CRANFIELD UNIVERSITY

OMAR IVAN HUERTA CARDOSO

FEASIBILITY STUDY OF A NOVEL BIO-BASED MATERIAL THROUGH A DESIGN THINKING APPROACH

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

Doctor of Philosophy
Academic Year: 2013 -2016

Supervisor: Dr. Adriana Encinas-Oropesa
Dr. Philip J. Longhurst

June 2018

CRANFIELD UNIVERSITY

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

Doctor of Philosophy

Academic Year 2013 - 2016

OMAR IVAN HUERTA CARDOSO

FEASIBILITY STUDY OF A NOVEL BIO-BASED MATERIAL THROUGH A DESIGN THINKING APPROACH

Supervisor: Dr. Adriana Encinas-Oropesa
Dr. Philip J. Longhurst

June 2018

This thesis is submitted in partial fulfilment of the requirements for the degree of PhD

ABSTRACT

Landfilling of non-biodegradable materials is one of the most significant long-term pollution legacies. This practice represents a loss of energy-intensive produced materials alongside with an opportunity for recycling. Environmental and economic concerns arising from the large-scale production and consumption of oil-based materials, have led to an increased interest in developing more sustainable alternatives.

Natural fibres (e.g. sisal, jute, flax, etc.) offer a potentially low environmental impact raw material for the packaging industry. Current research in the use of natural fibres in composite materials is reviewed initially in this work. This covers natural fibre properties, surface treatments, composite properties, and manufacturing processes. The rationale for the use of poly(lactic) acid (PLA) as a matrix system is defined. There are studies on the use of *Agave tequilana* fibres (ATF), but, there is no work reported to date attempting their use as a reinforcement/filler for poly(lactic acid) to replace polystyrene in consumer good applications. In this research, the importance of using a design thinking method in the development of more sustainable materials to be integrated into a circular economy, is established and principles for doing so are drafted.

An initial life-cycle approach was used to design a biodegradable ATF and poly(lactic acid) bio-based composite. Experimental work included the development of different grades of fully degradable ATF/PLA bio-based composites using two diverse manufacturing processes; extrusion-press moulding, and film stacking. Bio-based composite properties were modified by exploring several surface treatments. Their resulting bio-based composite properties were investigated to provide enough information about the material behaviour in order to evaluate its potential uses. Mechanical and physical properties (tension, flexural, impact, and moisture) were assessed using standardised tests and methods. The possible routes for recycling or energy recovery of the material to close the material life cycle loop were explored.

Despite the by-product character of ATF, it offers a potential low-cost alternative as a reinforcement source for bio-based composites. ATF were observed to have a density of 1.2±0.1 g/cm^3 with a tensile strength of 79±38 MPa, and Young's modulus of 3.3±1.4 GPa. Surface treatments improved ATF tensile properties and interfacial shear strength (IFSS) with PLA. Alkali-treated ATF resulted in a maximum improvement of ~50% in tensile strength and IFSS. According to the results obtained, ATF/PLA bio-based composites with a high fibre content of 60wt% have some properties capable of outperforming those of general purpose polystyrene in several conditions (i.e. ~15% in flexural modulus and ~17% in flexural strength), while in other cases properties did not presented significant improvements (i.e. Young modulus ~3 GPa).

The impact of the new ATF/PLA bio-based composite on the current waste management system in Mexico was studied in terms of the *"best"* economic-environmental-social balanced route at the end-of-life of the material. It is considered that a continuous looping with the least possible loss of carbon and energy is best achieved through biological recycling. Anaerobic digestion of the material was ~14% after 20 days of incubation, with production of ~20 mL CH_4/gVS.

Due to the performance presented regarding their economic viability and environmental acceptability within a circular economy, ATF/PLA bio-based composites have the potential to be used in non-structural applications within the consumer goods industry, e.g., packaging, casings for electronic appliances, crates, etc.

Keywords:

Agave fibres, green-composite, mechanical properties, by-products, natural fibres, bio-based material.

ACKNOWLEDGEMENTS

First and foremost, I am deeply grateful to my main supervisor, Dr. Adriana Encinas-Oropesa, at the SWEE, Canfield University for her suggestions, comments and support during these studies. I would like to express my gratitude to my second supervisor Dr. Philip J. Longhurst for his patient instruction and disposition. Without their guidance, this research would not have been possible.

I would like to express my sincere appreciation to Mrs Cristina Hernandez and Distillery “La Fortaleza” for the support and believe in the project, to Dr. Raffaella Villa for her support during the degradability test, and to all the Cranfield technical staff for their help, and openness to new approaches in the laboratories during the performing of the experimental work.

I also would like to thank my friends and colleagues who helped me through my study in Cranfield. Last, but not least, I am deeply indebted to my lovely wife, Citlalli, for her patience, love, and encouragement during the endless hours of this research. I also owe many thanks to my mother, and my brother and sister for their unconditional support and love.

This research was funded by the Mexican Government through the Consejo Nacional de Ciencia y Tecnologia (CONACyT) and the Secretaria de Educacion Publica (SEP).

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF FIGURES IN APPENDICES

LIST OF TABLES IN APPENDICES

GLOSSARY

Acetylation - is the process of introducing an acetyl group in replacement for an active hydrogen atom from the natural fibre.

Amorphous - or non-crystalline, are material that do not have uniformly packed molecules, therefore do not exhibit any crystalline structures in X-ray or electron scattering experiments.

Bagasse - is the residual lignocellulosic waste that remains from tequila production.

Bioscouring - is a process by which alkaline stable pectate lyase is used to remove pectin and waxes selectively from natural fibres.

By-product - a secondary or incidental product of a manufacturing process. It does not receive allocations of joint costs, can be useful and marketable or it can be considered waste.

Calendering - process where fibres pass through pairs of heavy rollers which flatten the loose fibrils improving quality and appearance.

Convergent thinking - problem solving technique in which ideas from different fields are brought together (synthesized) to find a single optimum solution to a clearly defined problem.

Coupling agent - a compound which provides a chemical bond between two dissimilar materials, usually an inorganic and an organic.

Crimp - property that allows corrugations on a packaging part to lock them in place.

Crystallinity- refers to the degree of structural order in a solid. In polymers it is associated with partial alignment of their molecular chains.

Deadfold - packaging property where a fold (as in soft foil/sheet) that does not unfold spontaneously.

Decorticating – a method for stripping the skin, bark, or rind off wood, plant stalks, grain, etc., in preparation for further processing.

Degumming - a method, which removes heavily coated, non-cellulosic gummy material from the cellulose part of the natural fibres.

Divergent thinking - a method used to generate creative ideas in a spontaneous, free-flowing and 'non-linear' manner by exploring many possible solutions in an emergent cognitive fashion.

Elementarization - refers to the degree of separation/extraction of elementary fibres from a bundle of natural fibres after any extraction process.

Esterification – reaction when a carboxylic acid is treated with an alcohol and an acid catalyst, an ester is formed along with water.

Glass transition - is the reversible transition state in amorphous materials from a hard and relatively brittle state into a viscous or rubbery state as the temperature is increased.

Grafting - technique involving the copolymerization of a polymeric backbone, resulting in segmented copolymers with a linear backbone of one composite and randomly distributed branches of another composite.

Holistic method - an approach characterized by the belief that the parts of something are intimately interconnected and explicable only by reference to the whole; therefore it attempts to deal with the whole system.

Interface - is the two-dimensional boundary region between two surfaces.

Interphase - is the three-dimensional region between two phases.

Interfacial shear strength - is the strength of a material or component against the type of yield or structural failure where the material or component fails in shear.

Lumen - is the tubular inside space of a cellular component or structure found in natural fibres.

Matrix – surrounds and binds together fibres or fragments of the other materials, called reinforcement in composites.

Melt density – density of a polymer material in molten state.

Mercerization – method used to treat natural fibres with caustic alkali under tension, in order to increase strength, luster, and affinity for dye.

Microfibrilar angle - refers to the angle between the direction of the helical windings of cellulose microfibrils in the secondary cell wall of fibres and the long axis of the cell wall.

Moiety - is a functional group that participates in similar chemical reactions in most molecules that contain it. In turn the parts of the group are termed moieties.

Neutral carbon footprint - refers to achieving net zero carbon emissions by balancing a measured amount of carbon released with an equivalent amount sequestered or offset.

Retting - is a process employing the action of micro-organisms and moisture on plants to dissolve or rot away the cellular tissues and pectins surrounding bast-fibre bundles.

Specific gravity - is the ratio of the density of a substance to the density of a reference substance; equivalently, it is the ratio of the mass of a substance to the mass of a reference substance for the same given volume.

Specific properties - depend on or are calculated based on another measurable property; they are derived from other intrinsic and extrinsic properties.

Steam explosion - extraction technique that is applied to fibrous organic materials to open up the fibres making them more accessible for subsequent processes.

Tensile modulus - Young's modulus or modulus of elasticity is a measure of stiffness. It is defined as the ratio of stress along an axis to strain along the axis, and is used to describe the elastic properties of objects when they are stretched or compressed.

Thermal conductivity - the rate at which heat passes through a specified material, expressed as the amount of heat that flows per unit time through a unit area with a temperature gradient of one degree per unit distance.

Thermoplastic - refers to a polymer that becomes pliable or mouldable above a specific temperature and solidifies upon cooling without any change of the inherent properties.

Thermoset - is a polymer joined together by chemical bonds, acquiring a highly crosslinked polymer structure when heated and once the material sets it cannot be remoulded.

Twist – is a packaging property where twisted material (as in soft foil) keeps its shape without untwisting spontaneously.

Waste – is any substance or object which is discarded or intended or required to discard.

LIST OF ABBREVIATIONS

ACF	Acetylated fibres
AD	Anaerobic digestion
AKF	Alkali-treated fibres
ATF	Agave tequilana fibres
ATW	Agave tequilana weber
APTES	(3-Aminopropyl)triethoxysilane
ASTM	American Society for Testing and Materials
BMP	Biomethane Potential
CAGR	Compound Annual Growth Rate
CE	Circular economy
CSA	Cross sectional area
DT	Design Thinking
DTGA	Differential thermogravimetric analysis
E	Young’s modulus
EDX	Energy-dispersive X-ray spectroscopy
ENF	Enzyme treated fibres
ESEM	Environmental scanning electronic microscope
EVA	Ethylene vinyl acetate
GDP	Gross domestic product
GPPS	General purpose polystyrene
GRAS	Generally recognised as safe

GHG	Greenhouse gas
HDPE	High-density polyethylene
HIPS	High impact polystyrene
IFSS	Interfacial shear strength
LDPE	Low-density polyethylene
MD	Material development
MJ	Megajoules
MSW	Municipal Solid Waste
OM	Optical microscopy
PC	Polycarbonate
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
PJ	Petajoule
PMC	Polymer matrix composite
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
SIF	Silane-treated fibres
TGA	Thermogravimetric analysis
T_g	Glass transition

T_m	Melting point
UNF	Untreated fibres
UTS	Ultimate tensile strength
VA	Vinyl acetate
vol%	Volume content percentage
WMS	Waste management system
wt%	Weight content percentage

1 Introduction

1.1 Background

In recent years, awareness has been raised over the environmental and economic concerns posed by the large-scale production of oil-based materials. Along with the growing production and consumption of plastics, the oil-based economy has been challenged by high oil prices and an increasing risk of scarcity as is shown in Figure 1.

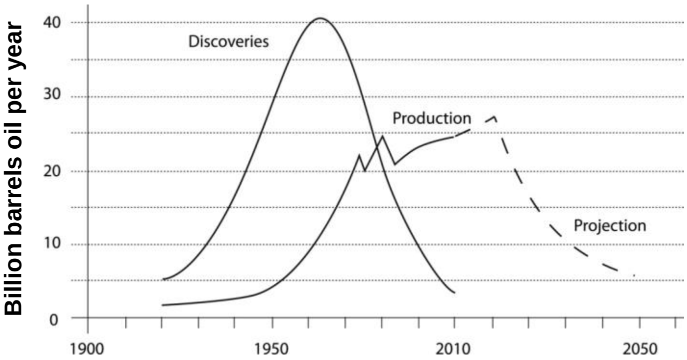


Figure 1. World oil supply. Discoveries and production curves. Adapted by the author [1].

One of the serious ecological problems that oil-based plastics present and which need to be addressed is their recyclability and biodegradability [2,3]. There is a need to end landfilling of non-biodegradable materials due to the environmental burdens this practice presents (e.g. carbon sequestration). Packaging applications (e.g. polystyrene) are one of the most significant concerns due to the problems created at the disposal phase by energy consumption and the major recycling costs at sorting, collection, and transportation stages [3].

Packaging remains the largest end-use application of plastics [4,5]. The global packaging industry is worth about £300 billion and the UK industry over £9 billion [6]. The packaging industry is expected to experience a steady growth in the years to come. This is due to several reasons: increasing urbanisation, investment in the real estate sector, widening health care, rapid development of emerging economies and the inherent rise of the middle class with a higher demand for consumer goods and more sophisticated packaging [7].

As shown in Figure 2, the second largest category within the packaging market is rigid plastics (tubs, pots and jars) with a 27 % share of the total market. This segment is growing fast and is forecast to increase more than real gross domestic product (GDP); about 4% per year until 2015 [8].

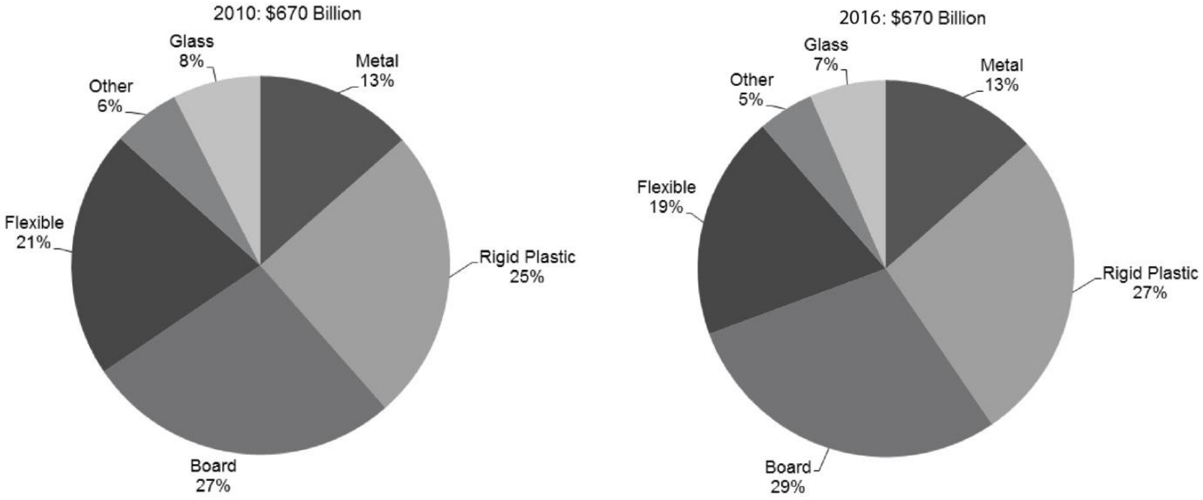


Figure 2. Global packaging sales by type 2010 vs. 2016 [7]**.**

Food packaging consumption (Figure 3) accounted for more than half of the packaging market share worldwide. This is the result of the food and beverage industry's growth driven by the demand in developing countries.

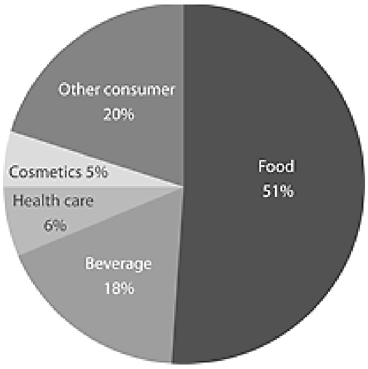


Figure 3. Global packaging by end market 2012. Total market size=US$ 400B. Adapted by the author [8]**.**

Plastic packaging includes trays and lids, films, pouches, bottles, and so on. More sophisticated packaging materials have been developed to achieve desired features such as gas and moisture barrier properties, UV and visible light transmission, flexibility, stretchability, heat sealability, low glass transition, and other mechanical properties indicative of strength or performance characteristics.

There are several types of plastics, but only a few are used in food packaging applications. The most common are polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyvinylidene chloride (PVDC), ethylene-vinyl alcohol (EVOH), polyethylene (PE) among others. A summary of the properties of the most common polymers used in packaging is provided in Table 1.

Table 1. Properties of some polymers frequently used for food packaging.

Polymer	*Tg*(°C)	*Tm*(°C)	Density (kg/m3)	Tensile strength (MPa)	Young's modulus (MPa)
LDPE	<125	110	910-940	8-12	200-400
HDPE	<110	126-135	941-965	10-60	600-1400
EVOH	72	191	1200	71.6	3138
PA	47 to 57	265	1140	36-79	2300-2500
PET	67 to 80	267	1400	55	1700
PVC	87	212	1220-1360	55.6	276-7584
PVDC	<35	198	1600-1700	73	483
PC	150	220	1200	62.1	2380
PS	100	240	1050	26-48	3200-4200
PP	<18	176	900	30-38	1100-150

Source: [9,10]. The data are based on 25-µm film thickness.

In developing countries, e.g. Mexico, even though these materials can be recycled or recovered, they are likely to be disposed in regulated landfills or incinerated. This is due to packaging materials received at recycling facilities being contaminated with food remains or other substances. Moreover, the lack of technology available to avoid contamination during the sorting of materials and waste makes the recycling process impracticable and not always economically viable [11].

Consumer convenience trends (i.e. single-use, ready-to-eat, portability) have increased the amount of packaging material, more than most other manufactured products, within the waste-stream. This is the result of the high visibility and bulky characteristic of packaging in the food industry (with a share of 60% of all packaging) [12]. Over one-third of the average household municipal solid waste (MSW) arises from these materials [13,14]. Specific data on the relationship between packaging consumption and MSW production is available, albeit has been changing along with consumer trends [15,16]. Discarded packaging materials remain a major problem, complicating efforts to address their environmental impact.

Packaging also contributes considerably to Greenhouse Gas (GHG) emissions [17], only 1 - 3% of its hydrocarbon content is degraded within a 100 year period and its impact has not been considered as a long-term emission [18,19].

The environmental and economic concerns arising from the large-scale production and consumption of oil-based packaging materials shown in a linear model (see Figure 4) [2,3,15,16], have resulted in increased attention to the development of new and more sustainable alternatives [20,21].

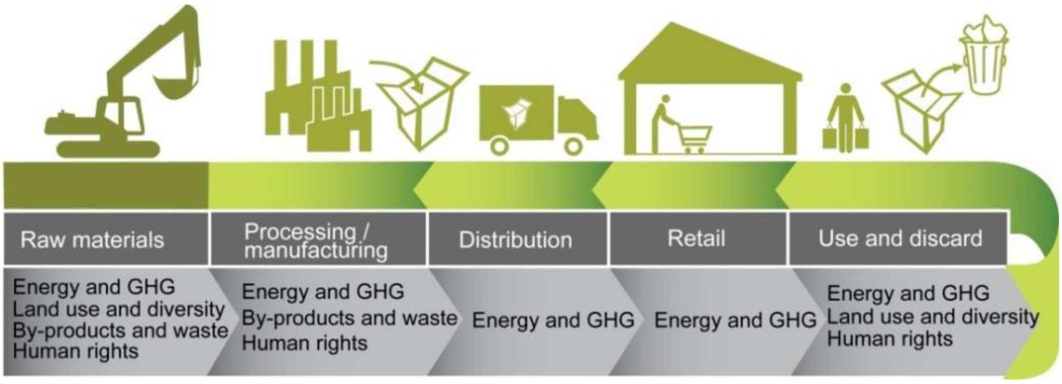


Figure 4. Linear model of oil-based materials.

Innovations and improvements in the field of sustainable materials [22] (i.e. new bio-based plastics, better recycling processes, waste treatment procedures, etc.) have been addressed by material scientists using different methods and frameworks [23–27]. However, these alternatives have proven to be too fragmented and uncoordinated to have a real impact to date. Furthermore, these material developments are commonly approached either from an economic or merely mechanical performance perspective. This leaves behind other important factors (i.e., sustainability) that may contribute to the overall function and contribution of the resulting material through its life cycle.

Linear models of innovation for new material developments have had many breakthroughs such as new polymers and superalloys. However, current environmental challenges require more holistic and systemic models of innovation to enable the consideration of real-world constraints [28–32], without undermining the importance of linear models [33]. Consequently, engaging the surrounding and constraining factors that influence the system that a material will become part of is essential in assuring a more sustainable material innovation. Therefore, a new material development should be seen as a dynamic and iterative process that forms part of a bigger system, so that is possible to take the most benefit out of it.

New ways of thinking and different approaches towards the use of materials have been implemented during recent years. The idea of materials never becoming waste, but rather having them re-entering the economy as valuable technical or biological nutrients has been embraced as the circular economy [34,35]. Furthermore, from the perspective of environmental innovation, also known as eco-innovation [36,37], if truly sustainable innovation in material developments for a sustainable behavioural change [38] is intended, then broad linked and interdependent levels must be considered [33].

“Design Thinking”, as a systemic innovation and problem-solving approach, has the potential and flexibility to work as a bridge between innovation in new materials and sustainability [39]. Hence, this approach is used in this work in an initial stage as a method to conceptualize the material. This is to allow the consideration of influential factors and sustainability constraints that would play an important role during the material’s full development.

The material conceptualization led to the development of a bio-composite material. These materials are an excellent example of the Cradle-to-Cradle principle [40], and their use for general packaging purposes or other applications has proven to satisfy some of the requirements (e.g., strength, density, specific gravity, etc.) in place of established thermoplastics [41–46].

Bio-based composites, from naturally occurring renewable resources, can be considered as a more efficient, sustainable and biocompatible solution than oil-based packaging materials. Using biodegradable and compostable materials can also help to improve the CO_2 balance in the atmosphere by closing the carbon cycle loop, in contrast to landfill disposal [47].

Despite the promising properties of bio-based composites, several problems remain, such as: the higher matrix cost that limits its use in broader packaging applications, the fibre processability and availability, and overcoming the inherent stiffness and brittleness from the material system where natural fibres under stress present failure due to crack propagation through the inherent fibre flaws and weak bonding between fibre cells, causing an early composite failure. Different alternatives to these issues have been explored. For example; the use of additives (i.e., plasticisers) or fillers (i.e., natural fibres) during material processing to tune mechanical properties and reduce the final material cost [42,48–50]; and the use of surface treatments to enhance the dispersion and interfacial adhesion between the fibre and matrix, to improve the final bio-based material properties has been reported [51,52]. However, there is always a compromise between the benefit obtained from such treatments and the final cost of the material.

Innovations in the development of these bio-based materials will be available for the market as long as they become economically viable. The accepted use of agricultural by-products or waste, as feedstock in new material developments is an early sign that bio-based materials do have the potential to achieve market competitiveness.

The use of agricultural by-products such as natural fibres (e.g., cotton, maize husk, etc.) as a filler or reinforcement, offers several advantages for bio-based composites and their possible applications, such as: low cost, low density, high toughness, acceptable specific strength properties, compostability, and biodegradability. However, the long-term ecological and economic sustainability of the industry that using these materials and their region could be endangered by conflicts between farmers and the companies that control the food industry, and by the related cycles of surplus and scarcity of the by-product.

The use of agricultural by-products as a raw material source not only offers a renewable source, but could also provide a non-food source of economic development for farming and rural areas if their use considers the persistent cycles of surplus and shortage of production, and the farm land use is not affecting directly the food supply chain. Considering these factors in the agricultural by-product use as a commodity, to stabilize the costs and supply could maintain the current agricultural practices, and the local environment. Thus, bio-based composites have the potential to overcome the ever-growing environmental pressure caused by the widespread consumption of oil-based polymers and plastic packaging. Consequently, encouraging and developing biodegradable and environmentally acceptable materials capable of being integrated into a sustainable cycle.

Some natural fibres such as; hemp [53], sisal [54], kenaf [55], etc., have been cultivated in an industrialised way and specifically for the development of bio-based materials. Nevertheless, during recent years, agricultural wastes or by-products have started to gain attention as valuable sources for raw materials in new applications due to waste reduction policies. These new applications include the production of chemicals, enzymes, fuel bio-composites, textiles, etc. The primary sources of these by-product materials are; maize, wheat, rice, sorghum, barley, sugarcane, pineapple, banana, and coconut. *Agave tequilana* fibres (ATF) are a lignocellulosic by-product from the tequila production. ATF composition varies from fibre source, but primarily contains cellulose, hemicelluloses, lignin, and extractives. Despite the high volume of lignocellulosic by-products from tequila production (around 300,000T per year), only a few studies on their use as a raw material source have been published [56,57]. This limits the commercial development of a possible bio-based material for new applications. Therefore, this research concentrates on the development of a novel material based on a by-product from tequila production using a “whole-system” and “design thinking” approach.

First, the development and synthesis of a method for sustainable new material developments based on agro-industrial by-products using a convergent-divergent thinking, is given. This method is then used to conceptualise the material that is developed in this study. The core part of the work presents the actual development of the bio-based material through each step of the process. The analysis of the ATF as a possible reinforcement source for a poly(lactic acid) (PLA) matrix is assessed using two manufacturing methods. The effect on mechanical properties from different surface modification methods is presented. Finally, different end-of-life routes are analysed for the developed material, to understand the implications of introduction on current waste management systems.

1.2 **Literature gaps**

Methods are available for material development, and traditionally these have been made by scientists following a rigorous scientific, quasi-linear method, often neglecting to address environmental challenges. Designing materials in isolation from surrounding factors tends to affect the whole system negatively; resulting in a system that is less efficient (e.g., polystyrene foam) [58], with its different components working against one another. Hence, this work develops a method to enable sustainable innovation in new material developments from a “design thinking” perspective, and it is presented as a tool for the material conceptualisation in this study and future applications.

PLA is a non-toxic polymer produced through the fermentation of annually renewable agricultural resources, such as maize or sugar beets [59,60] and therefore more environmentally friendly than its oil-based counterpart materials. The technologies for transforming PLA are ready for industrial use, and there is a strong industrial interest in materials with an environmental acceptability and economic and technical viability.

Several natural fibres are typically used in bio-composite studies as they are available as commercial commodities. However, the use of by-product ATF is not widely researched. Despite the fact that several studies [56,57,61] have attempted the use of ATF to produce paper or biomass, at present, no studies or technical data regarding the use of ATF within a PLA matrix have been reported, which has resulted in their limited use by the industry in broader applications such as packaging. Furthermore, there is a lack of studies on the influence of ATF configuration and surface treatments on the properties of a bio-based composite. PLA is commonly selected for bio-composite investigation, due to its mechanical properties [62,63] and environmental benefits. Therefore, PLA, in particular, can be combined with ATF to impart desirable characteristics such as reduced final cost and acceptable mechanical properties.

The use of by-product ATF with a renewable matrix (i.e. PLA) could help develop bio-based composites as a more sustainable alternative to support decoupling plastics from fossil feedstocks, therefore improving circular economies by integrating materials already considered waste into the resource flow. ATF bio-based material ideally offers an acceptable strength and energy absorption, weight and cost savings, as well as environmental advantages.

This research tries to fill these gaps by establishing a knowledge base for ATF and an ATF reinforced/filled PLA-based material. Various loadings and configurations of agro-industrial waste were studied to enable, and validate the use of an ATF/PLA bio-based composite to replace general purpose polystyrene in packaging applications or other non-load bearing consumer goods in a circular economy framework.

1.3 **Aims and objectives**

The aim of this research is to understand the potential applications and benefits of a novel ATF/PLA bio-based composite developed through a “design thinking” approach. Consequently, the following objectives were identified:

- To apply a “design thinking”-based method for the conceptualization and development of a more sustainable material from agro-industrial by-products.
- To characterise ATF properties.
- To analyse the effects of surface modification treatments (i.e. alkali, bioscouring, silane and acetylation) on ATF properties.
- To assess the effects of fibre treatments and fibre content on mechanical and physical properties, e.g. tensile, flexural and impact strength, and water absorption, of ATF/PLA bio-based composites compounded by extrusion moulding and film-stacking methods.
- To analyse the possible end-of-life alternatives for ATF/PLA bio-based composites, e.g. mechanical recycling, composting, incineration, anaerobic digestion and landfill.
- To understand and explain the implications of integrating a fully biodegradable ATF/PLA bio-based material within a Mexican waste management system.

The method used for the accomplishment of the above mentioned objectives is summarised in Figure 5.

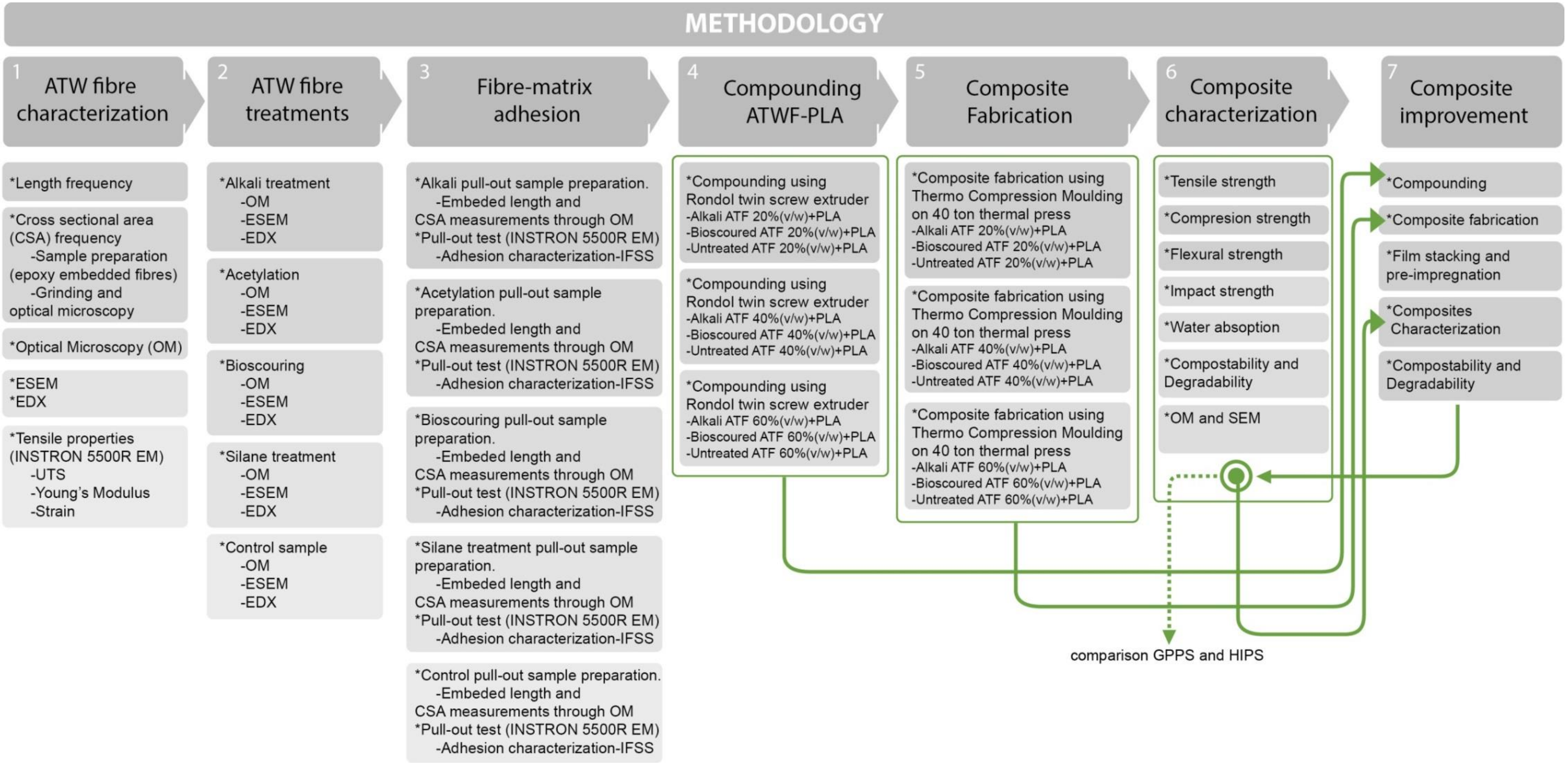


Figure 5. Graphical description of the methods used for the objectives' accomplishment and their interrelation.

1.4 **Thesis plan**

This thesis is structured into chapters which describe specific aspects of the study. All chapters in this thesis were written by the first author, Omar Ivan Huerta Cardoso, with the supervisors, Dr. Adriana Encinas-Oropesa, and Dr. Philip J. Longhurst recognised as co-authors. All experimental work and sample preparation carried out during this research was undertaken completely by Omar Ivan Huerta Cardoso using Cranfield University's facilities.

Chapter 1 defines the context and background of this work. It summarises the literature gaps, aims, and objectives of the research.

Chapter 2 provides a detailed literature review of the state-of-the-art of green composites. Current knowledge is presented regarding properties of ATF, other natural fibres (i.e. flax, jute, hemp, etc.), and composites based on different natural fibres and agricultural wastes, with various matrices and PLA. The knowledge gaps and advantages for using PLA as a matrix for ATF are also established. An insight regarding the current methodologies in the development of green composites is given. Furthermore, key findings of the literature are summarised.

Chapter 3 focuses on how sustainable innovation in new material developments can be enabled through the use of a "design thinking" approach. Initially, difficulties to consider sustainability issues, presented for traditional Research & Development (R&D) methods commonly employed in material developments are highlighted. "Design thinking" is presented as an alternative and holistic approach to developing socially responsible and environmentally sustainable materials. This holistic approach is then used along with different tools and techniques during the material conceptualization. This is used as a case study for describing the method potential as a sustainable innovation enabler in new material developments.

Chapter 4 describes a method for the selection and characterization of a bio-based waste from the blending of a design thinking and material science perspective. Mechanical and physical properties of ATF are determined as an initial step towards full material development.

Chapter 5 presents an investigation of surface treatment effects and compatibility properties of the agro-industrial by-products from tequila production with poly(lactic acid). Results presented in this study relate to the possible performance of a bio-based material (ATF/PLA) through its different development stages.

Chapter 6 investigates the influence of different fibre loading contents and surface treatments on the properties of an ATF/PLA composite material manufactured through extrusion moulding process. Quasi-static mechanical and physical properties (tensile strength, flexural strength, water absorption, etc.) are presented and compared to general purpose polystyrene (GPPS) and neat PLA. This study analyses the effects of three fibre treatments and vol% loadings in the development of the novel green composite material to tailor or improve its properties to the desired state. The knowledge obtained allows for the new material to be placed within a comparison spectrum, so predictions about possible applications can be proposed.

Chapter 7 studies the effect of a different manufacturing method, fibre configuration and a higher agro-industrial by-product % content on the mechanical and physical properties of an ATF/PLA composite material. The data obtained gives a better understanding of the new materials performance at higher ATF content for more accurate comparisons against GPPS, so that applications can be suggested.

Chapter 8 explores three different routes for the end-of-life of the novel ATF/PLA bio-based material. In this study, the biodegradability properties of the material are assessed through anaerobic digestion. A biomethane potential test is used to measure the biogas production from the digestion and co-digestion of complex organic substrates. Reprocessing, compostability, and energy recovery from combustion are also reviewed and compared as routes to re-integrate the ATF/PLA material into the value chain in a scenario where the material is likely to be disposed of. This chapter also looks at the possible sustainability impact an ATF/PLA bio-based material presents to a Mexican scenario within a circular economy framework.

Chapter 9 highlights the major findings of this research, summarising the obtained results regarding ATF/PLA material structure and properties, and overall sustainability benefits. Further material and product development are also suggested.

1.5 **Contribution to Knowledge**

- Huerta-Cardoso O., Encinas-Oropesa A. & Longhurst P. (2016) Innovation in materials for the circular economy. Talk at the 2014 Disruptive Innovation Festival. The Ellen MacArthur Foundation and Cranfield University. 20 October -14 November 2016.
- Huerta-Cardoso O., Encinas-Oropesa A. & Longhurst P. (2015) Novel materials through design thinking process. Oral presentation at XIII Symposium of Mexican Students and Studies. University College London (UCL) 23 - 25 July 2015.
- Huerta-Cardoso O., Encinas-Oropesa A. & Longhurst P. (2015) Sustainable materials for social change. Oral presentation at MEX-UK International Seminar: Energy, Materials and Technology: Human and Social Aspects. Cranfield University 27 April 2015.
- Huerta-Cardoso O., Encinas-Oropesa A. & Longhurst P. (2014) Sustainable materials from agro waste. Poster session presented at XII Symposium of Mexican Students and Studies. Leeds University 4-6 Agosto 2014.
- Huerta-Cardoso O., Encinas-Oropesa A. & Longhurst P. (2014), Bio-based material from waste. Talk at the 2014 Disruptive Innovation Festival. The Ellen MacArthur Foundation and Cranfield University. 20 October -14 November 2014.

2 Literature review

2.1 Composites

A composite is a material consisting at least of two combined constituents or phases mixed at macroscopic level (Figure 6). These phases; a reinforcing or dispersed phase, a matrix or continuous phase [64] and the boundary region between two phases [65], are not soluble in each other.

Polymer matrix composites (PMCs) are comprised of a variety of short or continuous fibres bound together by a polymeric matrix, and their increasing attention is due to the combination of low-cost materials and improved final properties.

The matrix holds the dispersed phase together, transferring the loads to the reinforcement while protects the composite system from the majority of degradative processes (i.e., delamination, water absorption, impact damage, chemical attack, etc.) that may cause failure in the PCM. Hence, the matrix is frequently the weak link in a composite system.

The matrix phase can be a thermoset or thermoplastic polymer. Some of the many significant advantages thermoplastics offer over thermosets are their softening behaviour when heated, their low processing cost, design flexibility and ease of moulding complex parts [66].

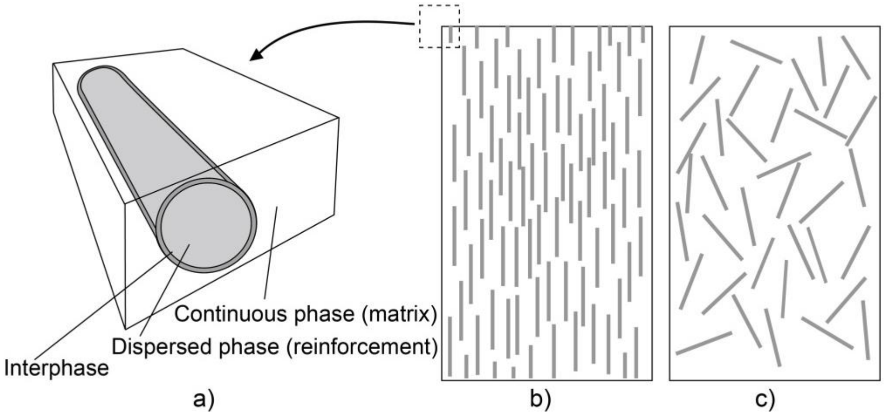


Figure 6. Composite configuration. a) Composite phases. b) Short fibre aligned composite. c) Short fibre randomly oriented composite. Adapted by the author [64].

2.2 **Green-composites**

In recent decades, as oil prices increased, so did the interest and research in bio-based materials. New developments were the result of this work; biodegradable films, sheets, and mould forming materials saw the light during the 1980's. Now plant-based materials have become increasingly more popular [67]. Looking at the use of bio- or renewable carbon, as opposed to petrocarbon for materials, has enabled attention to a reduced carbon footprint trend in new material developments. Thus, the use of annually renewable bio-feedstocks to manufacture materials may offer an inherently neutral carbon footprint value proposition [68] by balancing the amount of carbon released during material manufacturing with an equivalent amount sequestered or offset during plant growth and material use [69].

Bio-composite materials comprise at least one phase derived from a biological origin. However, fully green composites have both matrix and reinforcement derived from renewable resources [70], compounding biopolymers (e.g., PLA) with natural fibres (e.g., flax) or even by-products from food crops (e.g., rice husk) [71]. Bio-polymers reinforced with natural fibres are generally named green composites.

In recent years, several new polymers (Figure 7) derived from natural sources such as cellulose, starch, wood flour and PLA have emerged, leading the race as potential replacements for traditional plastics [72]. PLA has been considered for this study. The selection of a matrix polymer is based on availability, sustainability, and compatibility with cellulose fibres. PLA in particular, satisfies many favourable requirements as a thermoplastic material and can be used in conventional processing. Thus, it is suggested as commodity resin and as matrix material for non-critical and non-load bearing parts, such as packaging and casing applications. Biopolymers are an acceptable matrix for natural fibre-reinforced composites due to their highest percentage of renewable resources and environmental benefits offered.

Given the fact that natural fibres' cellulose degrades at ~200° C [66], it is hard to find a suitable thermoplastic matrix that can be used in biocomposite applications without damage to the fibre structure. A notable exception is PLA with processing temperatures well below the degradation temperature ranges of natural fibres.

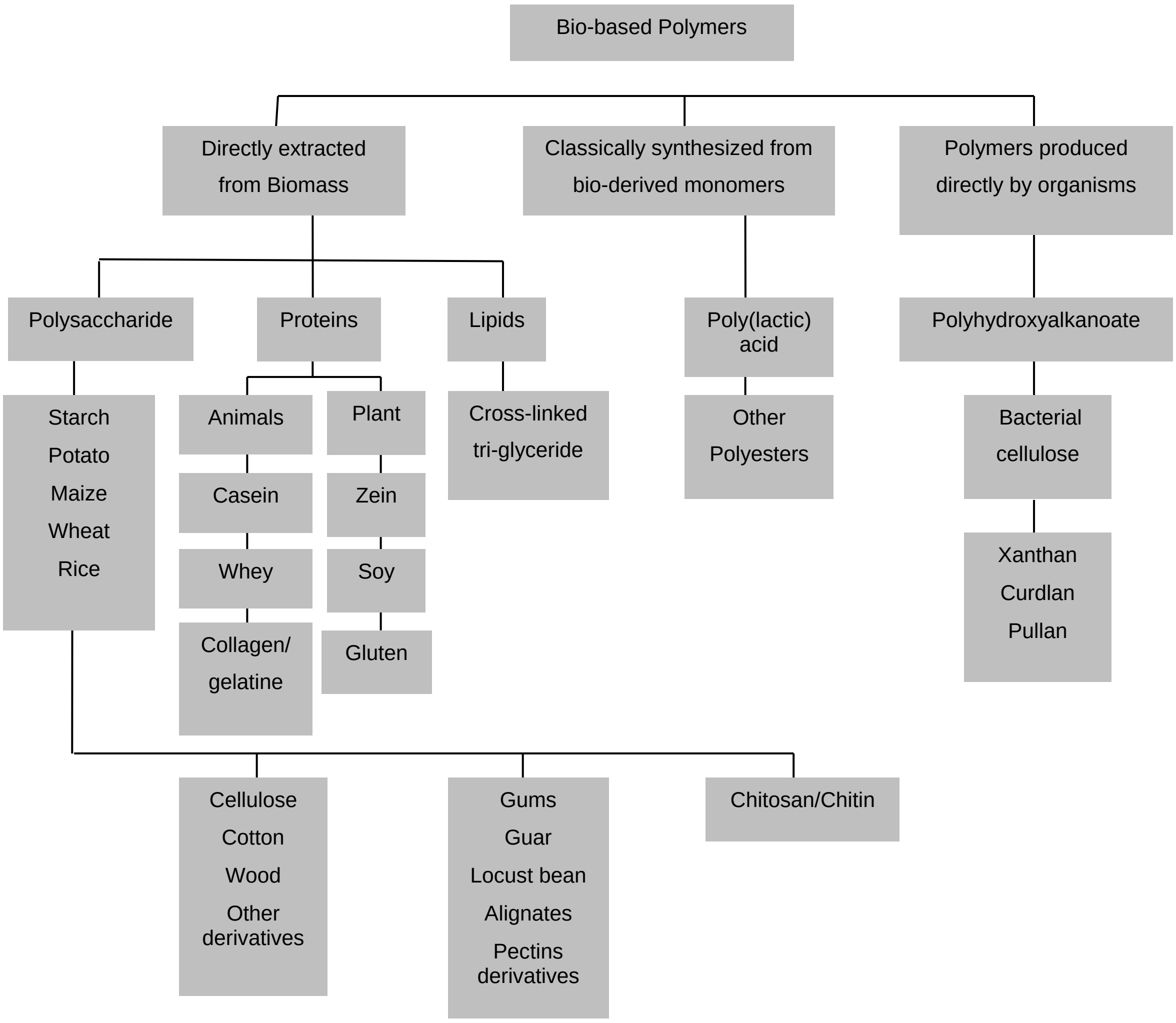


Figure 7. Classification of biodegradable polymers. Adapted by the author [73]**.**

2.2.1 **Poly(lactic acid) (PLA)**

PLA is a transparent and semi-crystalline polymer with a melting point (T_m) of approximately 130-175^o C and a glass transition (T_g) of about 55-65° C [74] requiring processing temperatures of 185-190° C [75]. PLA (Figure 8) is the first degradable polymer to be commercialised by the plastic industry on a big scale, therefore it has been widely embraced for compostable packaging applications without considering the disruption to current waste management systems. It has high strength and low elongation at break [76] and can be made from annually renewable resources [59]. PLA poses several advantages in comparison to oil-based polymers, which include:

1) Production from annually renewable resources such as maize or sugar beets.

2) Considerable carbon fixation quantities due to its natural origin.

3) Recyclability and compostability.

4) Use of 20-50% fewer fossil resources for production in comparison with oil-based polymers.

5) May improve farm and circular economies as it helps decoupling plastics from fossil feedstocks by exploring and adopting renewably sourced feedstocks. [74,77–79].

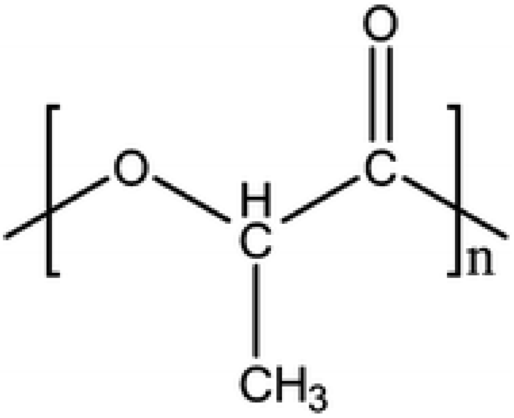


Figure 8. Basic structure of poly(lactic) acid.

Although PLA has been shown to be a brittle and stiff material, it can be processed similarly as other thermoplastics on standard equipment (e.g. extrusion and injection moulding) to produce moulded parts, films, or fibres [59,74,80].

To overcome the stiffness, brittleness and the low thermo-mechanical resistant properties that have limited the use of PLA in broader applications; additives like plasticizers or fillers, i.e. fibres, have been added during its processing [62,70,81,82]. PLA engineering and functional properties are given in Table 2 and Table 3 respectively.

Table 2. Engineering properties of commercial grade poly(lactic) acid - Ingeo^{TM}.

Property	Value
Thermal conductivity (amorphous sheet)	- 8° C 0.127 J/m -°K-s 25° C 0.130 J/m -°K-s 58° C 0.131 J/m -°K-s 124° C 0.126 J/m -°K-s 190° C 0.121 J/m -°K-s
Thermal conductivity (crystalline pellets – 25% crystallinity)	25° C 0.160 J/m-°K-s
Glass Transition Temperature, T_g	55 – 60° C
Peak Melt Temperature, T_m	145 – 170° C
Specific Gravity, ρ	1.24 - 1.25 g/cc
Melt Density (200° C), $\rho_{.melt}$	1.12 g/cc
Pellet Bulk Density, $\rho._{bulk}$	0.79 - 0.85 kg/litre (49 - 53 lb/ft3)
Typical Flake Bulk Density, $\rho._{flake}$	0.593 kg/litre (37 lb/ft3)

PLA degradation occurs by hydrolysis. It is degraded into CO_2 and H_2O by microorganisms under lab compost row, soil and ambient exposure conditions within a period of 60-120 days [83–87]. PLA degradation in the environment is about six months to two years, being this dependent on the size and shape of the sample, the isomer ratio, and temperature of hydrolysis [86,88].

Currently, only a limited quantity of bio-based polymers are used for food packaging at an industrial scale [89]. Poor material properties compared with oil-based equivalents, the diversion of food crop land use [90] and higher manufacturing costs make it difficult to achieve a competitive production.

Table 3. Poly(lactic) acid functional properties for packaging.

Material property	Functional property	Packaging Improvement
Heat seal initiation with vinyl acetate/ethylene vinyl acetate copolymer (VA EVA) between 80 and 85° C [29]	Deadfold, twist and crimp	Improved folding and sealing
Tensile modulus of 500-580 3500–4000 MPa [29; 57; 58].	High tensile modulus	
The CO_2 permeability coefficients for PLA (15.65+-0.63 - 19.44+-0.90) are lower than PS but higher than PET [59]	Barrier properties	Grease and oil resistance
	Renewable resource	Made from CO_2
	Flavour and aroma Properties	Reduced taste/odour issues
Heat seal initiation with vinyl acetate/ethylene vinyl acetate copolymer (VA EVA) between 80 and 85° C [29]	Low-temperature heat seal	Stronger seals at lower temperatures
High Gloss & Clarity	Wet paper strength, ability to downgauge coating	Package aesthetics
Critical surface energy of 38 dynes cm^2 [29]	Low coefficient of friction, Polarity	Printability
PLA migrants into the diet are lower than 18.0ppb. [56]	GRAS Status[56]	Food contact approved

2.2.2 **Natural fibre-based composites**

The use of biodegradable and environment-friendly plant-based fibres as feedstocks for composites has been a natural choice to make them ‘greener’. The availability of inexpensive plant-based fibres has encouraged their use in past years.

