameter about 10-20 $\mu$ m as shown in Figure 5, processing samples for single fiber pull-out test may be possible but the probability of failing the test would also increase due to the fragility of the elementary fiber. Another biocomposite made of PLA and untreated flax was studied via microbond testing by Wong et al. [53] , who obtained a value of  $\tau$  in the range of 8-17 MPa. Flax fibers have a higher value of

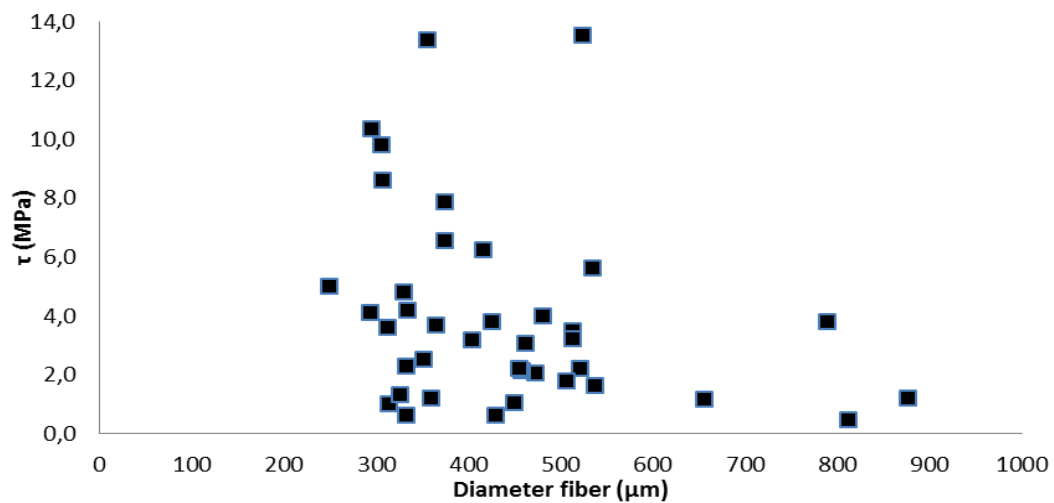
interfacial shear strength than bamboo fibers when associated with PLA. However a work comparing PVDF/bamboo fibers with a PP/fiber mentioned that the polarity of the polymer matrix could have an influence on the adhesion to the fiber surface. Indeed, PP is non-polar and PVDF is polar, and the authors discussed their results showing that a polar matrix has a better interfacial shear strength with natural fibers than non-polar matrices. PLA is polar and therefore probably more prone to have a good adhesion to natural fibers than other non-polar polymers.

Fiber pull-outs tests may give interesting information about the parameters that could influence the interfacial shear strength of the composite. According to Eq. (14), the diameter of the fibers and length embedded into the polymer matrix are two parameters that play a key role on the results of the test. Even if 26 out of the datasets interpreted in this work do not exactly represent the interface of the biocomposite, 38 datasets fulfilled all the requirements and could be used to evaluate the interfacial shear strength between the PLA matrix and the bamboo fibers. A scatter plot of the interfacial shear strength as a function of the embedded length is provided in Figure 43, and a global trend is detected corresponding to values of  $\tau = 1\text{-}13.6$  MPa dispersed over a range of embedded length ranging from around 250  $\mu\text{m}$  to 550  $\mu\text{m}$ . Apparently, there is no mathematical relationship linking the interfacial shear strength to the length of bamboo fibers embedded in the polymer matrix. The second parameter which may influence interfacial shear strength is the embedded length of bamboo fiber in PLA matrix. Similarly, Figure 44 presents a scatter plot of the interfacial shear strength as a function of the fiber diameter. Once again, no mathematical relationship can be pointed out between the interfacial shear strength and the

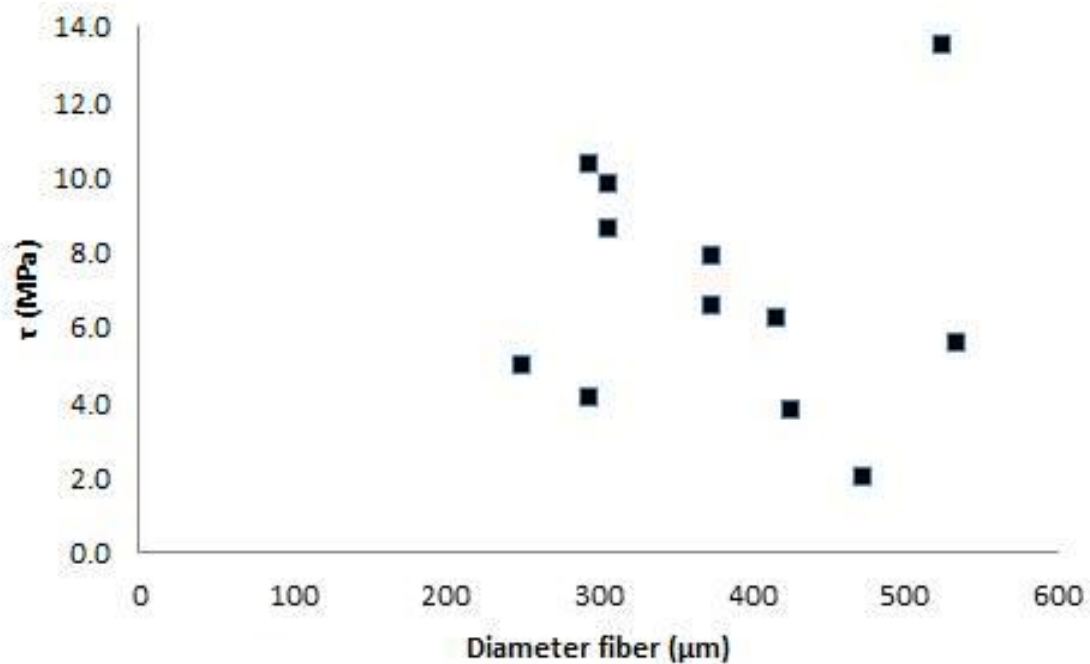
fiber diameter. Values of  $\tau$  between 1 and 8 MPa are obtained for embedded lengths going from 400 to 800  $\mu\text{m}$ ; only a few points are outside this range.



**Figure 43.** Interfacial shear strength between PLA and bamboo fibers as a function of the fiber length embedded into the polymeric matrix.