Studies have proven the importance of using natural fibres such as: cotton [91], jute [92,93], abaca [42], flax [62,94], wood [95], hemp [96], kenaf [97], and bamboo [98] as reinforcement. However, some natural fibre limitations (see

Table 4) such as the low processing temperature and moisture absorption must be considered when used in bio-composites. Natural fibres can be classified according to their origin in mineral, animal and plant/vegetable as depicted in Figure 9.

Table 4. Main advantages and disadvantages of natural fibres [99]**.**

ADVANTAGES	DISADVANTAGES
Low cost	High moisture absorption
Renewable resource	Poor dimensional stability (swelling)
Low density	Poor microbial resistance
High Young's modulus	Low thermal resistance
Good tensile strength	Discontinuous fibre
Non-abrasive to tooling and moulds	Anisotropic fibre properties
No skin irritations	Low transverse strength
Low energy consumption	Low compressive strength
CO_2 neutral	Local and seasonal quality variations
Biodegradable	Demand and supply cycles

Fibre choice is usually determined by selection criteria such as ultimate mechanical properties, interfacial adhesion with the matrix, strength, cost, availability of resources, chemical properties, and resistance to moisture, among others [100]. These are often dictated by fibre constituents and origin.

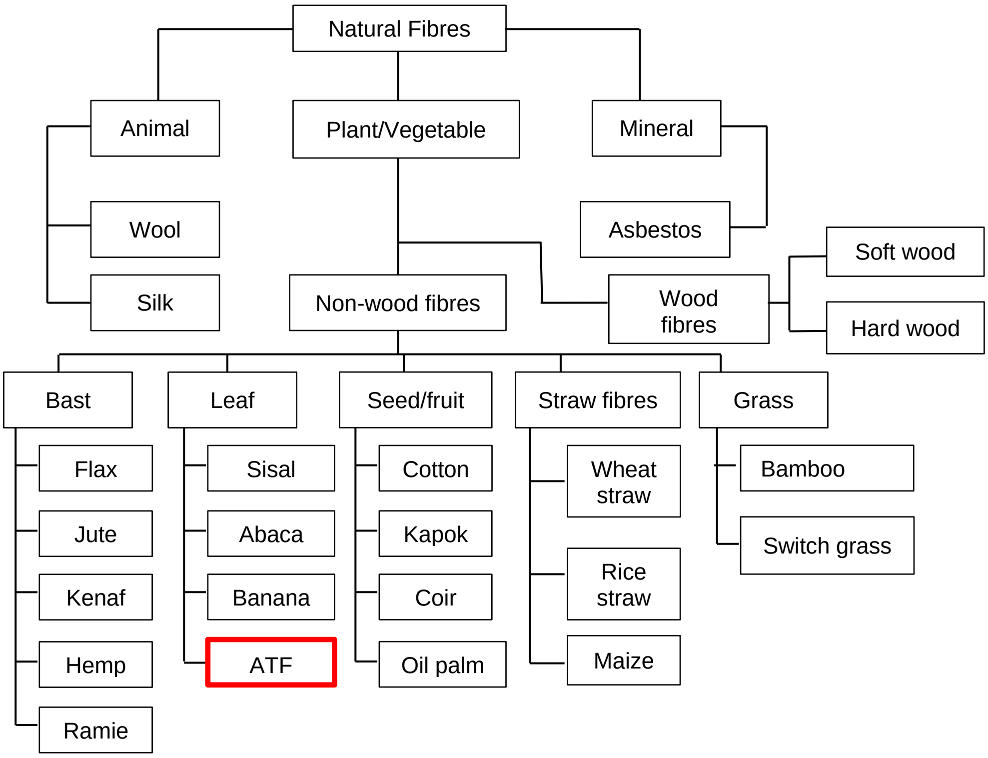


Figure 9. Classification of natural fibres. Adapted by the author [82].

Natural fibres are lignocellulosic in nature. Composition varies from fibre source, but primarily contains cellulose, hemicelluloses, lignin, and extractives. Commonly, extractives, such as waxes, are present in small amounts contrary to the first three components which are found in higher proportions. These substances are not evenly distributed within the fibre cell wall, and their concentrations change from one region to another [101]. The properties of each constituent contribute to the overall fibre properties, and consequently to the final performance of the green composite material. Figure 10 shows a typical cell wall with principal components.

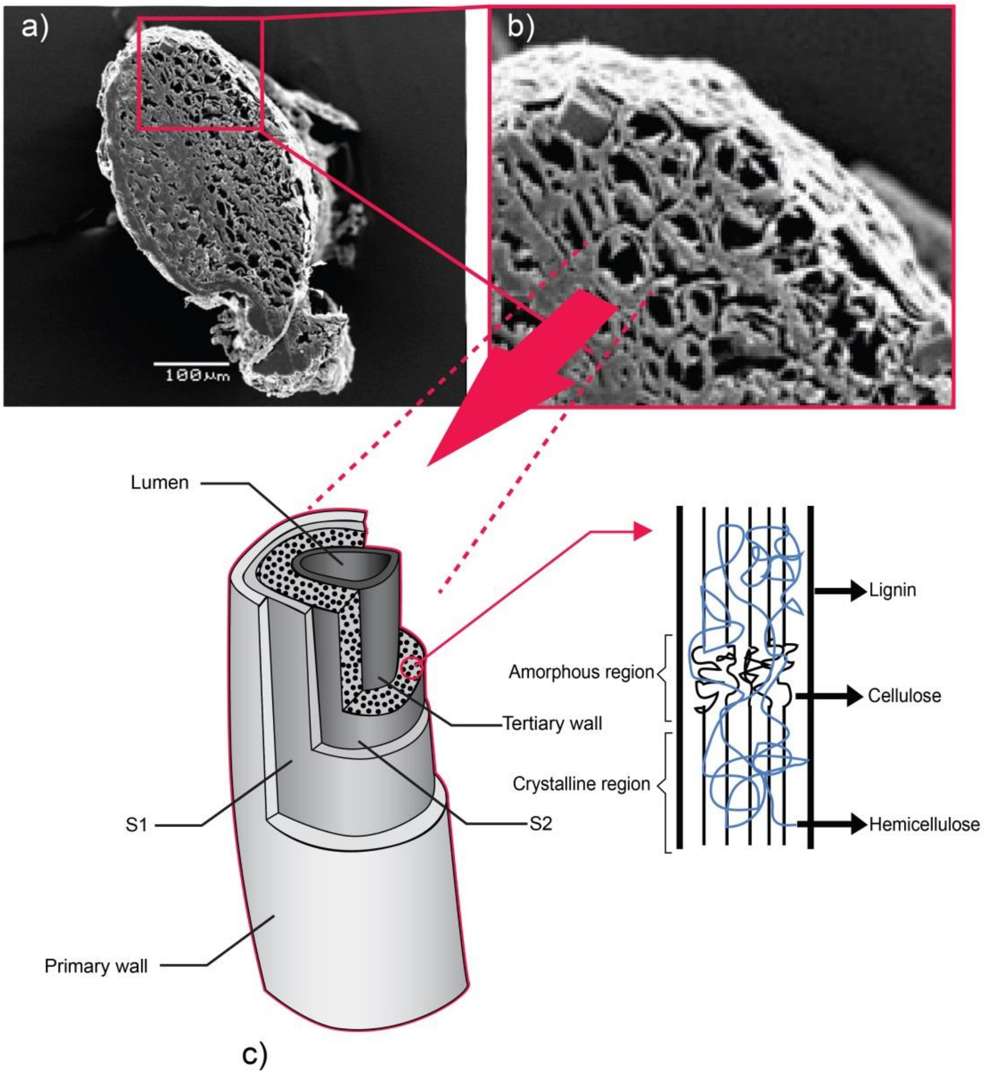


Figure 10. Main structure of a typical *Agave tequilana* fibre (fibre-cell microstructure). a) cross-section view showing the fibre-cells, lumens and middle lamellae. b) magnification of the cross-section. c) schematic drawing showing the different layers of an individual fibre-cell. Adapted by the author [102]**.**

2.2.3 **Cellulose**

Cellulose is a carbohydrate, (carbon, hydrogen, and oxygen) present as structural material in plant cell walls in the form of microfibrils. Cellulose is one of the most abundant and essential components of natural fibres in composites manufacturing. Higher cellulose content leads to higher stiffness making the fibres suitable for resin reinforcement [54,103–105]. Cellulose chains have three free hydroxyl groups (as shown in Figure 11) on each glucose unit that have a fundamental role in fibre modification.

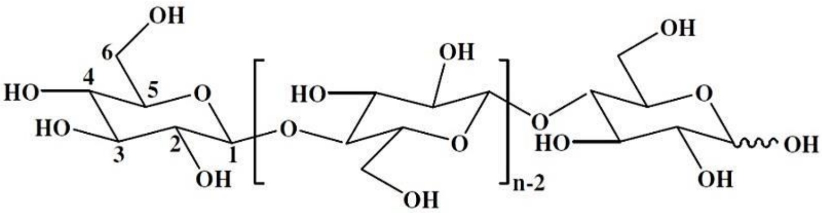


Figure 11. Cellulose chemical structure showing the multiple hydroxyl groups forming hydrogen bonds with oxygen atoms on the same or on a neighbour chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength [106]**.**

2.2.4 **Hemicellulose**

Hemicellulose is a polysaccharide. It binds bundles of cellulose fibrils into microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions (see Figure 10c); and it is crosslinked to lignin. Hemicellulose hydrophilicity is greater than cellulose due to its low molecular weight and amorphous structures. Hence, is responsible for the biodegradation, moisture absorption, and thermal degradation of the fibre.

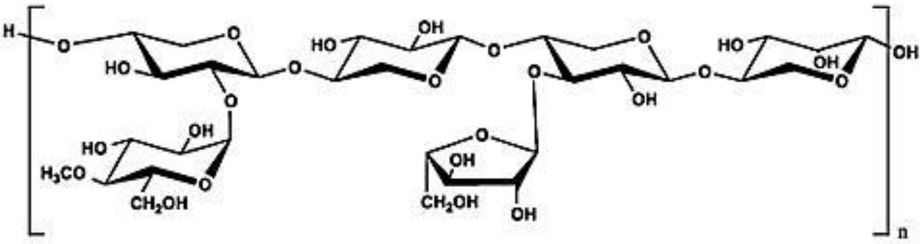


Figure 12. Hemicellulose chemical structure showing its random and amorphous nature.

2.2.5 **Lignin**

Lignin is a macromolecule composed of aliphatic and aromatic constituents (see Figure 13). It works as a biological barrier and binder for hemicellulose and cellulose to form fibre cell walls. Lignin is much less hydrophilic than either cellulose or hemicellulose [107]. Lignin is more thermally stable, and it allows better response to chemical modifications such as acetylating, as well as reduces the level of biodegradation [66].

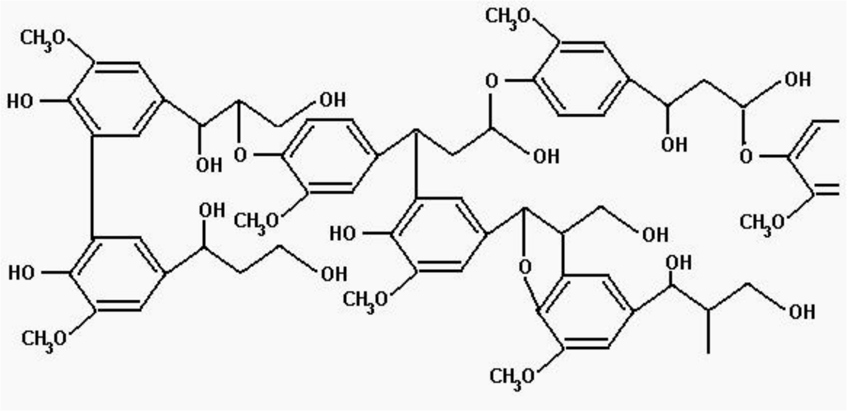


Figure 13. Portion of a possible structure of lignin. Lignin is a huge molecule that is interwoven with, and chemically bonded to cellulose. All kinds of linkages occur in lignin and it is not possible to show a complete structure.

2.2.6 **Extractives**

In addition to the major chemical components, natural fibres contain small amounts of inorganic materials, and low molecular mass organic materials usually referred to as "extractives". This non-cellulosic compounds (except proteins, inorganic salts, and colouring matter, which are found in the lumen) [108] create the majority of issues for bio-based composites such as poor absorbency and poor wettability [109].

2.2.7 **Mechanical properties of natural fibres**

Mechanical properties of natural fibres depend on their composition, morphology and crystalline structure [52]. It is also well known that climate, extraction methods, and experimental conditions are factors that affect natural fibre properties.

2.2.8 **Thermal behaviour of natural fibres**

Thermal degradation of natural fibres is essential in the development of bio-based composites. It influences the curing temperature for thermoset-based composites and extrusion temperature in thermoplastic composites. The thermal degradation of natural fibres has been recognised as a two-stage process, shown in Figure 14. The first stage is associated with hemicelluloses degradation at temperatures between 220-280° C, and a second stage related to lignin degradation is at 280-300° C [66].

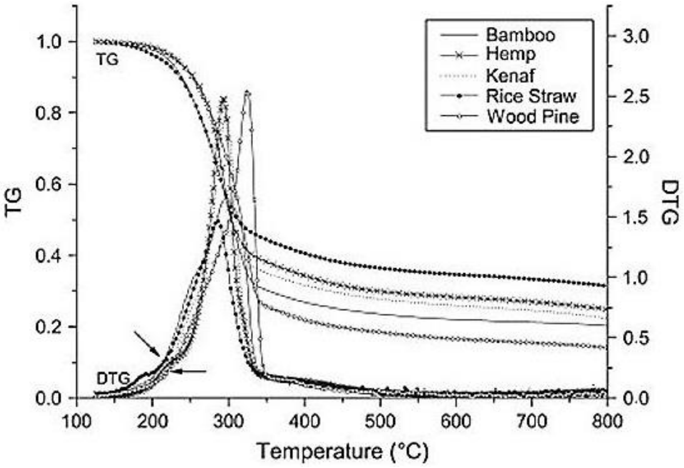


Figure 14. Typical thermogravimetric analysis and differential thermogravimetric analysis curves for natural fibres [110]**.**

Thermal degradation of the ligno-cellulosic materials within a bio-based composite system could result in the production of volatiles at processing temperatures above 200° C. Thermal degradation could lead to porous composites with lower densities and inferior mechanical properties. In order to improve thermal stability, and thus mechanical properties of most common natural fibres used in bio-based composites several treatments/methods such as mercerization, esterification, grafting, etc. have been reported [111–113].

2.2.9 Modification of natural fibres

Due to a large number of hydroxyl groups in cellulose, natural fibres are hydrophilic; leading to poor interfacial adhesion and poor moisture resistance properties when compounded with hydrophilic polymers (i.e., PLA). Thus, their potential as reinforcement/filler for bio-based composites is reduced. Nevertheless, natural fibre modifications are considered to improve these drawbacks [114–117]. Natural fibres must be treated or modified considering the following factors:

- Maximum homogenization of the fibre properties
- Degree of elementarization and degumming
- Degree of polymerization and crystallisation
- Adhesion within the fibre-matrix system
- Moisture resistance [118].

2.2.9.1 Physical modification

Physical treatments change the structural and surface properties of the fibre and thereby influence the mechanical bonding with the matrix. During tequila production (section 2.3); fibres are semi-extracted from the plant using several processes similar to common physical modification methods, such as stretching [119], calendering [120,121], thermotreatment [122], and steam explosion [123]. These processes change the structure and surface of the fibres, thereby leaving them already prepared for further chemical modification or interaction with the polymeric matrix.

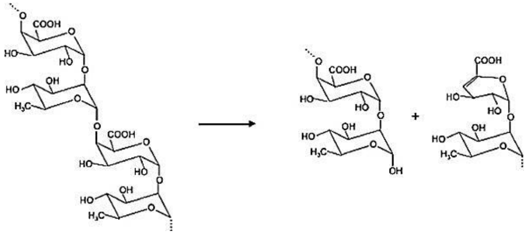
2.2.9.2 Chemical modification

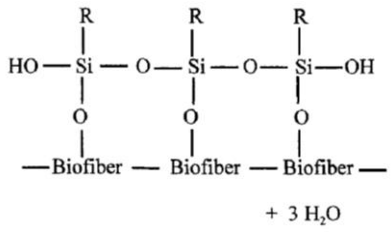
Modification of natural fibres by chemical means is used to modify the surface of the fibres or the whole fibre by changing its structure or by the introduction of new functional groups into the surface of the fibre.

Dewaxing [124–131], coupling agents [55,129,132–134], alkali [53,55,93,103,124,129,132–139], and enzymatic treatments [62,140–145]; have been widely reported in the literature for other lignocellulosic fibres. However, the effect of such modification treatments on fibres from the tequila production waste stream, and its influence on interfacial adhesion with PLA has not been reported. Thus, a better understanding of the chemical composition, physical properties and surface’s adhesive bonding of this natural fibre source is necessary for developing bio-based composites.

The main reactions, improvements to mechanical properties and other benefits, and drawbacks of these chemical modification methods for other natural fibres are depicted in Table 5.

Table 5. Chemical surface modification methods used for lignocellulosic fibres.

Treatment	Chemicals / Enzyme	Reaction	Treated fibre / Matrix	Influence on mechanical properties of composites / Improved properties	Drawbacks
Alkali	Sodium Hydroxide (NaOH)	$\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber} - \text{O} - \text{Na} + H_2O$ Main treatment effect Increases fibre roughness by disrupting its hydroxyl group (–OH), removing lignin, wax, and oils from the surface of the fibre cell wall, depolymerising cellulose and exposing crystalline regions.	• Kenaf / PLA [55,133] • Kenaf / Epoxy [133] • Hemp / PLA [53,135] • Hemp / Epoxy [133] • Hemp [103,133,135] • Flax / PLA [138] • Flax / Epoxy [133] • Henequen / Epoxy [133] • Henequen / HDPE [132] • Agave Americana [137] • Sisal / PLA [134] • Sisal / Rubber [103,136] • Sisal [103] • Jute / Epoxy [93] • Jute [103] • Kapok [103] • Bamboo / PLA [138,139] • Oil palm fibres [129]	• Increase in composite's tensile strength and higher compression strengths related to the enhanced mechanical interlocking of the fibre and the resin. • Composite's flexural strength and modulus was found to be greater. • Higher interfacial friction stress between matrix and fibre. • Better mechanical properties as compared to just detergent washed, dewaxed and bleached fibre based composites [146]. • Increased high deflection temperature, lower in comparison to that of silane treated composites [55].	• Negative impact on economics. • Energy, chemical, and water intensive. • The effluent is ecologically undesirable because of its high alkalinity, biochemical, and chemical oxygen demand. • No influence in forming transcrystalline regions [134]. • In jute / epoxy composites, the rougher surface morphology after treatment did not improve the adhesion [93]. • Reduces strength of the fibre. • Lower tensile strength composite in comparison to that of silane treated [132].
Enzymatic	Enzyme: Pectate Lyase	 Main treatment effect It is an alternative method to Alkali treatment and field retting by microorganisms with a lesser impact on the environment. The enzyme breaks down the pectin and removes waxes, oils and other impurities. The enzyme cleaves de-esterified pectin in plant cell walls through	• Flax / PLA [62,141] • Flax / PP [62,145] • Hemp / Cellulose acetate butyrate [144,147] • Kenaf / PP [142] • Ramie [140] • Cotton [143]	• Reduced environmental pollution and energy consumption. • Higher mechanical properties attributed to the removal of the surface finish [142]. • Minor but positive thermal properties were improved [141]. • Composite strength is about 50% better compared to similar PP/flax fibre composites [62]. • The modulus of the single fibres decreased gradually with enzyme concentration due the reduction in the non-cellulosic content that binds the cellulose fibres [144].	• Negative impact on economics. • Prolonged treatment fibres could decrease the tensile modulus and stress at the break of fibres [144]. • Although considered natural substances, may need to be regulated by specific legislation covering biotechnology products [148]. • Require proper conditions for enzyme production, monitoring enzyme yielding, the recovery, and finishing stages to ensure a good manufacturing practice

Treatment	Chemicals / Enzyme	Reaction	Treated fibre / Matrix	Influence on mechanical properties of composites / Improved properties	Drawbacks
		cleavage of the internal glycosidic bond by beta-elimination.		• Pectate lyase enzyme improved the mechanical properties more that Alkali treatment [144]. • Improvement in pull out behaviour [141].	[148]. • Degumming does not improve flexural properties of the composite [144].
Acetylation	Acetic anhydride (CH3-C(=O)-O-C(=O)-CH3)	$\text{Fiber} - OH + CH_3 - C(=O) - O - C(=O) - CH_3 \rightarrow \text{Fiber} - OCOCH_3 + \underbrace{CH_3COOH}_{\text{Acetic Acid}}$ Main treatment effect Plasticization of cellulosic fibre through the reaction of hydroxyl groups (–OH) of the fibre with acetyl groups (CH3CO–).	• Flax / PP [125,149] • Flax [130] • Hemp [130] • Rayon / PS [126] • Cotton / PS [126] • Wood / PS [126] • Oil palm fibres [129] • Sisal / LDPE [127] • Sisal / Epoxy [128]	• Increased tensile and flexural strengths [125]. • Improvements in fibre surface morphology and moisture resistance properties [125]. • Increased interfacial shear strength [126]. • Heterogeneous and smoother fibre surface [125,130,149]. • Increased fibre's surface energy. • Improvement in fibre dispersion.	• Negative impact on economics. • Energy, chemical, and water intensive. • The effluent is ecologically undesirable because of its high alkalinity, biochemical, and chemical oxygen demand. • Decrease in Charpy impact strengths [125]. • Decrease the resistance to stretching. • Tensile strength of acetylated composites is slightly lower than that of untreated ones [128].
Coupling agent	(3-Aminopropyl) triethoxysilane H2N(CH2)3Si(OC2H5)3 (Silane)	 Main treatment effect Forming of covalent bonds through the reaction of silanol with the hydroxyl group (–OH) of the fibre.	• Sisal / PLA [134] • Hemp / Epoxy [133] • Flax / Epoxy [133] • Oil palm fibres [129] • Kenaf / PLA [55] • Kenaf / Epoxy [133] • Henequen / Epoxy [133] • Henequen / HDPE [132]	• Higher increase in modulus than that of alkali treated fibre composites [55]. • Improved composite's flexural strength in comparison with Alkali treated composite [55]. • Increased High deflection temperature, higher than that presented for alkali treated composites [55]. • Silanes may reduce the number of hydroxyl groups rendering natural fibres more hydrophobic	• Negative impact on economics. • No influence in forming transcrystalline [134]. • Decreased impact strength in comparison with alkali treated composite [55]. • Lower tensile modulus composite in comparison to that of alkali treated [132].

2.3 ***Agave tequilana* fibres**

Agave is the name of a succulent plant of a large botanical genus of the same name, belonging to the Agavaceae family. The most commonly grown species of Agave include *Agave americana*, *Agave angustifolia*, *Agave attenuate*, and *Agave tequilana* Weber *var.* azul (ATW).

The ATW plant shown in Figure 15 is typically grown in Mexico for tequila production, and lately has been considered for biofuel (i.e. ethanol) production [150]. ATW has spirally arranged leaves forming a rosette about 1.2±1.8 m tall. The leaves are bluish green in colour, about 90±120 cm long and 8±12 cm width [151]. Its cultivation has been an inexpensive activity; the plant grows in semi-arid desert lands requiring very low field labour, watering, or agrochemicals.

Figure 15. *Agave tequilana* Weber *blue* variety.

The heart of the plant is used to produce tequila. In basic terms, tequila production process starts with the harvesting where *Agave tequilana* heart (commonly referred as “head” within the tequila industry) (Figure 16a) is separated from the leaves, to then be taken to the oven where it is steam cooked, and finally milled to extract the juice from which tequila is produced. The *Agave* head milling process generates a by-product usually called bagasse (Figure 16b); which represents around “40% of the total weight of the milled

Agave on a wet weight basis"… The head weight is around …"20 and 60 kg although some can reach 100 kg" [151]. In 2013 more than 300,000T of bagasse were co-produced with tequila (Figure 17) [152]. These by-product fibres extracted from the heart of the ATW plant have been used for the development of the novel green material studied in this research.

Figure 16. Tequila production stages. a) ATW heads being transported. b) ATW bagasse after milling. Source [153]**.**

Although some studies have shown there are cost-effective uses for the low-value waste/by-product from the tequila production [56,61], the remaining leaves that are left in the fields as soil nourishment after harvesting are not used for commercial purposes. From this residue, only the material from the leaves has enough mass to be considered for fibre production.

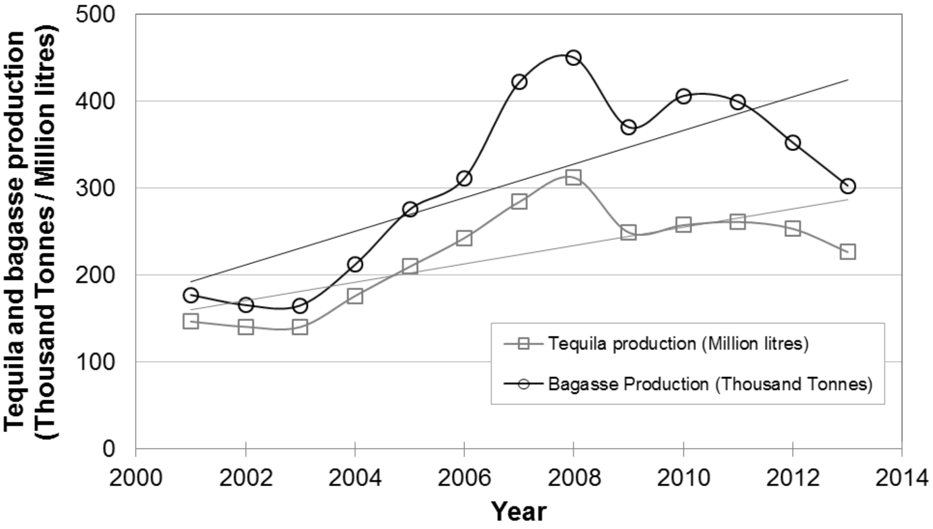


Figure 17. Tequila and bagasse production trend. Adapted by the author [152]**.**

Bagasse and leaves from ATW are basically composed of cellulose, hemicellulose, and lignin. As shown in Table 6, this by-product presents high α-cellulose content similar to other lignocellulosic fibres widely used in PMCs.

Table 6. *Agave tequilana* Weber chemical composition in comparison with other lignocellulosic fibres used in PMCs.

Item (%)	ATW fibrous bundle (a)	ATW head (a)	Sisal fibres (b)	Hemp fibres (b)
Ethanol-benzene extracts	5.3	3.1		
Ethanol extracts	2.9	5.5		
Hot water extracts	5.8	3.9		
Lignin	15.9	16.8	11	4
α-cellulose	64.8	64.9	73	74
Hemicellulose	5.1	5.5	13	18
Ash	1.0	2.0		

(a) [61]. (b) [103].

ATF is thermally stable between 100-220° C which suggests safe use up to a maximum temperature of 220° C (Figure 18) [102]. These values and the TGA curve behaviour are in agreement with most common natural fibres used in bio-composites which have a thermal degradation in a two-stage process within the ranges of 220-280° C and 280-300° C (Figure 14).

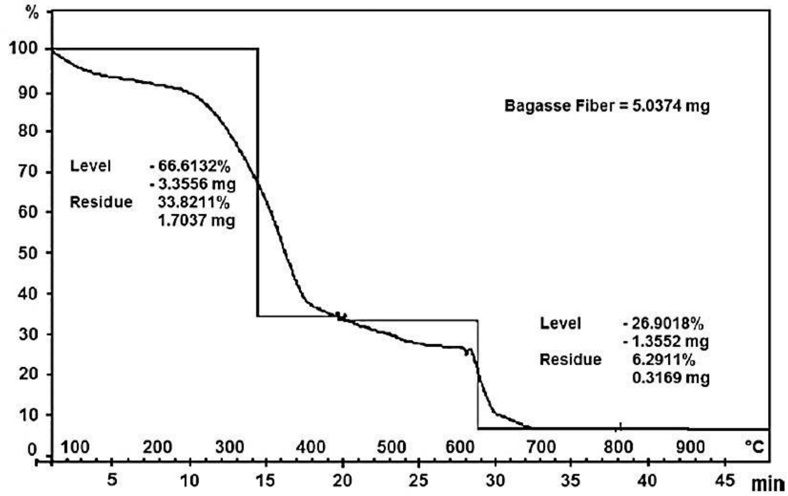


Figure 18. Thermogravimetric analysis curve of *Agave* tequilana fibres [102]**.**

ATF mechanical properties depend on its composition, morphology and crystalline structure [52]. It is also well known that climate, extraction methods, and experimental conditions are factors that affect natural fibre properties. Table 7 shows tensile properties of *Agave* fibres extracted from the leaves of a different species (*Americana L*).

Table 7. Mean tensile properties of *Agave* fibres (*Americana L*) [154]**.**

Radius of Agave fibres (μm)	σ (MPa)	ε (%)	E (GPa)
60–80	154 ± 47	16.4 ± 8.2	2.9 ± 1.2
80–100	65 ± 42	13.6 ± 11.9	1.9 ± 0.6
100–120	80 ± 12	22.3 ± 6.0	1.3 ± 0.2
120–140	70 ± 21	19.1 ± 10.7	1.4 ± 0.3
60–140	100 ± 32	19.3 ± 8.2	1.7 ± 1.1

Values are mean ± SD.

2.4 Material development and selection

The research and development of a new material is a complex task, and especially when waste or by-products are being used as a raw material source. Methodologies and databases are available for new developments and material selection [23–27]. Nevertheless, traditional approaches to materials selection often rely on previously used materials, which results in safe, but, limited solutions [24,155]. Traditional material developments commonly rely on rigorous scientific procedures from the material paradigm perspective (i.e. structure, performance, properties and processing). These linear methodologies are mainly focused on technical/mechanical performance, and often leave unaccounted some other factors that are important to consider in view of current environmental and social challenges. Designing materials in isolation from surrounding factors is to the detriment of the entire system it takes part. Therefore, it is important to consider all the different factors/elements, interdependency, and constraints when designing a new material that may eventually take part of a more complex and already existent system.

Designing a new material using agro-industrial by-products must comprise a multidisciplinary approach, where knowledge from different areas, such as materials science, marketing, performance evaluation, and environmental sciences, among others, is interconnected in a complex and iterative system. This is to forestall complications regarding economic, legal, geographical, environmental, business, and social barriers. Therefore, a “synergy among diverse industries, agriculture and communities resulting in a profitable conversion of by-products and wastes into resources promoting sustainability” may be feasible [156], as has been recognized and defined by the Environmental Protection Agency (EPA) in the “Green Twinning” concept or by the Business Council for Sustainable Development for the Gulf of Mexico (BCSD-GM) as by-product synergy.

“Systems thinking” involves the understanding of a system by analysing the linkages and interactions between the different components that comprise the whole. “Whole-systems thinking” brings along radical resource efficiency through integrative design.

A method that could bring together the elements for the development of materials based on agro-industrial by-products, and for multidisciplinary research teams to consider all possible interconnections involved, rather than just a sequence of steps to follow under a traditional research and development (R&D) could be very useful. An understanding of this is presented in chapter 3: Design thinking approach as a sustainable innovation enabler in new material developments.

2.5 **Key findings of the literature review**

New and more sustainable materials, such as green composites, offer a potential solution to the environmental and economic issues (e.g., landfilling disposal, energy intensive recycling, sorting and collecting) posed by the large-scale production, and consumption of oil-based packaging [70,157,158]. The use of these green composites represents a reduction in oil consumption and leads to lower CO_2 emissions as they exhibit renewability of the source, biodegradability/compostability, and environmentally friendly processing [60,83,159].

Despite PLA brittleness and stiffness, it is recognised as a possible replacement for oil-based polymers since it fulfils several characteristics to work as a thermoplastic matrix, for composite use and as an optimal material for food packaging applications. It can be processed similarly as other thermoplastics on standard equipment allowing PLA based composites to get introduced at faster rates in the industry. Studies related to the use of PLA as a matrix with other lignocellulosic fibres, such as kenaf, are found in the literature. However, there is a lack of data on the use of ATF by-products within a PLA matrix system.

Recent interest in reducing the environmental impact of materials is leading to the development of novel natural fibre-based materials that can reduce our dependence on petroleum, while the use of renewable materials is maximised.

A better understanding of ATF properties, modification treatments, and interaction with a PLA matrix is needed within the context of a novel development of a bio-based composite material for non-load bearing parts such as packaging, casings, crates, etc. To overcome some drawbacks presented by the use of natural fibres, surface modification treatments (e.g. alkali treatment) aim to improve the interfacial bonding between natural fibres and matrix. Bonding between matrix and reinforcement plays a major role in the resulting composite properties. Thereby, modified ATF are a potential new economic alternative as raw material source, to produce bio-based composites as a possible environmental solution to handle oil-based materials disposal.

3 Design thinking approach as a sustainable innovation enabler in new material developments.

3.1 Introduction

A great challenge today's economies are facing is to successfully integrate environmental sustainability with economic growth and welfare. Concerns arising from the large-scale production and consumption of oil-based materials [2,3,15,16] have led to increased attention to the development of new and more sustainable material alternatives.

Materials appeal to us in several ways: by their aesthetics, their properties, and the resultant relation between these qualities working together. The technical properties are often considered a constant characteristic. On the other hand aesthetics may change along with the society, forcing traditional materials use into new applications. Since the materiality of a product provides emotional connections associated with aesthetic and functional qualities of a certain material used, the rethinking of materials and their use is key for the development of more sustainable products and production processes. Different expectations and other stereotypical associations related to materials are usually assigned by the user perception and its context (regardless material life cycle stage), for example, polymers have been seen for many years as a durable and revolutionary material, and just recently a shift in this perception presents polymers as pollutants. Consequently, making the use of predetermined materials in preconceived applications a general rule within the industry. Additionally, the introduction of new materials and the unconventional use of the current ones may provoke confusion to the different users-stakeholders all along the material life cycle. Thence, an erroneous judgement about appearance and properties based on a limited knowledge or misconception may lead to the deficient use of the materials qualities and resources (i.e., single use plastic).

Special concerns related to materials during their use and end-of-life phase in open life cycles, have promoted actions towards more sustainable innovation practices. According to Rossy et al. 2010 [22], these actions can be classified into two levels; technological (e.g. material substitution, minimization of material use,…) and non-technological (e.g., dematerialisation, closing loops,…). However, this has not been the case for transitional economies where waste management systems have proven deficient and little reliable resulting in landfilling of valuable materials [3,11,160]. Furthermore and from the perspective of environmental innovation (short: eco-innovation) [36,37], if truly sustainable innovation in material developments towards a sustainable behavioural change [38] is intended, then broad linked and interdependent levels must be considered: technological, social and institutional [33].

3.2 **Sustainable innovation in material developments**

Sustainable innovation in materials is a complex task. Traditionally databases and methods from the material science perspective are available for new developments and material selection [23–27]. However, these approaches rely on a preconceived paradigm, where materials are designed or selected based on their technical and aesthetical qualities. Thus, leaving unaccounted other surrounding factors that have a stronger influence regarding a development of new and more sustainable alternatives.

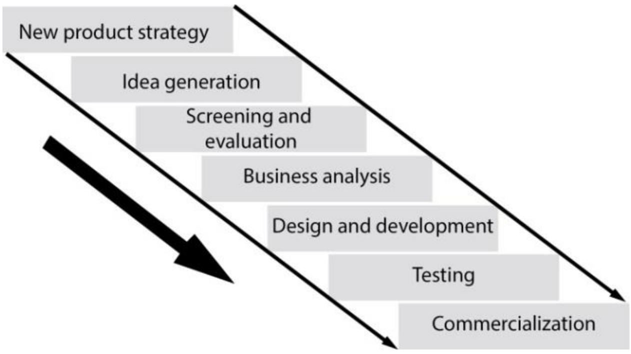


Figure 19. New product development model [161]**.**

During several years, linear models of innovation and other frameworks still linear (Figure 19) for new materials developments were successfully used, having many breakthroughs such as new polymers and super alloys. However, new needs and current environmental challenges require models of innovation biased against systemic and holistic perspectives; although, without undermining the importance of linear models [33]. “Systems thinking” involves the understanding of a system by analysing the linkages and interactions between the different components that comprise the whole [28–30]. Whole-systems thinking brings along radical resource efficiency through integrative design and real-world constraints [31,32]. Consequently, designing or selecting new materials, engaging the surrounding and constraining factors that influence the system they belong or they will become part, is essential in assuring a more sustainable material innovation, without the disruption of a system in place that works better in sustainability terms. For example, the new multi-layered films used for fresh food packaging, represent a bigger disruption to the current waste management system as they pose more difficulties for recycling that single layer films [162]. Therefore, it is important to consider all the different elements, connections, and constraints involved in new material developments since they will eventually take part of a more complex and already existent system.

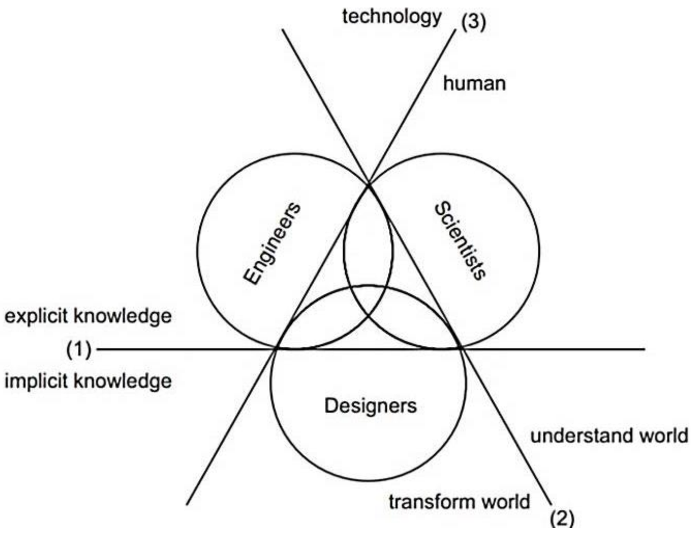


Figure 20. Theoretically hypothesised paradigm model of designers, engineers and scientists with the three main barriers distinguishing them [163]**.**

Designing or selecting a new material as in any innovation-led development must comprehend a multidisciplinary and cooperative approach as it has been previously recognized by Bartneck & Rauterberg (2007) [163]. However, the knowledge from the different areas involved is always interconnected in a complex and iterative system with well-defined boundaries of action as shown in Figure 20.

A model where integrative design and collaboration is encouraged will forestall complications regarding economic, legal, geographical, environmental, business, and social barriers. Therefore, promoting sustainability through a synergy among diverse industries, agriculture, communities and other possible stakeholders [156].

Design, as a systemic way of thinking, has the potential and flexibility to work as a bridge between new materials innovation and sustainability; understanding sustainability (Figure 21) from a systemic perspective as the interconnection of three fundamental macro-systems (environmental, economic and social) to everything else [164,165].

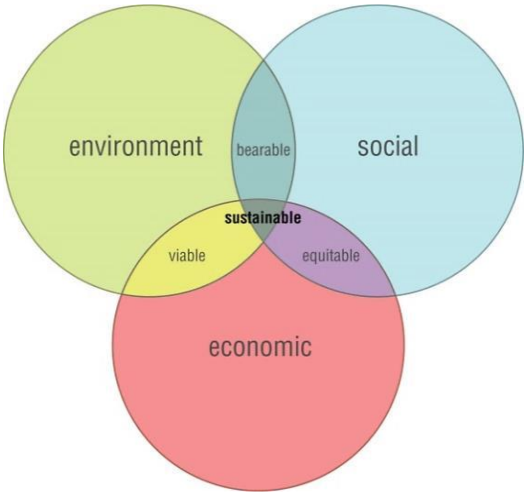


Figure 21. Venn diagram for sustainable development. Adapted by the author [164]**.**

In this chapter, a comprehensive “design thinking”-based method is drafted, to allow integrative or multidisciplinary research, to consider the possible interconnections, and to enable sustainable innovation in new material developments, rather than just give a sequence of linear steps to follow under a traditional research and development (R&D) work. Conceptualization of a new material is used as a case study example.

3.3 **Design thinking**

Previously, designers have focused on improving the look and functionality of physical products. During recent years, design tools have been used to successfully tackle more complex problems, such as reducing costs in the healthcare system [166]. This approach has been adopted now by businesses and non-profits as well.

As Richard Buchanan mentioned in his “Wicked Problems” [39], there is no single definition for design and design thinking (DT) that covers the diversity of ideas and methods gathered together under this always evolving label. However, under a broadened conception and for purposes of this paper DT can be defined as a human-centred, holistic, and abductive approach to innovation and problem-solving. It is integrative, emphatic, rational and systemic; and interconnects all the necessary elements that bring radical solutions to contextual problems. Moreover, because in abductive reasoning the solution is not derived from the problem, but it fits into it; DT may help influence a change towards a more sustainable material development as an integrative element to complement sciences.

A useful and general way to understand the complexity of decision making involved in a DT process can be seen at the give and take balance found in problem-solving situations in the real world. It can be seen that there is not such a thing as a linear design process in the sense of a step-by-step technique. There are many different ways to approach decision-making, and in this context, the solution or decision taken is influenced by constraints derived from the initial definition of the problem.

The DT process has been recognized difficult to standardize [167] but several stages in common can be identified across the different DT processes available in the literature as well as in the industry [168–173]. The process can be best summarised in four iterative stages:

- Discover
- Define
- Develop
- Deliver [174].

However, it is important to state that stages must be considered as innovation blocks rather than sequential steps to follow, as is shown in Figure 22.

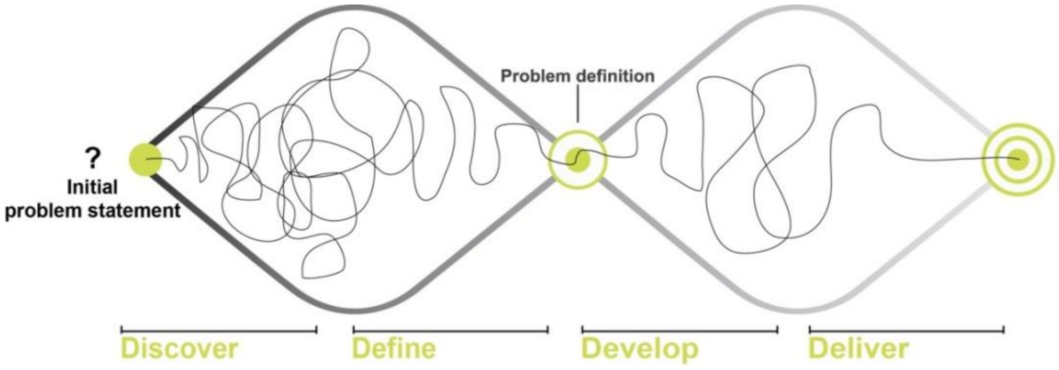


Figure 22. Double diamond design process. Adapted by the author [174]**.**

The method has proven efficient across different disciplines due to its generic nature, and it has the flexibility to be used for enabling sustainable innovation in material developments. Its stages consist of iterative loops where exploration and testing of hypothesis happen throughout the project. Contrary to other more linear methods that do not consider any similar stage, this approach makes special emphasis on the "Discover" phase at the fuzzy front end (FFE) as it has been referred by Rhea (2005) [175]. In material developments, where sustainable innovation is intended, this phase plays a critical role in defining the real nature of the problem that is being addressed, and it makes the best use of the designer's knowledge, skills, and tools. It is the early stage of the sustainable innovation process where ideas start to form, and the true problems emerge. However, at this stage, there is a certain level of ambiguity and a seeming unstructured process that may develop reluctances across the different stakeholders involved in the process, especially when they are from backgrounds different than design. Consequently, it is important to have a well-established, but flexible method, as a guideline, rather than a recipe to improve the confidence across reticent participants, to facilitate the dialogue, cross-fertilization, and innovation at early stages of sustainable material developments.

3.4 **Material conceptualization through a design thinking approach.**

A DT approach to enable sustainable innovation in new material developments is not intended to take over more conventional practices (i.e., material sciences approach-linear development method), but to tap into overlooked capacities humans have such as the ability to be intuitive, to recognize patterns and to build new ideas onto new discoveries in a systemic way, so that is possible to have an integrated approach towards new material developments as it is shown in Figure 23.

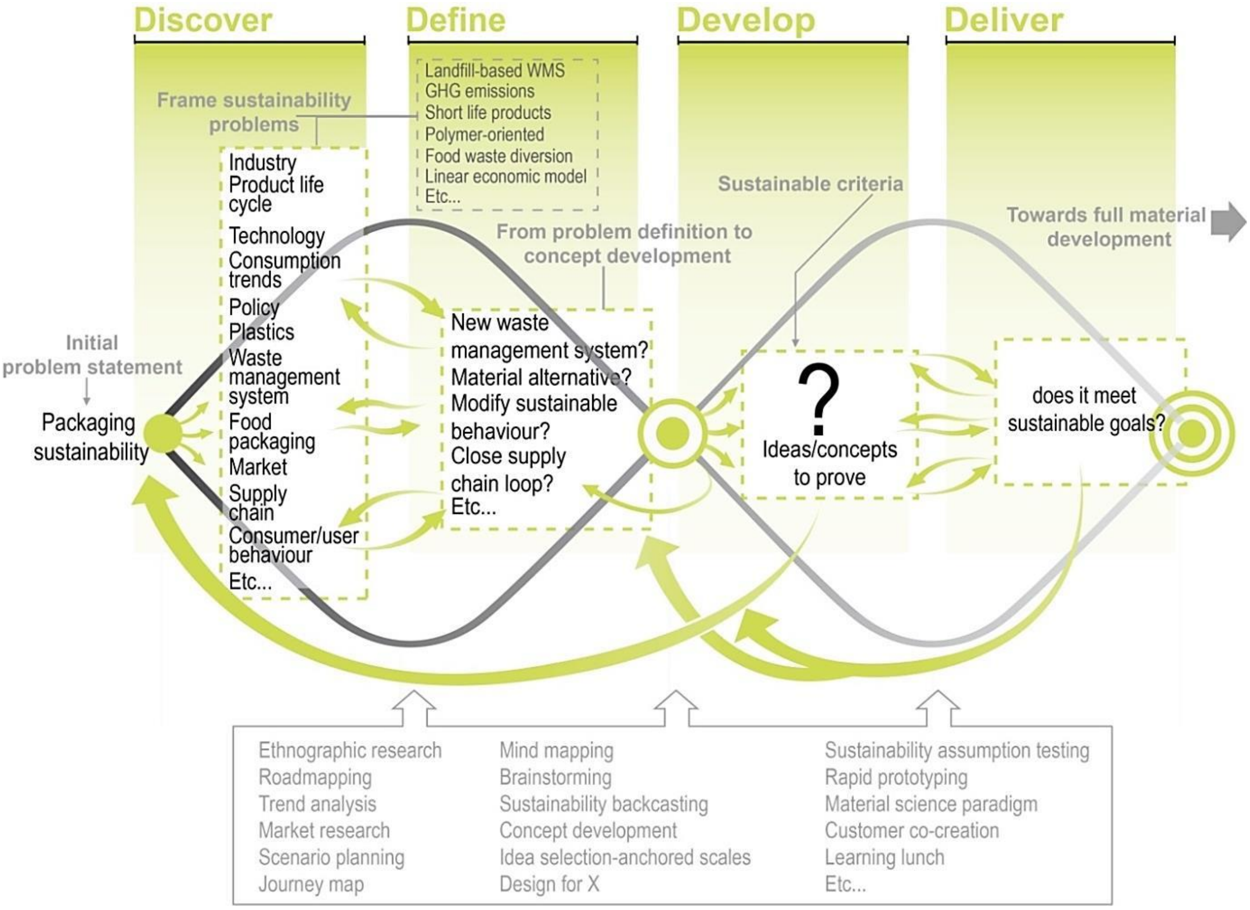


Figure 23. "Design thinking" model to enable sustainable innovation in new material developments.

The design thinking approach helped to understand the implications and interconnections between the influential factors related to the sustainability of packaging, in a Mexican scenario, as an initial problem statement. Then, it was possible to conceptualize the material through the definition of truly sustainability issues across the different phases of the method as follows:

3.4.1 **“Discover” phase**

During the start of “Discover” phase (Figure 24) the statement of what “the problem” is believed to be, allowed focusing efforts and contextualization of the problem. Therefore, influencing factors involved were easily identified and considered, so that their definition determined whether and how ideas were identified and analysed; and how the hypothetically new sustainable materials (at a conceptual level) can be selected and developed.

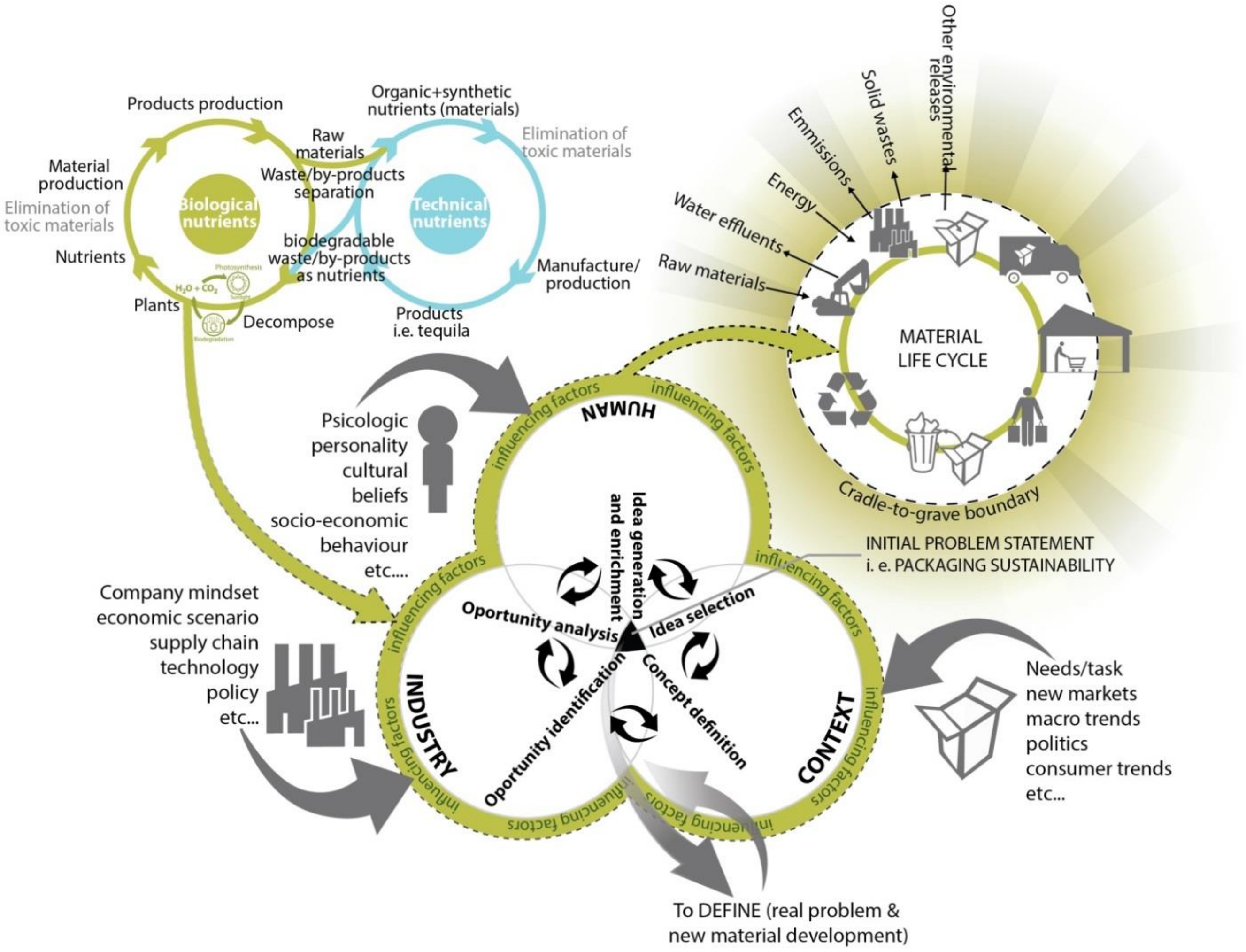


Figure 24. “Discover” phase.

The influencing factors related to the industry, context and human/user relations were contemplated initially since they impact more directly the development at first glance. During further stages, and as “Discover” stage progressed, more constraints were added to the equation making the system more complex and interconnected. However, the prioritisation of every influencing factor was necessary and defined according to the aim of the development.

An expanded understanding of the context related to the initial problem statement was achieved through data collection at this early stage (i.e., ethnographic research, desk research, reports, etc). This phase was built on iteration between data collection and data synthesis; where meaning derived from the data became the insight in the process.

Several methods and tools were used in this phase [176]. The idea of having little evidence at this point where constraints or influencing factors (intrinsic and extrinsic) and the initial ambiguity among them was involved in the process, was to facilitate the innovation at this stage of the material development. The intrinsic and extrinsic constraints (e.g., cultural beliefs, socio-economic structure, consumer trends, etc.,) considered at this phase helped define interconnected issues related to the original problem definition. The ever-changing human and contextual circumstances make design thinking process always subject to improvement and adaptation, and this adaptive nature worked as the basis in confronting uncertainty and ambiguity, and improvement was associated with the creation of better tools.

3.4.1 **“Define” phase**

While divergent thinking was encouraged during “Discover” phase by progressively expanding the vision as broad and extended as possible; a convergent thinking was embraced at the “Define” stage where the narrowing down of insights generated was achieved. This was done by the interpretation and alignment of the needs/requirements, from the influencing factors, while envisioning alternative futures and different and more sustainable solutions.

At this phase, the needs and insights from the influencing factors were framed as discrete, but well-defined, “sustainable problem statements” that functioned during the “Develop” phase as separated starting points for idea generation.

3.4.2 **“Develop” phase**

The “Develop” phase was centred on the creation of different alternatives, ideas or concepts using “Design for Environmental Strategies”, established by Fiksel & Fiksel (1996) [177], with an emphasis in revalorization as an element covering all touching points during the development of the new material. Therefore, some materials were expected to be diverted from an end-of-life and up-cycled through the sustainable innovation process.

This phase is when a fast, but reliable, materials science paradigm approach in the mode of rapid prototyping and testing of ideas/concepts becomes useful. Ideas were framed, developed, and tested using several criteria and tools, according to the different trade-offs made during earlier phases between influential factors and sustainability aims. The level of development of the ideas was just enough to validate the principle of the concept tested; refinement and detailed of ideas were carried on as iterations through the process continued, allowing in this way a manifestation of different ideas/concepts by accelerating idea generation and feedback in a short period of time.

3.4.3 **“Deliver” phase**

The “Deliver” phase focused on gaining feedback; new knowledge on sustainability performance indicators and metrics, from the ideas developed earlier, was obtained to determine if sustainability goals had been met. This feedback from the sustainability embedded assumptions made was used to continue the iterations upon the idea, particularly at the first phase (“Discover”). Some metrics that were employed in the material design process have been suggested before by Fiksel (2011) [178] and McDonough et al. (2002) [40] and are summarised in Figure 25.

The objectives of “Deliver” phase were to obtain insight, as well as converging on the most promising ideas or elements of the ideas that were worthy to carry on beyond idea/concept testing to further “full material development”. The maturity of an idea/concept was likely to occur after several iterations at the different phases of the process. The number of iterations and phases where this happened, depended on how strong the idea/concept, influenced in a sustainable way the surrounding factors it was interconnected, and the knowledge available during the process. However, the initial constraints of influencing factors and objectives that were defined at the beginning of the process, and as the material development progressed, helped to decide how to proceed in whether to move and iterate between phases, or to a more traditional and linear development method once the idea/concept was well defined and evaluated.

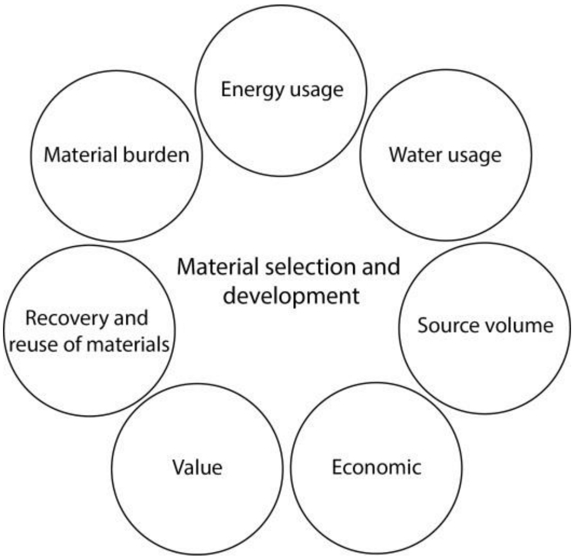
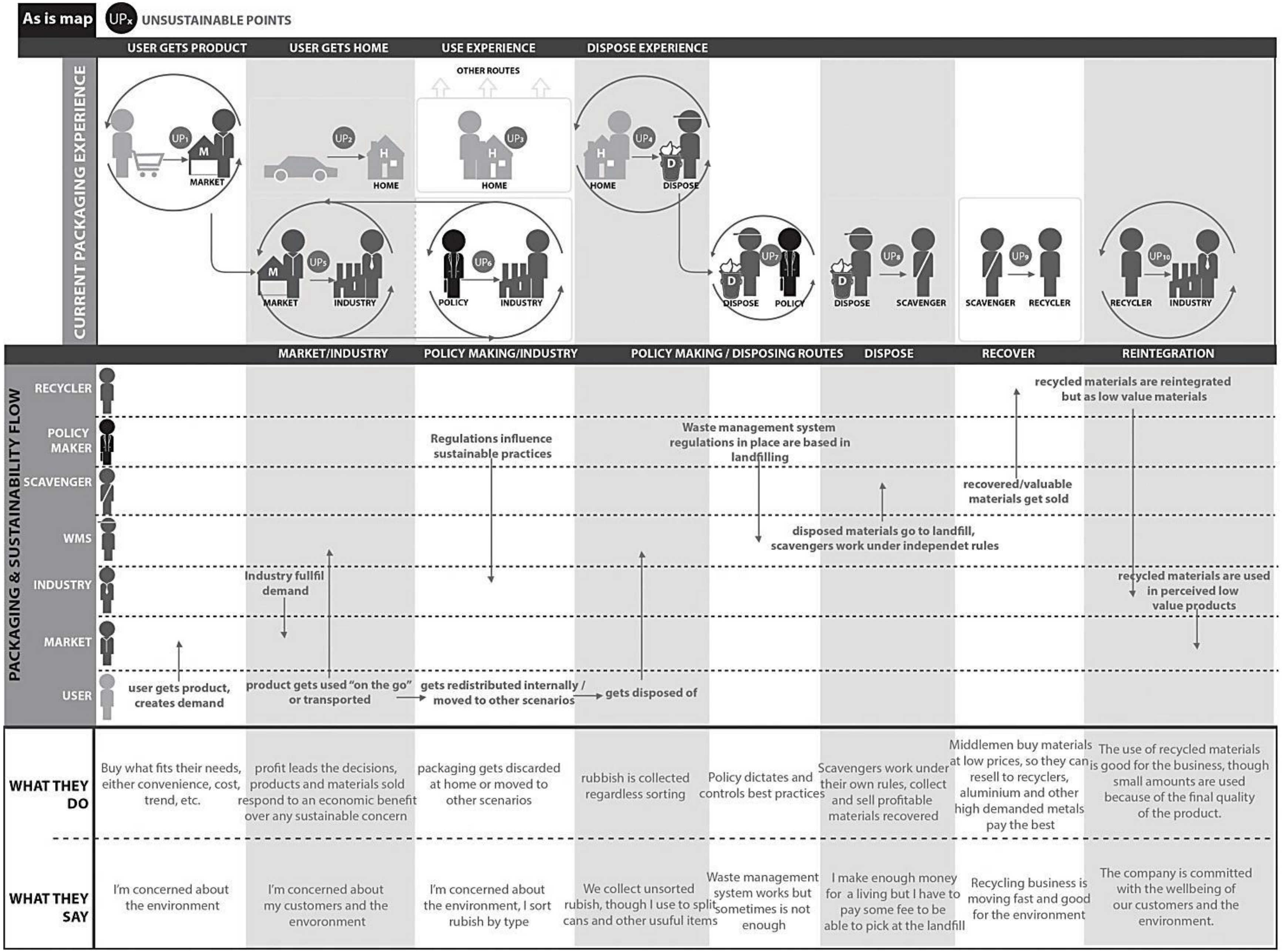


Figure 25. Sustainability metrics for material selection and development.

3.4.3.1 Design thinking tools to enable sustainable innovation in new material developments

As has been shown, the process itself presented an unavoidable uncertainty; however, it was possible to avoid the risk related by using some methods, tools and techniques often related to other areas such as anthropology, marketing or ethnographic research. Many of these tools are available for gathering data, synthesising information, facilitating the creation of innovative solutions or evaluate the different alternatives. For example:

- **Personas and Journey Map/experience mapping: “**Personas” are an ideal and prototypical presentation of end users based on behaviours and motivations of real people [179]. This tool provided a human-centred reference that allowed focusing on ideal stakeholders during the material development. The use of this tool helped taking an emphatic perspective during the process. “Personas” were developed at the beginning of the material design process and were useful in problem defining; furthermore, this tool was also used at the “Develop” phase for idea/concept generation along with other tools, such as “storytelling” and “brainstorming” to thoroughly visualise the problem-solution relation. Stakeholders defined through “Personas” (i.e. policy maker) influence the material development, and are the basis of journey map/experience mapping tool. Rather than bringing only a thorough understanding of person’s life, this tool was intended to bring a holistic stakeholder experience in the sustainable material development (Figure 26). Therefore, a satisfying leading solution was better embraced as this tool helped uncover hidden needs/requirements (Figure 27). The aim of this stakeholder experience map and its use along with other “design thinking” tools [180] at the “Develop” phase was to bring an innovation platform for a more sustainable material development.



user gets product, creates demand

product gets used “on the go” or transported

Industry fullfil demand

Regulations influence sustainable practices

gets redistributed internally / moved to other scenarios

gets disposed of

Waste management system regulations in place are based in landfilling

disposed materials go to landfill, scavengers work under independet rules

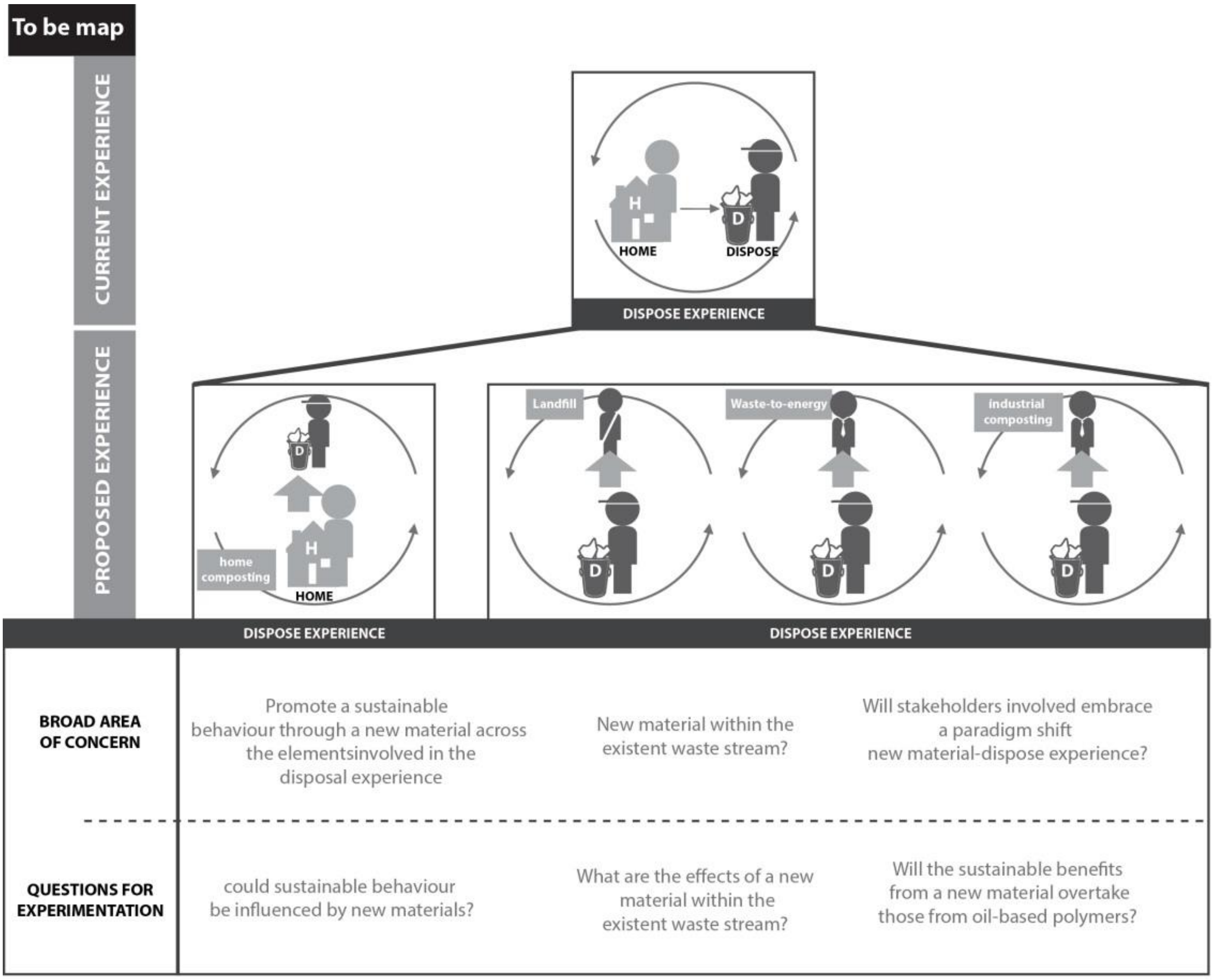
recovered/valuable materials get sold

recycled materials are reintegrated but as low value materials

recycled materials are used in perceived low value products

WHAT THEY DO	Buy what fits their needs, either convenience, cost, trend, etc.	profit leads the decisions, products and materials sold respond to an economic benefit over any sustainable concern	packaging gets discarded at home or moved to other scenarios	rubbish is collected regardless sorting	Policy dictates and controls best practices	Scavengers work under their own rules, collect and sell profitable materials recovered	Middlemen buy materials at low prices, so they can resell to recyclers, aluminium and other high demanded metals pay the best	The use of recycled materials is good for the business, though small amounts are used because of the final quality of the product.
WHAT THEY SAY	I’m concerned about the environment	I’m concerned about my customers and the envoronment	I’m concerned about the environment, I sort rubish by type	We collect unsorted rubish, though I use to split cans and other usuful items	Waste management system works but sometimes is not enough	I make enough money for a living but I have to pay some fee to be able to pick at the landfill	Recycling business is moving fast and good for the environment	The company is committed with the wellbeing of our customers and the environment.

Figure 26. “As is” experience map for packaging.



BROAD AREA OF CONCERN	Promote a sustainable behaviour through a new material across the elementsinvolved in the disposal experience	New material within the existent waste stream?	Will stakeholders involved embrace a paradigm shift new material-dispose experience?
QUESTIONS FOR EXPERIMENTATION	could sustainable behaviour be influenced by new materials?	What are the effects of a new material within the existent waste stream?	Will the sustainable benefits from a new material overtake those from oil-based polymers?

Figure 27. “To be” map, a proposed experience map for packaging disposal.

- **Mind Maps:** Mind maps are visual representations of diagrams connecting all the information regarding a certain theme [181]. This tool was used during problem definition to identify the different influencing factors at the initial problem statement and to illustrate probable relations amongst each other. Mind maps offered a full overview that facilitated holistic associations for reframing the problem. Figure 28 and Figure 29 show an example of mind maps used for the application, context and material selection process for packaging.

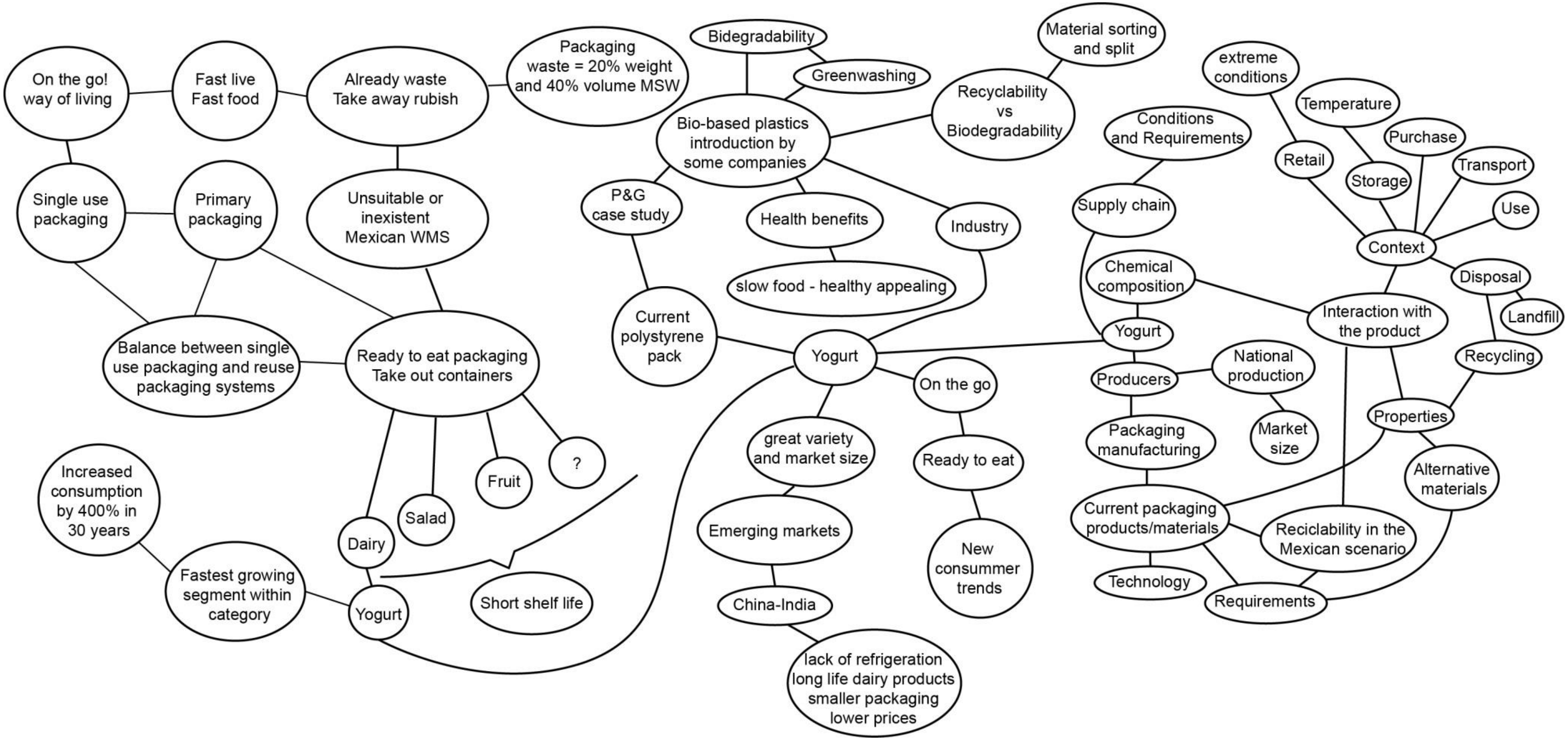


Figure 28. Application and context mind mapping.

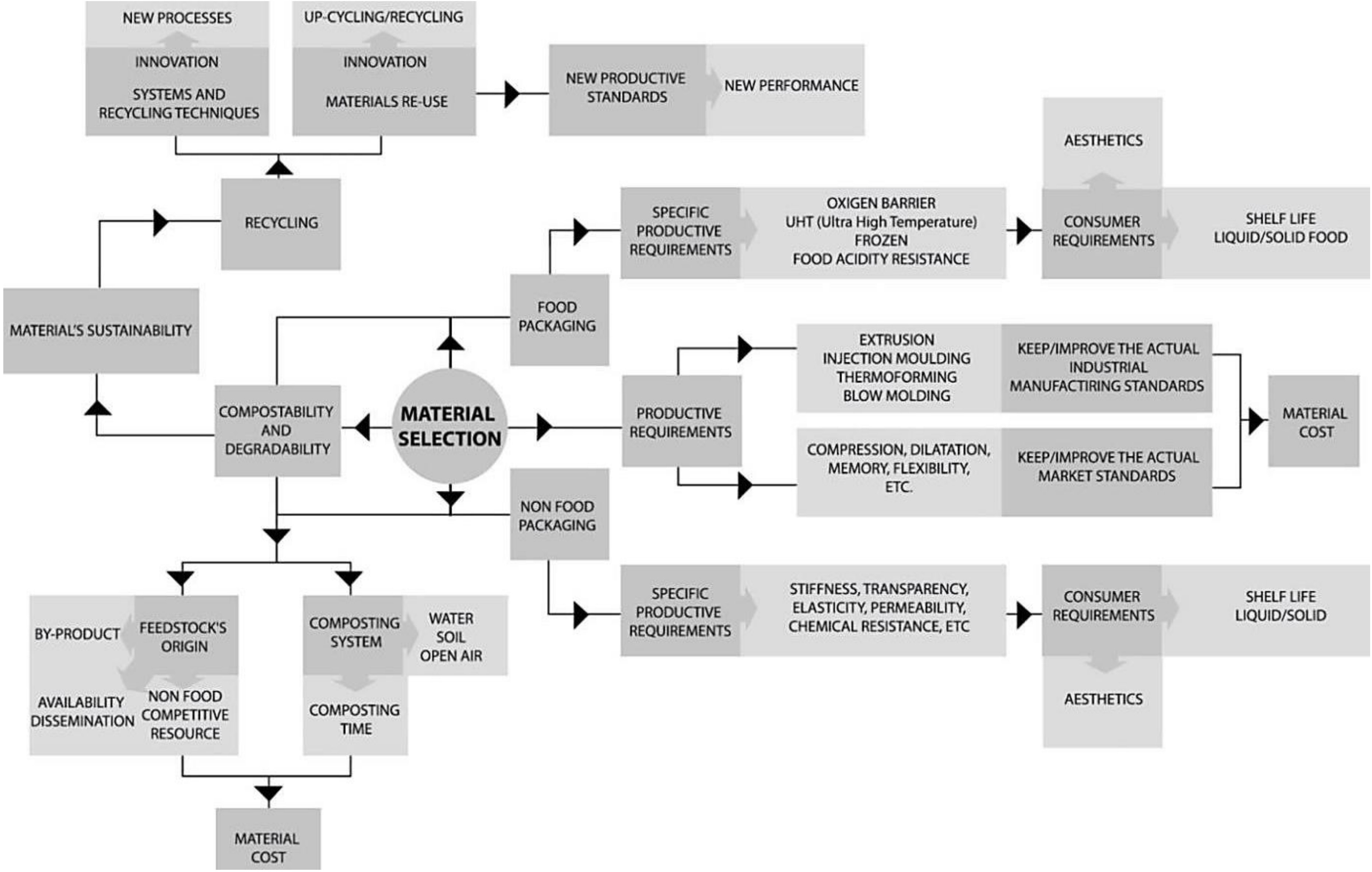


Figure 29. Material selection mind mapping.

- **Brainstorming:** Brainstorming (Figure 30) is a technique to enable idea generation through creative thinking. The main principle was to free inhibit, and avoid critics during the creation of ideas that were aimed to solve the initial problem statement, defined at early stages of the process, so that was possible to generate as many ideas as possible for further evaluation and testing. This, under the premise that a large number of alternatives generated will assure greater chances to produce an effective solution. Although the technique has been evolving and several variations are available, basic rules for brainstorming are:
  - Criticism is unwanted
  - Freewheeling
  - Quantity over quality (detail)
  - Combination towards improvement
  - Group interaction

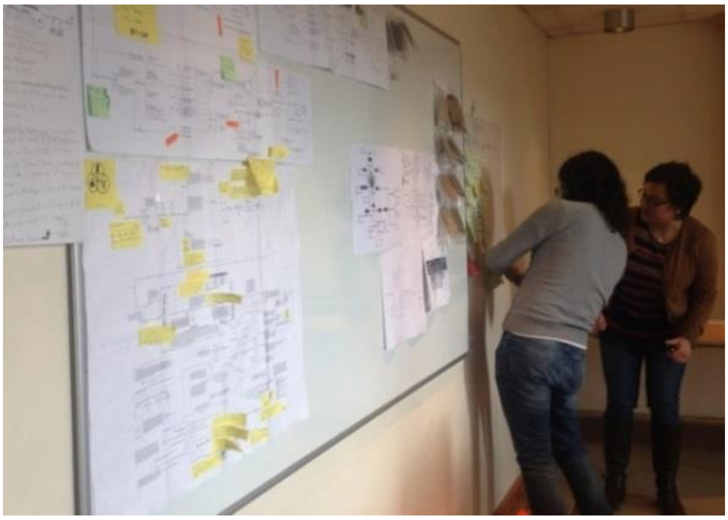


Figure 30. Brainstorming session for idea/concept creation.

- **Fast prototyping:** as it is described by Ogilvie and Liedtka (2011) [182], it is a way of thinking with the hands, a rapid iteration that allowed a fast learning and improvement of the idea. Within the iterative process of design, prototypes of ideas/concepts were delivered ("Deliver" phase) refined and evaluated within every iteration until the concept was mature enough to move to a full material development.

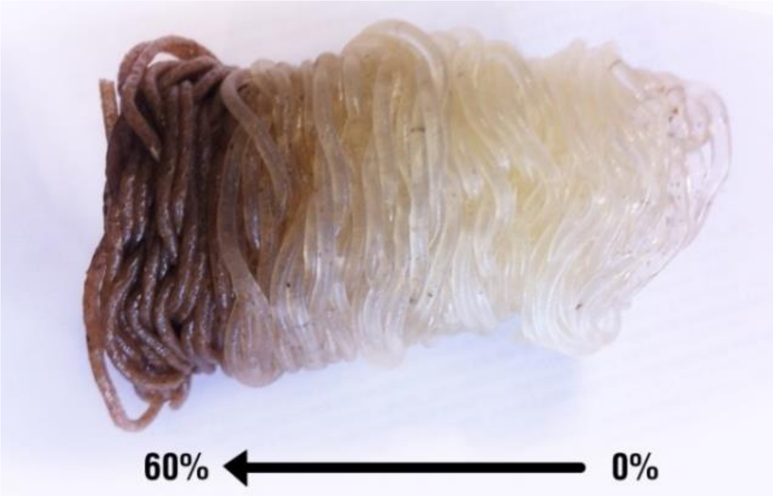
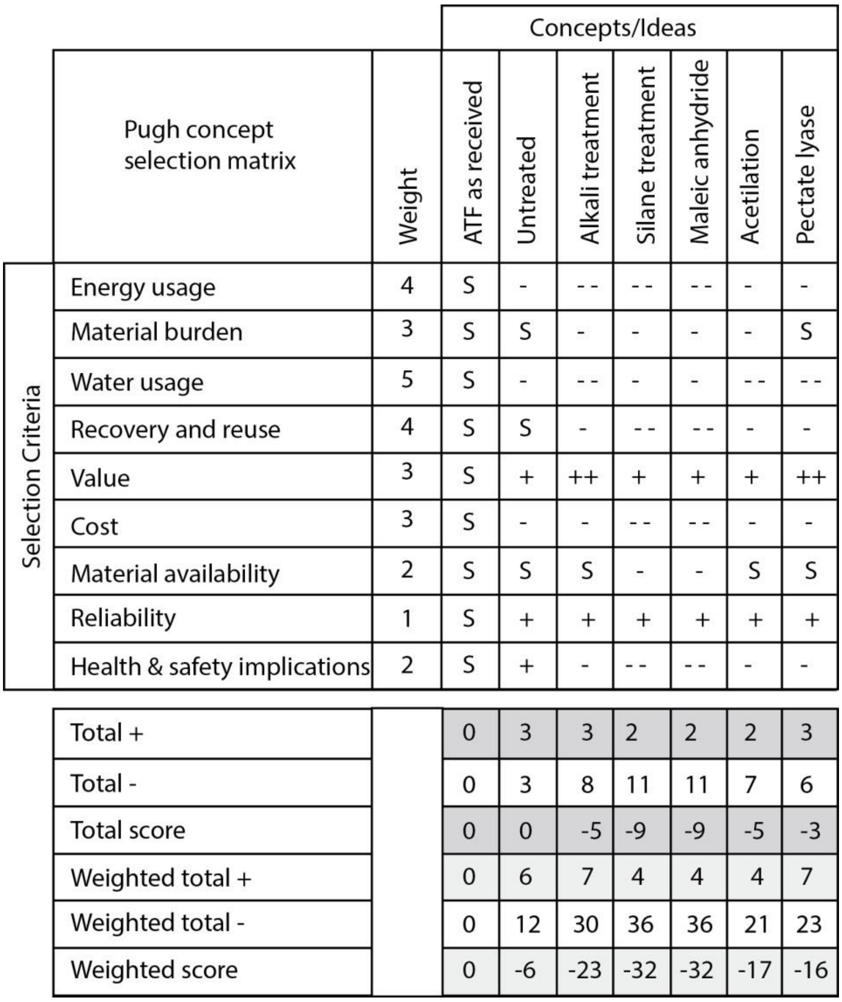


Figure 31. Material prototype used to assess material compatibility and processability.

- **Pugh matrix:** allowed idea selection through the comparison of criteria meet among the different concepts [183]. This tool also permitted the generation of hybrid ideas as quality optimisation was carried out during the comparison. An example of a Pugh matrix, used to decide between different surface treatments alternatives, is shown in Figure 32 where several sustainability criteria were used to make a pairwise comparison with a selected baseline. Six candidate treatments have been evaluated against 9 criteria and ATF as it was received is used as a “baseline”. This baseline is scored as “S” against all of the criteria. The treatment alternatives are then compared in a pairwise fashion against the baseline for each of the criteria. If a treatment alternative is better than the baseline a “+” is entered in the appropriate cell, on the other hand, if it is worse than the baseline, then a “-” is scored, and if it is the same than the baseline an “S” is assigned. It is also possible to add extra levels of discrimination by using “+ +” for much better or “- - “ for much worse. The overall evaluation is then made by adding the “+” and “-“ for each alternative criteria and the total score is calculated by summing the number of “+” and “-“[183].



			Concepts/Ideas						
	Pugh concept selection matrix	Weight	ATF as received	Untreated	Alkali treatment	Silane treatment	Maleic anhydride	Acetilation	Pectate lyase
Selection Criteria	Energy usage	4	S	-	- -	- -	- -	-	-
	Material burden	3	S	S	-	-	-	-	S
	Water usage	5	S	-	- -	-	-	- -	- -
	Recovery and reuse	4	S	S	-	- -	- -	-	-
	Value	3	S	+	++	+	+	+	++
	Cost	3	S	-	-	- -	- -	-	-
	Material availability	2	S	S	S	-	-	S	S
	Reliability	1	S	+	+	+	+	+	+
	Health & safety implications	2	S	+	-	- -	- -	-	-
	Total +		0	3	3	2	2	2	3
	Total -		0	3	8	11	11	7	6
	Total score		0	0	-5	-9	-9	-5	-3
	Weighted total +		0	6	7	4	4	4	7
	Weighted total -		0	12	30	36	36	21	23
	Weighted score		0	-6	-23	-32	-32	-17	-16

Figure 32. Pugh matrix for surface treatment selection using sustainability criteria.

Other tools, techniques, and mindsets such as:

- Collaborative culture
- Roadmapping
- Technology trend analysis
- Customer trend analysis
- Empathy maps
- Market research
- Scenario planning
- Visualization
- Concept development
- Idea selection / anchored scales
- Assumption Testing
- Customer co-creation

amongst others [180,182] are available, and can be adapted and integrated into the process at early stages and along the process for sustainable innovation in new material developments and according to the different needs of the project.

3.5 **Material concept**

The material “designed” at a conceptual level using the approach mentioned in previous sections is a bio-based material; in basic terms, it is a green composite made of renewable resources and organic waste from the tequila production. It consists of three phases; a continuous phase or matrix made of PLA, a dispersed phase made of organic waste from tequila production, and finally an interphase which is the area where the first both phases interact among them.

Figure 33. Material concept life cycle.

This bio-based and more sustainable material was conceptualized through a whole system approach, understanding the influence and implications it can have during the product life cycle, and the sustainable benefits it might bring towards a shift into a more circular economy as it is depicted in Figure 33. Therefore, it is considered that the integration of this material into a bio-based economy framework will bring reductions in energy and water consumption, and greenhouse gas emissions to the different stages of the cycle, thanks to its technical and quality properties along with its compostable and degradable nature.

3.6 **Conclusions**

Sustainable material developments usually involve linear or quasi-linear methods related to the new product development model. To enable sustainable innovation for new material developments, a more systemic approach is needed, at least at the initial stage. A fundamentally systemic “design thinking” approach presents a significant opportunity for enabling sustainable innovation in new material developments.

The most crucial phase when using a design thinking approach for new material developments is the “Discover” phase. The right definition of the “true problem” to solve (not the initial problem statement) will be dependent on the insights of this phase. “Discover” stage is essential in identifying gaps and assessing opportunities for new material developments; enabling in this way sustainable innovation, and therefore providing some degree of enhanced utility, cost avoidance, value, and quality improvement, among others.

The integrative and immersive character from the “design thinking” approach, at earlier stages of more sustainable material developments, will intensify cross-examination of the different influencing factors, or constraints that should be used to assure sustainability aims are accomplished in the best possible way. The cross-functional insight obtained from the various influencing factors may disclose what the true problem is and with it the probable answers to it towards a real sustainable solution. Consequently, successful sustainable innovation in material developments will only occur when these influencing factors are considered. Hence, a design thinking approach is flexible enough to work as a bridge between material sciences and sustainable innovation, bringing a new perspective to material developments.

4 Characterisation of natural fibres from tequila production waste stream to evaluate their reuse as composites reinforcement.

4.1 Introduction

Environmental and economic concerns, arising from the large-scale production and consumption of oil-based packaging [2,3,15,16], have led to increased attention towards the development of new and more sustainable alternatives. There is a need to end the landfilling of non-biodegradable packaging as this is one of the most significant problems that plastic packaging creates is at its disposal phase. Landfilling and recycling have been proven inefficient as they are energy-intensive and represent significant losses and costs related to sorting, collection, and transportation phases within the recycling process [3]. In developing countries, even though materials can be recycled or recovered, they are likely to end up either landfilled or incinerated. This is largely due to packaging being contaminated with food remains or other substances at recycling facilities. Technology to prevent contamination and segregate materials and wastes can be costly and energy intensive [11]. Similarly, recycling processes can often be impracticable and uneconomic.

Consumer trends such as single-use, ready-to-eat or convenience foods have increased the amount of packaging material; more than most other products in the waste stream. Commonly 60% of all food packaging is disposed of after single use [12]. Over 10% of the global solid waste composition arises from packaging [184]. Specific data on packaging and municipal solid waste (MSW) has been recorded to illustrate the constant change of relationship between packaging materials and the environmental impact their use represent [15,16].

Packaging contributes a considerable 8% to the total greenhouse gas (GHG) emissions [17], and about 1-3% [18,19] of the hydrocarbon content is degraded within 100 years. Thus its impact is not considered as a long-term emission due to the reduced GHG emissions presented by its slow degradation rates.

Within the product design cycle, several life cycle stages determine the packaging design and material choice. These can be positively influenced by raw material selection; which determines the final packaging properties such as weight, thermal insulation, mechanical properties, recyclability, compostability, degradability, barrier properties, etc.

There is growing interest from industry [20,21], market and developers in new green materials. Green composites from naturally occurring renewable resources can be considered a more efficient, sustainable and biocompatible solution than oil-based packaging materials (e.g., GHG emissions, oil depletion). Using biodegradable and compostable materials can also help to improve the CO_2 balance in the atmosphere by closing the carbon cycle loop in contrast to landfill disposal [47].

4.2 **Natural fibre properties**

Novel green composite materials with enhanced properties at a potentially lower cost [50,62,70,81,82] offer a promising option to overcome the limitations of bio-based polymers. This, along with an increased demand, may reduce costs and get materials into production at faster rates and bigger scales, decreasing our dependence on depleting fossil fuels without compromising the food supply chain. However, to ensure a sustainable development and avoid food crop competition during fibre crop production and supply to markets several considerations can be distinguished. For example, dependency to food crop land use can be avoided through the use of fibres produced in desert areas and their by-products (e.g., *Agave Tequilana* Weber *var.* azul), as well as the consideration of the impact factor on the environment as a relation between the production volumes of fibre and the size of the end-use market [70,150,185]. Hence, composites derived from natural fibres and their by-products can be considered as potential substitutes of oil-based plastics. This is particularly evident where natural materials are plentiful, renewable, and biodegradable [70,82,186].

Natural fibres require low production energy, are non-abrasive to processing equipment, are CO_2 neutral when incinerated, perform well as acoustic and thermal insulators [158], and have a low bulk density. Therefore, the use of biodegradable and environmentally friendly plant-based fibres as feedstocks for composites has been a natural choice to make composites ‘greener’ during the last 15 years.

The use of natural fibres such as; kenaf [55,97], flax [62,187,188], jute [42,103,189], hemp [96,190–192], bamboo [98], wood [193], and sisal [54,136,194,195] in composites has recently been the subject of intensive research. Moreover, the application of materials considered as waste or industrial and agricultural by-products, such as lignocellulosic fibres from tequila production, offers several advantages for the manufacturing of green composites for packaging applications [196], for example, low cost, low density, high toughness, compostability, and biodegradability [70,197,198].

Agricultural by-products are widely available in certain regions of the world. Their cost depends on the availability and potential use of the by-product. In developing countries, their use for fibre production does not add much value to the crops [199]. Agricultural by-products have been used for pulp and paper making [200], and they have promising potential as a reinforcement/filler source for green composite developments, although final properties in green composite materials have strong variations due to chemical composition of the natural fibres [201].

Natural fibres and agricultural by-products are mainly composed of cellulose, hemicellulose, lignin and waxes. Cellulose is the main structural component. Its content influences the properties, economics, and the utility of the fibre. Chemical compositions, physical and mechanical properties of most common natural fibres used in composites are presented in Table 8 along with fibres from agricultural by-products.

Ligno-cellulosic by-products commonly need additional processes for fibre extraction. Retting methods, using bacteria and fungi from the environment or other chemical means are used to eliminate non-cellulosic materials. Although mechanical separation using decorticating machines, steam explosion and other methods is available [202–204].

Natural fibre properties are influenced by their composition, structure and the number of inherent flaws present in each fibre. Higher cellulose content and a lower microfibrillar angle result in higher modulus and tensile strength with low elongation [205,206]. In contrast, fibres with higher lignin content, lower length/diameter ratio and a higher microfibrillar angle present lower strength and modulus with higher elongation.

Lignocellulosic by-products are already used in several composite materials [46,207,208]. These developments usually focus on technical aspects, such as mechanical strength. Economic and ecological assessments, when carried out, are performed after technical investigations are finished. The use of a life cycle approach, during early stages of a material development, with respect to technical, economic, and ecological aspects, may bring advantages for material and product development, as materials are strongly linked to other aspects, and the degree of freedom for changes in an early stage could be greater.

The material selection process is one of the most important factors at the early stage of the design process, because it helps to narrow the available range of materials; making the selection easy [209]. Material property charts are used as the simplest tool for material selection [24]. However, information or methodologies regarding the selection of new material sources or by-products are not fully available.

Table 8. Natural fibre properties.

	Fibre type	Density (g/cm^3)	Length (mm)	Diameter (μm)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Cellulose (wt.%)	Hemi-cellulose (wt.%)	Lignin (wt.%)	Ref.
common natural fibres for composites	Bamboo	0.6–1.1	1.5–4	25–40	140–800	11–32	2.5–3.7	73.83	12.49	10.15	[210]
	Cotton	1.51	15–56	12–35	400	12	3–10	82.7	5.7	-	[211,212]
	Flax	1.4	10–65	5–38	800–1500	60–80	1.2–1.6	64.1	16.7	2.0	[211,212]
	Hemp	1.48	5–55	10–51	550–900	70	1.6	74.4	17.9	3.7	[211,212]
	Jute	1.46	0.8–6	5–25	400–800	10–30	1–1.8	64.4	12	11.8	[211,212]
	Ramie	1.5	40–250	18–80	500	44	2	68.6	13.1	0.6	[211,212]
	Sisal	1.33	0.8–8	7–47	600–700	38	2–3	65.8	12.0	9.9	[211,212]
by-products/waste	Sugarcane bagasse	1.2	0.8–2.8	10–34	20–290	19.7–27.1	1.1	32–55.2	16.8	19–25.3	[212,213]
	Banana	1.35	0.17	13.16	355	33.8	5.3	60–65	19	5–10	[213,214]
	Coir	1.15-1.46	20–150	10–460	95–230	2.8–6	15–51.4	32–43.8	0.15–20	40–45	[215]
	Corncob	–	–	–	–	–	–	26.1	45.9	11.3	[216]
	Rice husk	–	–	–	–	–	–	25–35	18–21	26–31	[217]
	Rice straw	–	0.4–3.4	4–16	–	–	–	28–36	23–28	12–14	[218,219]
	Wheat straw	–	0.4–3.2	8–34	–	–	–	33–38	26–32	17–19	[202,220]

Several methods for material selection can be found in the literature and many start with the assumption of an already existing material from established databases of material attributes [25]. Despite the material selection process rely on powerful analytical methods (e.g., experimental characterization); new selection processes embracing both analytical and inductive thinking may pose an attractive approach to consider sustainability burdens, when looking at new material sources within the waste stream.

This research proposes a method to look at natural fibres within the waste stream to determine their potential use as a new material source in earlier stages of the research for developing green composites. The case study of by-product fibres from tequila production for its use in the packaging industry was evaluated.

4.3 **Waste fibres from tequila production**

Agave tequilana, shown in Figure 34a, belongs to the family Agavaceae. This succulent plant has spirally arranged leaves forming a rosette about 1.2±1.8 m tall. Its leaves are bluish green in colour, approximately 90±120 cm long and 8±12 cm width [151], and its cultivation is cheap. The plant grows in semi-arid desert land requiring low field labour, little watering, and no agrochemicals.

Tequila processing starts with harvesting the Agave head (Figure 34b). This is separated from the leaves, and taken to the oven where it is steam cooked and milled to extract the juice for tequila production.

The Agave head milling process generates a by-product referred to as bagasse (Figure 34c). This represents about 40% of the total weight of the milled Agave, some heads can reach 100 kg [151]. In 2013 more than 300,000T of bagasse were produced (Figure 35) [152].

There are cost-effective uses for the by-product leaves from tequila production such as animal feed, paper and fibre boards [56,61]. The volume from the leaves is enough to be considered as a potential fibre source for reinforced composites; notwithstanding leaves are still left in the ground as soil nourishment.

Figure 34. ***Agave tequilana*** **plant and fibres. a)** ***Agave tequilana*** **plants also known as blue Agave (Needham 2014)** [221]**. b)** ***Agave tequilana*** **heads are steamed cooked at 90-95 °C for about 18-24 hours** [153]**. c) Dry bagasse obtained after the heads have been shredded to extract plant juices.**

During tequila production, *Agave* heads are exposed to processes similar to physico-mechanical fibre extraction methods, such as; stretching [119], calendaring [120,121], thermal-treatment [122], and steam explosion [123]. These processes leave fibres partially extracted from the *Agave* head, with a structure and surface ready to interact with a polymeric matrix in a composite system, thus reducing fibre extraction costs. ATF constituents are reported to be similar to other lignocellulosic fibres used for composite applications [61,103] with high cellulose content.

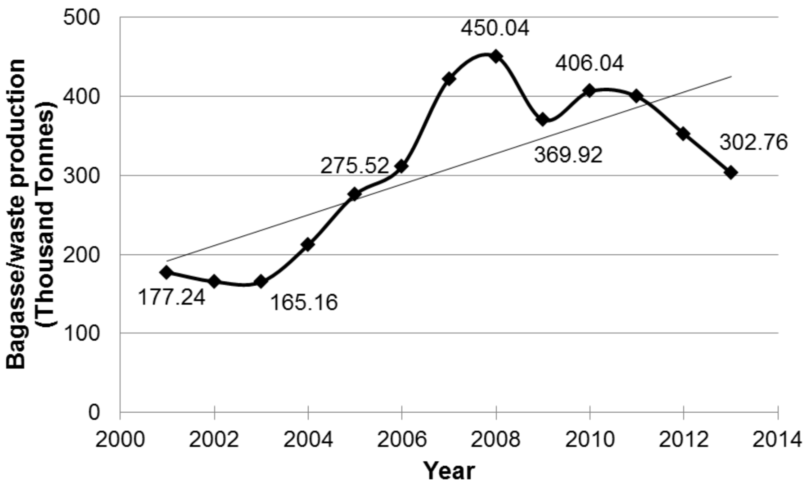


Figure 35. Production trend of bagasse for the past 13 years.

4.4 **Materials and methods**

4.4.1 **Materials**

Dry *Agave tequilana* bagasse was obtained after tequila extraction from distillery “La Fortaleza”, Mexico. Characterization methods used for preparing the samples and testing methods throughout the work are described in this section.

4.4.2 **Analytical method for fibre selection**

An analytical method for natural fibres within the waste stream (Figure 36) relies on looking at the properties of natural fibres. Many natural fibres have been studied and technical data is already available although, this is considerably less than other common materials such as metals and polymers.

The determination of mechanical and physical properties of the fibres, within the context of composite and packaging materials, represent the critical factors to determine the final composite material behaviour and properties. These composite materials are designed in terms of their macroscopic constituents (e.g., fibres, matrix) and properties can be tailored to meet specific requirements by controlling the choice of fibre, alignment and volume fraction.