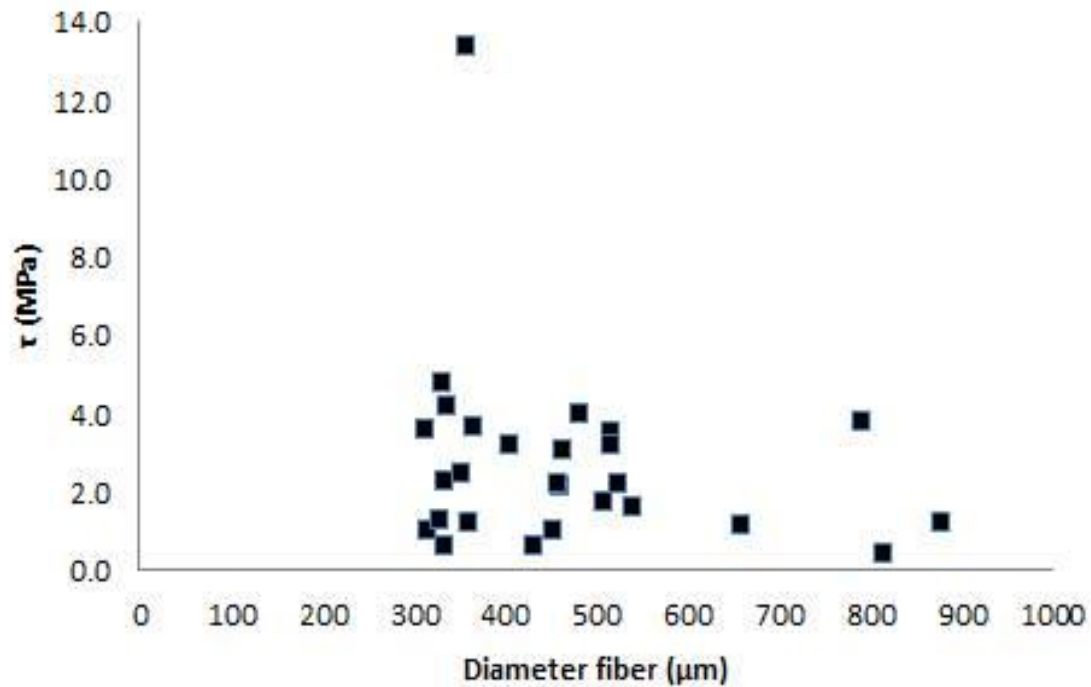


**Figure 44.** Interfacial shear strength as a function of the fiber diameter



**Figure 45. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber diameter (only uniform samples were selected).**

Sorting and classifying the samples allows better interpretation of the results. Indeed, the values of interfacial shear strength obtained for bamboo fibers considered as uniform are more representative of the actual interface between the PLA matrix and the fiber, as previously shown in Figure 45. By selecting the more representative values, the value of  $\tau = 7.0 \pm 3.1$  MPa is obtained. When only “uniform” fibers are taken into account, the interfacial shear strength is found to be higher than the value obtained by averaging the whole dataset (uniform + non uniform), meaning that “non-uniform” samples are probably too weak to cause interface failure as expected.



**Figure 46. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber diameter (only “non-uniform” sample were selected)**

The values plotted in Figure 46 do not exactly quantify the interface between PLA and the bamboo fiber because some defects found on the bamboo fibers caused problems during the test and did not allow testing the interface. The diameter of the fibers seems to play an important role in success of the pull-out tests. Indeed, the “non-uniform” were found to have a generally higher diameter of the fiber with respect to the samples considered “uniform”. A larger diameter reduces the risk of cohesive failure of the bamboo fiber and increases the surface stressed at the interface between the matrix and the reinforcement.

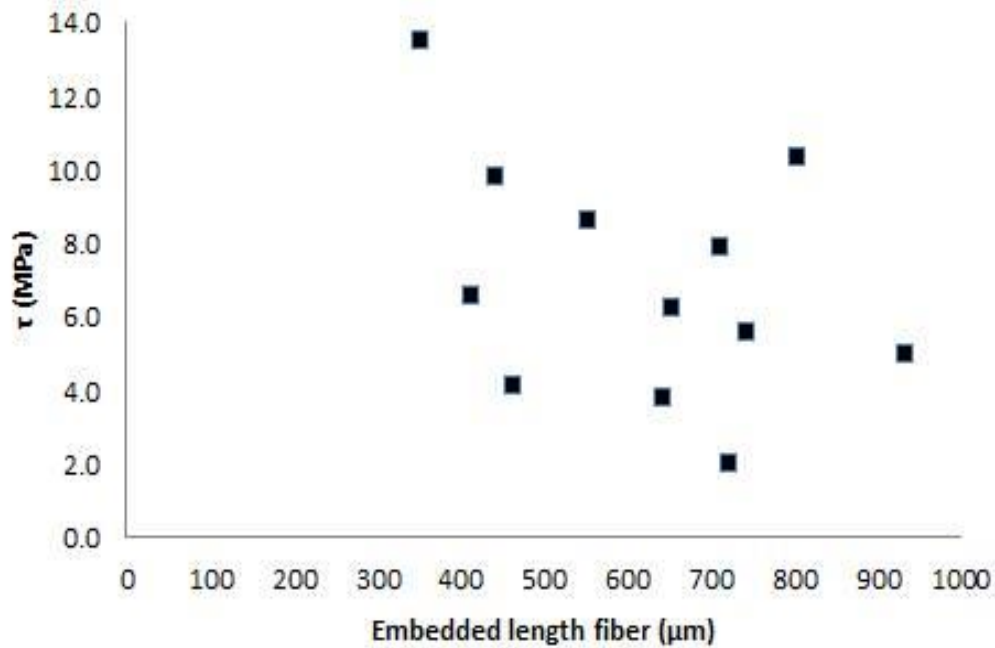


Figure 47: Interfacial shear strength between PLA and bamboo fibers as a function of the fiber length embedded into the polymeric matrix (only “uniform” samples were selected).