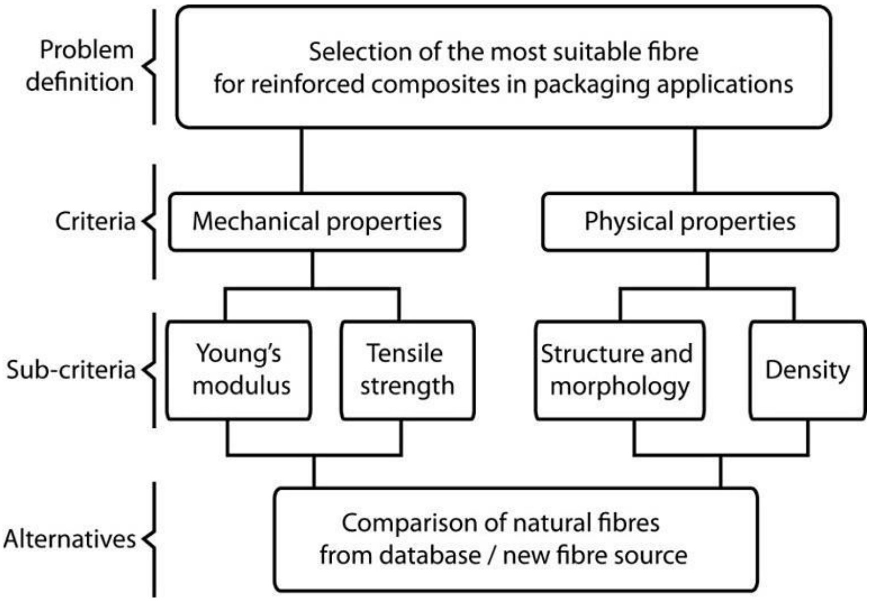


Figure 36. Analytical method for natural fibre selection showing the main sub-criteria.

4.4.3 **Fibre selection flow**

The fibre selection flow resulting from this work is a combination of analytical and inductive methods, where agricultural and industrial by-products within the waste stream are looked at as a new material source for fibre reinforcement or fillers for polymeric materials. The fibre selection flow seen in Figure 37, is divided into 3 sections; corresponding to fibre requirements, fibre constraints and relations, and fibre source selection process.

During the fibre requirements stage, the fibre is theoretically chosen according to company, market, and user requirements. In this section information from material databases, market research and other ethnographic studies are gathered, clustered, analysed and screened to obtain an ideal fibre that theoretically fulfils the established requirements. This step provides a starting point for comparisons between the applications for the final material. Ideal fibre is determined as a possible solution to already defined and specific applications that recognise each constraint from amongst the selection options. Constraints are expected to remain constant while the options for the application may change or be limited to each case.

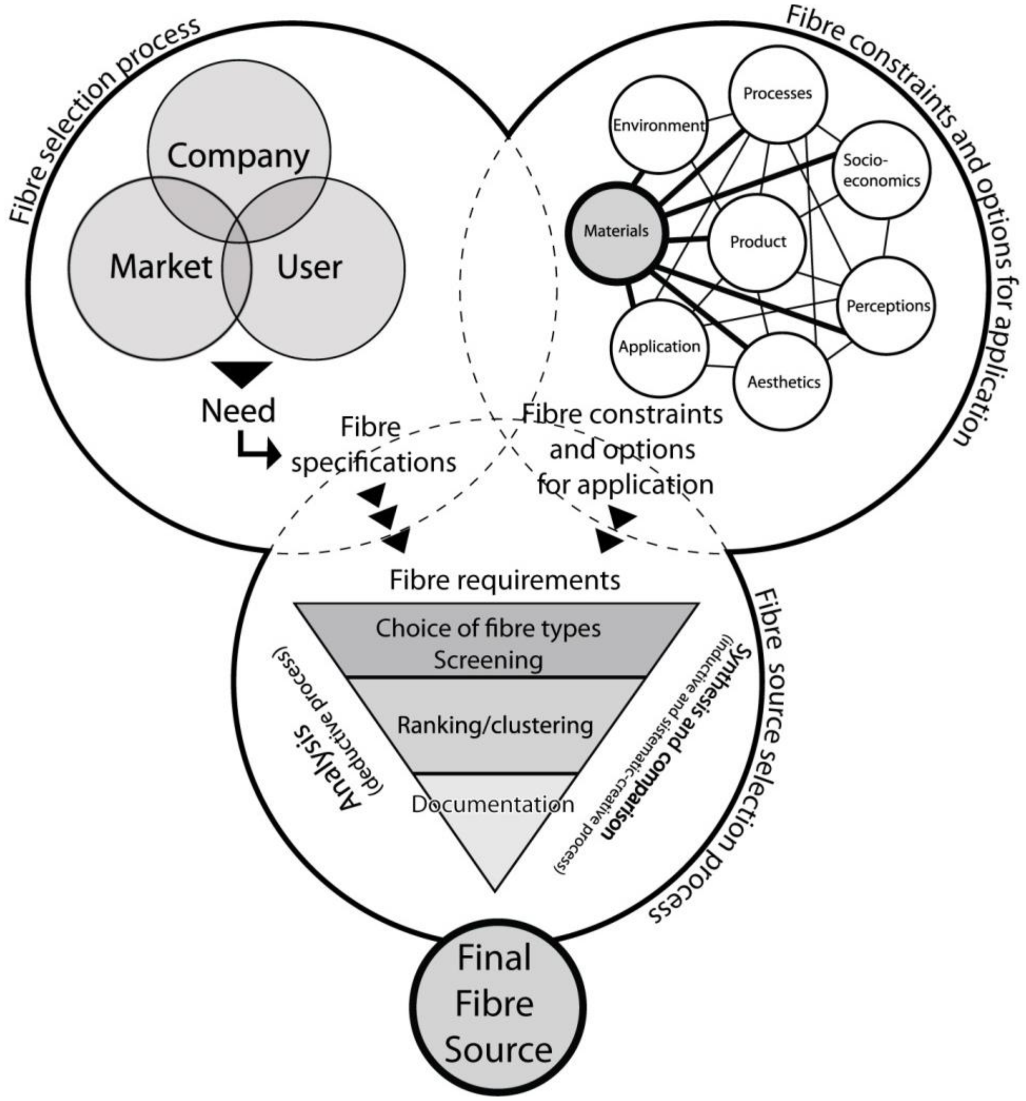


Figure 37. Fibre selection flow based in analytical and inductive methods.

Once an ideal fibre has been determined and the theoretical properties are known, it is possible to progress beyond the fibre source selection process. In this stage, waste stream materials are studied using a suite of analysis, synthesis and comparison methods; the most promising fibre sources are then analysed and screened according to the defined constraints.

The proposed analytical method looks at the material properties to match the technical requirements and ideal properties to the material during the fibre selection process. The method follows a deductive process where fibre properties are obtained whenever possible from databases. When information is not available, properties can be determined by direct testing using an analytical method (Figure 36).

Synthesis and comparison methods use previous experience and analogy to determine the usability of fibres from the waste stream. Despite biases inherent to this inductive thinking, the scope of opportunities increases the potential possibilities to be synthesised and tested as they match the requirements.

Once fibres have been identified to meet the required performance they are clustered and screened using established constraints. Fibres are then ranked and those that fail to meet the requirements and constraints are eliminated.

4.4.4 ***Agave tequilana*** **fibres physical and mechanical properties**

4.4.4.1 Morphology / structure

Several established characterization techniques were used. Optical microscopy and environmental scanning electron microscopy (ESEM) were used to characterise the ATF structure and morphology. Energy dispersive X-ray (EDX) was performed to determine the elemental composition of deposited materials on the fibre surface.

To determine the fibre length, 200 randomly selected ATF were mounted onto a thick paperboard and scanned at hi-resolution; images obtained were then processed and measured using Image J software [222].

Due the non-homogeneity of fibre length and the scatter in diameter across the fibres observed by planimetering [223,224], a variation from a previously reported cross sectional area (CSA) method [225] was applied to achieve more accurate measurements (see Appendix B). These measurements provide a better estimation of the fibre’s tensile properties. Individual fibres were held together in groups of 10 and embedded vertically in epoxy; samples were ground and polished; cross sections were photographed at 50x magnification. The process was repeated at every 2 mm steps along the 20 mm length of each sample to provide a total of 7 different micrographs for every sample. Each micrograph was then processed and analysed using Image J software to find the CSA. A total of 350 CSA measurements were taken.

4.4.4.2 Mechanical properties

Tensile tests were performed according to the American Society for Testing and Materials (ASTM) using ASTM D3379-75 [224]. To determine tensile properties, 60 single fibres were individually mounted on 90 gsm paper tabs. A 30 mm slot equal to the gage length was cut out in the middle of every tab. Samples were randomly chosen and pasted at both ends of the slot using ethyl-2-cyanoacrylate. The gage length of each fibre was measured using a Vernier calliper to the nearest 0.1 mm. Each specimen was mounted and aligned with the axis of the cross-head on an INSTRON 5500R EM with a 100N load cell and chart speed of 0.5 mm/min. From the data recorded ultimate tensile strength was calculated using:

$$\boldsymbol{T} = \frac{\boldsymbol{F}}{\boldsymbol{A}}$$

Where, $\boldsymbol{T}$ is the tensile strength, $\boldsymbol{F}$ the maximum load recorded during test, and $\boldsymbol{A}$ is the mean CSA previously obtained.

4.4.4.3 Density

To determine ATF volume density, 20 samples were oven dried until constant weight, and linear density was calculated by measurement of the masses and lengths using an analytical balance to the nearest 0.00001 g and an optical microscope at magnification 5X respectively. The average linear density and diameter were used to calculate the volume density of the fibre.

4.5 **Results and discussion**

4.5.1 ***Agave tequilana*** **fibres morphology / structure**

ATF shows non-uniform geometrical characteristics; its microstructure is assembled into bundles of fibres; each fibre consists of two cell walls arranged as concentric tubes with a middle lumen as shown in Figure 38a. Each fibre cell is united by the middle lamellae, which consists of cellulose, lignin, pectins and hemicelluloses [226], see Figure 38b. In addition, other minor components, such as waxes, inorganic salts and nitrogenous substances are also present. The longitudinal section (Figure 38c and d) of a fibre reveals a non-constant transverse dimension and a large number of flaws from its natural origin and extraction process.

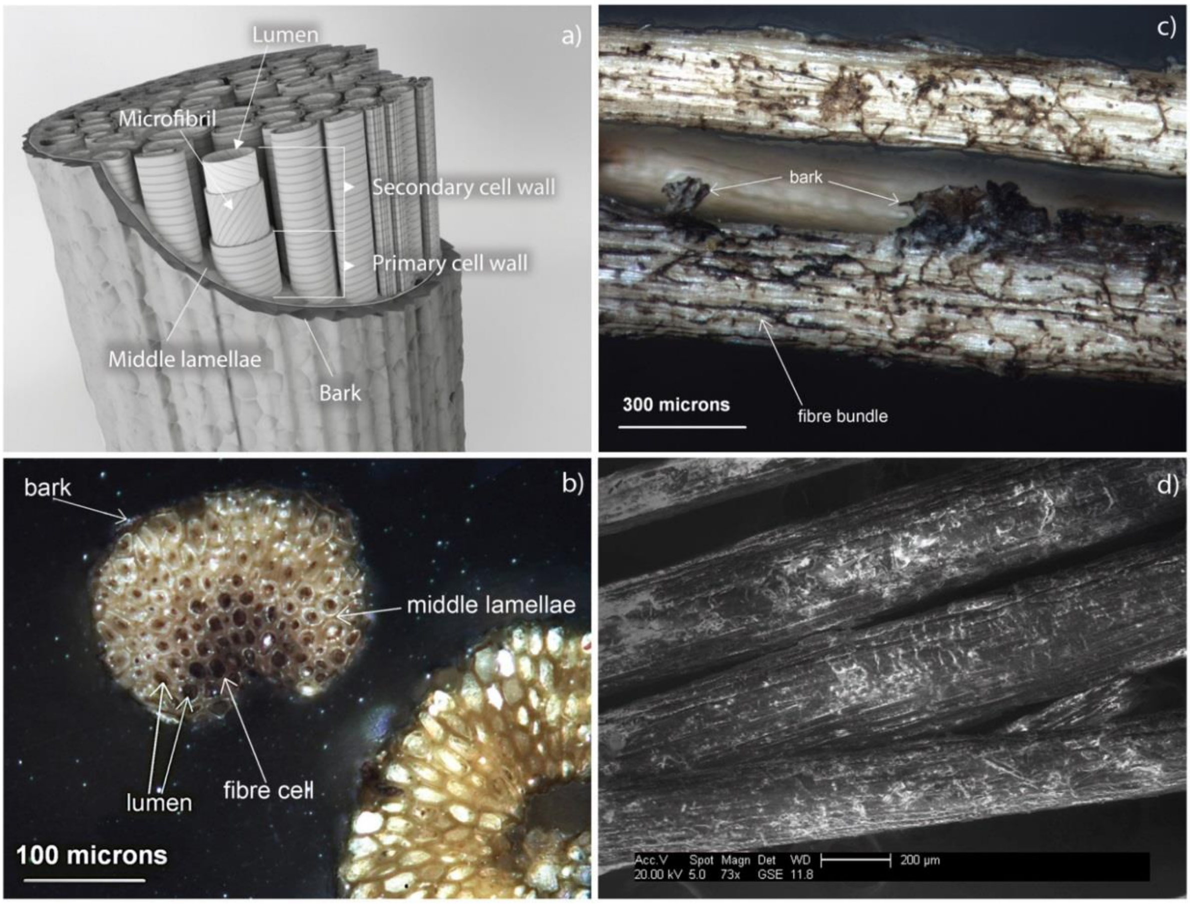


Figure 38. ***Agave tequilana*** **fibre morphology. a) Schematic ATF morphology showing a concentric arrangement of cells. b) ATF cross section shows the middle lamellae consisting of cellulose, lignin, pectins and hemicelluloses. c) Micrograph from ATF longitudinal section showing a non-uniform longitudinal section along the fibre length and remaining bark composed mainly of non-cellulosic materials. d) ESEM micrograph of ATF longitudinal section showing flaws along the fibre length.**

4.5.2 **Characterization**

Mean ATF length was found to be 77±18 mm with a mean CSA of 75±41 µm. Mean ATF density was found to be 1.2±0.1 g/cm^3. Length, CSA and density distributions are shown in Figure 39a-c respectively.

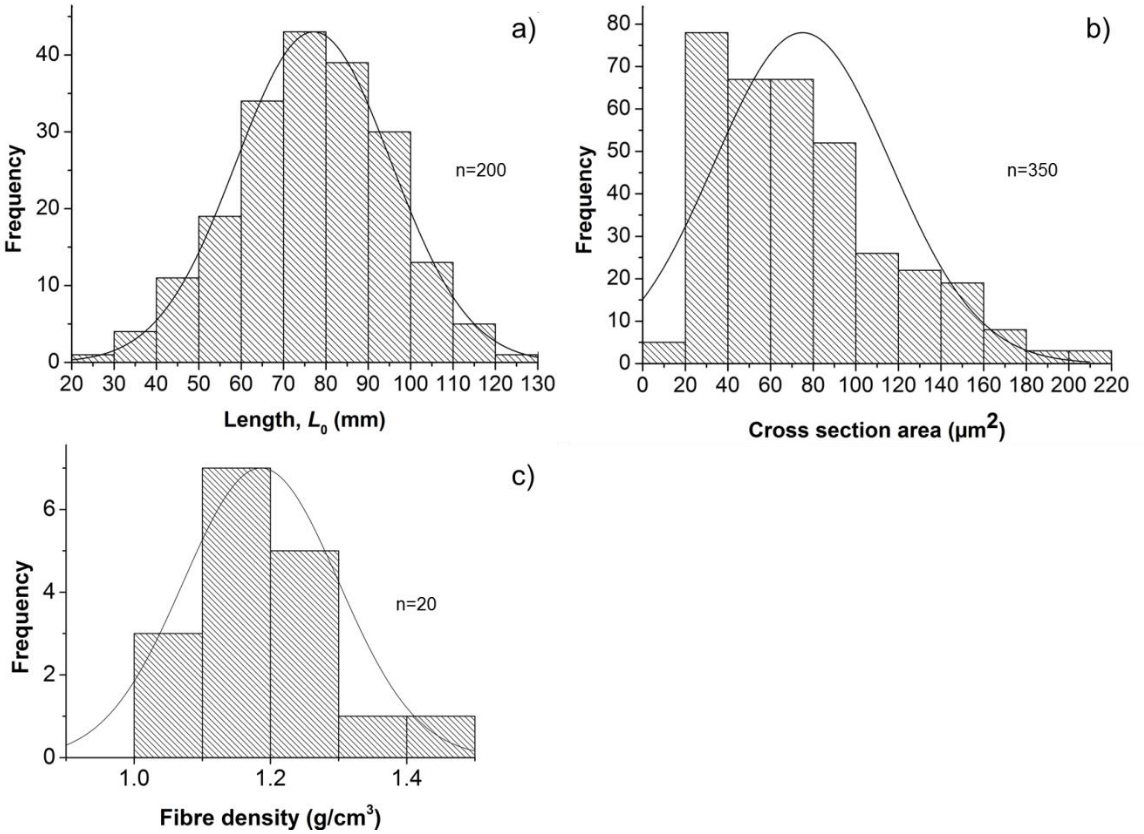


Figure 39. *Agave tequilana* fibres initial characterization. a) Length distribution of ATF for this work. b) CSA distribution of ATF for this work. c) Density distribution of ATF for this work.

4.5.3 **Mechanical properties**

ATF exhibit significant variability in tensile strengths and serration effects during tensile tests. This is a common characteristic of natural fibres, and can be explained by the structure and number of flaws present within the fibres. Under stress, cracks propagate through weak bonding between cells, causing intercellular fracture without the removal of microfibrils causing fibre failure. The long elongation ATF presented was primary a result of microfibrils orientation and angle. Mean stress-strain plot of ATF (Figure 40) shows ductile failure. This corresponds to the behaviour of a tough polymeric material.

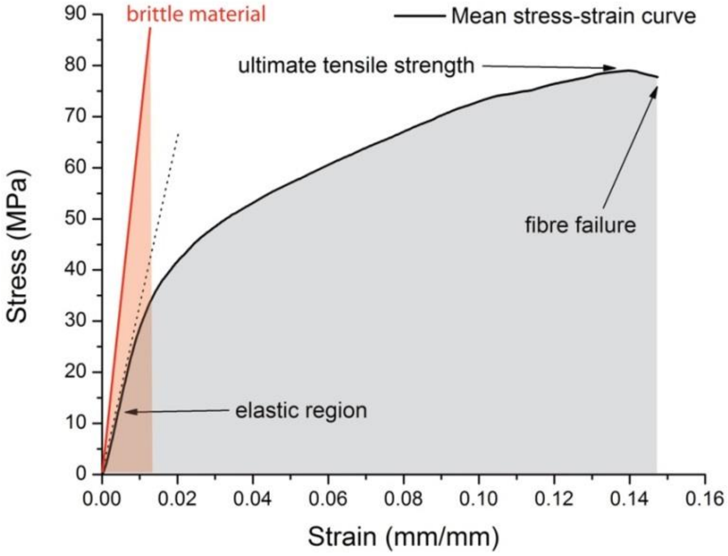


Figure 40. *Agave tequilana* fibres tensile behaviour. Mean stress-strain curve from experimental data (60 specimens tested).

Figure 41a (ESEM) and b (optical microscopy) show the fracture mode of ATF and the separation between fibre-cells. This individual fibre breakage at different planes results in the serration and small non-linear region presented in the stress–strain curve, prior to fibre failure. These results revealed that there is a strong relation between tensile properties and fibre failure due to morphological variations.

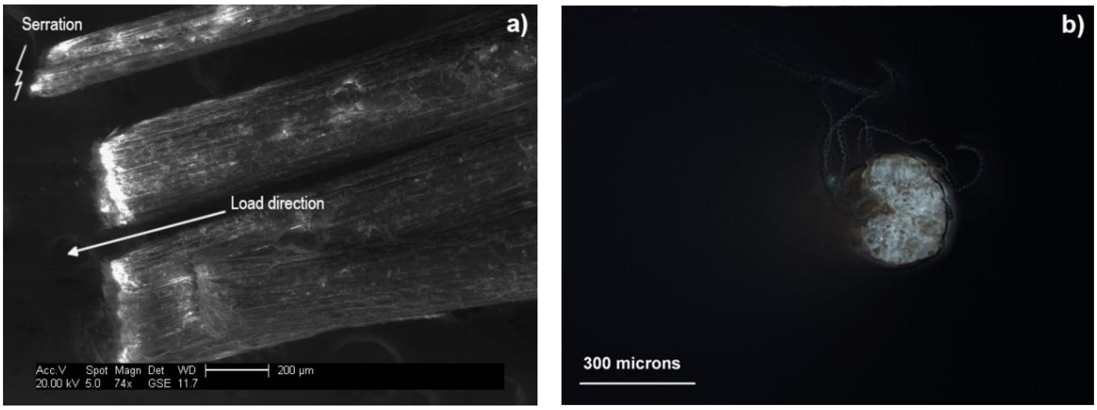


Figure 41. *Agave tequilana* fibre tensile failure. a) ESEM of ATF showing failure mode after tensile test. b) Micrograph of CSA of ATF after fibre failure.

Figure 42, 43 and 44 summarise known natural fibres currently used as reinforcement for composite materials as a function of mechanical properties, physical properties and chemical composition. Additionally, results from this study allow ATF to be placed for comparison. Ultimate tensile strength (UTS) and Young's modulus (*E*) values from ATF (see Table 9) were found to be higher (~36-90%) than those previously reported for the same *Agave* species within the waste stream (i.e., ATW 41.5-58.1 MPa) [102], while the strain was fully in agreement (12-15%). This may be due the CSA determination, different harvesting, and fibre extraction conditions since there is a significant positive relationship between CSA and UTS ($p<0.05$). However, YM and UTS values were lower in comparison to data reported for another *Agave* species (i.e. *Agave sisalana* 385-577 MPa) [195] widely used and produced specifically as reinforcement for composites. The values for asymmetry and kurtosis presented during ATF characterization between -2 and +2 are acceptable in order to prove normal univariate distribution [227,228]. The lower mechanical properties of ATF used in this study, in comparison with other non-waste natural fibres as shown in Figure 43, is likely to be the result of mechanical and thermal stresses during tequila production that partially removed cementing materials that kept the cohesion between fibre cells, due degradation processes during storing, and test parameters/conditions, although, same ATF fibres presented results within the normal ranges in comparison with other agricultural wastes used as fibre source. Therefore, it is possible to consider ATF use as reinforcement or filler for polymeric materials in low-performance applications.

Table 9. Properties summary of *Agave tequilana* fibres.

Parameter	Data No.	Mean	Median	Mode	Skewness	Max	Min	Scale
CSA	350	75±41	66.54	30.38	0.89	214.60	16.62	µm^2
Length	200	77±18	77.41	66.65	-0.13	125.94	27.02	mm
Density	20	1.2±.1	1.15	-	0.70	1.47	1.01	g/cm^3
Water uptake	3	47±1	47.26	-	0	48.57	45.96	%
*UTS	60	79±38	77.29	-	0.55	199.79	8.73	Mpa
**E*	60	3.3±1.4	3.18	-	0.29	6.83	0.59	Gpa
*Elongation	60	13±9	12.67	17.28	1.23	48.54	1.50	%

CSA - cross-sectional area; *E* - Young's modulus; UTS – Ultimate tensile strength. * Gauge length 30.00 mm

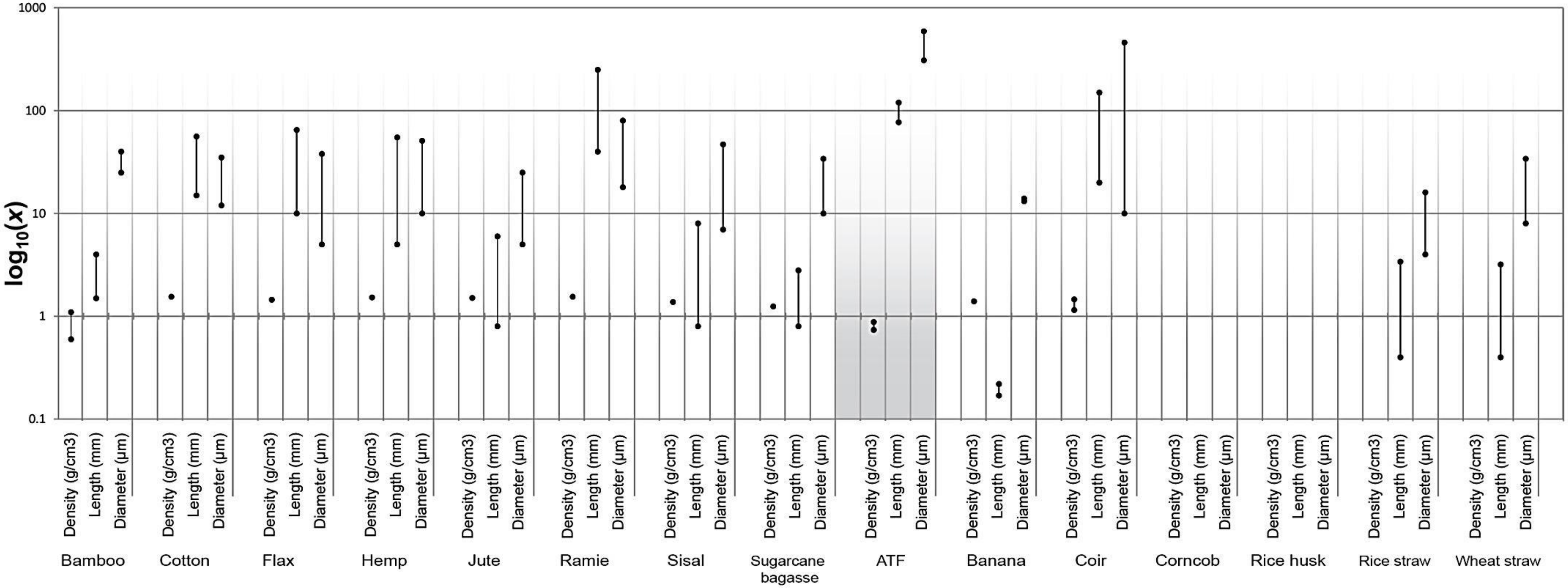


Figure 42. ***Agave tequilana*** **fibres physical properties compared with other lignocellulosic fibres.**

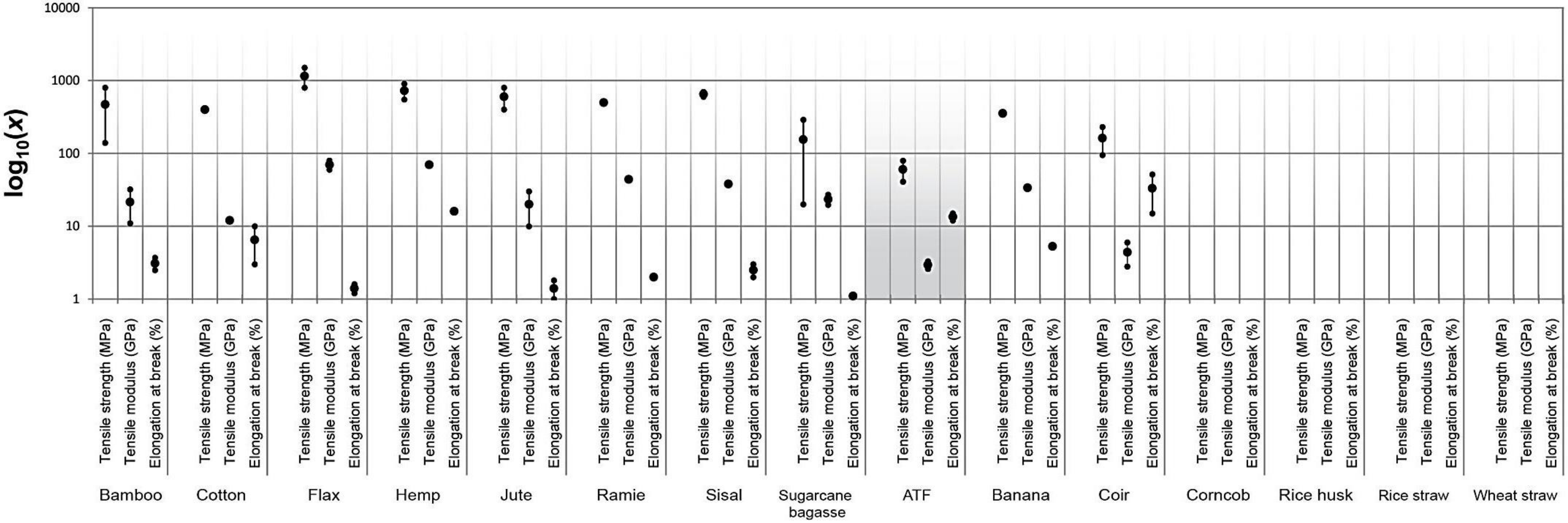


Figure 43. *Agave tequilana* fibres mechanical properties compared with other lignocellulosic fibres.

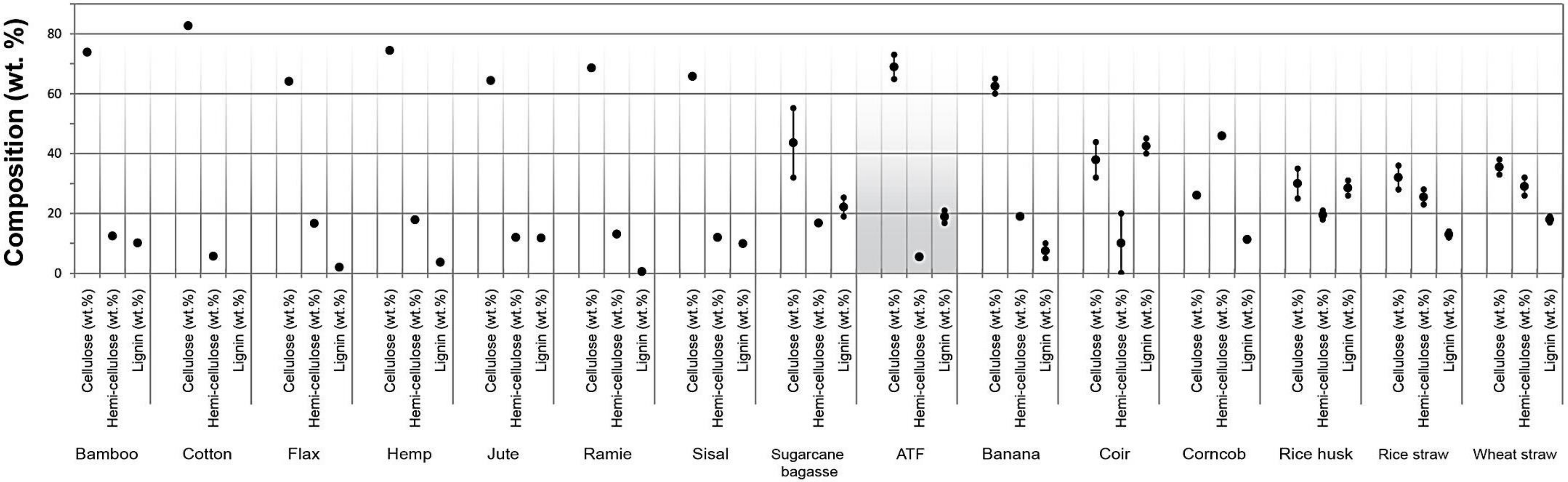


Figure 44. *Agave tequilana* fibres chemical composition compared with other lignocellulosic fibres.

4.5.4 **Energy-dispersive X-ray spectroscopy**

EDX is used to determine which chemical elements, are present in ATF samples, to estimate their relative abundance so it is possible to understand their suitability for surface treatments and predict ATF behaviour. The EDX spectrum for ATF shows peaks for carbon and oxygen corresponding to their binding energies. Generally, higher oxygen contents and higher oxygen/carbon ratios are found in natural fibre samples. This can be attributed to cellulose, whilst the peaks corresponding to inorganic mineral elements (i.e. magnesium, potassium and calcium) (see Figure_Apx C- 1) are present from essential requirements for plant growth. Fibres were analysed as received from the distillery and were found free of other elements or contaminants, leaving them ready for chemical treatments or surface modification previous to composite manufacturing. Table 10 summarises the corresponding X-ray EDX elemental analysis of ATF surface atomic composition and composition ratios.

Table 10. Energy-dispersive X-ray analysis for *Agave tequilana* fibres

Spectrum	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma
C	K series	15.37	0.04608	62.72	0.35
O	K series	12.22	0.04114	20.96	0.47
Mg	K series	0.11	0.00071	1.19	0.25
K	K series	0.16	0.00135	1.02	0.18
Ca	K series	2.08	0.01855	14.12	0.39
Total				100	

It is important to mention that the ATF oxygen/carbon ratio is less than the theoretical value of pure cellulose (0.83) from a cellulose molecule ($C_6H_{12}O_5$). It has been suggested that absorption of impurities on the cellulose surface or the presence of non-cellulosic compounds might lower the oxygen/carbon ratio, since they have fewer hydroxyl groups, and are rich in aliphatic and aromatic carbons [229].

4.6 **Conclusions**

Understanding the limitations and benefits of by-products as a material source is of paramount importance for the use of waste fibre as these constraints determine the use of natural resources. This work provides a method to test natural fibres from agricultural and industrial waste streams. The use of analytical methods to determine technical fibre properties, and an inductive approach to explore the phenomena associated to agricultural and industrial wastes to narrow down the most optimal alternatives between the available range of options, offers an attractive way to broaden and understand materials that can be integrated into new and greener productive cycles on early stages. This can be used as a primary tool for selecting proper lignocellulosic material sources within industrial and agricultural waste streams, for particular composite applications.

By-product fibres from tequila production were used as a case study. These lignocellulosic materials are a promising alternative for fibre production due the availability and economics its use may represent.

ATF presented a non-homogeneous morphology, characteristic of other natural fibres. The measuring of a cross-sectional area of ATF by image analysis of micrographs offered a more precise method to determine more accurately their tensile properties than CSA determination under the assumption of uniformly circular cross-section fibres [102,230]. Tensile properties of ATF are influenced by many factors including; their microstructure, the plant source, age, harvesting conditions, flaws caused by thermal and mechanical stresses during tequila extraction, fibre degradation due to storage and handling conditions, and notably the fibre extraction method. The lower ultimate tensile strength and Young’s modulus values presented by ATF when compared with data reported from other *Agave* species, such as sisal, which is widely used as reinforcement for composites in the automotive industry, could limit their use for load bearing applications. Tensile properties of ATF were within the ranges of data previously reported for the same *Agave* species under similar conditions, although the higher UTS observed was result of CSA measurements and gauge length used in this study. The values observed for ATF compared with other agricultural by-product fibres. Therefore, ATF can still be considered as a suitable material source for reinforcement in composite applications where load-bearing performance is not crucial such as in the packaging industry.

The use of ATF offers a new and potentially low-cost alternative as a reinforcement source for green composites. Several advantages of polymeric matrixes and other green composite applications in the food packaging industry are evident, such as; low cost, low density, toughness, acceptable specific strength properties, compostability, and biodegradability.

5 Surface treatments on natural fibres from tequila production waste.

5.1 Introduction

During the production of tequila, more than 300 000 tonnes of waste fibres are produced [152]. These waste fibres could be profitably used to produce green composites as they have shown acceptable physical and mechanical properties [102]. They are readily available as raw material source and at the present time have no value. However, tensile properties are influenced by many factors including microstructure, the plant source, age, harvesting conditions, flaws caused by thermal and mechanical stresses during tequila extraction, fibre degradation due to storage and handling conditions, and notably, the fibre extraction method. ATF present a lower ultimate tensile strength and Young's modulus values compared with data reported for other *Agave* species, e.g. sisal and henequen, which are widely used as reinforcement for composites in the automotive industry and with a joint global production estimated at around 300 000 tonnes with a value of $75 million [232].

Green composites from naturally occurring renewable resources can be considered as more efficient, sustainable and biocompatible solution to the environmental and economic concerns arising from the large-scale production, and consumption of oil-based materials [2,3,15,16].

The application of fibres from agricultural by-products as a filler or reinforcement offers several advantages for green composite applications, such as; low cost, low density, high toughness, compostability, and biodegradability. Natural fibres are mainly composed of cellulose, hemicellulose, lignin, pectin, fat, waxes and water-soluble substances [52,117]; they require low production energy, are non-abrasive to processing equipment, are CO_2 neutral when incinerated, have a low bulk density and perform well as acoustic and thermal insulators [158]. However, the incompatibility they present with the polymer matrices, the forming of aggregates during processing, and their low resistance to moisture represent a few drawbacks that limit their use [211]. This incompatibility results in poor interfacial fibre/matrix adhesion and low dispersion of the fibres, decreasing the mechanical properties of the final composite material. An improved interfacial bonding for natural fibre-based composites can be achieved by fibre modification with chemical/physical treatments or by the use of additives [51,116].

These modifications aim to improve the interphase through the addition of moieties or the activation of hydroxyl groups, as well as the enhancement of moisture uptake properties, fibre compatibility, dispersion, hygrothermal stability, and mechanical properties. Composites based on surface-modified natural fibres have, in general, better mechanical and physical properties due to improved adhesion and enhancement of polar interactions at the fibre/matrix interface that improve the reinforcing effect [233–236]. Consequently, leading to superior quality composites [114–117].

Chemical composition and structure of natural fibres help determine their properties and potential uses. Cellulose, lignin, and hemicellulose are rich in hydroxyl, carboxyl, and other functional groups; leading to a positive response to chemical modifications such as mercerization or acetylation. For example, acetylation is one of the most studied reactions for lignocellulosic fibres, where the basic principle is to coat the available hydroxyl groups (-OH) of the fibres that make them hydrophilic with other more hydrophobic molecules. A higher cellulose percentage increases stiffness, making the fibres more suitable for resin reinforcement. Cellulose is considered one of the most important chemical components of plant fibres in biocomposites manufacturing [103].

Dewaxing [124–131], coupling agents [55,129,132–134], alkali [53,55,93,103,124,129,132–139], and enzymatic treatments [62,140–145]; have been widely reported in the literature for other lignocellulosic fibres.

The alkali treatment is based on the principles of mercerisation. When the natural fibres are treated with an alkaline solution, such as NaOH, their properties are affected [238]. However, research has also shown that this has a positive effect on the properties of the composite material made using these alkali-treated fibres [135,137]. Hence, alkali treatment has been recognised as a simple and cost-effective method [239].

Another effective and low-cost method is the enzymatic treatment or bioscouring. As well as the mercerisation, enzymatic treatments remove non-cellulosic compounds from the fibres. Effectively, this results in selective pectin removal whilst leaving cellulose structures undisturbed; which favours the retention of the fibres strength [140,144,145,240]. In contrast to alkali treatment, enzymatic treatment is more energy efficient, less chemical and water intensive. Above all, the effluent disposal is more ecological due to its low alkalinity, biochemical and chemical oxygen demand [241].

Natural fibres from tequila production waste stream have suitable characteristics for their use as a raw material source for reinforcement/filler in green composite applications as it is depicted in Table 11. However, the effect of surface modification treatments on fibres from tequila waste stream, and their influence on interfacial adhesion with PLA has not been reported. Thus, a better understanding of the chemical composition, physical properties, and surface adhesive bonding, of this natural fibre source is necessary for developing green composites, and in consequence encourage its use while waste is being diverted from landfill.

Table 11. *Agave tequilana* fibre's properties.

Parameter	Data No.	Mean	CI 95%	Scale
Cross sectional area	350	79±41	79.32-70.65	μm^2
Length	200	77±18	79.64-74.57	mm
Density	20	1.2±0.1	1.22-1.04	g/cm^3
Tensile strength	60	79±38	88.86-69.84	MPa
Young's Modulus	60	3.3±1.4	3.64-2.95	GPa
Strain	60	13±9	15.46-10.72	%

In the present work a detailed investigation has been carried out on the effect of acetylation, silane, alkali, and enzymatic surface treatments on *Agave tequilana* fibres (ATF) properties in terms of surface morphology, water absorption, tensile properties and interfacial adhesion between fibre and poly(lactic acid) through pull-out test [242–246].

5.2 **Materials and methods**

5.2.1 **Materials**

ATF were obtained directly after tequila production from distillery, "La Fortaleza". Figure 34 shows fibres used in this study. NaOH, acetic anhydride, acetic acid, ethanol, perchloric acid, toluene, and 3-Aminopropyltriethoxysilane (APTES) were analytical grade and purchased from Acros organics. Pectate lyase enzyme was provided by Novozymes and PLA was provided by Mitsui & Co Europe PLC. Table 12 shows PLA properties, all other ingredients used were of commercial grade.

Table 12. Typical poly(lactic) acid material and application properties

Property		**Value**
Density		1.24 g/cc
Tensile strength	MD	110.1 MPa
	TD	144.5 MPa
Tensile Modulus	MD	3302 MPa
	TD	3852 MPa
Elongation at break	MD	160%
	TD	100%
Elmendor tear	MD	15 g/mL
	TD	13 g/mL
Spencer impact		2.5 joules
Optical characteristics	Haze	2.1
	Gloss, 20°	90
Thermal characteristics	Glass transition	52-58°C
	Melting point	150°C
Molecular weight		50 kDa

MD=Machine direction, TD=transverse direction

5.2.2 **Fibre treatments**

ATF were repeatedly washed with tap water, drained and oven dried for 24 hrs at 60° C. This ensured the removal of the residual matter present in the fibre from the tequila extraction process.

ATF were exposed to alkali, acetylation, enzymatic and silane treatments by immersion. Treatments were carried out with different percentage solutions concentrations, temperatures, and time ratios. A control sample was kept as a reference. Only the results for the best parameters tested for every treatment are reported. Details for the treatments procedures and solutions are given in Table 13. Different sets of specimens are referred hereinafter as untreated fibres (UNF), alkali-treated fibres (AKF) acetylated fibres (ACF), enzyme treated fibres (ENF), and silane-treated fibres (SIF).

Table 13. ***Agave tequilana*** **surface treatments**

Sample	Solution concentration %		Treatment time	Treatment temperature	Drying temperature and time
AKF	3% 8%	(w/v) NaOH water solution	60 min	21° C	60° C / 24 hrs
	3% 8%		180 min		
ACF	70:30 50:50	(w/w) Toluene + Acetic anhydride + 0.026% perchloric acid (70%)	60 min	60° C	60° C / 24 hrs
	70:30 50:50		120 min		
ENF	0.4% 2%	(weight percentage compared to the fibre) pectate lyase + 0.5 ml non-ionic wetting agent in a buffer solution pH 8.3	30 min	55° C	60° C / 24 hrs
	0.4% 2%		60 min		
SIF	3% 10%	3-aminopropyltriethoxysilane (weight percentage compared to the fibre) hydrolyzed in a water-ethanol solution (40:60 w/w) with a pH 5.5, 1 hour stirred previous treatment.	60 min	25° C	60° C / 24 hrs
	3% 10%		240 min		

The pre-dried fibres were first immersed in the correspondent aqueous solution for all treatments. Treated fibres were then drained, and subsequently rinsed with distilled water until acid-free, and to allow the removal of loosely bonded physisorbed compounds joined to the fibre surface. Finally, to remove moisture in the case of all treaded samples and to complete the chemical reaction in the case of SIF as polysiloxanes are mainly prepared by a multistep “hydrolytic polycondensation" consisting of elementary hydrolysis and condensation reactions, samples were kept for 24h in an oven at 60° C.

5.2.3 **Environmental scanning electron microscopy**

To determine changes in morphology, untreated and treated dry fibres were mounted with carbon tape on aluminium stubs for analysis at room temperature and under vacuum, using an environmental scanning electron microscope (ESEM) and according to a method reported elsewhere [133]

5.2.4 **Tensile test of treated *Agave tequilana* fibres**

Single fibre tensile tests were performed using an INSTRON 5500R EM with a 100N load cell and chart speed of 0.5 mm/min according to ASTM D3379-75 [224]. Single fibres were individually mounted using a thick paper tab with a slot of 30 mm length equal to the gage length was cut out in the middle of the tab. Samples were randomly chosen and pasted at both ends of the slot in the paper tab using fast glue. The precise gauge size of the fibre was measured using a vernier calliper to the nearest 0.1 mm. A total of 7 samples for every treatment were tested with the ultimate tensile strength calculated using:

$$\boldsymbol{T = \frac{F}{A}}$$

Where $\boldsymbol{T}$ is tensile strength, $\boldsymbol{F}$ is the maximum load recorded during test, and $\boldsymbol{A}$ is the mean Cross Sectional Area (CSA) determined using a method previously reported (see Appendix B) [225]. From the data obtained for every specimen tested, the strain was also calculated using the following equation:

$$\boldsymbol{\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}}$$

where $\boldsymbol{\Delta L}$ is the change in gauge length, $\boldsymbol{L_0}$ is the initial gauge length, and $\boldsymbol{L}$ is the final length. Young's Modulus (*E*) was calculated by dividing the stress ($\boldsymbol{\sigma}$), by the strain ($\boldsymbol{\varepsilon}$), in the elastic portion of the stress-strain curve.

The values obtained for the tensile strength were statistically interpreted using the Weibull distribution method [247]. This method is commonly used to determine the survival probability of fibres under tensile stress [248]. In this study, the form presented by Silva et al. (2008) has been used [195].

The survival probability ($\boldsymbol{S}$), was calculated using:

$$\boldsymbol{S} = \mathbf{exp}\left[-\left(\frac{\boldsymbol{\sigma}}{\boldsymbol{\sigma_0}}\right)^{\boldsymbol{m}}\right]$$

where $\boldsymbol{\sigma}$ is the failure stress and $\boldsymbol{\sigma_0}$ is a normalising parameter, and $\boldsymbol{m}$ is the shape factor usually referred as Weibull modulus. Rewriting this as:

$$\frac{\mathbf{1}}{\boldsymbol{S}} = \mathbf{exp}\left[\left(\frac{\boldsymbol{\sigma}}{\boldsymbol{\sigma_0}}\right)^{\boldsymbol{m}}\right]$$

and taking logarithm of both sides twice yielded:

$$-\mathbf{lnln}\left(\frac{\mathbf{1}}{\boldsymbol{S}}\right) = -\boldsymbol{m}\mathbf{ln}\boldsymbol{\sigma} + \boldsymbol{m}\mathbf{ln}\boldsymbol{\sigma_0}$$

From plotting $-\mathbf{lnln}\left(\frac{1}{S}\right)$ vs. $\mathbf{ln}\boldsymbol{\sigma}$**,** a straight line with slope $\boldsymbol{m}$ was obtained and from the intercept and slope $\boldsymbol{\sigma_0}$ value was calculated.

5.2.5 **Water absorption at saturation**

Water absorption was determined by immersion. Specimens composed of bundles of every treated and untreated fibres were dried at 60° C for 24 h, weighed in an analytical balance to the nearest 0.0001g, and placed inside a beaker containing distilled water at room temperature (25° C). The weight difference was measured at intervals of every hour until saturation and moisture content ($\boldsymbol{MC}$) was calculated using:

$$\boldsymbol{MC} = \frac{\boldsymbol{w_1} - \boldsymbol{w_0}}{\boldsymbol{w_0}} \times \mathbf{100}$$

where $\boldsymbol{w_0}$ is the mass of dry sample and $\boldsymbol{w_1}$ is the mass after immersion. Measurements were done by removing the fibres from the beaker, wiping them dry and weighting them to the nearest 0.0001g. Three replicates for every treated and untreated set of fibres were completed.

5.2.6 **Interfacial shear strength**

For the preparation of pull-out test specimens, 4mm diameter cylindrical shaped moulds were filled with PLA micro-pellets, and placed inside an oven heated at 175° C for 10 min. Single fibres were then embedded vertically into the cylinder-shaped PLA matrix at 175° C, then allowed to cool in air at room temperature (Figure 45). Further details on sample preparation are cited by Morlin and Czigany (2012) [243]. The fibres' CSA and embedded length were measured using an optical microscope at magnification 5X.

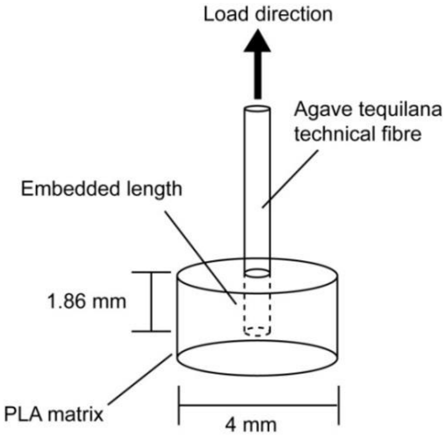


Figure 45. Schematic view of the pull-out specimen.

Optical micrographs of PLA/*Agave tequilana* fibre pull-out test specimens are shown in Figure 46a and b. Samples were aligned in-line with the axis of the cross-head on an INSTRON 5500R EM with a 100N load cell and a chart speed of 0.35 mm/min at room temperature. The load was applied by gripping the resin cylinder with a steel holder fixed to the lower machine clamp and pulling from the free end of the fibre. The load and displacements were recorded until the fibre pull-out completed. The procedure was repeated for every set of treated and untreated fibres, and at least 15 samples from every group were tested. From the data recorded, the debonding force was converted into interfacial shear strength (IFSS) ($\boldsymbol{\tau}$) using:

$$\boldsymbol{\tau} = \frac{\boldsymbol{L}}{\boldsymbol{D} \quad \boldsymbol{le}}$$

where L is the maximum load recorded during debonding, le is the embedded length and D is the fibre diameter obtained directly from CSA measurements of each sample.

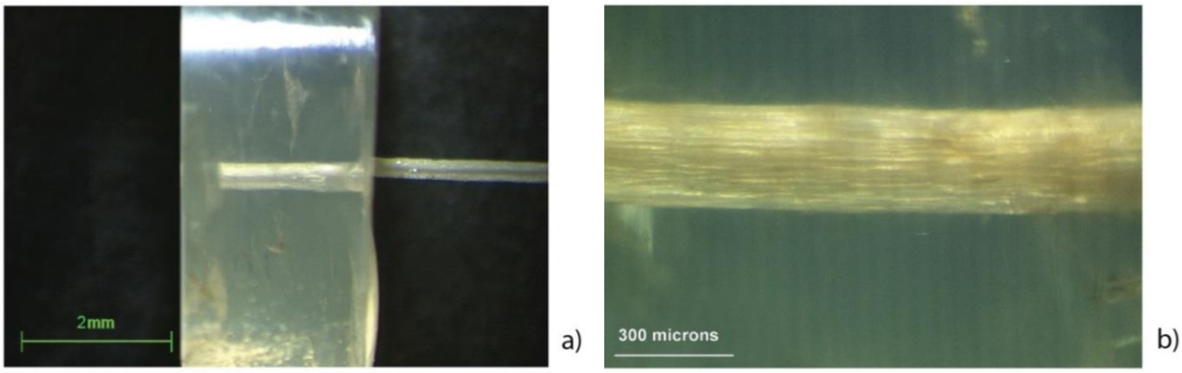


Figure 46. Pull-out specimens. a) Macrograph from pull-out specimen before test. b) Longitudinal section from pull-out specimen before test (magnification 5X).

5.3 **Results and discussion**

5.3.1 **Environmental scanning electron microscopy of treated fibres**

ESEM micrographs clearly show differences in the surface morphology of fibres. AKF (Figure 47a) and ENF showed relatively detached individual cells before treatment. Bundles presented a cleaner surface and more separated due the elimination of the interfibrillar material, hemicellulose and lignin in comparison with ACF and SIF. Therefore, an increased effective surface area available for contact with the matrix as well as the fibre surface roughness can promote a better mechanical interlocking [249].

ESEM images show a clear improvement in fibre surface morphology with a more uniform and smooth surface area for acetylated fibres (Figure 47b), indicating that fibres were successfully coated, and plasticized by the replacement of the hydroxyl groups from the cell wall with new acetyl groups (see Figure 48), making the fibres hydrophobic.

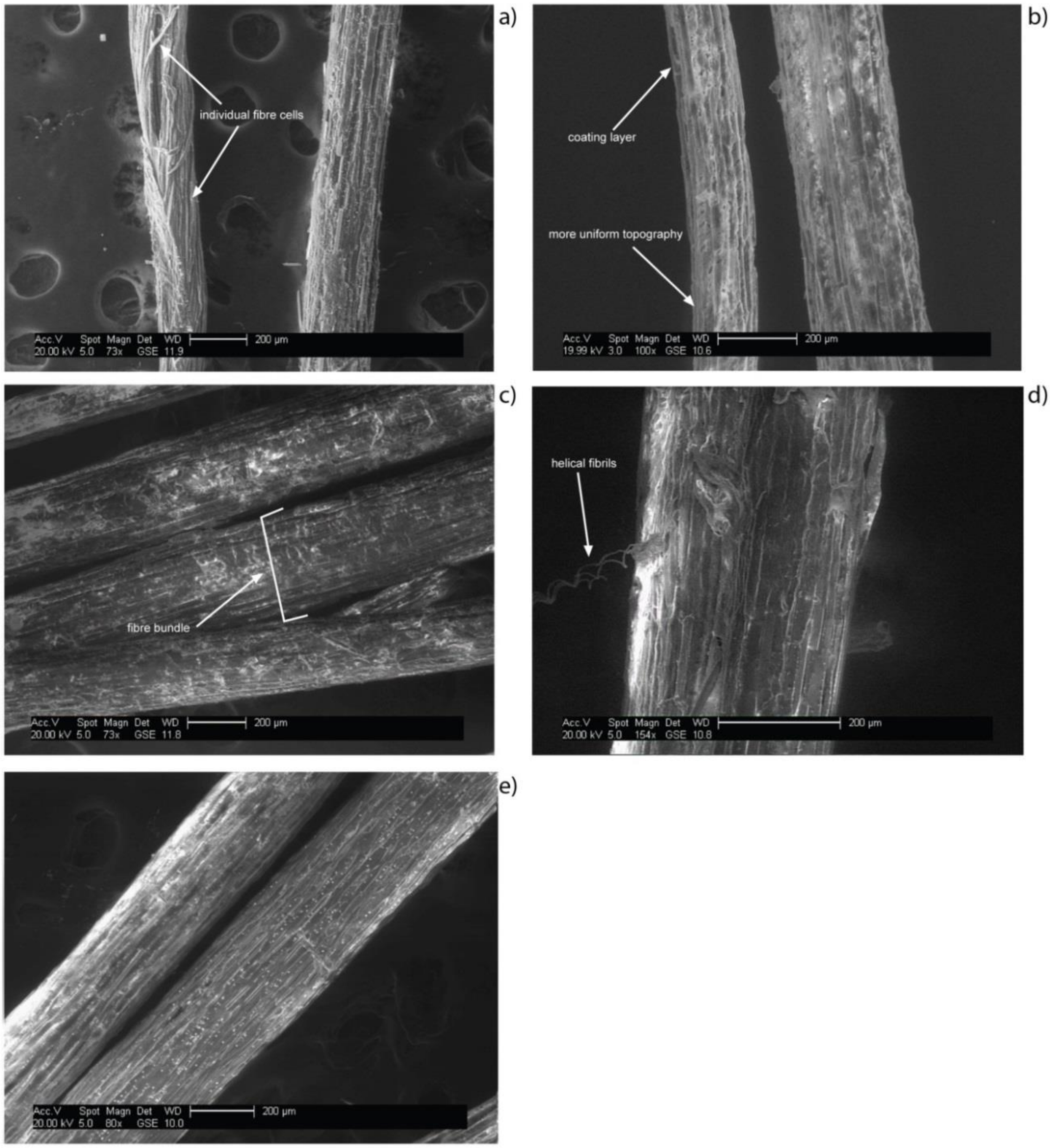


Figure 47. Micrographs of untreated and treated *Agave tequilana* fibres. a) AKF (NaOH 8% -180 min) showing loose fibre bundles, b) ACF ($(CH_3CO)_2O$ 50% - 120 min) showing a more uniform and coated fibre bundle, c) UNF presenting a closely packed fibre bundle, d) ENF (pectate lyase 4%- 60 min) showing partially loose fibre bundles, e) SIF (APTES 10% - 60 min) presenting a uniform fibre bundle.

Untreated ATF (Figure 47c) presented bundles covered by non-cellulosic materials. Whereas in Figure 47d, despite the fibres were still being arranged in bundles it was possible to see a partial fibrillation, i.e., the breaking down of the fibre bundle into smaller fibres. This resulted in the exposing of helical fibrils, by the action of pectate lyase enzyme leaving a considerable surface roughness, and increasing the effective surface area available for contact with the matrix. However, the fibre structure still presents non-cellulosic materials attached to the surface. This may be attributed to the incomplete activity of the enzyme to break the pectin molecules in partial areas of the fibre [144]. Roughness was not greater than that exhibited by alkali treatment (Figure 47a). An extended enzymatic treatment time, and constant pH monitoring, may be required to further eliminate undesirable cementing materials and thus ensure optimal enzyme activity.

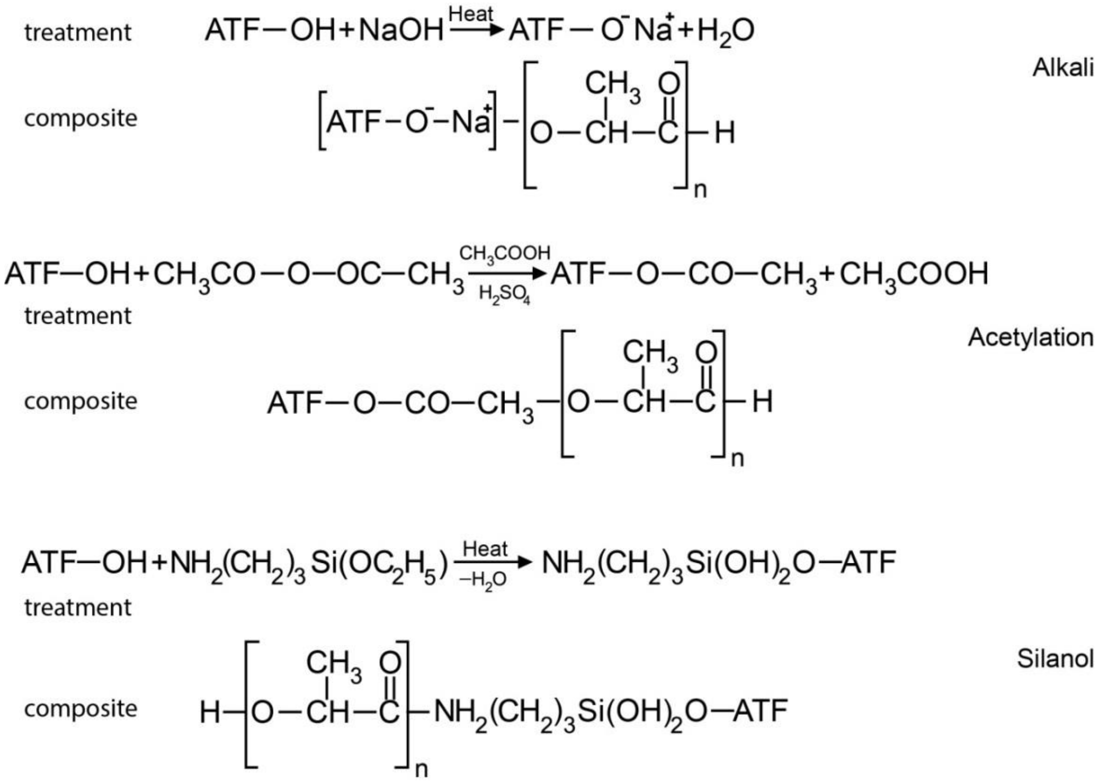


Figure 48. Hypothetical chemical reactions for treatments and between surface treated *Agave tequilana* fibres and poly(lactic) acid.

The forming of a polysiloxane coating bonded to the surface of ATW fibre can be seen in Figure 47e. The R-groups from this layer are likely to react in further composite preparation with functional groups present in PLA, forming a stable covalent bond working as a bridge between ATF and PLA as depicted in Figure 48. A significant change on fibres surface was confirmed through a weight percentage comparison from energy dispersive X-ray microanalysis (EDX) (shown in Table 14) of UNF samples against the final changes occurred in percentage variations in weight of respective elements for treated samples. This is corroborated by the presence of a 3.75% of silicon (Si) content bonded to the cellulose fibre surface for silane-treated samples. Therefore, ATF can be positively modified by chemical (i.e., alkali treatment) and enzymatic treatment (i.e., bioscouring). These processes delivered an active surface by the introduction of reactive groups or by the partial removal of lignin, waxes, and hemicellulose.

Table 14. Comparative energy-dispersive X-ray analysis for treated and untreated *Agave tequilana* fibres.

Sample spectrum	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
UNF								
O	K series	12.22	0.041	83.68	0.47	94.9	SiO2	Yes
Mg	K series	0.11	0.001	1.19	0.25	2.34	MgO	Yes
K	K series	0.16	0.001	1.02	0.18	2.37	KBr	Yes
Ca	K series	2.08	0.019	14.12	0.39	0.39	Wollastonite	Yes
	Total			100		100		
SIF								
O	K series	14.81	0.050	86.13	0.4	93.31	SiO2	Yes
Si	K series	0.45	0.004	3.75	0.24	2.31	SiO2	Yes
Ca	K series	1.43	0.013	10.12	0.34	4.38	Wollastonite	Yes
	Total			100		100		
ENF								
O	K series	12.35	0.042	95.91	0.45	98.32	SiO2	Yes
Ca	K series	0.26	0.002	4.09	0.45	1.68	Wollastonite	Yes
	Total			100		100		

5.3.2 **Effect of surface treatments on fibre strength**

Every surface modification method tested increased in some degree the strength of ATF. However, and as it is shown in Figure 49 the positive effect on fibre strength started to show a detriment after the maximum strength was reached for the surface treatment and parameters used for ATF. All treated fibres continued to display brittle failure within the maximum applied stress as that presented by untreated fibres. Table 15 shows a summary of the surface treatments effect on the ATF properties in comparison with untreated fibres.

Table 15. Summary of *Agave tequilana* fibres properties after surface treatments

Sample	Density (g/cm^3)	CSA (μm^2)	UTS (MPa)	*E* (GPa)	Strain (%)
UNF	1.2±0.1	75±41	79±38	3.3±1.4	13±9
AKF (8%-120 min)	0.88±0.1	59±25	119±33	3.1±1	25±8
ACF (50%-60 min)	1.1±0.1	74±14	99±12	3.3±0.3	13±7
SIF (10%-240 min)	0.9±0.1	57±23	87±15	3.0±0.6	17±8
ENF (0.4%-180 min)	1.0±0.1	67±29	93±37	3.0±0.9	18±8

Despite the growth of cracking during tensile stress induced by the formation of voids and porosity due to alkali treatment that is likely to allow moisture to penetrate into fibres and accelerate the failure; AKF samples treated with 8% NaOH for 120 min. presented the best outcome with a UTS of 119±33 MPa and an *E* of 3.1±1 GPa, where fibres were able to resist breakage and continue elongation after the maximum stress presented for UNF samples. This result may be attributed to a change in the chemical structure of cellulose within the fibres as the cellulose molecular chains in the microfibrils lose their crystalline structure as a result of the alkali treatment, and fibrils become more capable for rearranging themselves along the direction of tensile deformation. Hence, alkali treatment results in a higher stress development on ATF due to better load sharing among fibres [234].

ACF presented the second best results with a UTS of 99±12 MPa and an *E* of 3.3±0.3 GPa related to the forming of an additional coating layer to the fibre surface. Single fibre tensile test results of natural fibres are difficult to analyse due to widely scattered values [250]. Hence experimental data from treated and untreated ATF was analysed using a two-parameter Weibull distribution [247]. Results presented a good fit with a Weibull distribution at 95% confidence level, with an R^2= 0.94 for UNF as seen in Figure 50a, whereas the treated samples showed a distribution with less variation in strength ($\ln\sigma$) (see Figure 50b).

Through Figure 50a and b, it can be observed that for different fibre treatments, there was a fluctuation in strength ($\ln\sigma$), which is a behaviour that has been reported particularly for alkali treated fibres [248]. As the number of defects present on the fibres controls the Weibull modulus, it is concluded that AKF, besides having the highest mechanical behaviour, have a larger probability of failure when submitted to similar stress conditions. Results from tensile test are summarised in Figure 51 as a comparative to untreated samples.

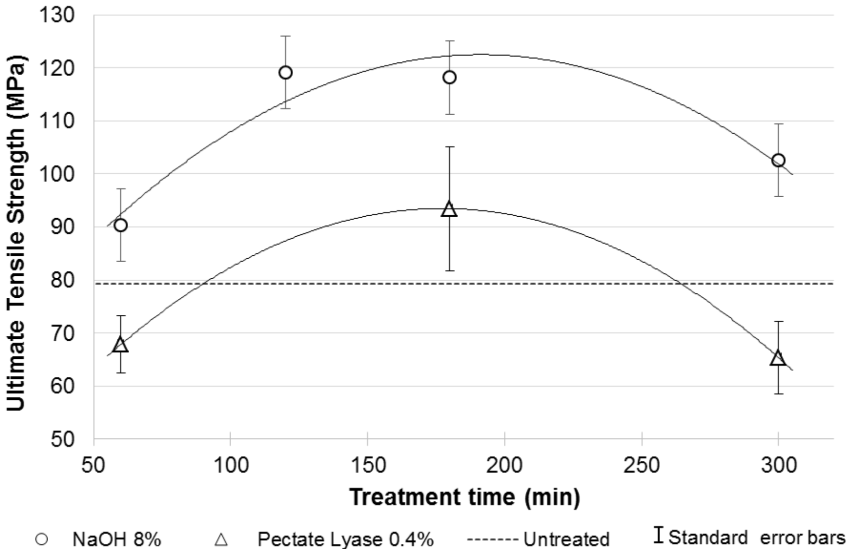


Figure 49. Treatment time effect on ultimate tensile strength for treated *Agave tequilana* fibres. AKF samples treated with 8% NaOH solution and ENF samples treated with 0.4% pectate lyase.

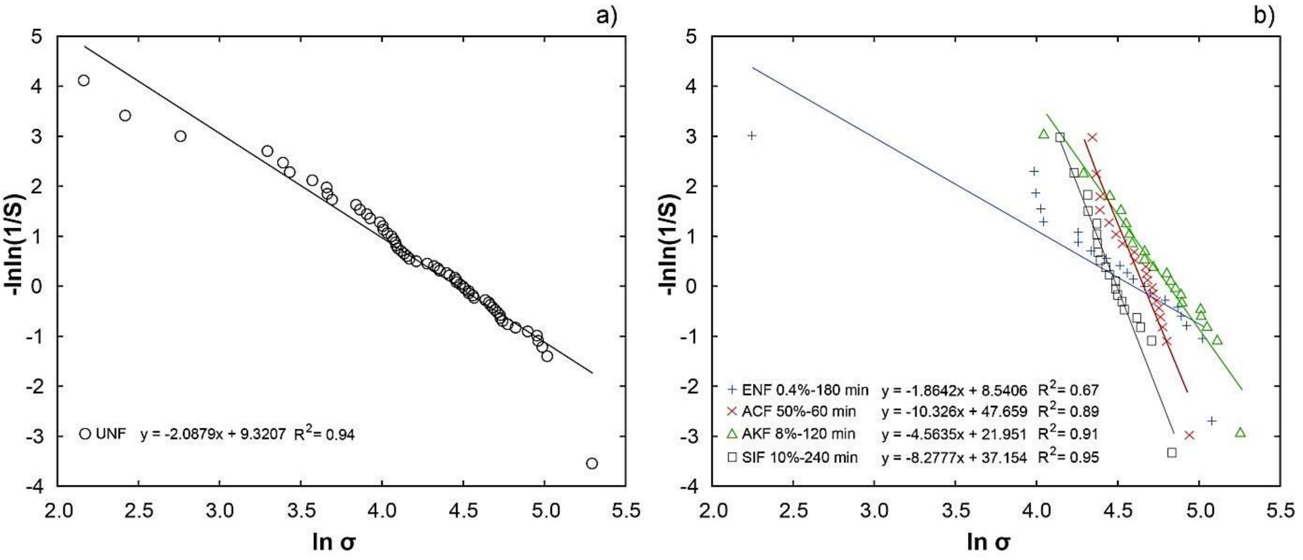


Figure 50. Weibull distribution for ultimate tensile strength for *Agave tequilana* fibres. a) Plot of –ln ln (1/S) vs. ln σ for the tensile strength for UNF. b) Plot of –ln ln (1/S) vs. ln σ for the tensile strength for all treated ATF.

Even though results from single fibre tensile test have shown lower values in comparison with other natural fibres (i.e., sisal ~80% [212]), and earlier failure attributed to inherent flaws in the fibre due to the tequila extraction processes and diameter variations; surface treatments effectively increased the UTS of ATF as can be seen in Figure 51.

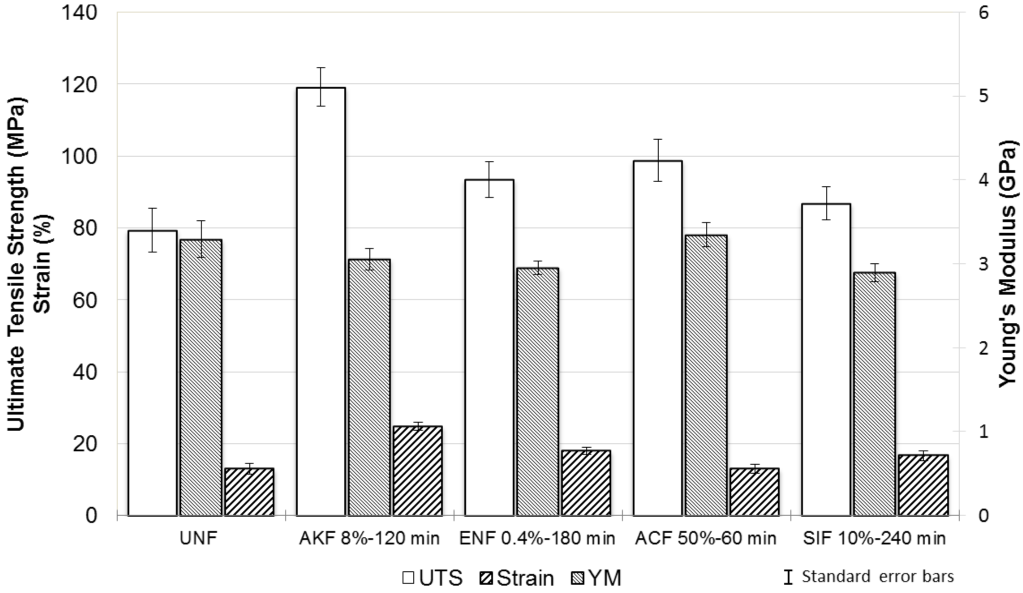


Figure 51. Effect of surface modification treatments on tensile properties for *Agave tequilana* fibres.

5.3.3 **Effect of surface treatments on water absorption at saturation**

The amount of water absorbed by the fibres was calculated by the weight difference between those samples saturated in water and dry samples. Figure 52 shows the best performance from the percentage of water absorbed plotted against time for the different treatments. Fibres absorbed water very rapidly during the first stages (0–60 min) reaching an equilibrium point, where no more water was absorbed and the content of water in the sample remained stable. UNF showed the highest water uptake with 47%. The hydrophilic character of cellulose is responsible for the water absorption in natural fibres, and therefore the higher cellulose content led to the higher amount of water being absorbed. Every treatment showed improvement in water absorption. ACF, as it was expected due to the hydrophobic layer coating ATF surface showed the best results with 29% of water uptake after 6 h of exposure. Pectate lyase, silane, and alkali treatments had a moderate effect on the amount of water absorbed as treated fibres accumulated approximately the same water content, i.e., between 35% and 37% after 6 hrs of exposure. This reduction in absorption properties in comparison with the UNF samples was attributed in the case of ENF and AKF to the partial removal of lignin and hemicellulose, and to the change of fibre’s hydrophilic nature to a more hydrophobic one as both treatments also promoted the activation of hydroxyl groups of cellulose units by breaking the hydrogen bonds.

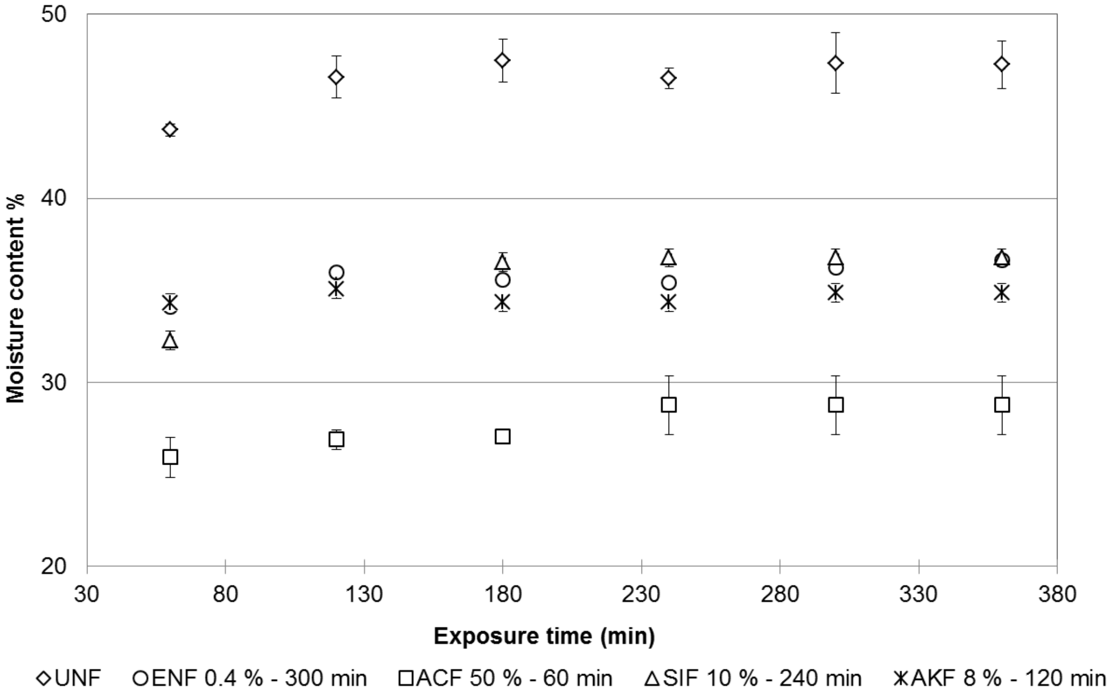


Figure 52. Water absorption at saturation for *Agave tequilana* fibres after surface treatments. Standard deviation marks are smaller than the markers in some cases.

5.3.4 **Effect of surface treatments on interfacial shear strength between *Agave tequilana* fibres and poly(lactic) acid.**

During tests, the debonding process started just after stage I with crack propagation until the maximum load was achieved and the fibre was consistently withdrawn from the matrix, to finally present a decreasing load with an extension trace as shown in Figure 53.

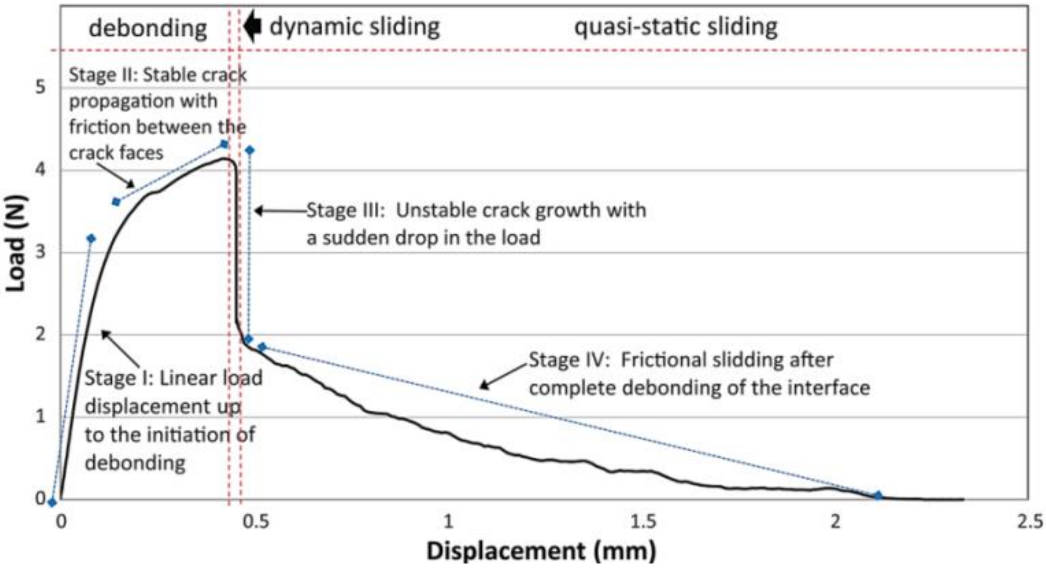


Figure 53. Experimental load versus displacement curve for a fibre pull-out test for PLA and untreated ATF.

The non-linear behaviour from the traces (Figure 54) shows the difference in the trend of the curves dropping after the load reached its maximum value. As the UNF gradually reached the maximum load there was a generally smooth transition, followed by a linear decrease with occasional stick-slip activity until the fibre was finally pulled-out from the matrix. This was a consistent behaviour from a weak interphase which is likely to be due to the low compatibility between ATF and PLA. In contrast, for AKF and ENF, this behaviour differed as a result of the higher roughness on the fibres surface, being the mechanical interlocking the main reason for the variability presented for these samples as shown in Figure 54. For silane-treated and acetylated fibres, the load-displacement trace has shown a weak bonding in comparison to AKF treated samples as the main factor improving the bonding between phases has been attributed to the increment in effective surface area due to the removal of non-cellulosic materials [249]. Notably, after interface failure, the curve decreased in an almost linear fashion, which is more evident for acetylated fibres, until the fibre was pulled-out leaving small traces of friction.

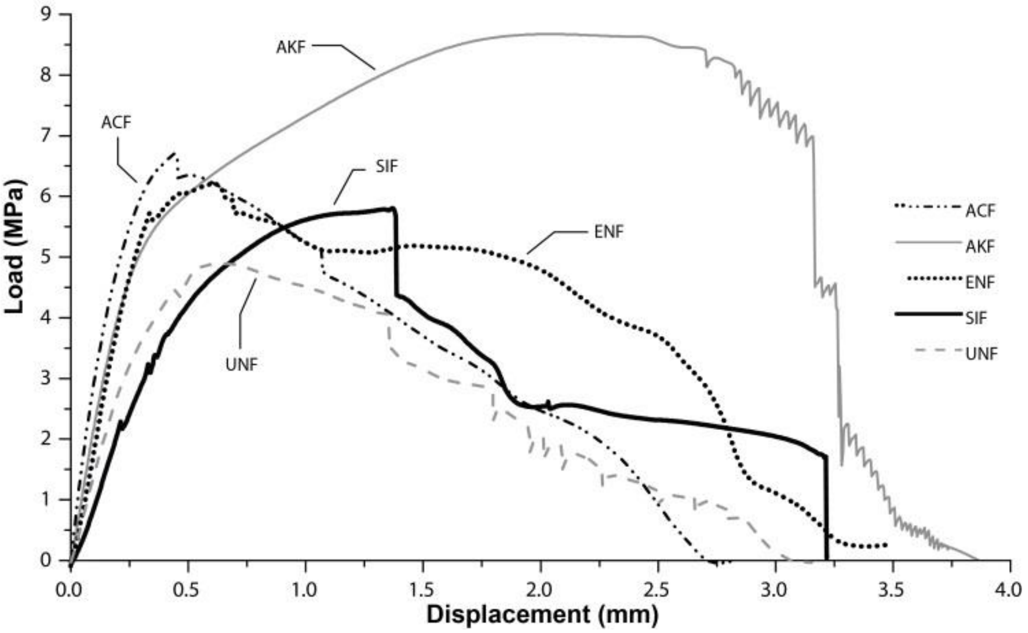


Figure 54. Typical load-displacement traces from untreated and treated *Agave tequilana* fibres during pull-out test. Load-displacement traces were obtained from the average of at least 18 samples tested.

The effect of different treatments and their concentrations for IFSS is shown in Figure 55 and Figure 56. Every treatment presented an increase in IFSS at different values in comparison with untreated fibres at 0.05 level of significance (Table 16). This was evidence of improvements in bonding within the PLA matrix. The highest IFSS, with a mean 5.2±1.3 MPa, was demonstrated by the samples treated with 8% NaOH for 60 min. This can be attributed to an increase of available hydroxyl (–OH) groups from the alkali treatment, the removal of the non-cellulosic materials, and above all to the increased roughness in the surface area of the fibre (Figure 47a). ENF samples presented a similar surface roughness from the enzymatic treatment (Figure 47b), although to a lesser extent with minor variations when compared to the UNF samples. ENF at 0.4% concentration for 60 min. presented the second best IFSS with a mean 4.0±0.7 MPa. Thus, a better mechanical interlocking promoted by alkali and bioscouring treatments within 60-160 ranges of time can be considered as the main factor improving the bonding between ATF and PLA (Figure 55).

Table 16. ANOVA results for interfacial shear strength differences between treated and untreated *Agave tequilana* fibres.

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	33.42	4	8.35	7.46	0.000046	2.50
Within Groups	78.36	70	1.11			
Total	111.77	74				

ATF exhibited variability in tensile properties as well as in IFSS, which is quite common to natural fibres. Therefore, the values obtained by pull-out test were statistically analysed using a Weibull distribution. Figure 56 shows that there is a reasonably good agreement between experimental IFSS data and the two-parameter Weibull distribution.

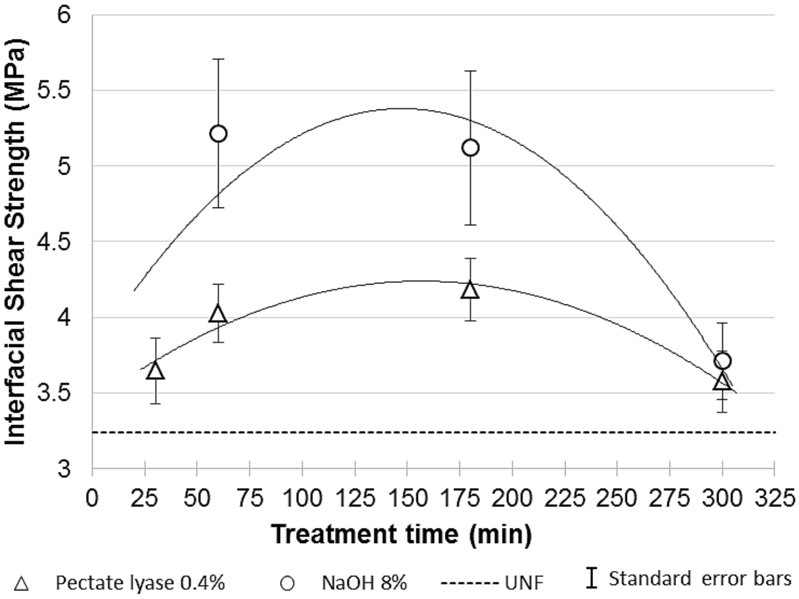


Figure 55. Effect of treatment time on interfacial shear strength for *Agave tequilana* fibres treated with 8% NaOH and 0.4% Pectate Lyase.

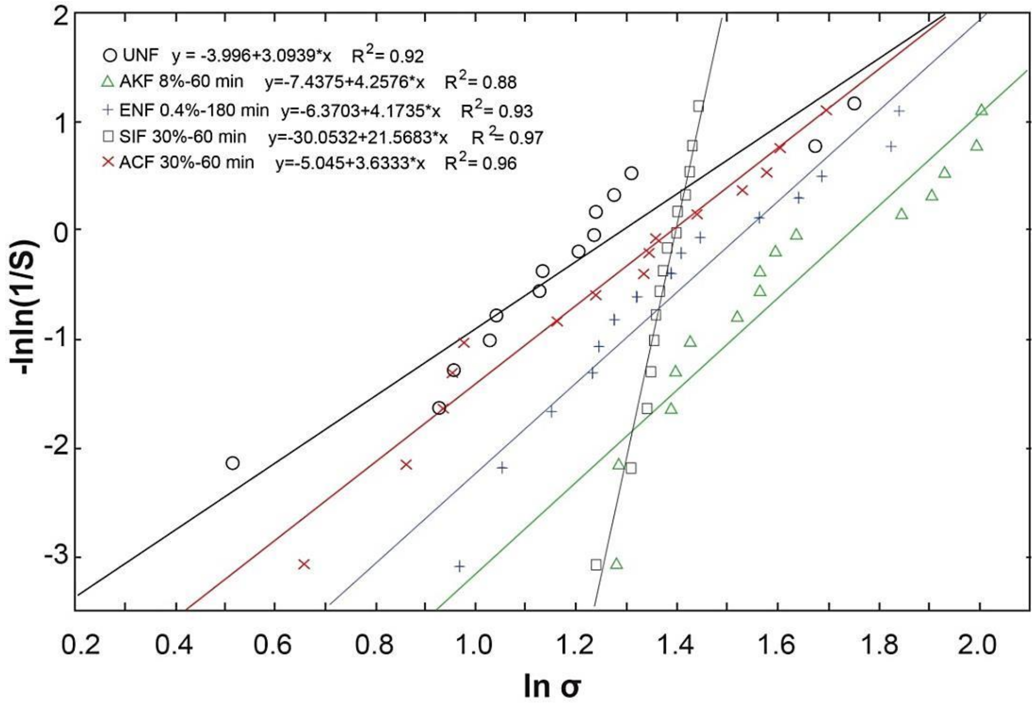


Figure 56. Pull-out test results in Weibull coordinates for all treated samples in comparison with untreated ATF.

5.4 **Conclusions**

The use of ATF, considered waste or by-products from the tequila production, offers a new alternative as a source of reinforcement fibres for green composites. This offers several advantages for PLA alongside other green composite applications, such as; low cost, low density, moderate toughness, acceptable specific strength properties, compostability, and biodegradability.

The bonding between matrix and reinforcement has a key role in determining the optimum performance of green composites, which can be improved by surface treatments. ATF tensile properties, interfacial bonding between PLA and ATF, and absorption properties are positively improved by surface modification methods. Alkali treatment presented the best results for ultimate tensile strength and interfacial shear strength in comparison with the UNF samples with an increment of ~50% and 60% respectively. Increased roughness in the surface area of the fibre and the removal of the non-cellulosic materials demonstrated by alkali and enzyme treated fibres are considered to be the main factors improving interfacial bonding (as seen in: Environmental scanning electron microscopy of treated fibres section). Therefore, it is possible to envision a green composite material based on treated ATF and PLA capable of performing under low stress conditions without compromising the integrity of the final composite product or the environment.

6 Extrusion moulding of a novel *Agave tequilana* fibre and poly(lactic) acid-based composite: a study of tensile, impact, flexural and water uptake properties.

6.1 Introduction

In recent years several new polymers derived from natural sources such as poly(lactic acid) (PLA) have been produced providing potential biodegradable replacements for hydrocarbon materials [251]. PLA is the first degradable polymer to be commercialized in the plastics industry on a large-scale; it has high strength and low elongation at break [76], can be processed in nearly the same way as other thermoplastics and is produced through the fermentation of renewable agricultural feedstocks such as maize or sugar beets [59,60]. However, some of its physical properties and the current high cost are some drawbacks that limit its broad application. The development of fully green composites presents a potential solution to these problems.

Interest in the use of natural fibres as reinforcement in composites has increased in recent years, as a solution to oil depletion, increasing plastics pollution, and as a mean to reduce material costs. The use of natural fibres and other agricultural wastes such as; kenaf [55,97], flax [62,187,252], jute [42,103,189], hemp [96,144,190,191], bamboo [98] wood [95], sisal [54,136,194,195], coir [215], rice husk [217], wheat straw [202,220,236], corncob [216], sugarcane bagasse [253], and banana [213,214], in composites has demonstrated the application and benefits of natural fibres.

Despite their benefits, natural fibres also have shown a few disadvantages inherent to its natural origin. These are associated to the presence of hydroxyl groups (OH) and include moisture uptake, variation in quality and poor dispersion and adhesion.

Chemical modifications aim to improve the interfacial interaction through the addition of moieties or the activation of hydroxyl groups. They also enhance moisture uptake properties, fibre compatibility, fibre dispersion, hygrothermal stability and mechanical properties; leading to superior quality composites [114–

117]. Several surface treatments on other lignocellulosic fibres have been reported including alkali, acetylation, silane and enzymatic treatments [130,135,140,144,145,194,249,254–257]. However, since fibre’s specific chemical makeup is influenced by the harvest conditions, their properties can exhibit great variation [197,236].

Composites based on surface-modified natural fibres have, in general, better mechanical and physical properties due to improved adhesion and enhancement of polar interactions at the fibre/matrix interface that improve the reinforcing effect [233–236]. A previous study on surface treatments for ATF and their mechanical behaviour indicated ATF as a possible candidate for their use in the production of biodegradable composites. The principal question would be, nonetheless, to understand ATF suitability as reinforcement for a PLA matrix. This is suggested by the fact that previous studies (see Chapter 5) demonstrated that most common chemical treatments, such as alkalization or enzymatic treatments, substantially improve the fibre properties. PLA-based composites have shown improved strength and Young modulus with the addition of natural fibres, although treated fibres present usually lower strength in comparison to untreated fibres due to cellulose reinforcement, could result in more brittle PLA limiting the tensile strength of the composites [258].

PLA has shown a significant potential to be used as matrix in green composite materials based on bast natural fibres such as kenaf [259], jute [92], hemp [260] and flax [138]. This study investigates the effect of ATF recovered from tequila production, after alkali and enzymatic surface treatments on the mechanical and moisture uptake properties of a PLA-based composite. The ultimate aim is the assessment of ATF as reinforcement/filler material in a PLA matrix-based composite with improved biodegradability, and capable of replacing oil-based polymers. The effect of alkali and enzymatic treatments on tensile and moisture uptake properties for ATF has been reported in the previous chapter. These treatments were found to improve interfacial adhesion between ATF and PLA through the mechanical interlocking caused by the removal of non-cellulosic materials.

Earlier studies have also shown that compounding of natural fibre-based composites can be done in one step using twin-screw extrusion [261–263]. Twin-screw extrusion is a suitable method for large-scale processing, but natural fibres present difficult feeding and poor dispersion of during melt compounding [264]. Particularly, if non-polar polymers are used as matrices, dispersion of natural fibres with polar surfaces is difficult [265]. Natural fibres, during compounding, tend to form aggregates which are difficult to break in order to achieve a good dispersion [266]. It is of paramount importance that current methods to manufacture natural fibre-based composites aim to be more efficient in terms of processing in order to obtain more commercially viable products.

The aim of this study is to compound ATF and PLA in one extrusion step in order to manufacture a bio-based composite. This kind of processing represents a more efficient and economical production of cellulose composites due to fewer processing steps involved. To study the effect of fibre treatments, several samples of treated ATF were used as the cellulosic raw material.

A preliminary investigation on the mechanical and physical properties of ATF/PLA composite materials is presented. Specifically, tensile, flexural, impact, moisture and water uptake properties. The morphology of the composites and failure mode are studied by optical microscopy and environmental scanning electron microscopy (ESEM).

6.2 **Materials and methods**

By-product ATF was supplied after tequila production by distillery “La Fortaleza” in Jalisco, Mexico. NaOH was analytical grade and purchased from Acros Organics, Pectate lyase enzyme (Scourzyme®) was provided by Novozymes. PLA (Ingeo Biopolymer 2003D) in pellet form was purchased from Natureworks™. PLA properties are given in Table 17. All other ingredients used were of commercial grade.

Table 17. Poly(lactic) acid properties.

Property	Value
Thermal conductivity (crystalline pellets – 25% crystallinity)	25 0.160 J/m-°K-s
Glass Transition Temperature, T_g	55 - 60° C
Peak Melt Temperature, T_m	145 - 170° C
Specific Gravity, ρ.	1.24 - 1.25 g/cc
Melt Density (200° C), ρ. melt	1.12 g/cc
Pellet Bulk Density, ρ. bulk	0.79 - 0.85 kg/litre (49 - 53 lb/ft3)
Tensile Strength at Break, D882	53 MPa
Tensile Yield Strength, D882	60 MPa
Tensile Modulus, D882	3.5 GPa
Tensile Elongation, D882	6.0 %
Notched Izod Impact, D256	16 J/m

6.2.1 **Fibre treatments**

ATF with a mean length of 10 mm were pre-washed and oven-dried at 60° C for 24 hrs. Fibres were further exposed by immersion to alkali and enzymatic treatments. Alkali-treated fibres were immersed 180 minutes in 8% (v/w) NaOH solution, while enzyme treated samples were exposed to 0.4% (v/w) of pectate lyase in relation to fibre content during 180 minutes. Details from every treatment have been reported in previous chapter. Untreated ATF samples were kept as control. Different sets of treated and untreated fibres were oven-dried after treatment at 60° C for 24 hrs. and kept in sealed desiccators to control relative humidity (RH) due to the hygroscopic nature of the fibres.

6.2.2 **Compounding**

Compounding was carried out in a 21mm LAB Rondol twin-screw extruder equipped with a 2 mm hole diameter die and controlling the temperature profile, speed crew and drive torque. Residence time was calculated to keep the melt flowing and to prevent degradation during all the runs, at least for 3 min. During processing of the different grades, a purge flow was passed through the extruder to clean residual materials and avoid cross-contamination. The screw speed was fixed at 50 rpm for the melt mixing, and 60% for the drive torque. Details from the heating temperature are given in Figure 57. 20, 40 and 60%

(v/w) of fibres and PLA pellets were separately premixed by continuous shaking before compounding to assure the uniformity during the material feeding. Extrudates were prepared and pelletized by adding the premixed fibres and PLA directly into the hopper. Samples are denoted hereinafter as AKF, ENF and UNF for alkali, enzyme and untreated specimens with 20, 40 and 60% (v/w) of fibre content respectively. Neat PLA was also pelletized and press moulded to keep it as a control material.

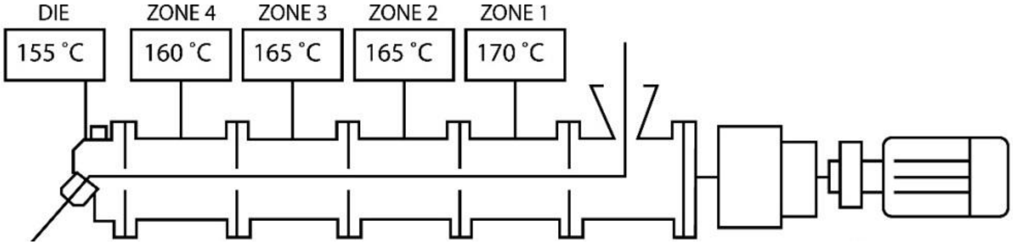


Figure 57. Extrusion profile temperature settings.

6.2.3 **Press moulding**

Pellets were oven-dried at 60° C for 24 hrs. and kept in sealed desiccators before press moulding. Composite plates were prepared in a 40 T hot press by press moulding the pellets in a steel frame at 160° C for 8 minutes at 55 MPa. Hot press frame dimensions (mm) are given in Figure 58. After pressing, the frame was quenched under room conditions and composite plates were unmoulded. Specimens were cut out from the composite plates by dynamic water jet cutting, inspecting the taper and tolerances in the cut out samples before further testing.

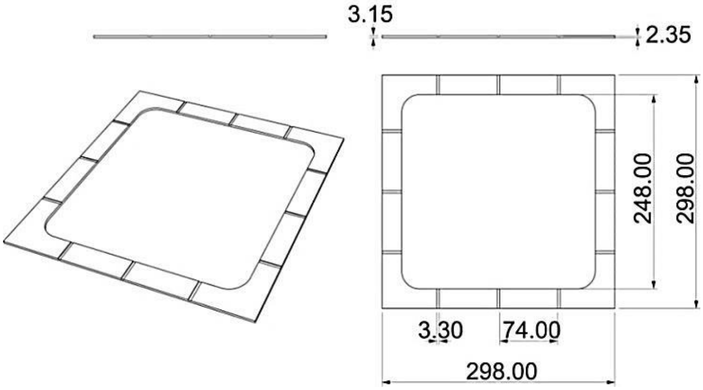


Figure 58. Hot press frame dimensions.

6.2.4 **Optical microscopy**

Morphology and failure mode of composites were analysed by optical microscopy using a Nikon Eclipse E600 at 5x and 10x magnification. The fractured specimens of the ATF/PLA composites were observed with an environmental scanning electron microscope (ESEM); samples were mounted with carbon tape on aluminium stubs to be analysed at room temperature and under vacuum.

6.2.5 **Mechanical testing**

Tensile testing was performed on type 1 specimens according to ASTM D638-10 standard on a calibrated Instron 5500R EM with a 100kN load cell at a crosshead speed of 2mm/min at room temperature (21° C) [49]. From the data recorded, ultimate tensile strength (UTS) was calculated using:

$$\boldsymbol{\sigma = \frac{L}{A}}$$

where $\boldsymbol{\sigma}$ is the stress, $\boldsymbol{L}$ is the maximum load recorded during test, and $\boldsymbol{A}$ is the specimen cross-sectional area. From the data obtained for every specimen tested, the strain was also calculated using the following equation:

$$\boldsymbol{\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}}$$

where $\boldsymbol{\Delta L}$ is the change in gauge length, $\boldsymbol{L_0}$ is the initial gauge length, and $\boldsymbol{L}$ is the final length. Young's modulus (*E*) was calculated by dividing the stress ($\boldsymbol{\sigma}$), by the strain ($\boldsymbol{\varepsilon}$), in the elastic portion of the stress-strain curve.

Three-point bending flexural test was realised according to ASTM D790 using a 5kN load cell and a crosshead speed of 1mm/min [132]. Calculation of flexural stress ($\boldsymbol{\sigma}$) was done according to:

$$\boldsymbol{\sigma = \frac{3FL}{2bd^2}}$$

where $\boldsymbol{F}$ is the maximum load on the load deflection curve, $\boldsymbol{L}$ is the support span, and $\boldsymbol{b}$ and $\boldsymbol{d}$ respectively correspond to the width and thickness of the tested sample. Flexural modulus ($\boldsymbol{E_f}$) was calculated using:

$$\boldsymbol{E_f = \frac{L^3 m}{4bd^3}}$$

where $\boldsymbol{m}$ is the gradient of the initial straight-line portion of the load-deflection curve. Impact testing was executed according to ASTM D4812 standard for unnotched Charpy impact on a Zwick pendulum impact test machine with a 1J hammer. Impact strength was calculated using the following equation:

$$\boldsymbol{I = \frac{E_c}{hb} \times 10^3}$$

where $\boldsymbol{E_c}$ is the corrected energy absorbed by the specimen; $\boldsymbol{h}$ and $\boldsymbol{b}$ are the thickness and width of the specimen respectively. Flexural and impact tests were performed flatwise and edgewise. Before testing and prior conditioning at room temperature, samples were oven-dried at 50° C for 24 hrs. and kept in sealed desiccators. At least 14 specimens were tested for every property assessed and for every material grade. Specimens' dimensions for every test are given in Figure 59.