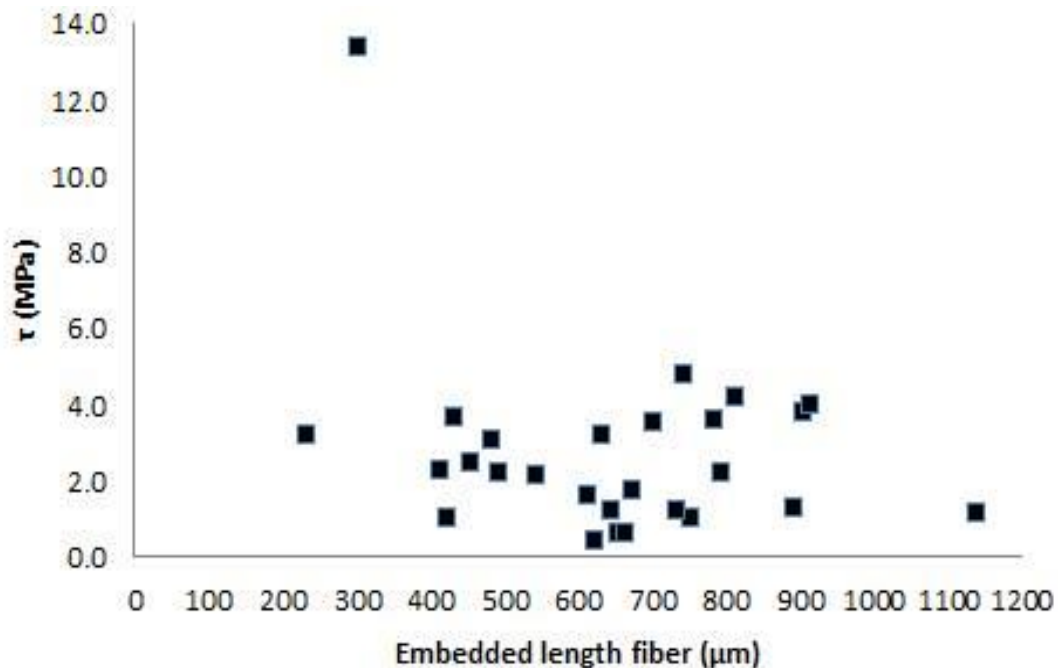


Figure 48. Interfacial shear strength between PLA and bamboo fibers as a function of the fiber length embedded into the polymeric matrix (only “non-uniform” samples were selected).

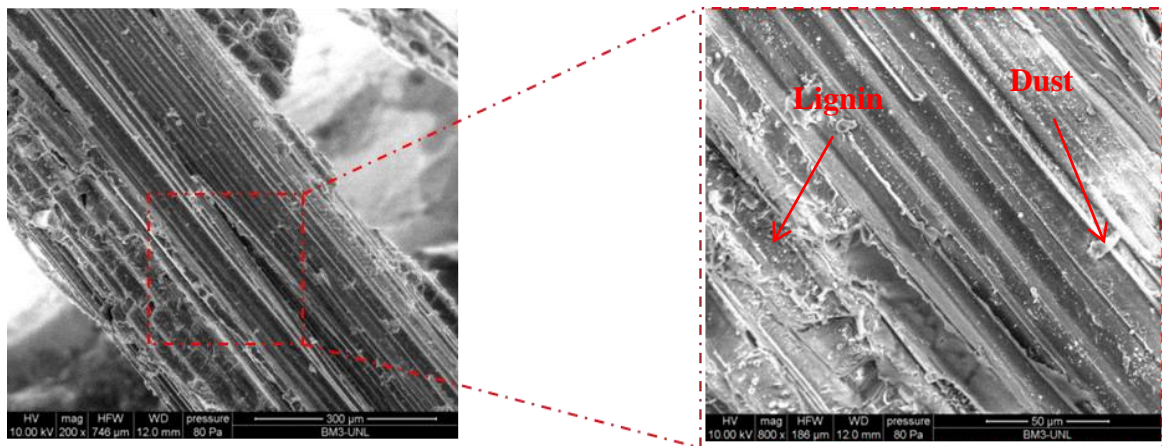
When the diameter of the fiber selected for the test reaches a limit (around 500  $\mu\text{m}$ ), the pull-out test has a high probability of failure. The results obtained for the interfacial shear strength were also evaluated as a function of the embedded length of bamboo fiber in the PLA matrix (Figure 47,  $\tau = 7.0 \pm 3.1 \text{ MPa}$ ). The length of fiber embedded in the polymeric matrix seems to have a high influence on the success of pull-out tests, as shown in Figure 48. A large number of the pull-out tests considered as “non-uniform” are located in the range of 600-900  $\mu\text{m}$ .

In conclusion, pull-out tests can be classified in two different categories on the basis of the results: some pull-out tests quantify the interface between the PLA matrix and the bamboo fiber (samples previously called “uniform”) whereas some others are not significant to evaluate the interfacial shear strength (samples previously referred as “samples with problems”). The analysis of both these categories of tests allowed the requirements for a sample to be understood to achieve a successful pull-out test, both in terms of length of the fiber embedded (<600  $\mu\text{m}$ ) in the polymeric matrix and of the fiber diameter (< 500  $\mu\text{m}$ ). These two parameters are connected to each other, as almost every time that the embedded length of the selected fiber was higher than its diameter, of the sample turned out to be a “non-uniform”. In order to have a successful pull-out test of a bamboo fiber from a PLA matrix, the selected fiber should have a diameter that is less than or equal to than the length embedded into the polymer.



### 3.2 Mercerized fibers

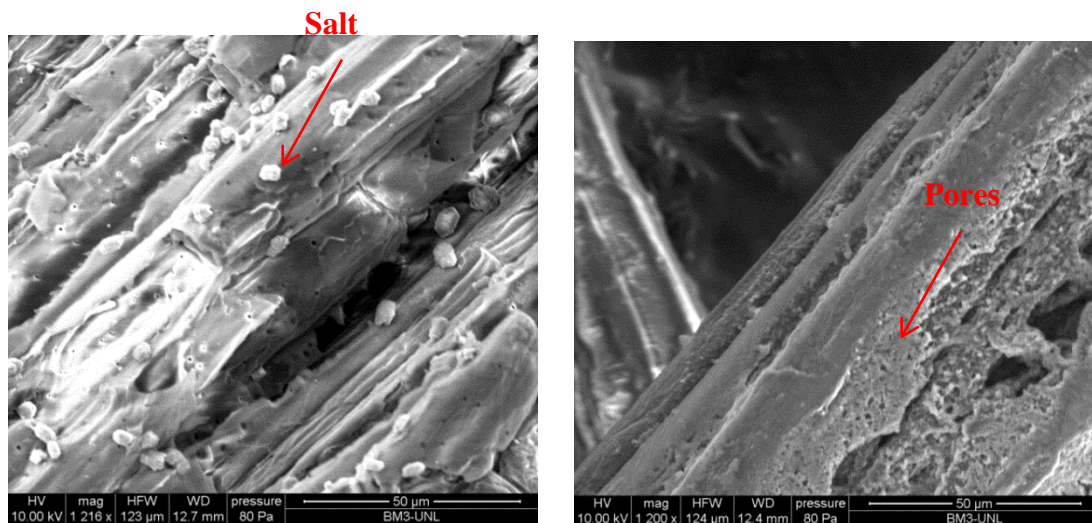
As one of the purposes of this work was to investigate the role of mercerization on the mechanical properties of bamboo fibers and, more specifically, on its interfacial shear strength with a polymer matrix, the fiber pull-out tests were also performed on samples prepared with mercerized bamboo fibers and then compared to the results previously discussed. Mercerization is a treatment with sodium hydroxide that is supposed to modify the surface of the bamboo fibers in order to remove some impurities and dust and therefore improve the quality of the contact surface. Sometimes, surface treatments may also lead to the formation of stronger (or eventually different) bonds between the polymeric matrix and the surface of the fibers.