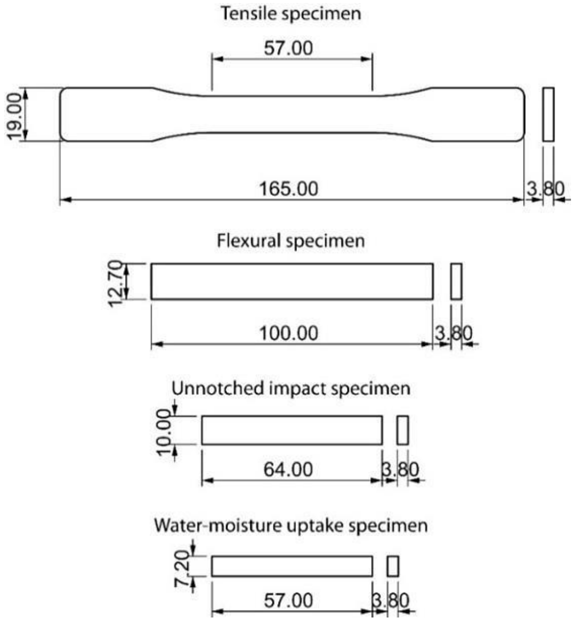


Figure 59. Specimen dimensions.

6.2.6 **Water and moisture uptake**

Due to the hygroscopic nature of the material, potentially leading to changes in dimensions as well as in mechanical properties; water absorption at saturation (WAS) and water absorption at equilibrium (WAE) were determined. These represent the % weight gain of the specimen due to water absorption after immersion in distilled water at 23° C or due to the exposure to a humid environment at 50% of relative humidity at 23° C respectively.

For every test, composite specimens were split up into two groups for WAS and WAE measurements correspondingly. Samples were dried at 50° C for 24 hrs. and weighed in an analytical balance to the nearest 0.0001g. The first set of samples was placed inside sealed beakers containing distilled water at room temperature (23° C), the second set was placed in a controlled chamber at 23° C at 50% of RH. The weight difference was measured at several intervals of time until equilibrium and moisture content (***MC***) was calculated using:

$$\boldsymbol{MC = \frac{w_1 - w_0}{w_0} \times 100}$$

where (w_0) is the mass of dry sample and (w_1) is the mass after exposure. Measurements were done by removing the samples from every beaker and chamber, wiping them dry and weighting them to the nearest 0.0001g. Three replicates for every set of samples were assessed for water and moisture uptake properties.

6.3 **Results and discussion**

6.3.1 **Compounding and press moulding**

The torque response of the ATF/PLA composites was recorded during the compounding process as a function of the mixing time. The torque values for ATF/PLA composites, corresponding to the stationary conditions, are shown in Figure 60. For all samples, during the mixing process, a slight but continuous decrease in the torque was observed, which could be accounted for, by the occurrence of some thermal and/or oxidative chain degradation phenomena at the applied mixing temperature. Such an effect was more marked in the presence of a high ATF content.

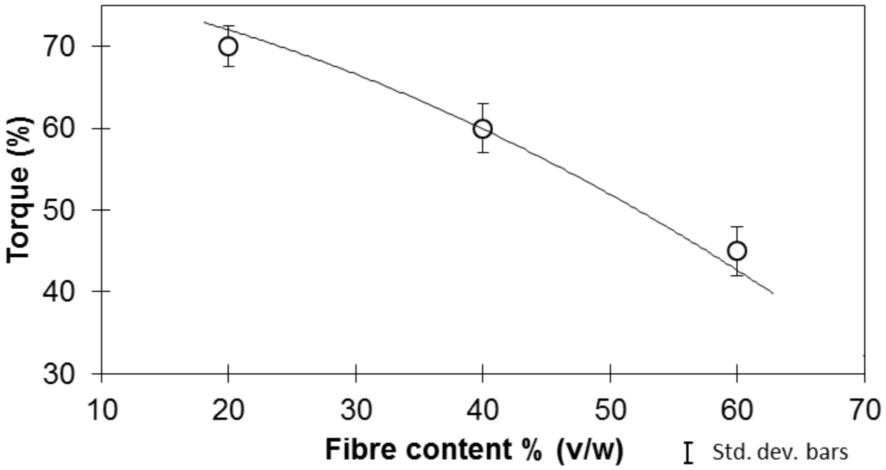


Figure 60. Continuous decrease of torque at increased fibre content.

ATF presented shearing during the compounding process due the extruder mixing elements configuration and the long distance ATF and PLA went through the compounding (see Figure_Apx E-2). Hence, the evident reduction in fibre length attributed to the mixing rather than the pelletizing as shown in Figure 61a and b. To preserve the fibres during compounding, the feeding must be done in the final zones of the extruder; therefore, minimising the passage through the kneading elements.

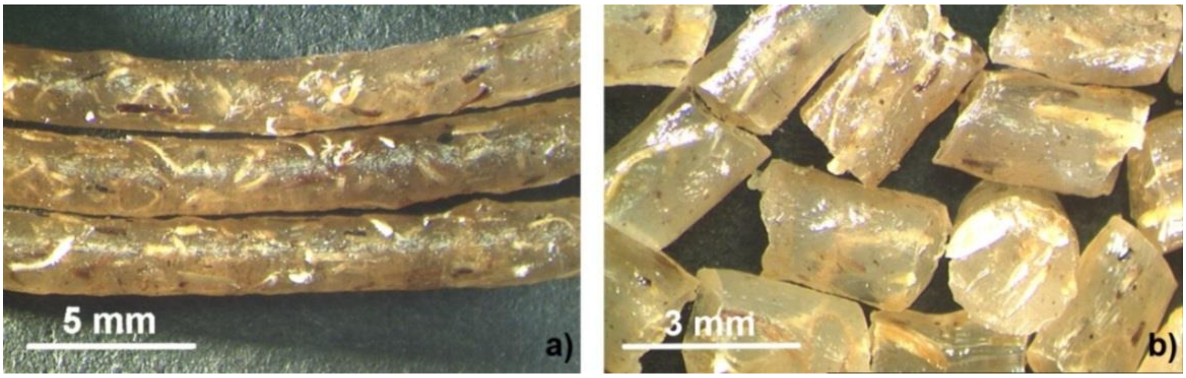


Figure 61. Macrograph of extruded filament and pellets of *Agave tequilana* fibres and poly(lactic) acid bio-based composites. a) 20% (v/w) ENF/PLA strand. b) 20% (v/w) ENF/PLA pellets.

Figure 62. *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens. a) Pelletized composites with different fibre volume content. b) 40% (v/w) AKF/PLA composite specimens. Top: Tensile test specimens. Middle: specimens used for three-point flexural bend test. Bottom: specimen used for impact test.

6.3.2 **Mechanical testing**

15 tensile tests were conducted for every set of specimens. During the tensile test, composite specimens fractured after yielding without necking, indicating a brittle failure mode as shown in Figure 63. Neat PLA had a tensile strength of 63±3 MPa, *E* of 2.8±0.1 GPa, and a strain of 2.9±0.2.

The decrease in tensile strength is attributed to the brittle nature of the ATF and the presence of damaged fibres below the critical fibre length (as seen in Figure 69) initiating failure due to stress concentration effects. Generally, the higher ATF content the lower the strength (Figure 64). However, a marginal improvement in comparison with the untreated samples was observed at 40% of fibre content.

The effect of the fibre volume fraction (% vol.) in ATF/PLA composites tensile and flexural strength is shown in Figure 64. ATF fibres did not provide a reinforcing effect, as augmented levels of elongation at the fibre ends within the composite, produced failure at the interface due to a weak bonding as confirmed by the ESEM analysis at the fracture section [267]. Increased fibre content results in a larger number of fibre ends; therefore, increasing the number of potential flaws within the composite system. The results observed are well within the range of other PLA-based composite materials prepared with other natural fibres specifically harvested for composite applications [62,96,97,268].

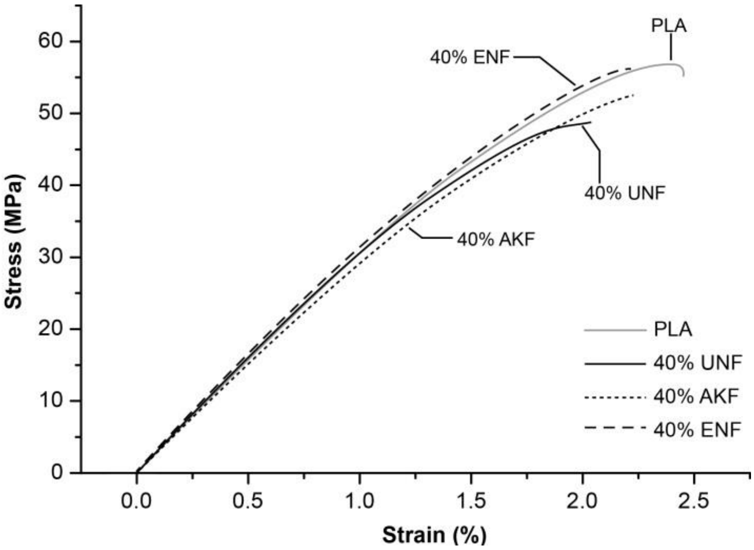


Figure 63. Mean stress-strain curves of neat poly(lactic) acid and 40% (v/w) Agave tequilana fibres and poly(lactic) acid bio-based composites. Standard error <0.65 for all cases.

The Young’s modulus of the ATF composite samples at 40 and 60% (v/w) fibre content presented higher values in comparison with pure PLA by the addition of fibres, indicating a stress transfer from the PLA matrix to the ATF as observed before by Rana et al. (1999) [269] with other natural fibre-based composites [269], whereas the elongation at break decreased more evidently. This increment in Young’s modulus is a common result from the additions of natural fibres [270]. Although stiffness was reduced with the addition of fibres with low aspect ratio for all the produced composites, when compared with neat PLA, significant variations have not been observed in *E*. Cellulosic ATF reinforcement may have increased the crystallinity of the PLA matrix, resulting in a more brittle matrix with limited tensile strength, and contributing to the improvement of *E*.

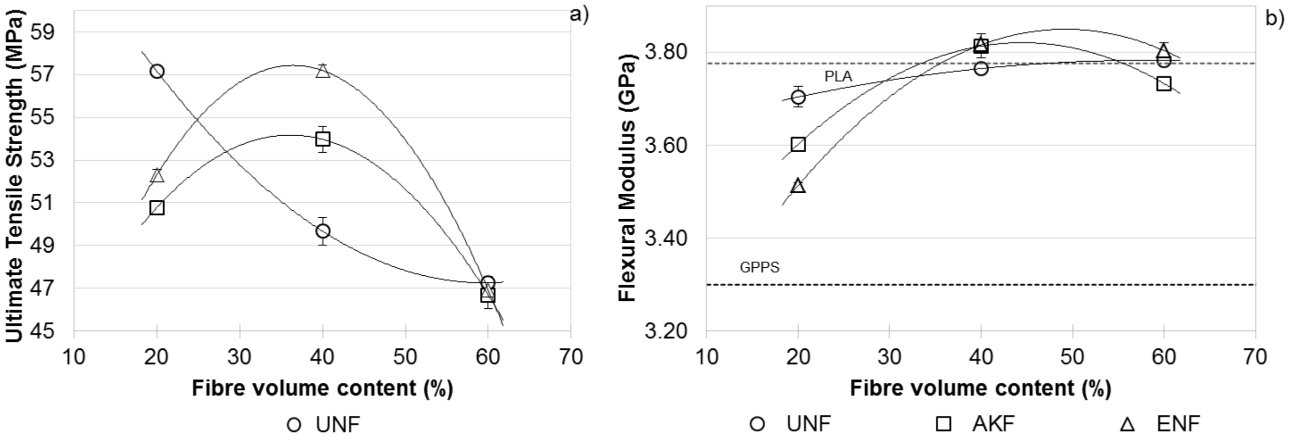


Figure 64. Tensile strength and flexural modulus for *Agave tequilana* fibres and poly(lactic) acid bio-based composites. a) Fibre content effect on UTS for ATF/PLA composites. b) Fibre content effect on Flexural modulus for ATF/PLA composites. In some cases error bars are smaller than the markers.

Additionally, moisture absorption and degradation by hydrolysis of the matrix due to high-temperature processing could also have affected the tensile strength. 40% ENF and AKF composites showed the higher results with mean UTS of 57.2±1 MPa and *E* of 3.0±0.2 GPa for ENF samples and UTS of 54±1 MPa and *E* of 2.8±0.1 GPa for alkali-treated samples. Composites containing 20 and 40% treated fibres presented differences at $p<0.05$ level of significance in comparison with UNF samples as seen in Table 18. However, for 60% fibre content samples, there was not enough evidence to conclude that there were significant differences between treated and untreated samples. Young's modulus and elongation of ATF/PLA composites were compared to those of GPPS (general purpose polystyrene) and.results have been summarised in Figure 65.

Overall, the addition of ATF improved the value of E, while the UTS, as well as the elongation of the composites were decreased. This result can be attributed to low adhesion between phases, ATF brittleness, and unfavourable perpendicular fibre orientation, leading to a low interface interaction and fibre pull-out.

Table 18. Effect of treatments on ultimate tensile strength for *Agave tequilana* fibres and poly(lactic) acid bio-based composites.

Sample	N	Mean (MPa)	UTS (Mpa) at 95% CI
20 % UNF	15	57.2±0.5	56.84-57.47
40% UNF	15	49.7±2.5	48.27-51.09
60 % UNF	15	47.3±1.2	46.59-47.91
20 % AKF	15	50.8±2.3	49.46-52.12
40 % AKF	15	54±1	53.62-54.31
60 % AKF	15	46.7±2.5	45.27-48.09
20 % ENF	15	52.3±1	48.42-49.29
40 % ENF	15	57.2±0.9	56.68-57.70
60 % ENF	15	46.9±1	46.30-47.52

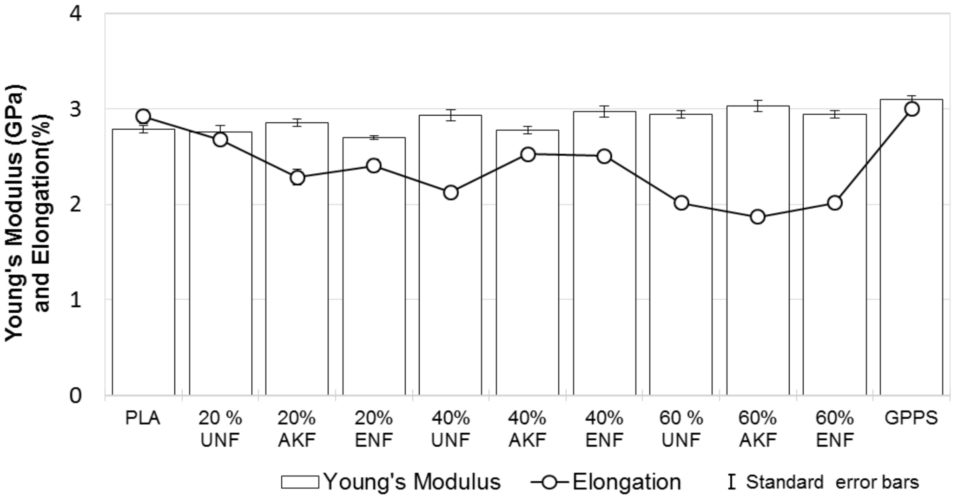


Figure 65**. Effect of treatments on Young's modulus and strain on *Agave tequilana* fibres and poly(lactic) acid bio-based composites.**

Although the flexural strength was reduced by the additions of the ATF, this still exceeded that of GPPS. However, the impact strength of the ATF/PLA composites was still below to the values reported from neat PLA. These observations were in agreement with previous results reported for other PLA-based composites with natural fibres with even higher strengths [43,270,271]. Flexural and Impact strength properties are given in Figure 66 and Figure 67 respectively.

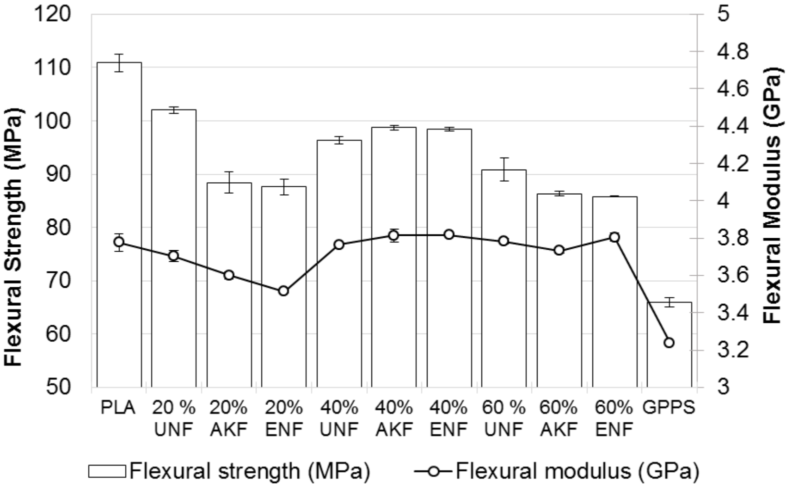


Figure 66. Effect of surface treatment on flexural strength and flexural modulus for *Agave tequilana* fibres and poly(lactic) acid bio-based composites in comparison with general purpose polystyrene. In some cases standard error bars are smaller than the markers.

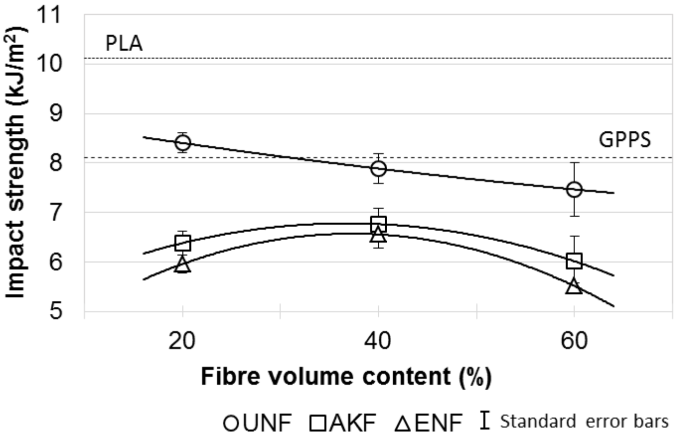


Figure 67. Impact strength of *Agave tequilana* fibres and poly(lactic) acid bio-based composites in comparison with GPPS and PLA.

ATF reduced impact strength presented by the material was attributed to fibres being ground during the extrusion process, and possibly fibre agglomeration at high fibre contents [272]. Crushed fibre particles have been reported to have a negative effect on mechanical properties of natural fibre-based composites [263,266]. Fibre ends may have caused increased levels of elongation in the interface of adjacent fibres, producing the breakdown at the interface [267] due to the insufficient adhesion and low PLA elongation at break. These reduced properties could be prevented by using a single-screw extruder and modified kneading elements [259]. However, inhomogeneous and directionally dependent properties due to molecular orientation of PLA and ATF alignment during manufacturing process should still be expected as shown in Figure 68.

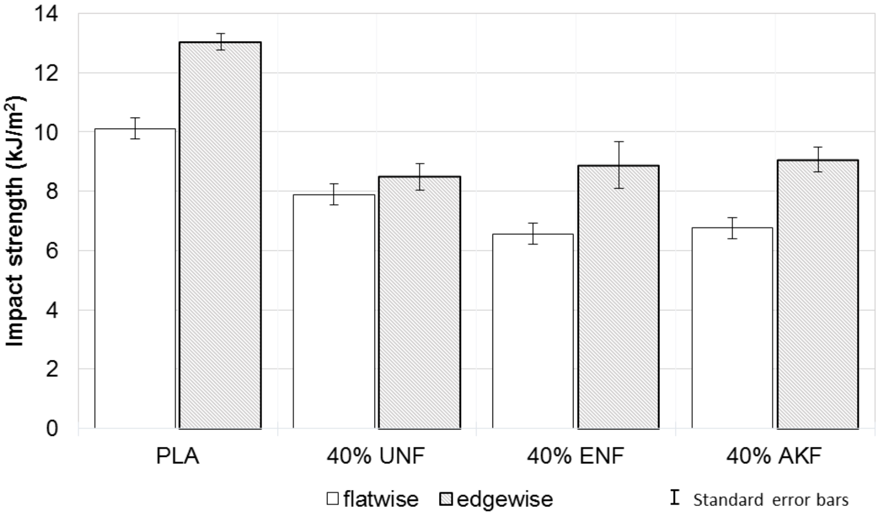


Figure 68. Impact strength in flatwise and edgewise direction for 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites.

6.3.3 **Optical microscopy**

Micrographs show large-scale variations in aspect ratio and morphology of ATF. It is observed that the length of the fibres varies significantly, the surface is rough with the adhesion of smaller fibres and particles, and presents breakage due kneading at the extrusion process. There was no evidence of developing transcrystallinity in the samples [273].

UNF composites presented clear fibre debonding before failure without evident crack propagation in the matrix (Figure 70a), while ENF and AKF composites have shown better adhesion as can be corroborated through the presence of crack propagation at the interface and the remaining traces of fibres after failure (Figure 70b and Figure 70c). Usually, the addition of high fibre content increases the probability of agglomeration and fibre breakage, creating regions of stress concentration that require less energy to elongate the crack propagation [43]. Additionally, the low transfer of loads may be attributed to a combination of factors such pre-existing fibre flaws from the extraction process, natural flaws from their origin, and also the non-evident transcrystalline interphase.

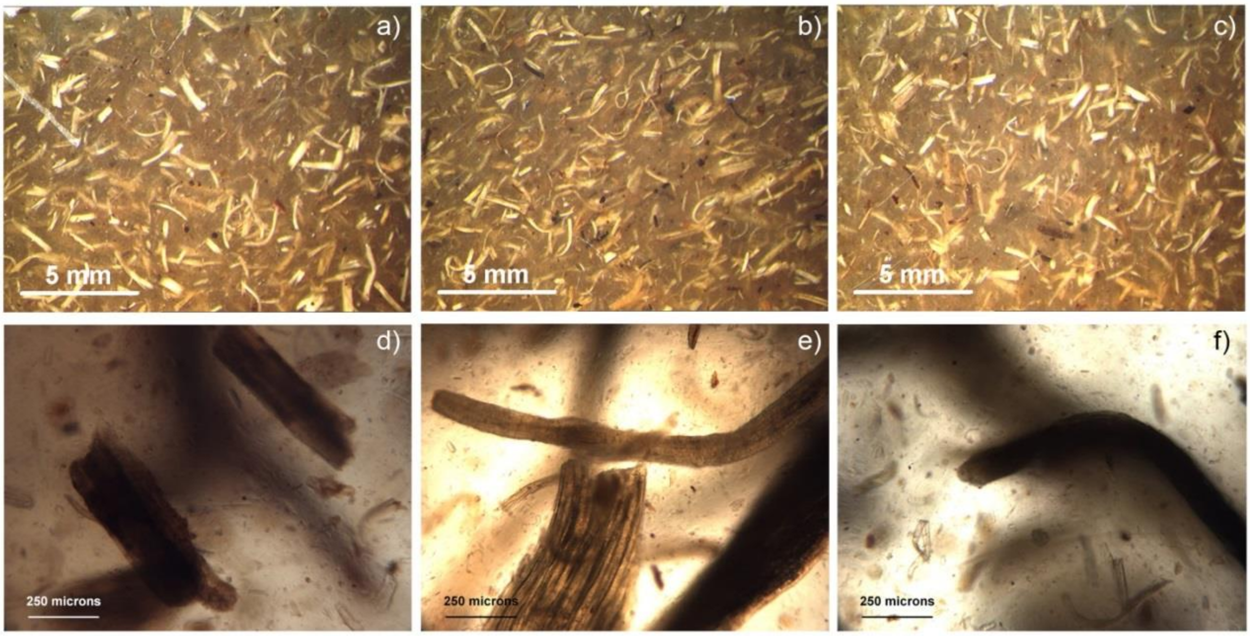


Figure 69. Macrographs of *Agave tequilana* fibres and poly(lactic) acid bio-based composites. a) b) c) Macrographs from 40% v/w composites after press moulding corresponding to UNF, AKF and ENF respectively. d) e) f) Micrographs at 10x magnification from 40% v/w composites corresponding to UNF, AKF and ENF respectively.

Environmental scanning electron microscope (ESEM) graphs were taken at the fracture surface of tensile, flexural and impact specimens to evaluate the adhesion between ATF and PLA. On 40% (v/w) UNF/PLA composites fibre surface was observed without traces of PLA matrix, indicating low fibre wetting. A gap between the matrix and the root of the fibres was noticed, indicating a weak adhesion, as it can be seen in Figure 71. On the other hand, fracture surfaces of 40% (v/w) AKF/PLA composites, presented a stronger adhesion, evidenced by the absence of a gap between the ATF and the PLA and by the wetting of the fibre by PLA (Figure 72b). Generally, improved tensile properties were observed at this v/w%. For 40% (v/w) ENF/PLA composites (Figure 72a), moderate adhesion was evidenced by the presence of remaining PLA on the fibre surface, although fibre pull-out observed at the fibre failure shows lower adhesion than that presented for AKF specimens. Thus, the better UTS value reported is attributed to the capacity of the fibres to withstand breakage longer than UNF and ENF specimens.

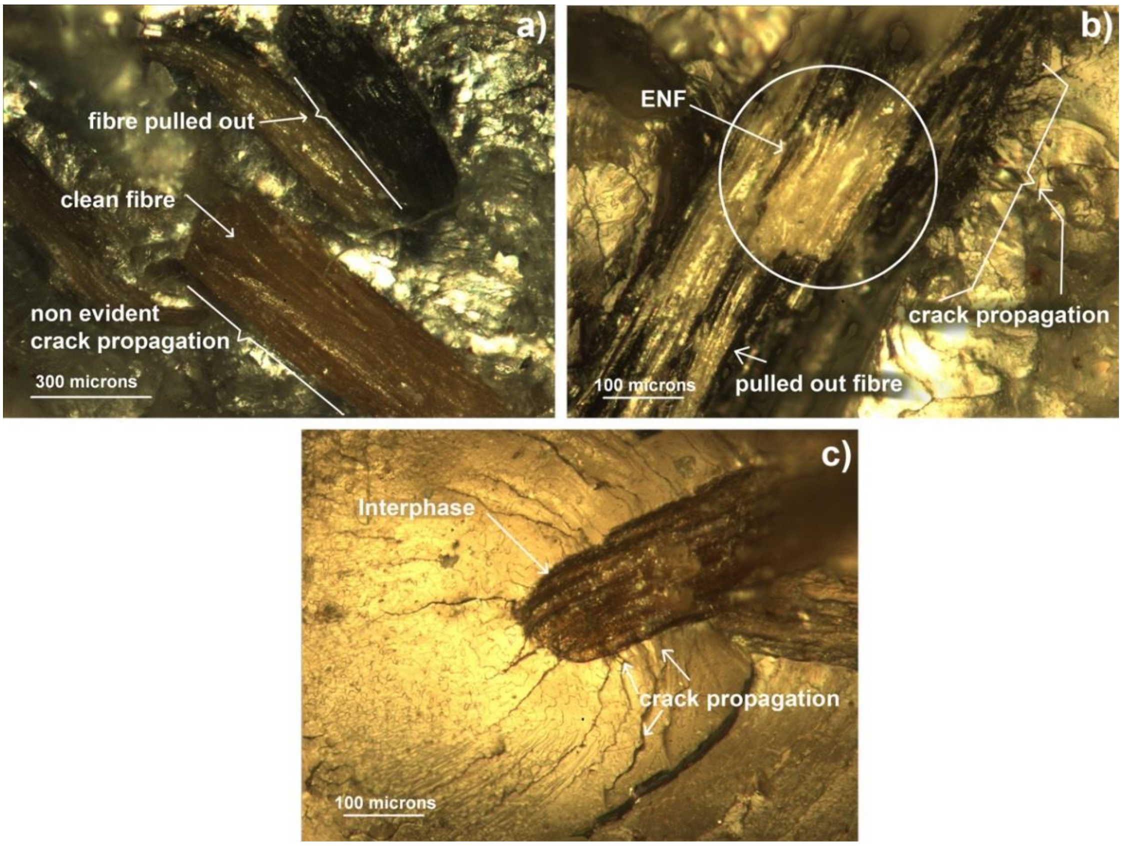


Figure 70. Cross section from 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites after tensile failure. a) UNF/PLA. b) ENF/PLA. c) AKF/PLA.

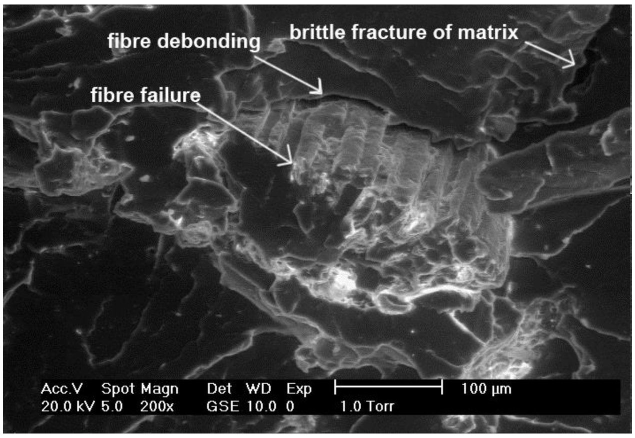


Figure 71. Micrograph from a tensile test specimen of 40% (v/w) untreated *Agave tequilana* fibres and poly(lactic) acid bio-based composite.

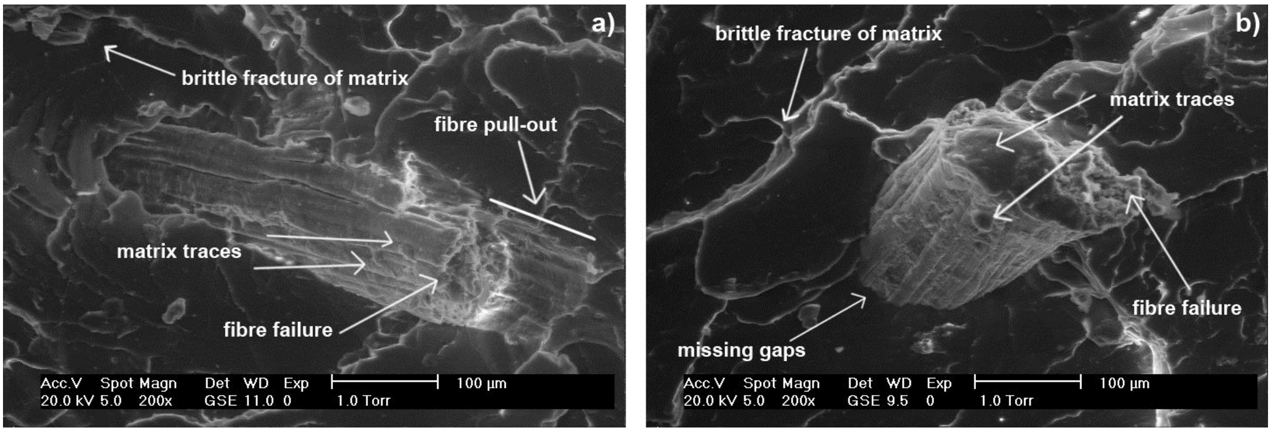


Figure 72. Micrograph from a tensile test specimen of 40% (v/w) treated *Agave tequilana* fibres and poly(lactic) acid bio-based composite. a) ENF composite. b) AKF composite.

6.3.4 **Water and moisture uptake**

Due to the hygroscopic nature of PLA and volume content of ATF, it was expected to observe an increase in moisture and water content in all the composites. The natural tendency to absorb water for the composite materials was evident. In the case of AKF this was clearer; reaching a saturation of 3.47% after 40 days of exposure (Figure 73).

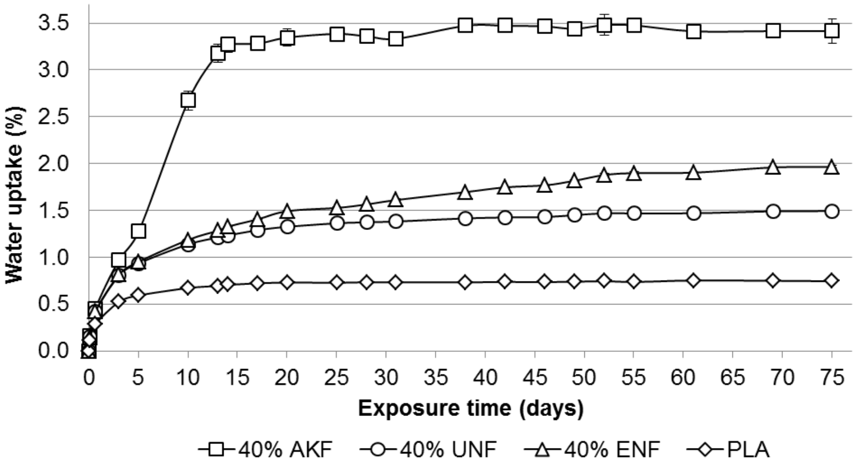


Figure 73. Water absorption at saturation for 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composite samples. In some cases standard error bars are smaller than markers. Standard error <0.13 for all cases.

Moisture absorption from 40% (v/w) composites was relatively low, reaching equilibrium after 30 days at about 0.4% of moisture content as shown in Figure

74 , whilst alkali-treated samples reached saturation at ~3.5% after 30 days. The difference in moisture and water uptake between samples is attributed to the delignification of ATF during treatments, as this rendered the fibres more hydrophilic. This may lead to important changes in dimensions as well as in mechanical and electrical performance that needs to be studied further.

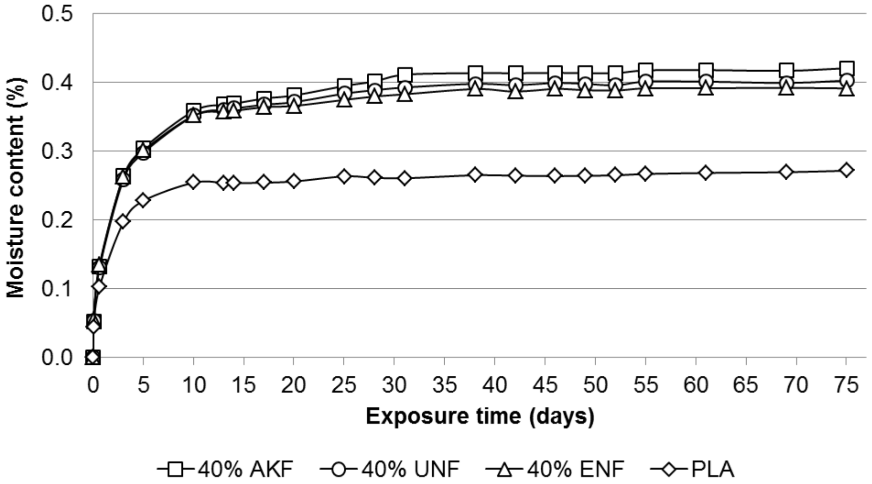


Figure 74. Moisture absorption at equilibrium for 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composite samples. Standard error <0.007 for all cases.

6.3.5 **Preliminary economic analysis**

To assess the feasibility of an ATF-based composite material, a preliminary economic analysis has been carried out. Table 19 reports the costs of the fibres used in the present study and the cost of the extrusion process for obtaining the masterbatch. The cost used for the extrusion calculations (0.71 £/kg) is a typical cost of a commercial extrusion in 2015 for 10 tonnes of material. On the other hand, the cost of the thermoplastic PLA matrix is 3.51 £/kg, although this value is strongly dependent on the market requests, showing a price reduction trend in last years. The actual cost of the fibres has been obtained from the chemicals needed to let the fibres ready for compounding and the operative costs for the treatments and transportation. The break-even point (BEP) has been estimated as the minimum percentage of fibres to be added to PLA in order to have the cost of the composite equal to that of pure polymer. In order to exceed the BEP, around 20 wt% filler is needed and thus the use of by-products/ wastes as fillers guarantees economic outcomes, notwithstanding the environmental aspect. Obviously, the costs reported in Table 19 could be further reduced by increasing the quantity of composites produced by extrusion.

Table 19. Preliminary economic analysis.

	Polystyrene cost	Fibre/filler cost (£/kg)	PLA cost (£/kg)	Extrusion cost (£/kg)	Break-even point (wt%)
UNF		.40	3.51	0.71	23%
AKF		.67	3.51	0.71	25%
FLAX		1.08	3.51	0.71	30%
KENAF		0.60	3.51	0.71	25%
SISAL		1.78	3.51	0.71	42%
COIR		0.70	3.51	0.71	26%
BANANA		1.02	3.51	0.71	29%
General purpose polystyrene	0.54-1.08				
High impact polystyrene	.64-1.27				

*Market prices by November 2015

UNF and AKF have a BEP of 23 and 25 wt% respectively because the used fibres are a by-product, still without commercial value. For this reason, changing the fibre source, surface treatments and with a wider acceptance of PLA within the supply chain, the bio-composite cost will become probably lower, and as consequence BEP will be reduced as well, making the price eventually more competitive to HIPS or GPPS.

6.4 **Conclusions**

It has been pointed out that the use of natural fibre-based composites may represent several environmental advantages in comparison to oil-based polymers and composites. Environmental impact can be reduced by the reduction of fossil-based resources, and biodegradable materials could help scale down waste related problems.

In the present study, green composites consisting of PLA and ATF obtained as by-product from tequila production have been prepared by melt compounding. The effect of different fibre ratios and surface treatments on ATF/PLA composites mechanical properties has been investigated

The collected data have shown that all the ATF/PLA green composites can be considered for applications which do not require demanding mechanical performance such as; packaging, containers, crates and other targeted applications. In comparison with neat PLA values, 60% (v/w) ATF/PLA green composites have been observed to have an increased Young’s modulus up to ~9% while observing ~10 GPa for flexural modulus, contrary to the reduction in flexural and tensile strength. All treated fibres-based composites have shown a substantial increase in adhesion by means of improved fibre wettability and surface morphology.

Tensile test results indicate that strength of ATF/PLA composites is not improved due fibre agglomeration, final aspect ratio of the ATF after compounding and fibre flaws inherent to its natural origin. Melt compounding using a twin-screw extruder critically reduced the fibre aspect ratio leading to decreased mechanical properties.

In particular, the best UTS values were reported for 40% (v/w) ENF/PLA composite with 57.2±0.9 MPa followed by the 40% (v/w) AKF/PLA with 54±1 MPa. The same formulations registered an improvement in flexural modulus, and although flexural strength was reduced, ATF/PLA composites’ characteristics are comparable or still superior to those of GPPS. Furthermore, the water and moisture properties of the green composites correlated well with the degree of delignification and removal of non-cellulosic materials, and to the level of adhesion resulting from an improved interfacial interaction. Also, in this case, AKF/PLA composites’ permeability with respect to the original value of neat PLA is less than 3.0% in water absorption at saturation and 0.14% in moisture absorption at equilibrium.

ESEM observations have shown that most ATF were well connected with the PLA matrix, but it is also shown that the dispersion and interfacial interaction between the phases could be improved especially at higher fibre loadings. Therefore, it is considered possible a further enhancement of the mechanical properties of ATF/PLA composites by optimising the interface interaction and compatibility. Consequently, the use of ATF and PLA to produce a bio-based material can provide a sustainable alternative to conventional oil-based thermoplastic materials. Future work will concentrate on the improvement of mechanical properties, and to evaluate the biodegradability of this developing and promising bio-based material.

Alkali treatment helped to overcome inherent problems favoured by the hydrophilic nature of the ATF and the lack of interfacial adhesion, improving the final properties of the composite. However, the use of high aspect ratio fibres could allow achieving a composite material based on ATF and PLA with better mechanical properties suitable for more demanding applications.

Despite surface treatments improved the composite properties, from the point of view of industrial applications, chemical modifications are being regarded little convenient or cheap, discouraging its use as a mere niche solution for specific applications, therefore, a better understanding of the benefits and possible implications regarding its use need to be addressed.

From an economical point of view, ATF-based green composites exhibited an acceptable performance, although their relative price may not be so competitive with that of other oil-based commodity resins. However, wider acceptance and demand for these novel materials along with a shift in consumption patterns may lead to a decreased overall cost. Additionally, in comparison with other natural fibre-based/PLA composites, and inasmuch as ATF is a by-product, its composites represent a competitive break-even point.

7 Tensile, impact, flexural and water uptake properties of an *Agave tequilana* fibre and poly(lactic) acid-based composite using film-stacking method.

7.1 Introduction

The increased environmental awareness and sharply risen prices of fossil fuels have encouraged the use of renewable carbon-based materials. Bio-based materials have helped decrease fossil fuel dependency and the related environmental impacts towards a reduced carbon footprint economy [157,158]. However, some challenges such as; processing, mechanical properties, cost, and recycling are yet to be addressed [159].

Green composites combine natural fibres and bio-based resins to develop materials with eco-friendly attributes that are technically and economically feasible while minimizing the generation of pollution. Biopolymer materials, such as PLA [274–276], made from renewable agricultural and forestry feedstocks, have witnessed considerable attention as a possible solution to the ever growing environmental concerns, and as an answer to fossil fuel dependency [52,186]. However, PLA has faced major challenges to get introduced to market because prices are still higher than its oil-based counterparts, for which supply chain and production has been gradually optimised since they appeared more than 60 years ago. Therefore, adding natural fibres to PLA has been a common practice to potentially lower manufacturing material cost; and in some cases increase biopolymer performance too [277].

The use of agro-industrial by-product materials (i.e. natural fibres) from natural and annually renewable sources is mainly driven by their eco-friendliness and economic reasons [63,278]. Natural fibres will play a fundamental role in the "green" and circular economy [35] based on their energy efficiency, use of renewable feedstocks, low CO_2 manufacturing processes, weight reduction, recyclability, and waste minimization [105,279].

Natural fibres-based composites have several advantages over synthetic counterparts in targeted applications not requiring high load bearing capabilities

[158]. Composites based on surface modified natural fibres and matrix have in general better mechanical and physical properties [55,146]. The potential applications of natural fibre-based composites in housing, automotive [280,281], packaging [198] and other low-cost, high volume applications is enormous [282,283]. Bio-based composite materials with reliable mechanical properties depend on the adequate formation of a strong interface and matrix-to-fibre stress transfer efficiency. Hence, a complete matrix fusion to facilitate thorough fibre impregnation is a vital requirement [285]. Additionally, new knowledge on ATF/PLA-based composites will intensify research and use of ATF as a raw material.

Agro-industrial waste materials can be reused and upcycled for the development of new and greener composites [46,286,287]. Lignocellulosic fibres obtained from the Tequila industry are a good example of these materials and a potential feedstock source for new bio-based composite developments [151]. Tequila by-products amount up to 300,000 t, concentrated in a small region in Mexico [152]. Despite upcycling of these by-products has proven to be feasible [56,61]; residual *Agave tequilana* leaves are still used as soil nourishment, and the bagasse is either treated as compost or disposed of by incineration or landfill [289].

Initial evidence from a bio-based material from the agro-industrial by-product fibres from tequila production has been reported in a previous chapter. However, the development of a usable bio-composite material with General Purpose Polystyrene (GPPS) comparable properties at higher fibre volume fraction has yet to be reported.

Final bio-based composite properties depend on the type of fibres and matrix used, as well as in the manufacturing process. Manufacturing processes exceeding 200°C cannot be used to manufacture composites due to natural fibres temperature degradation. Several processes such as injection moulding and film stacking used for thermoplastic composite manufacturing may be suitable to manufacture bio-based composites. Mechanical properties of bio-based composites are greater when processed using film stacking in comparison to injection moulding [290]. Injection moulding also has the tendency of creating non-homogeneous materials with fibre agglomeration and voids.

Film stacking method represents an advantageous alternative to extrusion and injection moulding, when high fibre volume is required without the loss of fibre properties because of the high shear strain that reduces the fibre aspect ratio [291]. Film stacking method consists of heating and compressing a stack of alternated layers of polymeric matrix and fibre mats during a determined amount of time as shown, in Figure 75.

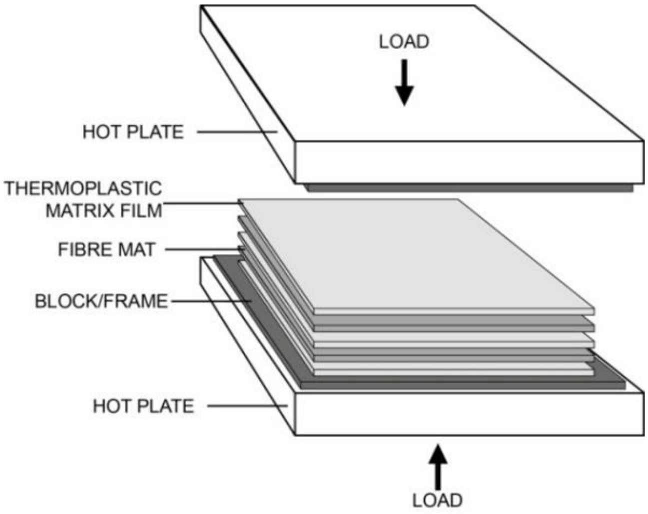


Figure 75. Schematic of the film stacking method.

With the increasing popularity of bio-based materials and composites, it is essential to carry out follow-up studies on ATF fibre-based composites, especially in their fabrication processes and properties, so that better knowledge can be obtained in order to move forward this kind of material developments into the market. In this study, a preliminary investigation on the fabrication of randomly oriented ATF/PLA based composites is presented. Combining film stacking and compression moulding, bio-based composite samples were prepared using pre-impregnated ATF mats and PLA film as a matrix as described in the following sections.

7.2 **Materials and methods**

Tequila by-product ATF were supplied by “La Fortaleza” distillery plant in Jalisco, Mexico. Materials used include analytical grade NaOH from Acros Organics; Pectate lyase enzyme (Scourzyme®) from Novozymes, pelletized PLA (Ingeo™ Biopolymer 2003D) by Natureworks™, and dichloromethane from Proton Scientific. All characterization techniques and methods used for preparing the samples throughout the work are described below.

7.2.1 **Fibre treatments**

ATF with a mean length of 10 mm and an initial moisture content of ~13% were pre-washed with distilled water to remove loosely physisorbed compounds from tequila production and oven-dried at 60° C for 24 hrs to remove any moisture content. Dried fibres were further exposed by immersion to alkali and enzymatic treatments. Alkali-treated fibres were immersed 180 minutes in 8% (v/w) NaOH solution, while enzyme treated samples were exposed to 0.4% (v/w) of pectate lyase enzyme in relation to fibre content during 180 minutes. Details from every treatment have been reported elsewhere in previous chapters. Untreated ATF samples were kept as control. Different sets of treated and untreated fibres were rinsed with distilled water and oven-dried after treatment at 60° C for 24 hrs. and kept in sealed desiccators to control relative humidity (RH) due to the hygroscopic nature of the fibres. Different set of specimens will be referred hereafter as alkali-treated fibres (AKF), enzyme treated fibres (ENF) and untreated fibres (UNF).

7.2.2 **Composite manufacturing**

ATF/PLA composite manufacturing was carried out using a 4 step process as it is summarised in Figure 76. Randomly oriented ATF mats were prepared during the first phase of the process by spreading 10 mm length (mean) ATF onto a vibration plate until an even distribution was achieved. During a second stage, mats were pre-impregnated with a 15% (w/w) PLA/dichloromethane solution and dried at 23° C at a 50% of RH during 20 minutes. Final moisture content for pre-impregnated mats was kept below ~2%. Laying up was done by stacking by hand pre-impregnated ATF mats and PLA films according to 20, 40, and 60% (w/w) of fibre content onto a metallic frame. On a final stage, the manufacturing of the randomly oriented ATF/PLA biocomposite specimens was carried out by compression moulding on a 40T thermal press at 160° C at a pressure of 55 MPa. Residence time was calculated to keep the melt flowing and to prevent degradation during all the runs, for at least for 10 min. After pressing, the frame was quenched under room conditions. Samples are denoted hereafter as AKF, ENF and UNF for alkali, enzyme and untreated specimens with 20, 40 and 60% (w/w) of fibre content respectively. Neat PLA was also press moulded under the same conditions to keep it as a control.

Specimens for mechanical testing were cut out from composite plates using a water jet cutting machine and according to specific ASTM standard D638-10, D790 and D4812. Samples were then oven-dried at 60° C for 24 hrs. and kept in sealed desiccators before mechanical testing.