**Figure 49. SEM pictures of the surface of a bamboo fiber before mercerization (untreated fiber)**

Figure 49 clearly shows that the surface of untreated bamboo fibers contain some lignin, dust and impurities. As previously explained, these components may greatly affect the quality of the interface. Figure 44 shows that performing a treatment with sodium hydroxide (NaOH) has clear consequences on the quality of the surface: the roughness of

the surface is surprisingly decreased and some small particles pollute it (these particles are likely to be salt crystals residual from the treatment and not removed by the washing procedure). The surface is also smoother with small microscopic pores as shown in Figure 50, and that probably allows a better interlocking of the PLA matrix with bamboo fiber in local area. As expected, mercerization induces a chemical and morphological modification of the surface of the bamboo fibers [32], which is supposed to improve their interface with a polymeric matrix; however, the presence of residual salts may also affect the quality of the interface and should be taken into account (salts should be entirely removed) for future tests.



**Figure 50: SEM pictures of the surface of a mercerized bamboo fiber. Residual salts (NaOH) can be seen on the surface of the fiber.**



**Figure 51: SEM picture of a mercerized bamboo fiber (technical fiber, i.e. bundle of elementary fibers).**

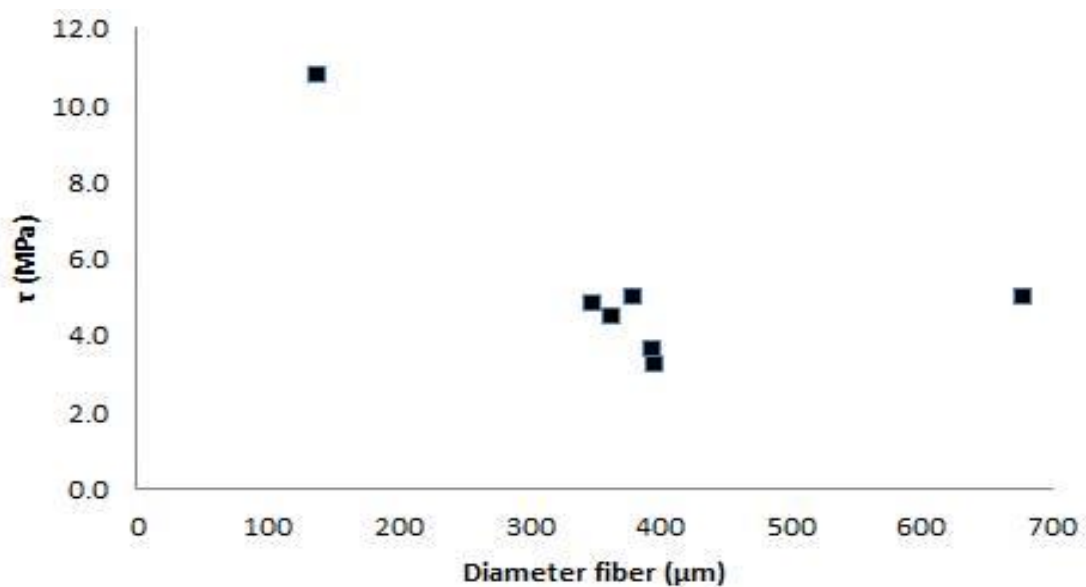
Figure 51 shows another benefit produced by the NaOH treatment on bamboo fibers. Indeed, in the literature it is reported that the mercerization causes swelling of the fibers, resulting in an improvement of the internal surface area which breaks internal bonds and therefore leads to the disorganization of the lignin structure. The interface between the fiber and the matrix is difficult to quantify in this case because there is also an internal interface between elementary fibers.

17 pull-out tests were performed on samples prepared with mercerized fibers; 7 of them were successful and interpreted, whereas 10 failed. A value of  $\tau = 4.3 \pm 3.3$  MPa was obtained for the interfacial shear strength when averaging the results of all the tests. This value is close to the one obtained for untreated fibers ( $\tau = 4.1 \pm 3.3$  MPa).

As 10 out of the 17 tests should be considered as “non-uniform” , only the samples containing “uniform” fibers were selected and the results are plotted in Figure 52, giving a value of the interfacial shear strength of  $\tau = 5.3 \pm 2.3$  MPa. This result is even lower than the one obtained for the samples with untreated fibers. However, most of the papers previously published claimed that the treatment should enhance the mechanical properties

of bio-composites. Thus, the results here lead to is a worse interface of the natural fibers with the surrounding polymeric matrix. Interpretations were also made on the statistics of the two populations of data, (untreated and treated data of interfacial shear strength, with via the t-test using a spreadsheet [55]. The value of the t-test reaches 0.22, meaning that the treatment has statistically no significant impact on the data about the interface shear strength, the limit being at 0.05.

Analogously to what was previously presented, Figure 52 shows the influence of the fiber diameter and Figure 53 the embedded length on the values of the interfacial shear strength determined by pull-out tests. Similarly to the values obtained on the untreated samples, the data for treated samples seem to be largely dispersed. Once again, the statistical t-test confirmed that the values of  $\tau$  do not depend on the treatment of the fibers. Data dispersion is mainly due to the fact that bamboo fibers are natural fibers, therefore their properties are intrinsically dispersed.



**Figure 52. Interfacial shear strength between PLA and treated bamboo fibers as a function of the diameter of the fibers (only “uniform” samples were selected).**

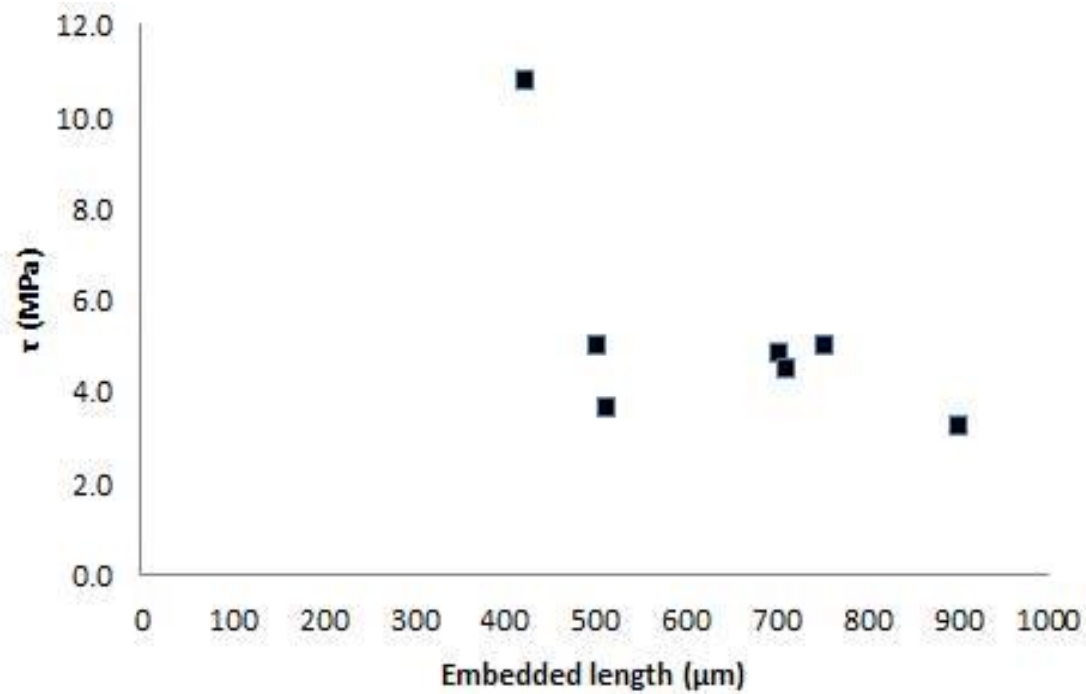
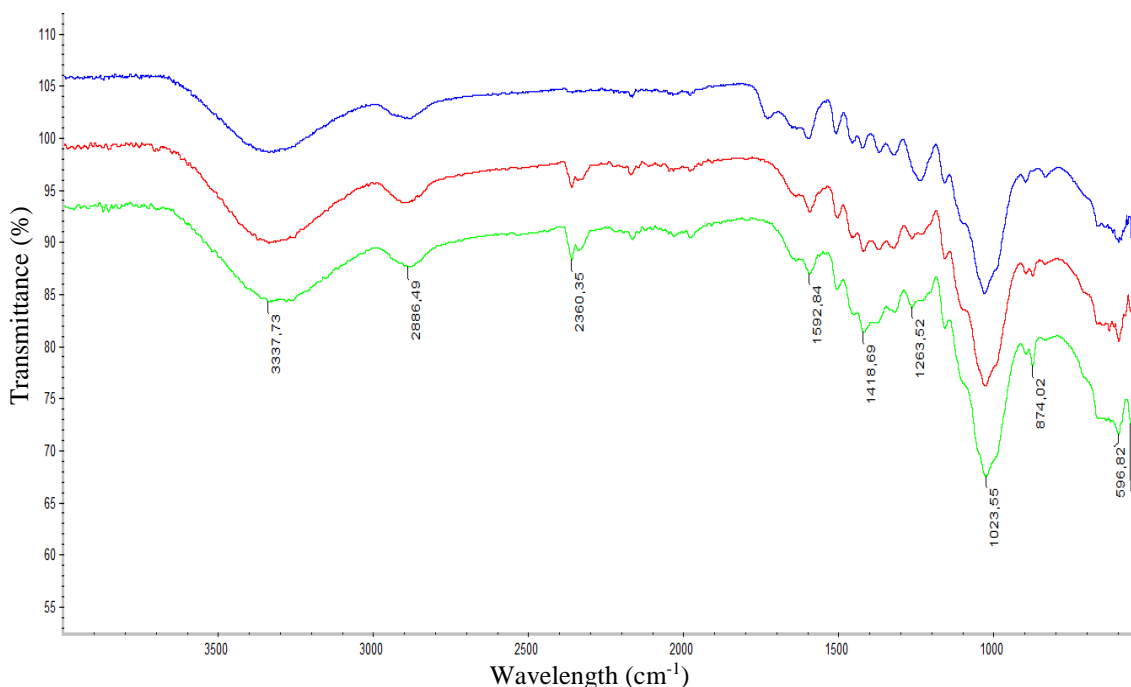


Figure 53. Interfacial shear strength between PLA and treated bamboo fibers as a function of the fibers length embedded into the polymeric matrix (only “uniform” samples were selected).

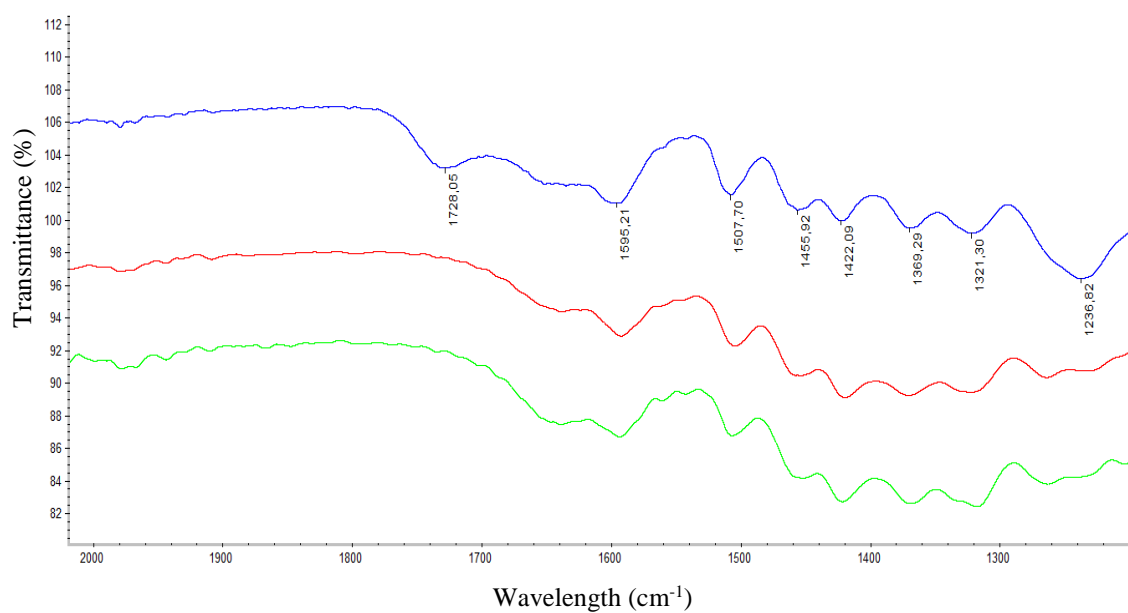
### 3.3 Fourier Transform Infrared (FT-IR) Spectroscopy

Once the fibers were treated with sodium hydroxide, FTIR spectroscopy was performed on a Nicolet Avatar 360 FT-IR device in the attenuated total reflectance (ATR) mode. Three pellets were obtained from (1) the bamboo fibers without treatment, (2) the bamboo fibers treated and washed once by filtered water, and (3) the bamboo fibers treated and washed twice. The aim of FT-IR spectroscopy is to evaluate the chemical consequences of the NaOH treatment on the fiber composition. However, quantitative analysis is difficult to obtain with infrared measurements and the interpretation of the peaks gives only a qualitative characterization of the chemical bonds on the fibers.