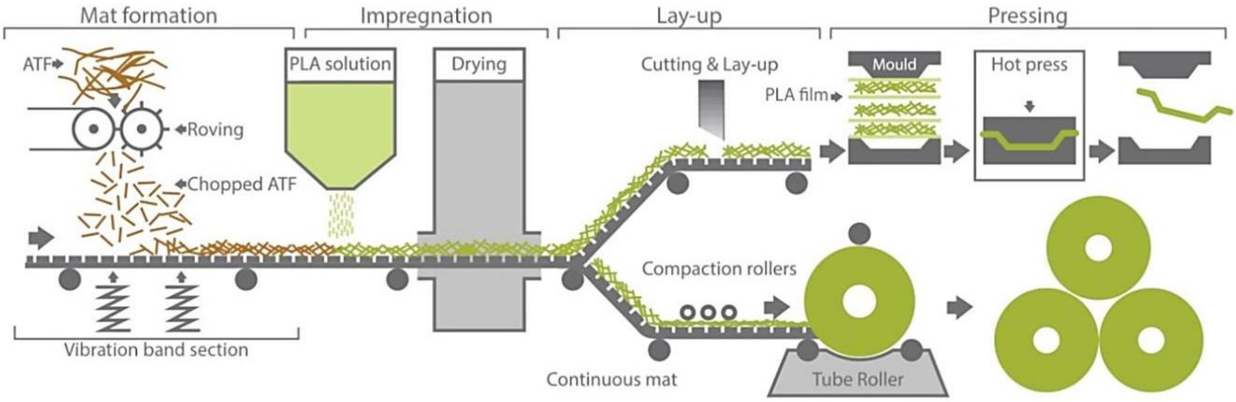


Figure 76. Schematic from *Agave tequilana* and poly(lactic) acid bio-based composite manufacturing using pre-impregnation process.

7.2.3 Environmental scanning electron microscopy and optical microscopy

ATF/PLA biocomposite specimens were examined pre- and post-failure using an optical microscope Nikon Eclipse E600 at 5x and 10x magnification, a macro at x0.75 and x1.5 and an environmental scanning electron microscope (ESEM) to analyse the test results and investigate possible correlations between processing conditions, mechanical performances and type of fracture.

7.2.4 **Mechanical testing**

Quasi-static mechanical properties were evaluated from tensile, impact and three-point bending tests. Tensile testing was carried out on type 1 specimens according to ASTM D638-10 standard on a calibrated Instron 5500R EM with a 100kN load cell and a crosshead speed of 2mm/min at room temperature (21° C) [49]. Ultimate tensile strength (UTS) was calculated using:

$$\boldsymbol{\sigma = \frac{L}{A}}$$

where $\boldsymbol{\sigma}$ is the stress, $\boldsymbol{L}$ is the maximum load, and $\boldsymbol{A}$ is the specimen cross-sectional area. Strain was also calculated using the following equation:

$$\boldsymbol{\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}}$$

where $\boldsymbol{\Delta L}$ is the change in gauge length, L_0 is the initial gauge length, and L is the final length. Young's Modulus (*E*) was calculated by dividing the stress ($\boldsymbol{\sigma}$), by the strain ($\boldsymbol{\varepsilon}$), in the elastic portion of the stress-strain curve.

Three-point bending flexural test was performed according to ASTM D790 standard using a 5kN load cell and a crosshead speed of 1mm/min [132]. Flexural stress ($\boldsymbol{\sigma}$) was calculated according to:

$$\boldsymbol{\sigma = \frac{3FL}{2bd^2}}$$

where $\boldsymbol{F}$ is the maximum load on the load deflection curve, $\boldsymbol{L}$ is the support span, and b and d correspond to the width and thickness from the specimen. Flexural modulus ($\boldsymbol{E_f}$) was calculated using:

$$\boldsymbol{E_f = \frac{L^3 m}{4bd^3}}$$

where $\boldsymbol{m}$ is the gradient of the initial straight-line portion of the load-deflection curve. Impact testing was executed according to ASTM D4812 standard for unnotched Charpy impact on a Zwick pendulum impact test machine with a 1J hammer. Impact strength was calculated using the following equation:

$$\boldsymbol{I = \frac{E_c}{hb} \times 10^3}$$

where E_c is the corrected energy absorbed by the specimen; h and b are the thickness and width of the specimen respectively. Flexural and impact tests were performed on a flatwise direction. Before testing, specimens (see Figure 77) were oven-dried at 60° C for 24 hrs. and kept all the time in sealed desiccators due to the hygroscopic nature from the phases. 14 specimens were tested for every material grade.

Figure 77. 60% (w/w) *Agave tequilana* and poly(lactic) acid bio-based composite specimens. Top: specimen used for tensile test. Middle: specimen used for three-point flexural bend test. Bottom: specimen used for impact test.

7.2.5 **Water absorption**

Water absorption at saturation (WAS) was determined for ATF/PLA composite materials. WAS is expressed as the increase in weight percent of the material according to:

$$\boldsymbol{MC = \frac{w_1 - w_0}{w_0} \times 100}$$

where (MC) is the moisture content, (w_0) is the mass of dry sample and (w_1) is the mass after exposure.

Specimens were first dried in an oven for 24 hrs at 60 °C and then placed in a desiccator to stabilise at room temperature (23 °C). Upon cooling, samples were weighed in an analytical balance to the nearest 0.001g and immerse in sealed beakers containing distilled water at room temperature. The weight difference was measured at several intervals of time by removing samples from the beaker, wiping them dry and weighting them to the nearest 0.001g until equilibrium. Three replicates for every set of samples were assessed and MC calculated.

7.3 **Results and discussion**

7.3.1 **Composite manufacturing**

Pre-impregnation and compression moulding process used for this research extend ATF capability of absorbing PLA, hence, improving interfacial interaction and allowing higher ATF ratio content in comparison with results presented previously where compounding via extrusion moulding was used. Despite, these open mould processes produce composites with high levels of voids (porosity), a better PLA impregnation and flow can be optimised by an appropriate control of PLA melting viscosity within the narrow processability window offered by ATF. Compounding through conventional extrusion moulding would yield inferior mechanical properties when compared with current process used in this research, due to the incorporation of even longer fibres contrary to the low fibre aspect ratios obtained from the extrusion moulding process. Furthermore, higher fibre wt% content through the use of this method offers the possibility of achieving a material with acceptable properties using as much as possible a raw material source with a marginal cost that was considered waste previously.

14 composites samples were manufactured with a wt% ranged from 20, 40 and 60%. As it was expected from the additions of a less dense ATF, density of composites decreased gradually with the increasing of ATF content. In general, a maximum reduction of ~28% was presented at fibre contents of 60%. ATF/PLA composite density values are within the ranges of GPPS as depicted in Figure 78. However, ATF/PLA bio-based material at 60 wt% of fibre content indicated a specific gravity lower than 1 g/cm3. These ranges are lower than GPPS and PLA. Thus, the use of ATF/PLA bio-based material could represent energy savings when transport is involved.

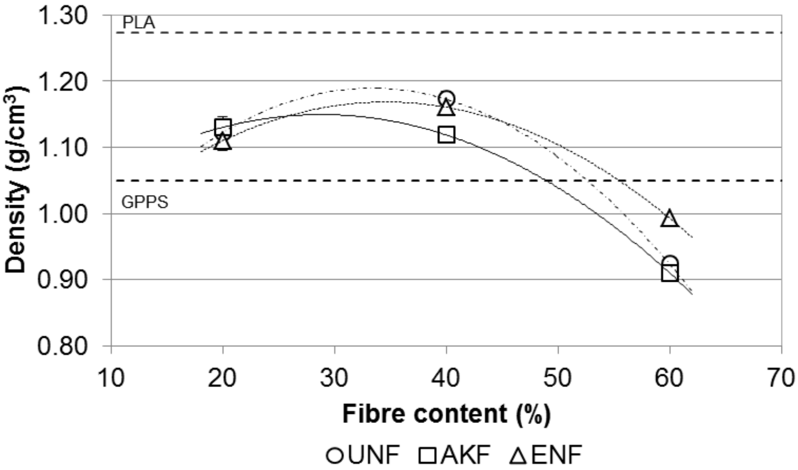


Figure 78. *Agave tequilana* fibres and poly(lactic) acid bio-based composites density mean values. Error bars are smaller than the markers. Standard error <0.02 in all cases.

Impregnation process formed consistent and uniform ATF/PLA mats (Figure 79a), losing uniformity only near the borders of the mat (Figure 79b). During the manufacturing process, ATF and PLA were subjected to a pressure-temperature cycle in only one occasion; whereas at compounding by extrusion moulding, the materials were exposed twice at shear and temperatures cycles affecting negatively the thermo-mechanical properties of the compound. The main constraint during processing was the hygroscopic nature of ATF and PLA due to moisture release during the process. Despite fibres and matrix were subjected to a moisture removal stage and kept in sealed desiccators during the time prior press moulding, traces of moisture release in the form of minuscule bubbles were present (Figure 80b).

Figure 79. Impregnated *Agave tequilana* fibres mat. a) Section from an ATF mat impregnated with PLA/dichloromethane solution. b) Impregnated ATF/PLA Mat dimensions.

Temperature sensitivity of the fibres (well above processing temperature) and PLA, along with the resilience time during processing showed evidence of a uniform flow and fibre-matrix interaction (Figure 80a). However, an effective compatibilization of the fibre/matrix interphase was not completely reached through a film stacking-press moulding method with pre-impregnated ATF mats (see Figure 80b).

7.3.2 Environmental scanning electron microscopy and optical microscopy

Microscopy observations revealed the scale variations in diameter and morphology of AKF; some effects of moisture and processing as discussed in the previous section are also presented (Figure 80b). Although void formation was minimal and air trapped bubbles were present in small amounts and only at opposite direction to press moulding, it is one of the main factors accounted for the reduction in interfacial adhesion and mechanical properties. Notwithstanding this was observed in small areas and close to the mould border, it was finally attributed to the insufficient matrix flow across the mould section. Therefore, a better control of PLA viscosity within ATF thermal degradation threshold and an increased resilience time might reduce this effect.

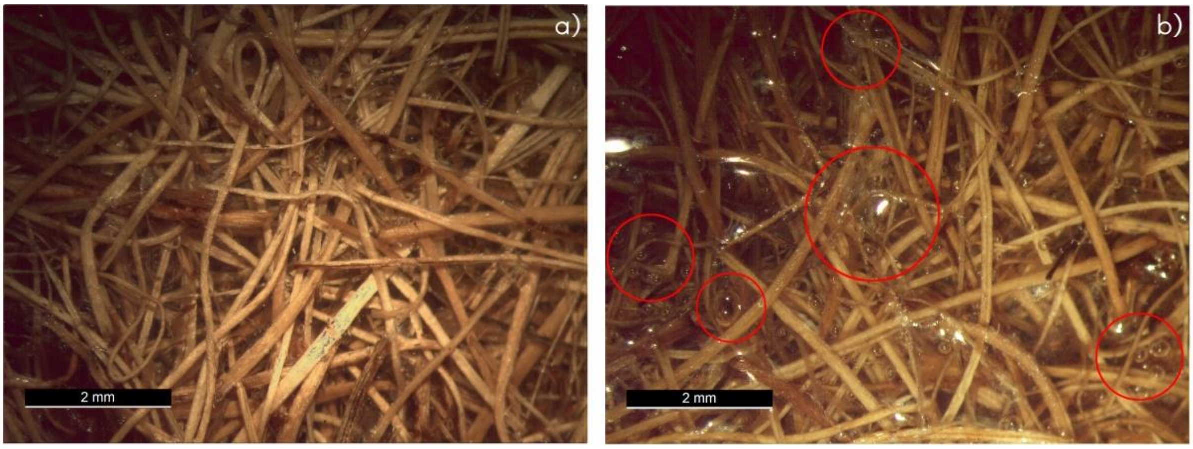


Figure 80. Macrographs from a 60% w/w *Agave tequilana* fibres and poly(lactic) acid bio-based composite. a) Section at 2x magnification showing randomly oriented ATF. b) Sample section indicating the formation of air bubbles.

Images obtained at the fracture surfaces of tensile test specimens shown in Figure 82 and Figure 81, presented pulled out fibres. Further, fibres are still present in the form of non-separated bundles. This indicates that the fibres have suffered less damage during compounding, contrary to what is observed for extrusion processed composites. However, it can be seen that the surfaces of the pulled out fibres are not totally clean. These observations suggest a low adhesion between the fibres and the matrix, as presented in other natural fibre/PLA based composites [62]. Nevertheless, treated samples depicted an improvement in adhesion contrary to the reduced interfacial interaction presented by untreated samples as can be corroborated by Bax and Müssig (2008) [292].

Observations performed on mechanical-tested ATF/PLA composites highlighted that treated samples showed a reduction in fibre pull-out with better matrix impregnation as compared to the UNF samples. Fracture processes of ATF/PLA materials presented yield crazing in accordance to Jiang, Zhang and Wolcott (2007) [293]. Fracture surface of composite materials is brittle due to the less plastic deformation properties inherent to the matrix. This brittle fracture is accompanied by longitudinal fibre pull-out found for the majority of the fibres arranged in a transverse direction to the crack plane as shown in Figure 82. This delamination phenomenon (Figure 81) arises because ATF lying in the plane of a laminate do not provide reinforcement through the thickness, and so the composite relies on the relatively weak and brittle PLA matrix to carry loads in that direction.

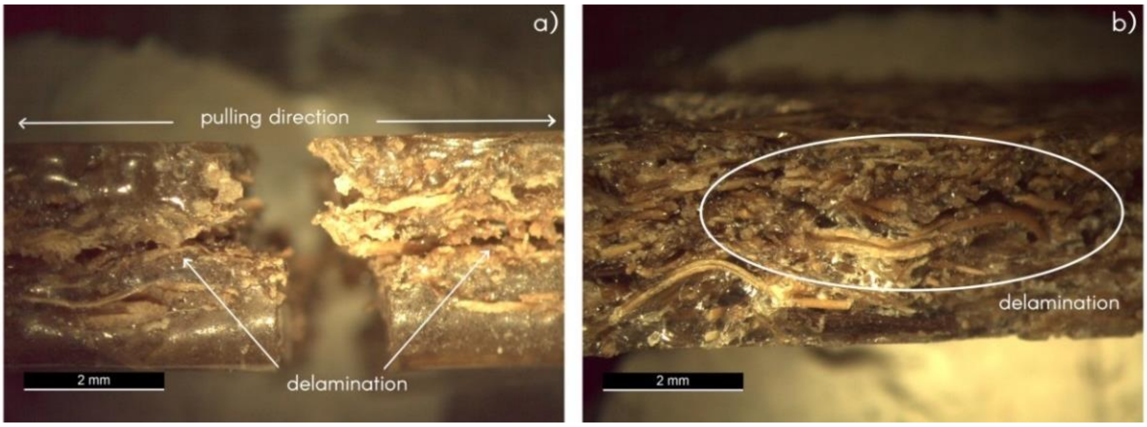


Figure 81. Fracture section from 60% w/w *Agave tequilana* fibres and poly(lactic) acid bio-based composites showing delamination after failure at the tensile test.

In the case of untreated samples (Figure 82b), pull-outs occurred more frequently than with alkali-treated fibres. AKF/PLA composites have shown better fibre-matrix bonding due to the removal of hydrophobic materials (i.e. lignin, pectin and extractives) as shown in Figure 82a. This better compatibility provided better mechanical properties that untreated samples due to a more evident interlocking between fibre and matrix. However, PLA melting viscosity appeared to be insufficient to facilitate the proper impregnation of AKF.

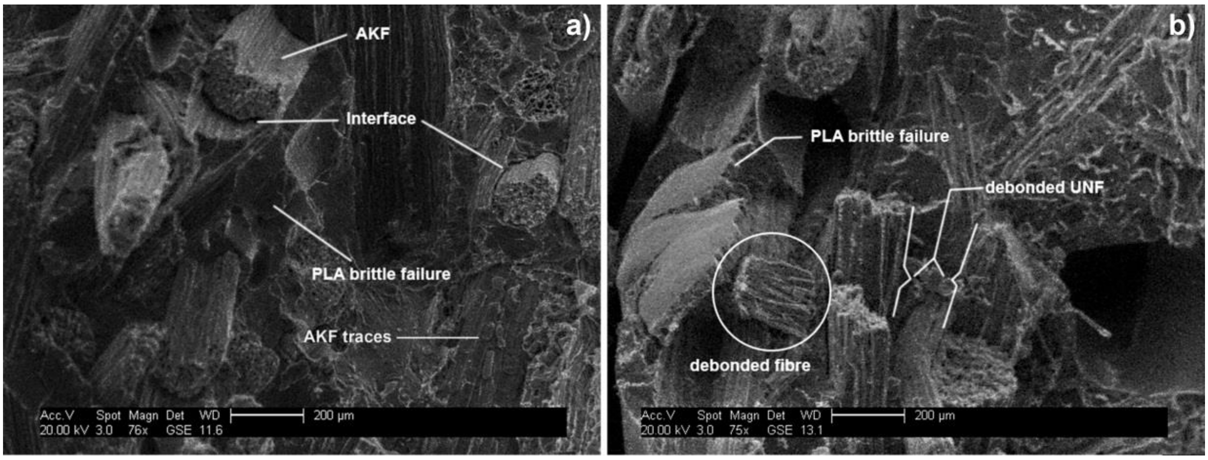


Figure 82. Micrographs of tensile tested *Agave tequilana* fibres and poly(lactic) acid bio-based composites. a) 60% w/w AKF/PLA. b) 60% w/w UNF/PLA.

7.3.3 **Mechanical testing**

126 tensile tests were conducted using specimens of different “weight percentage” and treatment. Figure 83 shows the mean value of the effect of the tensile test for UNF specimens. As observed, specimens with the highest fibre wt% exhibit a reduced elongation before failure. ATF/PLA composites that contained 60wt% of alkali-treated ATF have shown superiority in tensile and bending properties by ~13% and ~150% respectively in comparison to untreated specimens.

Fibre loading generally degraded the mechanical properties of the ATF composite material, as reported in other studies where PLA was used as matrix [62,268], although in some cases an improvement was observed, in particular for samples that were manufactured with 40 wt% and 60 wt% of treated fibre content. In these cases, it appears that the removal of non-cellulosic components from ATF specimens contributed positively to fibre/matrix interfacial interactions leading to a better matrix to fibre stress transfer in comparison with the UNF specimens. However, reinforcing effects decreased in line with the addition of higher ATF wt% content. ATF/PLA composites presented a matrix's inherent brittle failure without necking during tensile test (Figure 83).

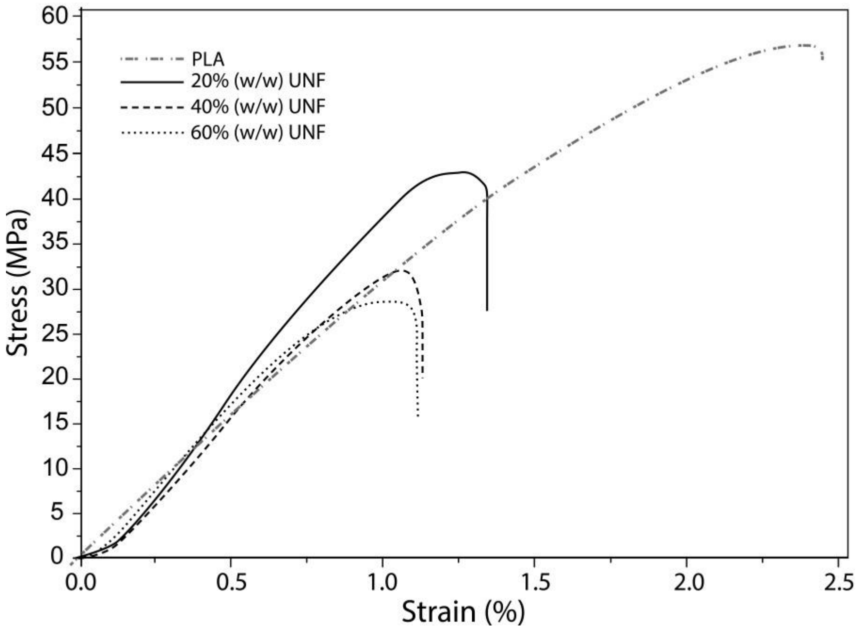


Figure 83. Mean stress-strain curves of 20, 40 and 60% (w/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites. Standard error <0.91 in all cases.

Despite the improved behaviour presented by ATF/PLA composite materials using treated ATF at 40 wt% and 60 wt% content indicated a stress transfer from the matrix to the ATF, the low interfacial interaction is considered the result of a non-perfect adhesion between ATF and PLA. However, adhesion and enhancement of polar interactions at the fibre/matrix interface can be improved [233–236] through the use of compatibilizers [269].

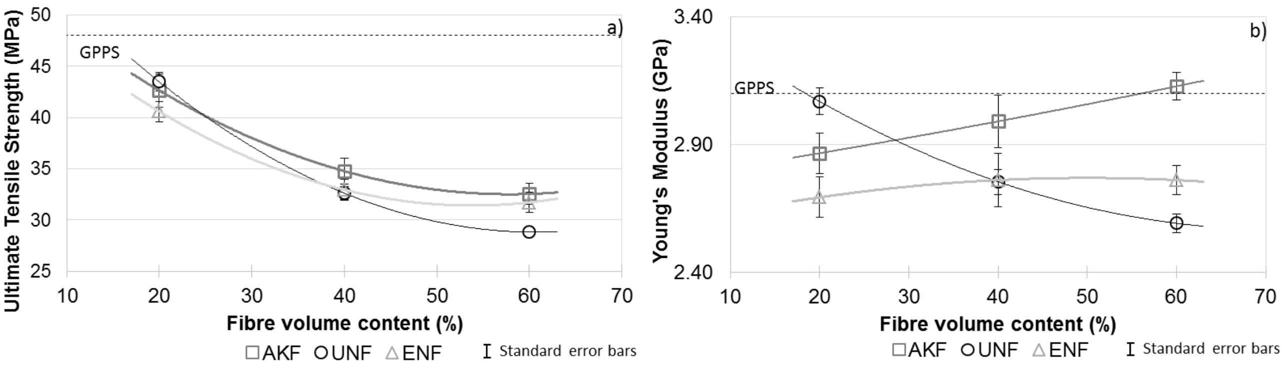


Figure 84. Tensile properties for *Agave tequilana* fibres and poly(lactic) acid bio-based composites manufactured by film stacking method. a) Fibre content effect on UTS for ATF/PLA composites. b) Fibre content effect on Young's modulus for ATF/PLA composites.

This reduction in mechanical properties has been shown before by ATF/PLA composites compounded by extrusion moulding. The decrease in properties was attributed to the low fibre aspect ratio resulted from the inherent crushing of fibres by the extrusion moulding process as referred previously by Keller (2003) [190], coupled with the initial thermal and mechanical degradation fibres have suffered during tequila production.

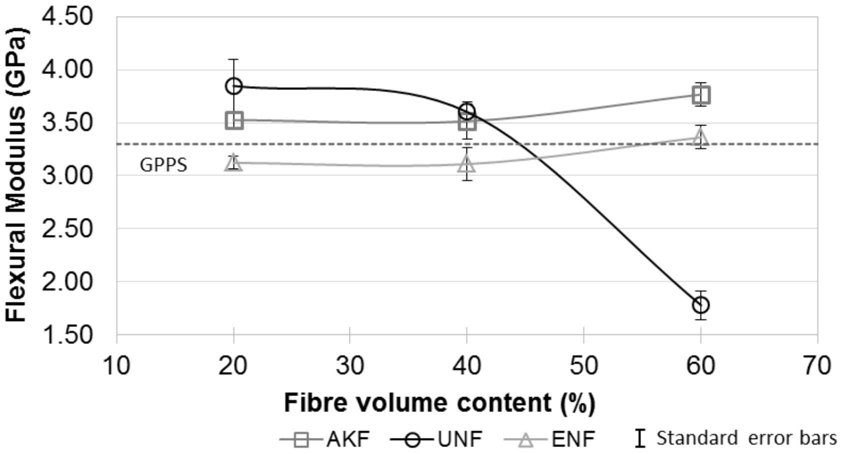


Figure 85. Fibre content effect on Flexural modulus for *Agave tequilana* fibres and poly(lactic) acid bio-based composites in comparison with GPPS.

15 specimens of each group of samples were tested for three-point bending flexural test. Figure 85 presents the flexural modulus results as a function of the fibre volume content by surface treatment applied. Flexural and tensile modulus of the ATF/PLA composite at the maximum fibre wt% content

remained approximately the same, without any detriment to original matrix modulus as shown in Figure 84b and Figure 85. The maximum tensile and flexural stress of ATF/PLA composites containing treated fibres were better than the UNF only at 40 and 60 wt% with improvements of ~13% and ~150% respectively as presented in Figure 86 and Figure 87. However, only at 60 wt% the differences were statistically significant at a P-value < 0.05.

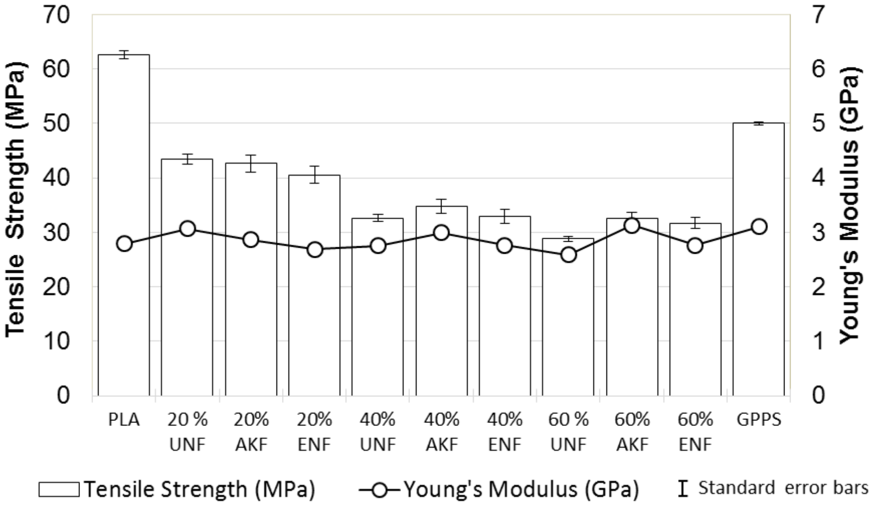


Figure 86. Effect of treatments on ultimate tensile strength and Young's modulus for *Agave tequilana* fibres and poly(lactic) acid bio-based composites manufactured by film stacking method. Standard error bars are smaller than the markers in some cases.

Generally, alkali-treated fibre-based composites show better tensile and flexural strength than untreated fibre-based composites at these fibre wt% contents [53]. However, neat PLA still presents better mechanical properties than its ATF-based composites. These findings are in agreement with works previously reported where the addition of natural fibres increased the modulus but the higher fibre content did not improve the modulus in the PLA composites [62]. This behaviour is the result of a reduced adhesion between the fibres and the PLA, therefore, the stress is not transferred from the matrix to the fibres. However, it is important to consider that the reduced effect on mechanical properties is expected from fibres with a lower strength than the matrix.

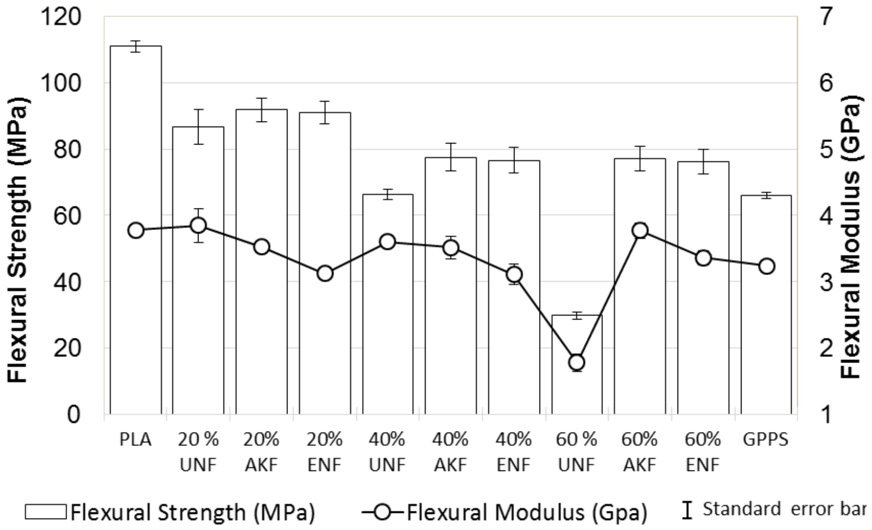


Figure 87. Effect of surface treatment and fibre content on flexural strength and flexural modulus for *Agave tequilana* fibres and poly(lactic) acid bio-based composites (flatwise) in comparison with general purpose polystyrene. Standard error bars are smaller than the markers in some cases.

Impact strength values of ATF/PLA composite materials are presented in Figure 88. 15 tests for each set of specimens were conducted to investigate the effect of surface treatments on impact strength of composite materials. Although treated ATF increased the amount of energy required to pull-out and fail fibres in comparison to UNF, the impact strength has shown reductions as an effect of the increased ATF content. An improvement of ~25% for AKT samples at 60 wt% fibre content in comparison to untreated samples was also observed. However, fracture analysis presented predominant fibre pulled-out over fibre failure without big traces of PLA matrix remaining on the fibre surface. In general, these results show that the ATF/PLA material properties are improved when treated ATF are used. Although this improvement is not significant, further treatments, compatibilizers and better processing conditions controls are possible to improve the toughness of the ATF/PLA composite materials.

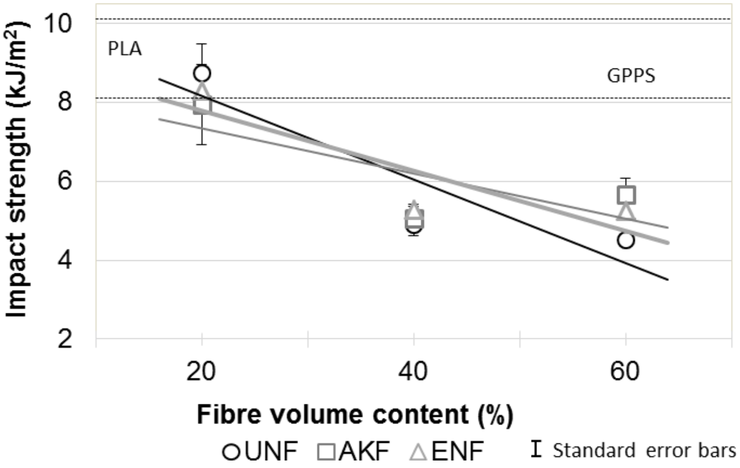


Figure 88. Impact strength of *Agave tequilana* fibres and poly(lactic) acid bio-based composites in comparison with GPPS and PLA.

The most important factor originating the decreasing trend in mechanical properties of the ATF/PLA materials lies in the flaws presented at the interface of the material and the structure and by-product character of the ATF. After the apparently improved interfacial interaction due pre-impregnation process and surface treatment, the ATF fibre structure still is the weakest component in the system. However, ATF/PLA composite materials at higher fibre ratio contents yet have comparable properties to GPPS.

7.3.4 **Water absorption**

Water uptake of treated ATF/PLA composites was found to be reduced more evidently after 20 wt% of ATF content. This reduction was attributed to the physical and chemical changes occurred at ATF during treatments and strictly correlated to the degree of delignification and removal of non-cellulosic materials, and to the level of adhesion presented due to an improved interfacial interaction. Also, in this case, AKF/PLA composites at 60 wt% content presented the major difference with a reduction in water uptake of ~15% in comparison with untreated samples as shown in Figure 89.

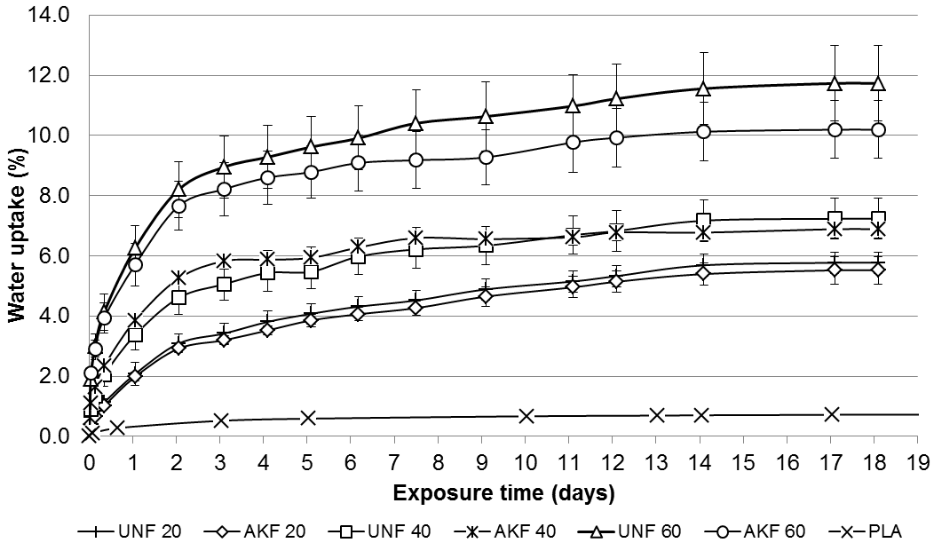


Figure 89. Water absorption properties of *Agave tequilana* and poly(lactic) acid bio-based composites. Standard error bars are smaller than the markers in some cases.

7.4 **Conclusions**

This paper has reviewed the mechanical properties of an ATF/PLA based material manufactured though film stacking method, as well as the associated constraints encountered in bringing together by-product ATF and PLA, to develop a bio-based material for non-structural applications. The effect of different fibre ratios and surface treatments on ATF/PLA composites mechanical properties has been investigated.

There was an inherent compatibility between ATF and PLA, and despite surface modification helped to some extent to overcome intrinsic problems in the use of ATF by showing better mechanical properties in comparison with untreated ATF, results are almost negligible when economic benefits are sought. Therefore, from an environmental point of view, these improvements through surface modification treatments might be considered little convenient, encouraging its use only for specific applications. Other ways of promoting interfacial interaction between ATF and PLA (e.g. melt viscosity control) to achieve a composite material with better mechanical properties suitable for more demanding applications might prove more economical, environmental and efficient.

Results obtained in this work give an overview of the possibilities of an ATF/PLA bio-based material compounded by film stacking method by comparing its properties against GPPS. It has been shown that the mechanical properties of ATF/PLA bio-based composites within a range of fibre volume fraction from 20% to 60% are greater when processed using film stacking method in comparison to injection moulding used in chapter 6. It was observed that ATF suffered from less shear strain during compounding by film stacking, hence preserving the size and the aspect ratio length to diameter. This process allowed the manufacturing of more homogeneous materials in comparison to those observed in chapter 6 where composites presented fibre rich zones in contrast with other poorly charged zones. Therefore, mechanical properties from film stacking compounded materials were observed superior to those compounded by extrusion moulding composites studied in chapter 6. In particular, the best UTS values were reported for 20% (w/w) UNF/PLA composites with 43±4 MPa followed by 40% (w/w) AKF/PLA with 35±4 MPa and 60% (w/w) AKF/PLA with 33±5 MPa respectively. All composites have shown the same decrease trend in properties with the increase of ATF content regardless the surface treatment used. However, and considering the high % content of discarded material used, characteristics and benefits are comparable or within the range to those of GPPS and other PLA based composites where natural fibres are specifically produced for composite applications [62]. Furthermore, the water uptake of ATF/PLA composites was found to be reduced for treated samples, being ~15% of water uptake reduction the major difference observed by AKF/PLA composites at 60 wt% content in comparison with untreated samples.

Data from experimental results have shown that ATF/PLA composites present comparable properties to those of GPPS and can be considered as materials for non-load bearing applications such as; packaging, containers, crates and other targeted applications, where high strength is not sought, but environmental benefits for a fast moving consumer product are the main concern. Due to ATF characteristics and by-product origin, there are still many stages through to harvest-procurement and processing at which variability in properties (degradation) can be introduced. Therefore, a significant opportunity window for improvement is presented.

8 Disposal route analysis of a bio-based material and its integration within a circular economy framework.

8.1 Introduction

Plastics are man-made long-chain polymeric molecules derived primarily from fossil fuel [294]. Synthetic plastics have been a dominant material in almost every field and nowadays are present everywhere as an indispensable part of our life (i.e. packaging). Research in polymers has improved continuously over the years along with the stability and durability of plastics. Thus, plastics are perceived as a synonym of a resistant material capable of enduring many environmental influences and wearing. The majority of these materials are virtually non-biodegradable, and in the case of packaging materials, some are difficult to recycle or reuse due to being complex composites having varying levels of contamination. Moreover, the energy-intensive and growing consumption, and the major recycling costs have led to serious ecological problems i.e. landfilling of non-biodegradable materials [2,3].

The intensive industrialisation presented during last century; especially in developing and transitional economies, has increased the demand for raw materials to satisfy the ever-growing consumption patterns. Consequently, the packaging industry has presented a steady growth during past years as a result of urbanisation and the rapid development presented by emerging economies with a higher demand for consumer goods and more sophisticated packaging [7] [8].

In the case of Mexico, these factors brought the growth of the municipal solid waste (MSW) along with problems associated with an inadequate waste management system. Difficulties in properly managing MSW have been recognised by Mexican organisations [295]. In the country, sanitary landfills and dumps, are the two predominant practices to manage municipal waste streams. These methods have been considered the worst case scenarios for disposal routes due to the environmental and social problems they pose. However, the number of landfills has been increasing considerably, and the practice is still embraced as one of the main disposal routes in Mexico. “From the 41 million tonnes of MSW generated in Mexico during 2011, around 77% was disposed of in landfills, 23% in non-regulated places (open dumped), and only 5% recycled, as shown in Figure 90. The recycled volume of plastics in comparison with the corresponding type of MSW produced was only 0.5%” [296]. This low volume is due to the high prices perceived for scavengers for other materials recovered (i.e. metals), and due plastics materials (mainly arising from food packaging) being contaminated with food remains or other substances, making sorting and recycling process impracticable and not always economically viable [11].

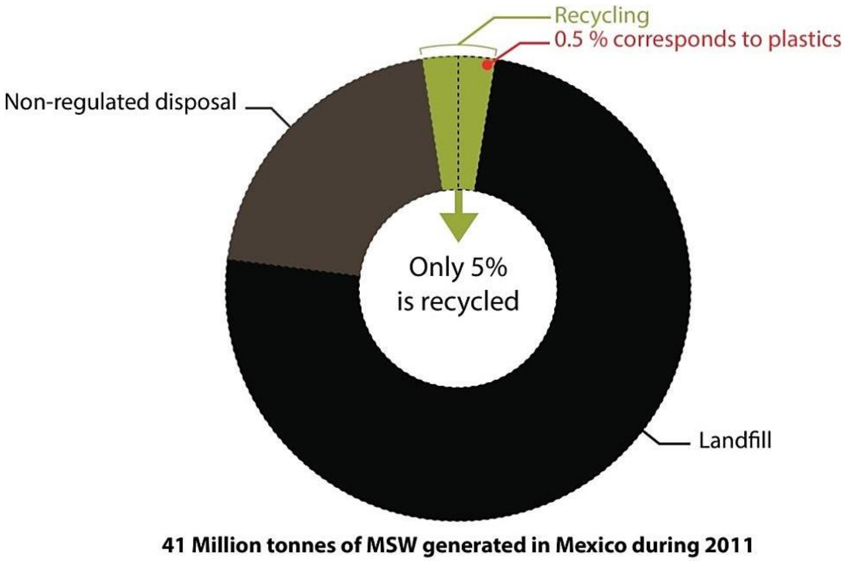


Figure 90. Waste management situation in Mexico. Adapted by the author [296]**.**

The use of packaging materials results in greenhouse gas (GHG) emissions through production, transport and end-of-life management. The carbon that is captured/embedded in the plastic packaging and the release of GHG emissions is strongly dependent on the packaging’s after-use pathway [297]. Only 1 - 3% of plastic packaging hydrocarbon content is degraded within a 100 year period in landfill conditions. Thus its impact is not considered as a long-term emission [18,19]. Additionally, products with a short lifespan (e.g., single-use packaging) are often consumed within days to months of initial production and end up being discarded. The most effective steps towards a more sustainable solution, according to McDonough (2002) [40] and the circular economy (CE) principles, are those that are likely to “move away from technical nutrients (e.g. oil-based materials) to biologically-based loops. This, in order to make these products serve a restorative purpose, rather than an exploitive one” [35].

These environmental, social, and economic concerns arising from the large-scale production and consumption of oil-based materials (i.e. packaging), within a current linear model [2,3,15,16], have resulted in increased attention towards the development of new and more sustainable alternatives such as the green composites or other bio-based materials. The use of these materials can also help to improve the CO_2 balance in the atmosphere by closing the carbon cycle loop in contrast to landfill disposal [47]. However, many of these materials have been designed to solve oil dependency and other problems related to mechanical performance. Therefore, leaving behind other factors such as the GHG contributions at the end-of-life of the material, or the possible disruption to a WMS already in place, that may contribute to the overall life cycle of the material and products where it is used.

It is the view of the author (see Figure 91) and under CE principles, that an ideal recovery scenario for these bio-based and biodegradable materials will allow them to get reinserted into the cycle of value. This, in a closed loop without losing any value, and where disposal, as well as recycling, represent large amounts of embedded energy and labour lost [3,35].

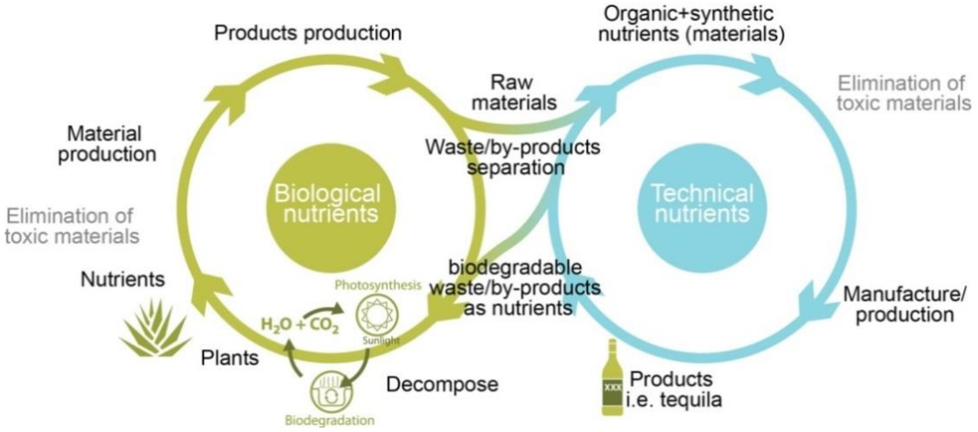


Figure 91. Proposed closed loop cycle for an *Agave tequilana* fibre and poly(lactic) acid bio-based composite, where biological nutrients are intended to remain as long as possible within a restorative circular economy. Adapted by the author [40].

In this section an ATF/PLA bio-based material manufactured and analysed in chapters 6 and 7 is studied in terms of the possible contributions and effects its introduction represents into an already existing WMS, based majorly in landfilling. However, other routes for the re-integration of the material into a closed loop as valuable technical or biological nutrient are also explored, so that is possible to draft a better proposal for the management of the material when it has accomplished its main function.

Different waste management solutions are in place for traditional materials such as plastics [298]. However, new materials such as ATF/PLA bio-based composites require a better understanding of the implications a disruption in the current waste stream represent [299,300].

The objective is that these materials of great sustainable interest can finally be introduced on a large scale as a real alternative, for appropriate and targeted cases, to the conventional non-biodegradable plastic materials. The aim of these materials is not merely a reduction in landfill volume, but on the contrary to enhance the collection of targeted applications (i.e. food contaminated packaging) to facilitate its diversion from landfill to composting or waste-to-energy (WtE) facilities when reuse and recycling are not feasible for after mentioned conditions.

8.2 **Recycling and conversion technologies**

There are numerous ways to keep the embedded carbon within the ATF/PLA bio-based composites looping the cycle. Recycling of these materials makes possible to keep the whole carbon content and save primary resources [301]. For example, the recycling of ATF/PLA bio-based composites through biogas production as a possible end-of-life scenario for this material enables carbon sequestration [302] while transforms the biomass available in the material into a renewable energy source [303]. However, these recycling routes may be appropriate for some types of materials and contexts and not work for others. Therefore, the importance of understanding the yield and behaviour that an ATF/PLA bio-based material has under different end-of-life routes. Consequently, making possible to draft better conclusions regarding the optimal waste management system and useful energy conversion forms for sustainable growth [304], at least while new waste prevention initiatives, improved WMS and a shift to more sustainable consumption patterns are in place. Moreover, energy from waste as recovery of these materials must be approached only as a support of the waste management, as depicted in Figure 92.

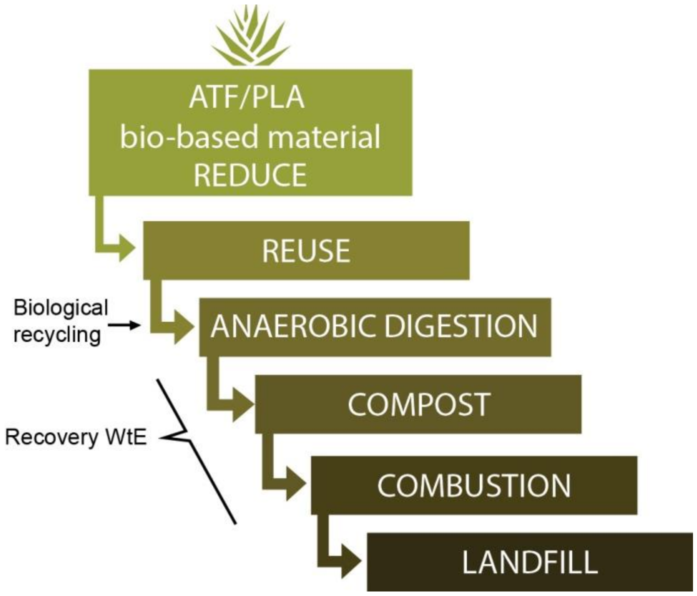


Figure 92. ***Agave tequilana*** **fibre and poly(lactic) acid bio-based composite waste management hierarchy. Adapted by the author** [305]**.**

There are two main types of conversion routes for producing energy as shown in Figure 93; thermochemical and biochemical. Thermochemical conversion is the process where heat and chemical reactions convert biomass materials or feedstocks into other forms of energy. Biochemical conversion involves the use of enzymes, bacteria or other microorganisms to break down biomass to produce energy. Production of power, heat, and transportation fuels are the possible outcomes for the different available conversion technologies.

Amongst the options for energy conversion, combustion (thermochemical), anaerobic digestion (AD) and composting (biochemical), are the main focus of this study, as they have been considered by the author as fundamental when evaluating possible short-lived consumer products made out of ATF/PLA bio-based composites.

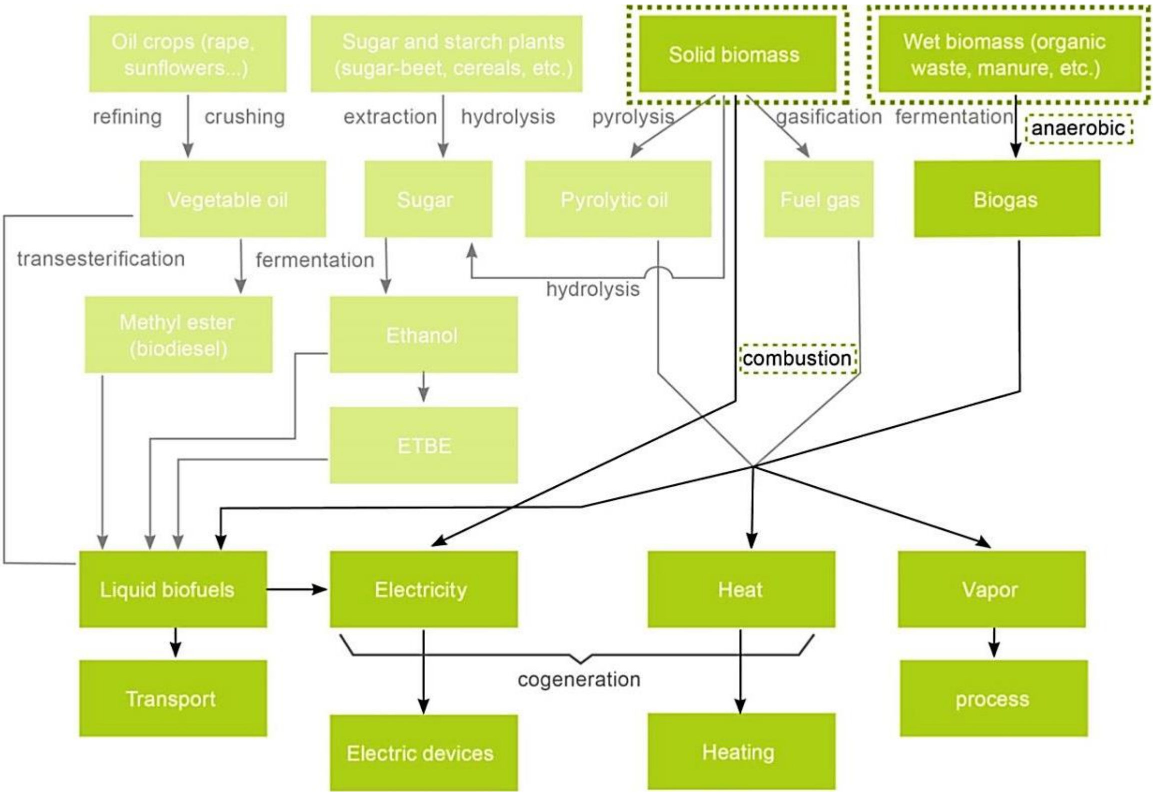


Figure 93. Biomass energy conversion.