**Figure 54.** Infrared analysis performed on untreated bamboo fibers (blue curve), treated fiber with one washing with filtered water (red curve), and treated fiber with two washing with filtered water (green curve).

As shown in Figure 54, the peak at  $3337.73\text{ cm}^{-1}$  (corresponding to the stretching of the hydroxyl bond  $\text{-OH}$ ) is present before and after the NaOH treatment. This result is normal because natural components of bamboo fibers form a high quantity of hydrogen bonds, whereas the peak at  $2886.49\text{ cm}^{-1}$  justifies the presence of methyl groups ( $\text{-CH}_2\text{-}$ ,  $\text{-CH}_3$ ) associated with cellulose, hemicelluloses and lignin [56], which are the main components of natural fibers. The stretching of C-O groups from cellulose is indicated at  $1023.55\text{ cm}^{-1}$  and logically present before and after mercerization. At  $2300\text{-}2400\text{ cm}^{-1}$ , one peak appears as a consequence of the treatment, indicating that intramolecular  $\text{OH}\cdots\text{O}$  hydrogen bonds are created by the mercerization [57]. Some papers mention a peak associated with  $\text{CO}_2$  appearing in the range of  $2300\text{-}2400\text{ cm}^{-1}$  [58]. The absorption peak at  $874.02\text{ cm}^{-1}$  becomes slightly more intense when the fiber is treated and washed, due to the C-H out-of-plane stretching [59]. The N-H stretching from amine salts detected (peak at  $2360\text{ cm}^{-1}$ ), meaning that salts are not completely removed after the treatment and the double washing. The shape of the peak at  $1595.21\text{ cm}^{-1}$  and the peak at  $1507.70\text{ cm}^{-1}$  respectively confirmed the presence of lignin carbonyl groups [60]. Moreover, the disappearance of the peak at  $1728.05\text{ cm}^{-1}$  shown in Figure 55 is also attributed to the aromatic ring vibrations of the phenylpropane skeleton from the lignin [61], which proves once again that lignin was actually removed (or at least chemically modified) by the NaOH treatment.



**Figure 55. Zoom of Figure 54 on 1200-2000 cm<sup>-1</sup> wavenumber**



## **CHAPTER 4: CONCLUSIONS AND PERSPECTIVES**

Bio-based composites represent an important alternative to composites based on synthetic polymers, which are nowadays produced in mass in our society. The renewable aspect of biocomposites is a subject of interest from scientific research and the industrial community. A possible definition of biocomposites is that the matrix is bio-sourced, and the reinforcements are natural fibers, meaning that the final material may be biodegradable and/or biocompostable. A previous research work performed by Sarah Royse [26] involved creation and characterization a biocomposite made of a polylactic acid matrix and containing short bamboo fibers. The mercerization of the fibers was then performed to improve the dispersion and distribution of the fibers into the polymeric matrix, with the final purpose of improving the mechanical properties of the final biocomposite. However, contrarily to what was expected, the treatment did not result in a material having higher strength or toughness or Young's modulus; a more homogeneous material having equal (or less) mechanical properties was quite surprising, and the reason was probably to be found in the adhesion between the bamboo fibers and the polylactic acid matrix in which they were embedded. Many works in the literature claimed that fiber treatment would increase the performances of the composite, but no clear evidence was found.

As a consequence, the decision was made to focus this thesis on the adhesion of a PLA matrix on the surface of bamboo fibers, both treated and untreated, in order to

understand better the mechanisms controlling the stress transfer during loading and therefore better design new composites for the future. The quality of the interface between the PLA matrix and the natural fibers was evaluated by mechanical pull-out testing of a single technical fiber (cohesive bundle of elementary fibers) embedded in a polymeric matrix of controlled thickness. This kind of test is largely used in the literature to characterize polymer-based composites.

First of all, a novel process to create samples was established and allowed pertinent fiber pull-out tests to be performed. 38 tests (out of the 74 tests totally performed) were considered significant and their results were interpreted to quantify the shear strength at the interface between the matrix and the fiber. The value of interfacial shear strength determined for the selected tests was  $\tau = 4.1 \pm 3.3$  MPa. All the samples employed for the pull-out tests were successively observed by optical microscopy and scanning electron microscopy to evaluate the failure mode that occurred at the end of the test. These investigations allowed the samples to be sorted in two different categories: the “uniform” samples and the “non-uniform”. First of all, the optical and electronic microscopes were used to observe the morphology of every single sample, and several aspects were taken into account: the fiber diameter, the surface morphology of the fiber as well as the aspect of the fiber tip. On the basis of these criteria, some samples were classified as “uniform” when the fiber diameter was found to be quite constant along their length, when the fiber tip was cohesive and well preserved even after the fiber pull-out test, and finally when the fiber and/or all of the elementary fibers composing the technical bundle did not break during the tensile portion of the recorded curve, before the complete debonding of the fiber

from the matrix. Only the samples and the measurements that fulfilled these criteria could be used to evaluate the interfacial shear strength. If any of these requirements was not fulfilled, the interfacial shear strength could not be determined and the sample and/or the test had to be discarded because too many complex mechanisms took place at the same time. Being very strict in the selection of the datasets, only 12 measurements could be considered as relevant resulting in the interfacial shear strength of  $\tau = 7.0 \pm 3.1$  MPa. This result is logically higher than the value obtained without selection of the samples because the highest debonding forces are recorded only when the pulled-out fiber is not broken during the extraction from the matrix.

After the pull-out tests on samples with untreated fibers, the bamboo fibers were mercerized (NaOH treated) and fresh samples were prepared and tested with the same protocol for comparison. 17 pull-out tests were performed and interpreted, similarly to what was previously done with untreated fibers. A morphological study of the treated fibers showed that some salts remained on the surface of the fiber even after two-cycle washing by filtered water, and that some portions of the fibers were significantly modified (the surface appeared sometimes smoother, sometimes rougher). FT-IR spectroscopy confirmed that, as expected, some of the lignin surrounding the cellulosic fibers was removed or at least chemically modified as a consequence of the treatment. A value of the interfacial shear stress equal to  $\tau = 5.3 \pm 2.3$  MPa was found, with a statistical t-test revealing that the NaOH treatment actually had no significant impact on the adhesion properties.

Perspectives for this work:

- Depending on the final purposes, separating any single technical fiber in elementary fibers could improve the homogeneity of polymer-based bio-composites, eventually improving the adhesion properties of the polymeric matrix to the natural reinforcement, but in terms of pull-out test the preparation of the sample could become very tricky.
- If any treatment has to be done on the fibers, a deeper understanding of the chemical changes on the fiber surfaces should be provided, with the purpose of establishing the best treatment for the desired final result (NaOH or something else? What concentration? What consequences? What about cellulose polymorphism? What about pentosans and other secondary components of the natural fibers?)
- Profilometry in BM3 may be used to obtain more information about the hole left in the matrix, eventually with samples having different thickness of polymer surrounding the fiber (and therefore different embedded lengths)
- Microbond tests should be performed and the results compared to the ones obtained by fiber pull-out testing

## BIBLIOGRAPHY

- [1] European plastics, "Plastics – the Facts," 2010.
- [2] Resinex, [Online]. Available: <http://www.resinex.fr/types-de-polymeres/pla.html>.
- [3] E. Vink, K. Rabagob, D. Glassner and P. Gruber, "Applications of life cycle assessment to NatureWorks™," *Science Direct*, vol. 80, pp. 403-419, November 2002.
- [4] C. Fuentes, L. Trana, C. Dupont-Gillain, W. Vanderlinden and S. De Feyter, "Wetting behaviour and surface properties of technical bamboo fibres," *Colloids and Surfaces A: Physicochem. Eng. Aspects* 380, no. Sciences Direct, p. 89–99, 2011.
- [5] K. A. Porter, "Ring Opening Polymerization of Lactide for The synthesis of Poly (Lactic Acid)," Illinois, 2006.
- [6] K. Charlet and A. Beakou, "Mechanical properties of interfaces within a flax bundle–PartI," *International Journal of Adhesion & Adhesives*, vol. 31, pp. 875-881, 2011.
- [7] P. Haque, A. Parsons, I. Barker, I. Ahmed, D. Irvine and G. Walker, "Interfacial properties of phosphate glass fibres/PLA composites: Effect of the," *Composites Science and Technology*, vol. 70, pp. 1854-1860, 2010.

- [8] X. Li, L. Tabil and S. Panigrahi, "Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review," *J Polym Environ*, vol. 15, pp. 25-33, 2007.
- [9] M. Bourgeois, "Fibres agrosourcées," *Techniques de l'Ingénieur*, vol. n2520.
- [10] O. Faruka, A. Bledzka, H. Fink and M. Sain, "Biocomposites reinforced with natural fibers: 2000–2010," *Progress in Polymer Science*, vol. 37, pp. 1552-1596, 2012.
- [11] C. Baley, "Fibres naturelles de renfort pour," *Techniques de l'Ingénieur*, no. am5130.
- [12] N. Defoirdt, S. Biswas, L. De Vriese, L. Ngoc Tran and J. Van Acker, "Assessment of the tensile properties of coir, bamboo and jute fibre," *Composites: Part A*, p. 588–595, 2010.
- [13] G. Raj, E. Balnois, C. Baley and Y. Grohens, "Interfacial studies of polylactic acid (PLA)/flax biocomposite; from model to surface fibre treatment," [Online]. Available: <http://www.iccm-central.org/Proceedings/ICCM17proceedings/Themes/Materials/NATURAL%20FIBRE%20COMPOSITES/D9.2%20Raj.pdf>.
- [14] K. Charleta, J. Jernota, J. Breard and M. Gomina, "Scattering of morphological and mechanical properties of flax fibres," *Industrial Crops and Products*, vol. 32, pp. 220-224, April 2010.

- [15] J. Andersons, E. Sparnins and R. Joffe, "Stiffness and Strength of Flax Fiber/Polymer Matrix Composites," *Polymer Composites*, vol. 27, no. 2, March 2006.
- [16] D. Garlotta, "A Literature Review of Poly(Lactic Acid)," *Journal of Polymers and the Environment*, vol. 9 no 2, april 2001.
- [17] J. Ahmed, J. Zhang, Z. Song and S. Varshney, "Thermal properties of polylactides," *Journal of Thermal Analysis and Calorimetry*, vol. 95, pp. 957-964, 2009.
- [18] N. Jarroux, "Les biopolymères : différentes familles, propriétés et applications," *Techniques de l'Ingenieur*, 10 2008.
- [19] P. Whittaker, *Bambous rustiques*, ULMER ed., 2007.
- [20] Company, *Bamboo Fiber Technology*, "Bamboo Fiber Technology," Lahontan.
- [21] H. Abdul Khalil, I. Bhat, M. Jawaaid, A. Zaidon, D. Hermawan and Y. Hadi, "Bamboo fibre reinforced biocomposites: A review," *Materials and Design*, vol. 42, p. 353–368, 2012.
- [22] L. Jiang, F. Chen, J. Quian, J. Huang, M. Wolcott and L. Liu, "Reinforcing and Toughening Effects of Bamboo Pulp Fiber on," *Ind. Eng. Chem. Res.*, vol. 49, pp. 572-577, 2010.
- [23] S. Amada, Y. Ichikawa, T. Munekata and Yukito, "Fiber texture and mechanical graded," *Composites*, vol. Part B, pp. 13-20, March 1996.

- [24] C. Fuentes, L. Trana, M. Van Hellemont, V. Janssens and C. Dupont-Gillain, "Effect of physical adhesion on mechanical behaviour of bamboo fibre reinforced thermoplastic composites," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 418, pp. 7-15, 2013.
- [25] A. Valadez-Gonzales, J. Cervantes and R. Olayo, "Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites," *Composites*, vol. 30, no. Part B, pp. 309-320, 1999.
- [26] S. E. Royse, "Fabrication and characterization of biocomposites from polylactic acid and bamboo fibers," 2012.
- [27] M. Jawaaid and H. Abdul khadil, "Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review," *Carbohydrate Polymers* 86, vol. 86, no. SciencesDirect, pp. 1-18, 2011.
- [28] M. Arifur Raman, D. De Santis, G. Spagnoli, G. Ramorino, M. Penco and V. Thanh Phuon, "Biocomposites Based on Lignin and Plasticized Poly(L-lactic acid)," *Journal of Applied Polymer Science*, october 2012.
- [29] T. Lu, M. Jiang, Z. Jiang, D. Hui, Z. Wang and Z. Zhou, "Effect of surface modification of bamboo cellulose fibers on mechanical," *Composites: Part B*, vol. 51, pp. 28-34, 2013.
- [30] M. Sreekala, M. Kumaran, S. Joseph and M. Jacob, "Oil Palm Fibre Reinforced Phenol Formaldehyde," *Applied Composite Materials*, vol. 7, pp. 235-329, 2000.



- [31] B. Pejic, M. Kotic, P. Skundric and J. Praskalo, "The effects of hemicelluloses and lignin removal on water," *Biosource Technology*, vol. 99, pp. 7152-7159, February 2008.
- [32] H. Wang, K. Sheng, T. Lan, M. Adl, X. Qian and S. Zhu, "Role of surface treatment on water absorption of poly(vinyl chloride) composites reinforced by *Phyllostachys pubescens* particles," *Composites Science and Technology*, vol. 70, pp. 847-853, 2010.
- [33] G. R. N. Rao, Rao, G. Goud and R. N., "Effect of fibre content and alkali treatment on mechanical properties of *Roystonea regia*-reinforced epoxy partially biodegradable composites," *Bull. Mater. Sci.*, vol. 34, pp. 1575-1581, december 2011.
- [34] M. E. Himmel, Biomass Recalcitrance, Deconstructive the Plant Cell Wall for Bioenergy, M. E.Himmel, Ed., Golden: Blackwell Publishing, 2008.
- [35] G. Onyeagoro, "Composite, influence of surface lignin concentration on fibre surface characteritics and tensile properties of oil palm fibre/urea formaldehyde resin," *Academic Research International*, vol. 3, no. 1, july 2012.
- [36] J. Caia, P. Fei, Z. Xionga, Y. Shia, K. Yana and H. Xionga, "Surface acetylation of bamboo cellulose: Preparation and rheological properties," *Carbohydrate Polymers*, vol. 92, pp. 11-18, August 2012.
- [37] J.Banoub, 2003. [Online]. Available: <http://biomass-chemistry.com/structure-lineaire-lignine/structure-lignine.html>.

- [38] N. Mosier, Wyman, C. Dale, B. Elander, R. Lee, Y. Holtzapple and M. Ladisch, "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresource Technology*, vol. 96, p. 673, 2005.
- [39] S. Deng, L. Ye and Y. Mai, "Measurement of interfacial shear strength of carbon fibre/epoxy composites using a single fibre pull-out test," *Adv Composite Mater.*, vol. 7, no. 2, pp. 169-182, 1998.
- [40] C. Di Francia, T. Ward and R. Claus, "The single-fibre pull-out test. Review and interpretation," *Composites*, vol. Part A 27 A, pp. 597-612, 1996.
- [41] L. Greszczuk, "Theoretical studies of the mechanics of the fiber-matrix interface in composites, Interfaces in Composites," *Interfaces in Composites*, p. 42, 1969.
- [42] R. Rodriguez and J. Cauch, "Investigation of the micromechanisms of the microbond test," *Composites Sciences Technology*, vol. 58, pp. 907-914, 1998.
- [43] C. Liang and J. Hutchinson, "Mechanics of the fiber pushout test," *Mechanics of Materials*, vol. 14, pp. 207-221, 1993.
- [44] H. Chen, M. Miao and X. Ding, "Influence of moisture absorption on the interfacial strength of bamboo/vinyl," *Composites Part A*, vol. 40, pp. 2013-2019, September 2009.
- [45] Adhesivetechnology, [Online]. Available: [www.adhesivetechnology.com](http://www.adhesivetechnology.com).
- [46] Olympus, "Instructions BX51 / BX52 system microscope," *Technical informations provided by Olympus*.

- [47] Technology, Bamboo Fiber, [Online]. Available:  
<http://www.bamboofiberstechnology.com/>.
- [48] Lincoln-Nebraska, University of, [Online]. Available:  
<http://www.chem.unl.edu/nmr/ftir.shtml>.
- [49] PerkinElmer, [Online]. Available:  
[http://www.uts.utoronto.ca/~traceslab/ATR\\_FTIR.pdf](http://www.uts.utoronto.ca/~traceslab/ATR_FTIR.pdf).
- [50] Nebraska, University of, [Online].
- [51] U. G. Wegst, "Bending efficiency through property gradients in bamboo, palm, and wood-based composites," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 4, no. 5, pp. 744-755, july 2011.
- [52] A. Le Duigou, P. Davies and C. Baley, "Interfacial bonding of Flax fibre/Poly(l-lactide) bio-composites," *Composites Science and Technology*, vol. 70, no. 2, pp. 231-239, 2010.
- [53] S. Wong, R. Shanks and A. Hodzic, "Effect of additives on the interfacial strength of poly(L-lactic acid) and poly(3-hydroxy butyric acid)-flax fibre composites," *Composites Science and Technology*, vol. 67, no. 11-12, pp. 2478-2484, 2007.
- [54] R. Tokoro, D. Vu, K. Okubo, T. Tanakaa, T. Fujii and T. Fujiura, "How to improve mechanical properties of polylactic acid with bamboo fibers," *Journal of Materials Science*, vol. 43, no. 2, pp. 775-787, 2008.
- [55] Microsoft, Excel, [Online]. Available: <http://www.physics.csbsju.edu/stats/t-test.html>.

- [56] M. Das and D. Chakraborty, "Influence of Alkali Treatment on the Fine Structure and Morphology of Bamboo Fibers," *Journal of Applied Polymer Science*, vol. 102, no. 5, september 2006.
- [57] F. Karipcin and F. Arabali, "Synthesis and characterization of 4 arylaminobiphenylglyoximes and their complexes," *J. Chil. Chem. Soc.*, vol. 51, pp. 982-985, 2006.
- [58] L. Wang, M. Zhang and S. Redfern, "Infrared study of CO<sub>2</sub> incorporation into pyrophyllite [Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>] during dehydroxylation," *Clays and Clay Minerals*, vol. 51, no. 4, pp. 439-444, 2003.
- [59] J. Wen, B. Xue, R. Suna and A. Pinkert, "Unmasking the structural features and property of lignin from bamboo," *Industrial Crops and Products*, vol. 42, pp. 332-343, April 2012.
- [60] J. Cai, P. Fei, Z. Xiong, Y. Shia, K. Yana and H. Xiong, "Surface acetylation of bamboo cellulose: Preparation and rheological properties," *Carbohydrate Polymers*, vol. 92, pp. 11-18, August 2012.
- [61] M. Li, Y. Fan, F. Xu, R. Sun and X. Zhang, "Cold sodium hydroxide/urea based pretreatment of bamboo for bioethanol production: Characterization of the cellulose rich fraction," *Industrial Crops and Products*, vol. 32, pp. 551-559, June 2010.
- [62] H. Wang, K. Sheng, T. Lan, M. Adl, X. Qian and S. Zhu, *Composites Science and technology*, vol. 70, pp. 847-853, january 2010.

- [63] J. Kim and Y. Mai, "Engineered Interfaces in Fiber Reinforced Composites,"  
*Elsevier Science*, pp. 6-10, 1998.