8.3 **Reprocessing**

Despite these bio-based materials have proven to have mechanical recycling capabilities [274,306], the current Mexican waste management conditions [295], and the always critical mass needed for recycling feasibility and viability at the introduction of a new material, suggest other ways of recovery to be considered. Furthermore, energy costs savings through recycling are minimum when compared to WtE conversion routes due to the non-homogeneous nature of the waste stream (pre-sorting expense), and the close break-even energy cost of recycling when compared to current feedstock prices [307]. Additionally, from an environmental point of view and besides the ATF/PLA bio-based composites presented a decreasing trend in property retention during re-processing (see Figure 94) similar to that shown by neat PLA [308], recycling of pure PLA underperform other methods such as incineration, composting and AD according to life cycle assessments (LCA) (Figure 95) [309]. On the other hand, the major inputs are given by the PLA matrix [78,310]. Hence, a higher ATF content above 40 wt% will reduce drastically the total percentage of the environmental impact of the whole material as the content of PLA inversely decreases, making the ATF/PLA bio-based composite to perform better at LCA.

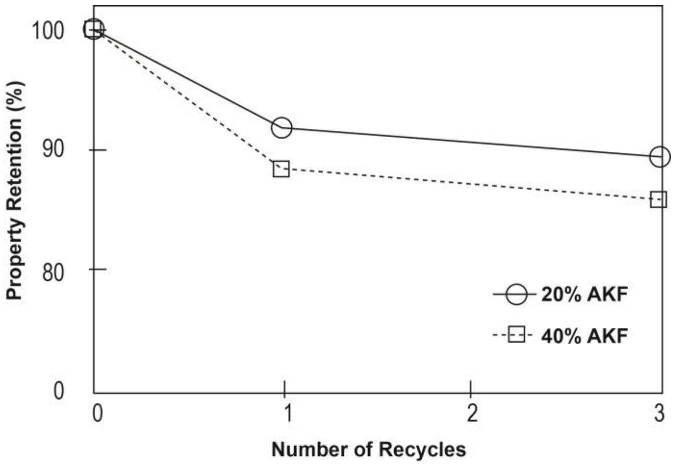


Figure 94. Influence of mechanical recycling on tensile strength for bio-based composites at 20 and 40 wt% of alkali-treated fibres after continuous reprocessing during compounding by extrusion. Standard error bars are smaller than the markers (<5% for all cases).

Reprocessing of ATF/PLA bio-based composites was carried out through repeated extrusion moulding and pelletising cycles, as it is described in chapter 6. The reduction in mechanical properties presented after reprocessing was inherent to the thermo-mechanical degradation occurred at both PLA matrix and ATF. Degradation under high processing temperatures, shear forces, and the reduction of ATF length, resulted in the decreased property retention of the material as it has been reported before [311,312]. Therefore, the high energy involved, and the loss in properties makes mechanical recycling through reprocessing little economic or viable, if performance retention is the main concern.

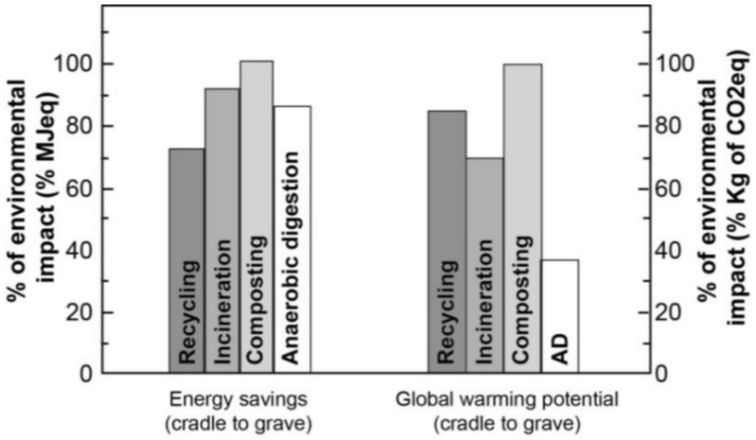


Figure 95. Energy savings and global warming potential for different disposal routes of neat poly(lactic) acid. Adapted by the author [309]**.**

8.4 **Compostability**

As it has been mentioned before, the ideal scenario for the ATF/PLA bio-based composites will be to stay cycling in the loop as long as possible (i.e., reuse). However, since this scenario could not be feasible, one option to keep the material value within the cycle as biological nutrients is composting. Nonetheless, composting global warming potential (GWP) is higher than that presented in AD [313].

Biodegradation is the most important precondition when a material is designed for being reintegrated as a nutrient for bacteria or fungi, and it should not be confused with the term composting. In a complete aerobic degradation process (mineralisation), organic substances are broken down to water and carbon dioxide, with the consumption of oxygen [314] contrary to anaerobic processes where the breaking down of the organic material is done in the absence of oxygen.

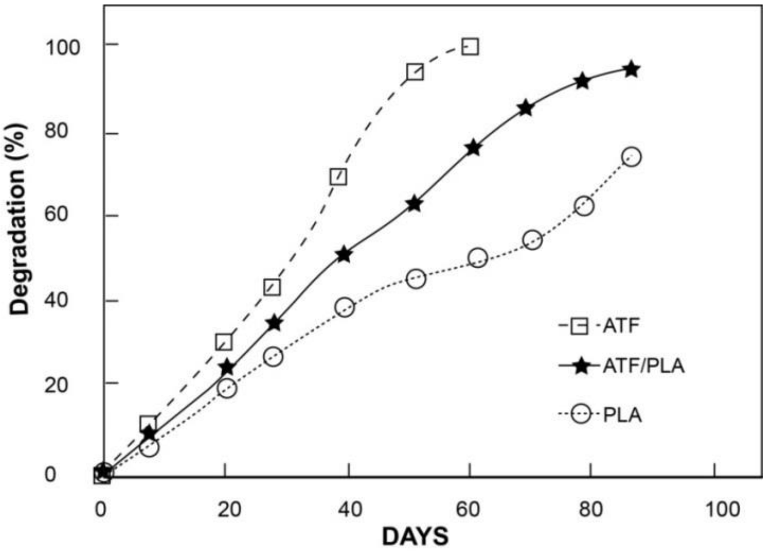


Figure 96. Mineralisation rate of 60 wt% *Agave tequilana* fibre and poly(lactic) acid bio-based composites. Adapted by the author [315]**.**

Due to the inherently compostable nature of PLA [84,85,87] and ATF, the recovery of a new ATF/PLA bio-based material through composting can be concluded as feasible, as it is shown in Figure 96. However, composting is not entirely viable for scenarios where landfilling is embraced as the main WMS and where technological difficulties prevent the widespread of industrial composting [316].

Mineralisation of ATF/PLA bio-based composites has been reported to be quicker than the observed by neat PLA. This is attributed to an initial hydrolysis at the fibre-matrix interface during composting facilitated by the hydrophilic nature of ATF. The degradation rate was observed to be major for the NaOH-treated materials and at higher ATF % contents due to the absence of lignin and waxes [315,317]. However, it is important to consider that home, and industrial composting differ in their degradation rates and emissions (i.e. nitrous oxide and methane) [313]; and that mineralisation of PLA at mesophilic temperatures is not feasible [318] making home composting a non-practical route.

8.5 **Incineration - Biomass combustion**

Incineration is a waste treatment process that involves the combustion of waste for energy recovery. Biomass combustion is the main technology route for bioenergy and is continuously gaining more attention due to its potentially CO_2-neutral and renewable energy source. The concept behind this principle is that plants such as *Agave tequilana*, or maize (used to produce PLA) take carbon (C) from the atmosphere during their growth, and return it during combustion. The impact of this biogenic carbon dioxide released is considered negligible; opposite to the impact represented by the carbon dioxide (CO_2) released by the combustion of fossil carbon materials. Although incineration with energy recovery has a higher GWP that AD, it is still lower than that presented by composting [309,313].

Combustion is a chemical reaction and the easiest process by which biomass and other wastes can be used for energy through the heat produced during the combustion in the presence of oxygen. During the process, oxidation of carbon and hydrogen (present predominantly in lingo-cellulosic materials) forms CO_2, water (H_2O) and heat [319].

The energy resulted from combustion is used in the form of heat, power, or a combination of both. The technology and the process itself have been improved with electrical efficiencies (only for biomass) of 30-40% [319,320].

The produced amount of heat is dependent on the biomass source, but normal values are expected to be around 20 Megajoules (MJ) of energy per dry kilogramme of biomass [321], while oil-based polymers present higher heating values ~18-39 MJ/Kg [322,323].

Table 20. Heating values of *Agave tequilana* fibre and poly(lactic) acid bio-based composites in comparison with other oil-based polymers and agricultural wastes.

Material	**Lower Heating Value (MJ/Kg) as received (including ash and moisture)**
PE	37.44 [323]
PS	38.74 [322]
PET	21.85 [324]
PVC	18.11 [323]
Flax	18.86 [321]
Hemp	15.93 [325]
Kenaf	17.83 [321]
Sugarcane bagasse	15.62 [326]
Coir	17.79 [327]
Rice husk	13.07 [328]
ATF	19.04 [315]
60% (w/w) ATF/PLA composite	21.30 [315]

When combustion is used as WMS for ATF/PLA bio-based composites, is important to consider that biopolymers generally have lower heating values than most petrochemical bulk polymers [315] (see Table 20). In some cases, the difference is negligible (i.e., PVC, PET) while it is substantial in other situations (i.e., PS). In practice, the difference in recoverable heat may have bigger variations than those indicated previously on Table 20 due to the feature of most biopolymers to absorb water rather easily or materials being contaminated by food remains. When recycling of the material through composting or AD cannot be achieved due to technical limitations or lack of economic viability; energy recovery by combustion is one of the best ways to recover the value of these bio-based materials in terms of non-renewable energy use and GWP [309,313].

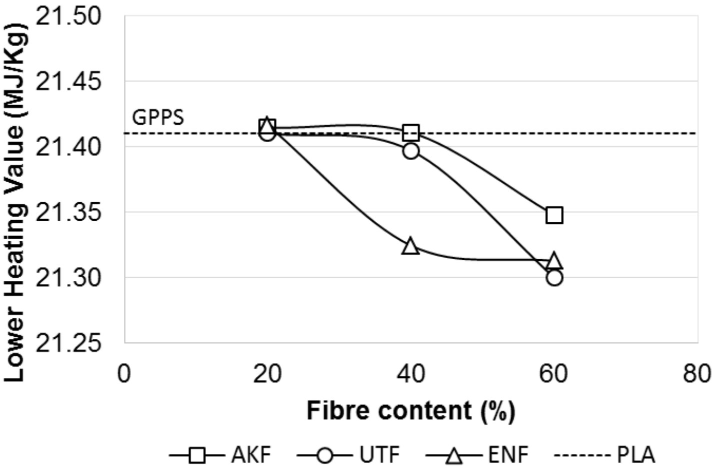


Figure 97. Experimental lower heating value (MJ/Kg) from an *Agave tequilana* fibre and poly(lactic) acid bio-based composite. Adapted by the author [315]**.**

As it was expected due to the similar amounts of carbon, hydrogen, oxygen and volatiles content in other biomass fuels, the calorific value (CV) for AFT/PLA bio-based composites (Figure 97) was within the same range presenting a negligible decreasing of CV at increased ATF content ratios. The concentration of carbon during the combustion process of ATF/PLA bio-based materials was present in oxidised C form (i.e., CO_2), accounting for the low CV obtained when compared to coal (~27-31 MJ/Kg) or other high carbon content materials such as oil-based plastics. However, fossil fuel alternatives are not anymore a sustainable option; besides, harmful compound release (e.g., chlorine, ammonia, etc.) is one of the main objections for the use of oil-based plastics in energy recovery through combustion. As a consequence, efficiency and total capacity have a considerable impact on the overall conclusions when selecting the *“right”* waste management system for this kind of materials. For example; energy usage, cradle-to-factory gate analyses, landfilling, and waste incineration without energy recovery favours the use of ATF/PLA bio-based composites; on the other hand, incineration in waste-to-energy facilities, especially with high energy-recovery yields, is in favour of oil-based polymers (in energy terms).

It should be taken into account that energy recovery yields from waste-to-energy facilities are generally low at present, and It is estimated that only one-quarter of the heating value of the waste is converted to final energy in the form of power and usable heat [329]. The generation of the same amount of final energy from conventional fuels in power plants and district heating plants requires only half of the energy input. As a consequence, the use of fossil fuels is still favoured from a short-term economy-performance relationship.

Mexico had a consumption of 4.8% of biomass as a % of primary energy from a total 7392 PJ/year during 2006 according to the OECD (Organization for Economic Co-operation and Development) [319]. Although bioenergy has shown to have potential, it has not been entirely exploited [330]. Thus, political support, a major energy policy and strict regulations to promote the use of renewable energy sources and biofuels in economically, environmentally and socially responsible forms might be urgently needed [331,332].

8.6 **Anaerobic digestion and biochemical methane potential**

Despite PLA has shown to be compostable [87,333,334] its anaerobic biological degradation at typical landfill conditions will require 100+ years [335]. Therefore, assessing the overall environmental burdens of a new PLA-based material in an existing WMS dominated by landfilling may help draft better management routes and strategies.

AD is the conversion of organic material into a biogas mainly composed of methane (CH_4), CO_2, and small traces of other gases like hydrogen sulphide (H_2S). There are two basic AD processes, mesophilic digestion (temperature range 35-40° C and retention time for about 30 days) and thermophilic digestion (reaches a temperature up to 60º C and can take 12-14 days to complete).

AD has increasingly gained attention during last years. The process occurs in an anaerobic and warm environment (i.e., digester) with the proper conditions for bacteria to growth, ferment the organic material and produce biogas with an energy content of about 20–40% of the lower heating value of the feedstock. In a typical scenario, biogas production will be formed with a normal distribution pattern over time. Biogas production is then used to determine when the process of digestion of the organic matter has been completed.

In Mexico AD has been a practice accepted late in comparison to European countries, but nowadays it can be considered a mature technology yet with a long way to go in terms of a broader embracement [336].

Due to PLA glass transition (T_g) ~60° C, it is expected for ATF/PLA bio-based composites to show a slow anaerobic degradation at mesophilic temperatures, contrary to the accelerated degradation it may present at thermophilic temperatures higher than PLA T_g [318]. On the contrary, organic materials (i.e. grass, leaves, and food scraps)have a faster degradation [337]. Therefore, an increased degradation rate from the ATF/PLA bio-based material can be expected in comparison to neat PLA. However, some difficulties for degrading the lignin present at ATF can be anticipated [338].

The biochemical methane potential (BMP) is a valuable, quick and inexpensive assay used to determine the ultimate CH_4 yield of organic material [339–341]. Consequently, it is used as an index of the anaerobic biodegradation potential of a determined material. Common procedures are given elsewhere [342]. In the case of ATF/PLA bio-based composites, this assay will yield useful information to predict, and understand the behaviour of this type of materials at AD waste treatment facilities, and particularly and most importantly at landfilling. This is important once it is known that landfilling is the predominant WMS in the context of this study, and that neat PLA will face difficulties for bacteria growth at anaerobic conditions presented at landfills.

8.6.1 **Enhanced anaerobic digestion by pre-treatment**

Pre-treatment of wastes for AD in materials such as ATF/PLA bio-based composites with high ligno-cellulosic fibre contents aim to enhance the biological process, improving by consequence the performance of the digesters.

Pre-treatments can be biological, mechanical or physico-chemical. However, a balance between the benefits of digestion enhancements and economic aspects of these pre-treatments are crucial for the industry, and not usually covered in the literature.

Size reduction and comminution lead to improved gas production and a more rapid digestion [343]. Natural fibres have been found to present an increase up to 25% of biogas potential. Open lignocellulosic structures, with more accessible and hydrolysable cellulose, may yield better results for biogas production [344].

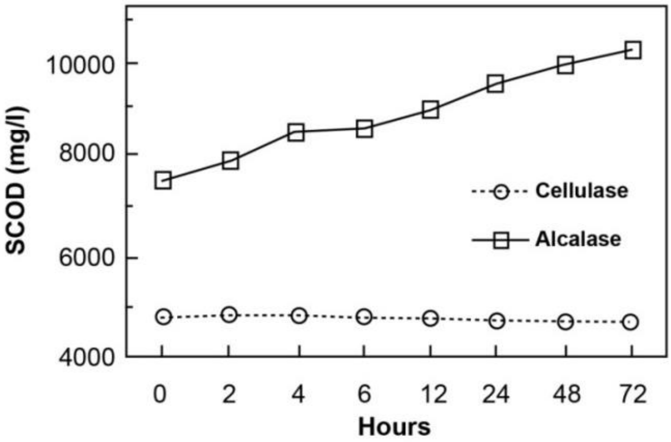


Figure 98. Soluble chemical oxygen demand results for enzymatic pre-treatment of an *Agave tequilana* fibre and poly(lactic) acid bio-based composite at 40 wt%. Adapted by the author [345]**.**

AD of PLA-based materials is feasible under the right conditions, as stated before. However, the change in parameters may affect the full operation and efficiency of the AD plant. Enzymes and other mechanical pre-treatments have been reported for increasing hydrolysis and degradation of PLA [346]. In other work, alcalase and cellulase enzymes have been used as pre-treatments to enhance ATF/PLA bio-based material degradability [345]. Soluble chemical oxygen demand (SCOD) values reported for alcalase, concluded the effectiveness of the pre-treatment (Figure 98), however, SCOD values presented for cellulase were either conclusive or significant. Lower cellulase's SCOD values can be attributed above all to the inaccessible cellulose being covered by non-cellulosic materials (e.g. lignin) within the whole fibre since ATF used in the study by Jeanne-Espinosa (2016) [345] were not pre-treated for their removal. Provided that AKF utilised in the present study have been pre-treated to remove non-cellulosic compounds before material manufacturing, it is also expected to have a better yielding in comparison to those samples that have lignin and other non-cellulosic materials not removed.

8.7 **Materials and methods**

8.7.1 **Anaerobic digestion**

In a laboratory-scale experiment, AD of ATF/PLA bio-based composites was investigated, as a simulation of the long-term anaerobic fermentation the materials will suffer at landfill conditions, and to assess continuous production of methane (CH_4), as a possible source of renewable energy at either AD facilities or landfill sites with gas collection.

Figure 99. Mechanically treated *Agave tequilana* fibres and poly(lactic) acid bio-based composite sample ground at 25,000 RPM.

The bio-based material samples (Figure 99) with a 20 and 60 wt% content of alkali and untreated ATF, as well as neat PLA samples, were subjected to the same anaerobic sludge digestion at 35° C. Samples were prepared using the method previously reported. From now on, samples are referred as AKF for alkali-treated samples and UNF for those untreated. Pure sludge was kept as a control to monitor microbial activity. Anaerobically digested sludge for the BMP assay was collected from the wastewater treatment plant at Milton Keynes, United Kingdom.

Before starting the tests, ATF/PLA bio-based composites were analysed for total solids (TS), volatile solids (VS), ash and carbon content according to standard methods [347]. The results are summarized in Table 21.

Table 21. Overview of analyses and reference items.

Test item	Total solids (%)	Volatile solids (% of TS)	Total organic carbon (%)	Ash content (%)
PLA	99.37	99.37	50.86	0.63
UNF 20%	95.30	98.48	49.51	1.52
UNF 60%	97.33	97.90	48.59	2.10
AKF 20%	98.20	99.68	45.25	0.32
AKF 60%	95.36	97.75	48.59	2.25

For BMP assay, ATF/PLA bio-based composites and inoculum sludge were added and stirred into a gas-tight closed reactor (Figure 100). Biogas was then produced during degradation time causing an increase in the pressure inside the bottles. Pressure evolution was registered by measuring the changes in pressure at different intervals, and the percentage of degradation was calculated. Biodegradability (%) was calculated as indicated by the following equation:

$$\textbf{Biodegradability (\%)} = (\Sigma V_{(1)} - \Sigma V_{(2)} / V_{(max)}) \times 100$$

where $\Sigma V_{(1)}$ is the total biogas volume from the bioreactor with the material tested. $\Sigma V_{(2)}$ is the total biogas volume from the control bioreactor. $V_{(max)}$ is the theoretical volume of the biogas evolved after complete biodegradation of the test material. In $V_{(max)}$ calculation, it is assumed that all the carbon in the materials tested is converted to only CO_2 and CH_4 after complete biodegradation. All samples were tested in triplicate.

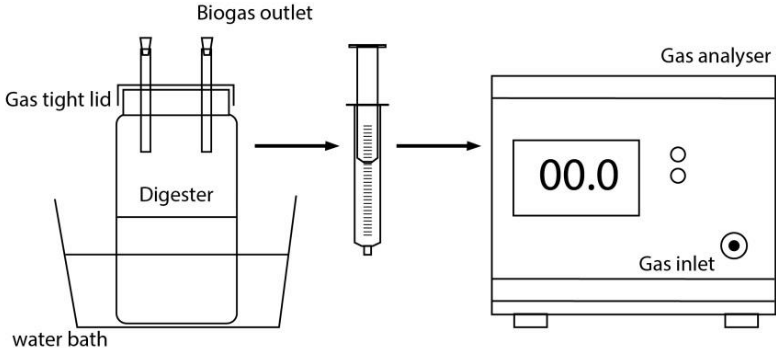


Figure 100. Biomethane potential assay setting.

8.8 **Results and discussion**

Anaerobic digestion gave new information about the material. After 3 days of incubation, mass variations were expected as biogas production started with a maximum of ~1.60 ml CH_4/gVS obtained for 60wt% AKF/PLA bio-based materials as shown in Figure 102. This was twice the values presented for samples with lower fibre content during the first days. Biogas production continued gradually during the incubation period. However, CH_4 ratio from the sludge was found to be lower than the normal ranges observed under same conditions (~60%). This was attributed to the low methanogenic bacteria activity caused by the absence of complete anaerobic conditions and above all the reduced pH originated by the accumulation of volatile fatty acids as the pH values measured at the end of the test were below 5.0 [348,349]. Figure 101 shows the CH_4 ratio presented by the pure sludge used in the experiment.

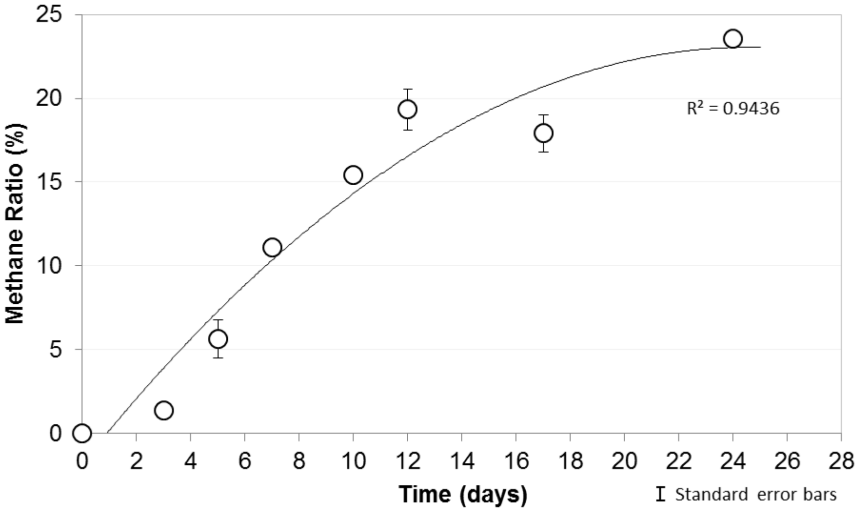


Figure 101. Methane ratio during incubation of the sludge. Incubation was done at 35 °C. After incubation pH was below 5.0.

Biogas production during 24 consecutive days allowed a qualitative analysis of the biogas. Biomethane gas production presented a 3-day lag phase where microbial adaptation has taken place to then increase constantly during the length of the test up to a maximum ~20 CH_4/gVS at the end of 24 days of incubation for 60% AKF samples. The other ~78% of biogas produced is accounted for CO_2 with small quantities of other gases like H_2S.

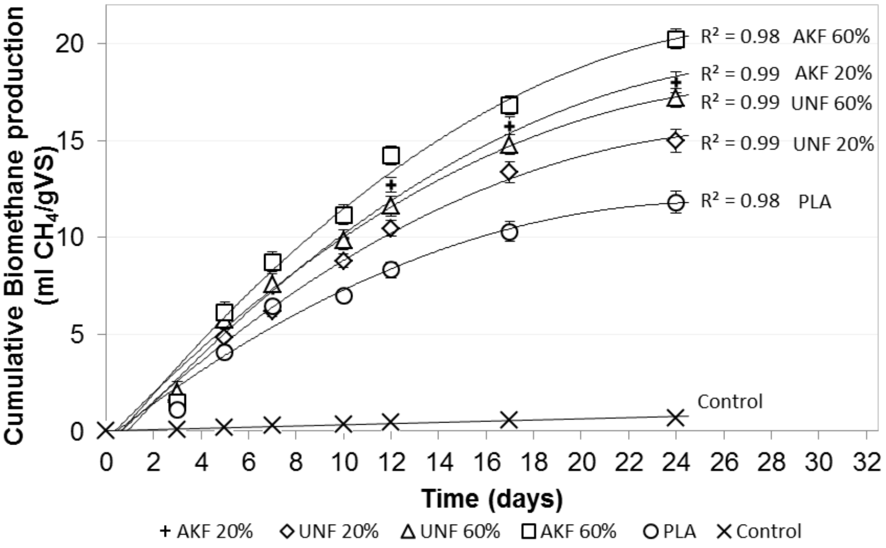


Figure 102. Cumulative biomethane production from *Agave tequilana* fibre and poly(lactic) acid bio-based composites as a function of time under anaerobic conditions. In some cases standard error bars are smaller than the markers.

These results show valuable information about the higher CH_4 production rate for samples with higher fibre contents. During the incubation, methanisation of samples containing higher fibre contents exhibited a higher conversion. For neat PLA, the conversion rate to biomethane was ~10% above the control (see Figure 102). Therefore, a very slow mineralisation process was observed for neat PLA over the entire period of incubation [350,351].

The biodegradation process of ATF/PLA bio-based composites was monitored by measurement of the increase in biogas produced in the test reactors. Correspondingly, among the samples tested, AKF 60% and AKF 20% gave the higher biogas production results as presented in Figure 102. According to the results, higher fibre % contents have shown a major degradation percentage

~14-16% above to that presented by samples with lower fibre content. Furthermore, alkali-treated ATF/PLA bio-based composites were degraded at a ~14% faster rate in comparison to untreated samples with a statistical significance of $p<0.05$ (see) . Thus the difference, at these incubation periods with low activity sludge, is rather small. This difference between alkali-treated and untreated samples was attributed to the difficulties to biodegrade the still existing lignin on untreated samples [338]. Biodegradability of PLA was within the ranges presented under mesophilic conditions during the same period of time [351].

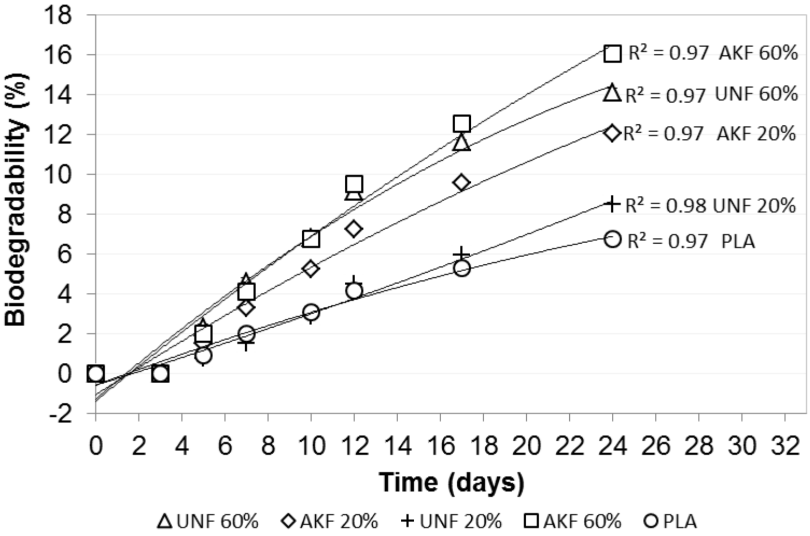


Figure 103. Provisional cumulative biodegradability of *Agave tequilana* fibre and poly(lactic) acid bio-based composites calculated from the evolved biogas volume. Standard error bars are smaller than the markers.

Despite CH_4 rate was ~30% below the commonly reported values, the information obtained through the test gives a confirmation of higher degradation rates for samples containing higher ATF contents and with more accessible carbohydrates (i.e. cellulose and hemicellulose). However, other experiments could be carried out to assess this behaviour, and the extended effect of a complete anaerobic digestion with more active sludge to clearly understand the phenomena on the maximum biodegradation of this kind of materials.

The mesophilic temperatures used were selected to replicate to some extent the conditions exhibited at landfills [352]. Although temperatures might be lower and present variations [353], these results give a general view of the implications ATF/PLA bio-based composites have within different waste management systems. If landfilling is considered the most likely end-of-life route for these materials, it can be expected that some of the biogenic material will break down with the carbon converted to a mixture of carbon dioxide and methane (i.e. landfill gas). Consequently, CH_4 could be captured and burnt, as energy from waste strategy. This makes landfill gas utilisation, in general, a very attractive GHG mitigation option. However, if the landfill conditions are not adequate some of the methane could escape into the atmosphere as a greenhouse gas with stronger implications that CO_2 [303].

When comparing composting with AD it appears that with anaerobic technology a variable amount of energy could be recovered, whereas composting seems a net energy consumer. However, AD requires a larger investment, and the process is more complex than composting. From an ecologic and economic point of view, AD has the advantage over composting and incineration, mainly because of its improved energy balance [354]. Composting of ATF/PLA bio-based composites might produce significant and uncontrolled emissions of volatile compounds, such as methane [355,356]. Furthermore, in terms of global warming, AD scores are better than other options [357,358].

While the arguments presented above are indicative and simplified, there are many more factors than the exhibited in this study that should be considered when trying to find the right balance to select the "*best"* end-of-life route for ATF/PLA bio-based composites. It is necessary to review and study in specific the application where the material is used on a case-by-case basis.

As discussed previously landfill as an end-of-life route presents many issues, even for a bio-based material. For example: the fact that materials degradation behaviour is strongly related to landfill conditions, and these appear to be scattered and non-strictly regulated, makes difficult to establish real long-term implications; the level of gas capture at landfill sites; the efficiency of the capture process; and the probable amount of GHG that could be released over the years. Consequently, WtE alternatives currently display a better option than landfill for managing ATF/PLA bio-based composites waste. However, it is important to bear in mind that every material application case is different, and that new and more efficient technologies and management systems might imply a shift in the waste management hierarchy for ATF/PLA bio-based composites.

Additionally, the use of an ATF/PLA bio-based material with compostable and biodegradable properties, within the fast-moving consumer goods industry, should be considered as a mean to enhance the collection of food waste and food-contaminated packaging, to enable diversion of these materials from the landfill to composting or to anaerobic digestion facilities.

The embedded energy from ATF/PLA bio-based composites waste which could otherwise be managed higher up in the waste hierarchy is a concern that needs to be addressed not only for this kind of materials. When a continuous cycling of the material (i.e. re-use) without energy inputs larger than mechanical or chemical recycling is not feasible, then WtE poses a better environmental solution than landfill, provided that the material’s waste has a high biogenic content and assuming that WtE facilities are in place and efficient at turning the material at its end-of-life into usable and renewable energy.

8.9 **Conclusions**

In a perfect scenario, waste from ATF/PLA bio-based composites would be prevented and make a waste hierarchy unnecessary. However, social, economic, practical and technological reasons force this kind of materials to be dealt with the available technologies at different levels of the waste management hierarchy (including WtE or even landfill). Also, it is considered that the final use of the material in question (different from packaging) must require specific waste management considerations, life cycle analysis and sometimes to depart from the hierarchy given altogether.

It has been acknowledged that ATF/PLA bio-based composites could be recycled in terms of having the carbon content cycling the value chain for longer periods than oil-based polymers. It is of paramount importance that although there is a possibility of energy recovery for the material, that does not imply a reduction in efforts to overcome the barriers to keep the material cycling the value chain. Moreover, while cultural, technical, and waste management issues are overcome, WtE presents an efficient way to ensure these types of materials do not go to a worse environmental case scenario in a landfill. In the long term, waste from these materials should be treated as an input rather than as waste, at its optimal level in the hierarchy in environmental and economic terms.

According to this study, it is shown that the ATF/PLA bio-based composites tested can be potentially biodegradable, according to the conditions under which they were placed to incubate and that they can be cycled within a closed loop as long as technology embracement, cultural shift and governmental support are in place.

9 Overall discussion: Implementation of the work

This work provided an early stage development of a bio-based material from the agro-industrial by-product fibres from tequila production and poly(lactic acid), as an alternative to oil-based polymers (i.e. polystyrene) in the FMCG industry; but offers, above all, a holistic approach that could be beneficial towards the development of other bio-based and non-bio-based materials.

The holistic approach used at the beginning of the study allowed to preconceive a material through the consideration of either sustainable or non-sustainable factors involved in the material development. However, the organic and adaptive character of the design thinking approach used will work as long as it is blended in harmony with stricter and linear methods such as those used in traditional material development. Therefore, it is considered that in new sustainable material developments, a design thinking figure/role should be at the core of the process, to facilitate the switch from one approach to another whenever it is necessary. This is to enhance sustainable innovation in a *“design-driven material development”* scenario.

This research involved assessing the feasibility of a new material produced from lignocellulosic fibres from the waste stream of tequila production. In this study, ATF observed acceptable properties for being considered as an attractive raw material source for new applications when looking forward the up-cycling of a “waste” that has big amounts of embedded energy on it, and that is almost ready for its use. Despite natural fibres from tequila production have lower mechanical properties (~80-86% for UTS) when compared to other lignocellulosic fibres such as sisal [195] due to their inherent origin as a by-product, structure and chemical makeup, they still offer competitive mechanical and physical properties at low cost such as UTS of 79±38 MPa, *E* 3.3±1.4 GPa, elongation of 13±9% and a density of 1.2±0.1 g/cm^3.

Surface treatments on these by-product fibres improved to some extent their mechanical and physical properties such as an increase of UTS ~10-50% and a reduction of water uptake in comparison to untreated samples of ~22-39%.

Alkali treatment with NaOH at 8% (w/v) for 60 minutes at 21° C was found to present the best-balanced results in terms of UTS, IFSS and water uptake. However, overall properties observed from treated ATF were lower when compared to other natural fibres specifically harvested for composite applications [212]. ATF compatibility with PLA was also improved by means of surface treatments. The higher IFSS observed was for alkali-treated fibres with an increment of ~60%. Surface treatments change ATF hydrophilic properties with a water uptake reduction of ~25-40%. Generally, improvements due to surface treatments were observed in ATF and ATF/PLA interaction. Thus, the previously given concept of *"waste"* assigned to ATF was changed into a raw material for new composite applications. However, the significance of these improvements should be balanced in a cost-benefit relationship for further applications.

The feasibility of a new material for its introduction into the supply chain involves the consideration of already existent manufacturing methods and their adaptation for the production of the new material. ATF/PLA bio-based composites were manufactured using two different procedures; extrusion-press moulding, and film stacking. These methods were selected to maximise the use of ATF in terms of the higher % of fibre volume content, to avoid disruption of existing manufacturing processes in place, and to facilitate the embracement of a new ATF/PLA material in the current supply chain.

ATF/PLA bio-based composites produced by extrusion-press moulding presented a UTS of 47±2 MPa with an *E* 3±0.2GPa, a flexural strength of 87±1 MPa and an impact strength of 6±2 kJ/m^2 at a maximum of 60% (v/w) content of alkali-treated ATF. At 60% (v/w) of AFT content, surface treatments presented a marginal difference over untreated samples. Major differences favouring surface treatments were observed at 40% of ATF content. These results were attributed to the increased surface roughness and delignification leading to the improved mechanical interlocking between ATF and PLA as it has been corroborated by other alkali-treated fibres [135,201,253]. Generally, ATF/PLA properties were below the values observed for other PLA-based composites [42,292]. However, it is important to bear in mind that the natural fibres used in this study have previously undergone thermo-mechanical degradation and that additives-plasticizers were not used during the compounding of the materials. The reduced properties presented in samples produced by extrusion moulding were attributed to the ATF shearing suffered during compounding. Although impact properties at maximum 60vol% ATF content were observed to be 10-30% lower than those of GPPS, tensile and flexural properties of samples at the same vol% are still within the ranges of GPPS. Additionally, the break-even point estimated for untreated ATF at 23wt% and for alkali-treated ATF at 25wt% in PLA-based composites is lower when compared to flax, kenaf, sisal and coir [62]. This represents an economic advantage over mechanical performance. Therefore, low load-bearing applications are suggested for the ATF/PLA bio-based materials.

On the other hand, samples produced by film stacking method presented a UTS of 33±4 - 32±4 MPa, with an *E* 3.2±0.2 – 2.8 ±0.2 GPa, a flexural strength of 77±10 - 76±10 MPa, an impact strength of 5.60±1.6 – 5.30±0.8 kJ/m^2, and a maximum WAS of 10.20% at 60wt% content for treated samples. ATF/PLA bio-based composites with treated ATF presented the best results in terms of properties retention, contrary to the increased drop in properties presented by the untreated ATF samples. Despite alkali-treated samples presented the best results as an effect of the improved interfacial interaction between phases; tensile strength values of ATF/PLA bio-based materials were lower than the observed for GPPS. These results were attributed to the non-perfect adhesion corroborated through the ESEM analysis at the fracture sections, and to the reduced capacity of ATF to withstand stress transfer before failure. However, final properties observed by ATF/PLA bio-based composites offered a comparison point against GPPS. Consequently, it is possible to place ATF/PLA materials within the ranges of GPPS, PP, and other PLA-based materials [277]. Therefore, applications, such as packaging, casings, crates, etc., with high fibre contents and non-load bearing dependence can be suggested for further development.

The initial life-cycle approach used in the materials conceptualization, allowed the design of a biodegradable ATF/PLA bio-based composite. Every new material that gets into the supply chain and waste stream somehow represents the disruption of the whole system. Landfilling was recognized as main WMS in Mexico [295]. However, it has been observed a shift towards new waste management technologies. Although, this change has been presented at a low pace and influenced by economic and political constraints.

The impact that a new ATF/PLA bio-based composite represents to the current WMS in Mexico was studied in terms of the *"best"* economic-environmental-social balanced route at the end-of-life of the material. In accordance with CE principles [35], and restorative-regenerative concepts [40], the ideal scenario at the end-of-life of this kind of materials is a continuous loop with the less possible loss of carbon and energy. This continuous looping is best achieved through the reuse of the material in a first instance. However, recovery and reuse of ATF/PLA bio-based composites might imply the development of new waste management systems to divert the material from an end-of-life with carbon or energy losses towards a solution better suited for a sustainable behaviour change [359].

Despite, mechanical recycling could be embraced as a way to recover these materials [274,306], this practice represents big amounts of embedded energy and labour cost [78,309,310]. However, the biggest contributions are made by PLA, favouring in this way the high % content of ATF above 40wt%. On the other hand, since Mexican WMS conditions favour only recycling of materials with higher economic value (i.e. aluminium), and energy costs savings through recycling are minimum when compared to WtE conversion routes [307], other routes offer a more sustainable option from the economic, environmental and social point of view.

The next best alternative after reuse, on the waste management hierarchy for ATF/PLA bio-based composites, is biological recycling through composting and AD. Initially, composting was preferred since AD has presented difficulties to fully biodegrade PLA-based materials under mesophilic conditions [318].

However, its GWP is higher when compared to other WtE conversion routes [313]. Furthermore, pre-treatments to enhance AD offer a real alternative [345,346]. ATF/PLA bio-based composites reached ~20% of biodegradation after 20 days under composting conditions [315], whereas under AD at mesophilic temperatures biodegradation presented a lower rate with ~16% after 20 days for 60wt% of ATF. Degradation rates, as well as CH_4 production values, were higher for alkali-treated samples when compared to untreated counterparts. The maximum CH_4 production was observed by alkali-treated samples at 60wt% of ATF content, with a cumulative of ~20 ml CH_4/gVS, whereas untreated samples at 60wt% of ATF content produced ~17 ml CH_4/gVS. Alkali and untreated samples at 20wt% of ATF content observed a reduction in CH_4 of about 10% and 13% respectively. Neat PLA produced a marginal ~11 ml CH_4/gVS. The difference observed in biodegradation and CH_4 production was the result of the difference in ATF wt% content, as well as the level of delignification of ATF as lignin has been recognised to present issues to biodegrade [338]. The lower biodegradation observed by the materials under AD was the result of a high fatty acid concentration, as indicated by the acidic 5.0 pH of the sludge recorded at the end of the test. Therefore, degradation values observed during AD serve this study only as an indicative element of the increased degradability rate of the material above neat PLA by ~2.5 factor. Additionally, more experiments at thermophilic temperatures and with a constant pH monitoring are needed to completely understand the AD process, maximum biodegradation and CH_4 rates for ATF/PLA bio-based materials.

Energy recovery through incineration of ATF/PLA bio-based composites represents the last alternative considered for this material before landfilling on the waste management hierarchy for the material.

Landfilling is considered the worst scenario as an end-of-life route for ATF/PLA bio-based materials. Despite its CO_2 neutral character, ATF/PLA bio-based composites under landfilling conditions will still produce ~2.0 times more CH_4 than neat PLA. This is important to be considered as CH_4 capture in landfills have an efficiency between 55-91% [360] and methane released into the atmosphere has major implications than CO_2 [303]. Landfilling should be avoided, and the use of ATF/PLA bio-based composites should be seen as a way to divert organic materials from the landfill to WtE facilities as a mitigating solution as long as new technology embracement, a cultural shift towards a more sustainable behaviour and governmental support are in place.

10 Conclusions and future work

The conclusions provided in this section are general and related to the objectives stated in section 1.3 Aims and objectives. For detailed conclusions, please refer to each chapter. Further work is included for every objective.

Objective 1: To outline a design thinking-based method for the conceptualization and development of a more sustainable material based on agro-industrial by-products.

This objective was covered in chapter 3 "Design thinking approach as a sustainable innovation enabler in new material developments". Here, the holistic approach offered by the “design thinking” method, used at the early stage of the material conceptualization, allowed the identification and better understanding of sustainable constraints in the new material development. The systemic nature of the method delivered insights from the different factors that influence sustainability in a new material development. Additionally, the “design thinking” approach had the potential and flexibility to work as a contingent framework in supporting the R&D strategies in the material development. It was concluded that the engagement of sustainable issues through holistic approaches such as “design thinking” enable sustainable innovation, and provide some degree of enhanced utility, cost avoidance, value, quality improvement, among others to the development of new materials.

Objective 2: To advance in the understanding of *Agave tequilana* fibres properties through characterisation.

This objective was dealt in: “Characterisation of natural fibres from tequila production waste stream to evaluate their reuse as composites reinforcement”.

In this section, a thorough understanding of the waste was achieved through its characterization in order to validate its use in new material developments, and more importantly, to comprehend its limitations as a raw material source for bio-composites. *Agave tequilana* fibres from tequila production were found to have higher mechanical properties to those reported in earlier studies [102]. Although these properties were lower when compared to other well-used fibres specifically produced for bio-composite applications [195], it has been determined their use as a feasible raw material source in bio-based materials for non-load bearing applications. The use of ATF represents a low cost with acceptable specific strength, compostability and biodegradability properties. However, the inherent non-homogeneous morphology and structure of *Agave tequilana* fibres requires further study, to unify and improve their technical and quality properties and to understand the major variations between sources. The pre-treatments used offered a shift in the perception of ATF, from waste into a raw material source.

Objective 3: To analyse the effects of surface treatments on ATF properties.

The effect of several surface treatments on ATF properties and interfacial bonding with PLA, as well as the determination of the best parameters for ATF were studied experimentally in: “Surface treatments on natural fibres from tequila production waste”. It was concluded that the best outcomes regarding tensile strength and interfacial shear strength, were observed for the alkali-treated fibres, and results were correlated to the increment in roughness on the fibre’s surface area, due to the removal of non-cellulosic compounds. New knowledge related to the effect of surface treatments for ATF has been provided as a result of this study. New possibilities for ATF use as a raw material source in other bio-based composites can be derived from these results. From an environmental point of view, some implications must be reviewed as some treatments are more energy intensive in comparison with others. A balance between benefit, cost and environmental impact must be at the centre of whether or not a treatment must be contemplated.

Objective 4: To assess the effects of fibre treatments and fibre content on mechanical and physical properties (e.g. tensile, flexural, impact and moisture) of ATF/PLA composites, compounded by extrusion moulding and film-stacking method.

This objective was covered in: “Extrusion moulding of a novel Agave tequilana fibre *and poly*(lactic) acid-based composite: a study of tensile, impact, flexural and water uptake properties" and in: “Tensile, impact, flexural and water uptake properties of an Agave tequilana fibre *and poly*(lactic) acid-based composite using film-stacking method" through the manufacturing of the actual material via extrusion moulding, as it was considered a fundamental process from an industrial embracement perspective, and through film stacking method, as it allowed a higher fibre volume fraction. Despite ATF and PLA presented an inherent compatibility, a reinforcing effect from ATF was not observed in both cases. The properties of the material were comparable and in some cases superior to those presented by GPPS. Hence, ATF/PLA bio-based composite was proposed for applications that do not demand high mechanical strength. However, extrusion moulding as manufacturing process presented some setbacks, as ATF fibre aspect ratio was reduced and a high ATF % content was hard to reach. On the other hand, and despite film stacking manufactured materials contained a higher fibre volume fraction, the method itself shown some flaws in the processability of the material as matrix flow was not uniformly distributed. Further research to optimise extrusion process with higher natural fibre content, as well as better matrix melt flow in the film stacking manufacturing method, is considered the main step towards industrialisation of this kind of materials as it will offer a bigger range of applications and a wider acceptance.

Objective 6: To analyse the possible end-of-life alternatives of ATF/PLA composites (i.e. reprocessing, composting, incineration, aerobic digestion and landfill) and **Objective 7:** To draft the implications from the possible integration of a fully biodegradable ATF/PLA bio-based material in a circular economy framework within a Mexican waste management scenario

These objectives were dealt with in chapter 8 ”Disposal route analysis of a bio-based material and its integration within a circular economy framework”. through the assessment of different end-of-life routes for the AT/PLA bio-based composite within the Mexican WMS. Despite results from AD were not conclusive, they offer and indicative point of comparison between different WtE technologies available. The *“best”* option as an end-of-life rote, for the material studied, is the biological recycling through AD or composting, only followed by energy recovery through combustion. The higher % content of ATF increases the BMP in the material. Further work regarding maximum CH_4 yield is suggested. Landfilling, with and without energy recovery, has been considered the worst but the most probable route to be followed for the ATF/PLA bio-based composite due to the present waste management conditions in Mexico. The potential for WtE for ATF/PLA bio-based composites which could otherwise be managed higher up in the waste hierarchy is a concern in the Mexican scenario. This is not an issue arising from WtE as a process, but rather as a result of opportunities not being taken to divert materials from waste streams.

11 References

1. Campbell, C. J. and Laherrère J. H. (1998) 'The end of cheap oil', *Scientific American,* 278(3): 60–65.
2. Sorrentino, A., Gorrasi, G. and Vittoria, V. (2007) 'Potential perspectives of bio-nanocomposites for food packaging applications', *Trends in Food Science & Technology*, Elsevier, 18(2): 84–95.
3. Zikmund, W. G. and Stanton, W. J. (1971) 'Recycling solid wastes: a channels-of-distribution problem', *The Journal of Marketing*, 34-39.
4. PlasticsEurope, (2007) *The compelling facts about plastics*. Available at: http://www.plasticseurope.org/DocShareNoFrame/docs/2/LPKOHJHDDAJFEAAJLHBNMOOAF6U9YCF9SO63Q68THNPD/PlasticsEurope/docs/DLS/Final_F actsFigures2007_PublishedOct2008_final-20081020-002-EN-v1.pdf (Accesed: December 2013)
5. PlasticsEurope, (2009) *The compelling facts about plastics 2009*. Available at: http://www.plasticseurope.org/DocShareNoFrame/docs/4/LPKOHJHDDAJFEAAJLHBNMOOART4LTAYD49BCF9SO63Q6/PlasticsEurope/docs/DLS/Brochure_UK_FactsFigures_2009_22sept_6_Final-20090930-001-EN-v1.pdf (Accesed: December 2013)
6. Miller, R. (2005) *The landscape for bioploymers in packaging*. Available at:http://miller-klein.com/wp-content/uploads/2016/12/2007LandscapeforBiopolymers.pdf (Accesed: January 2015)
7. Pira. S. (2012) *The future of global packaging to forecasts to 2016*. Available at: https://www.smitherspira.com/market-reports/global-packaging-industry-expected-to-reach-820-billion-by-2016.aspx (Accesed: January 2014)
8. Ernst & Young Limited, (2013) *Unwrapping the packaging industry: Seven factors for success*. United Kingdom: EYGM Limited. Available at: http://www.ey.com/Publication/vwLUAssets/Unwrapping_the_packaging_industry_%E2%80%93_seven_factors_for_success/$FILE/EY_Unwrapping_the_packaging_industry_-_seven_success_factors.pdf (Accesed: January 2014)
9. Robertson, G. L. (2016). *Food packaging: principles and practice*. CRC press.
10. Mark, J. E. (1999) *Polymer data handbook Oxford Univ*. Press New York, NY p. 363.
11. Green Industries, (2013) *Food packaging wastes and environmental impacts*. Available at: http://www.greendustries.com/unido.pdf (Accessed: 1 November 2013)
12. Northwood, D. and Oakley-Hill D. T. (1999) *Wastebook*, Luton friends of the earth, environment agency and the building research establishment.
13. LRRA. Recycling Audits (1996) *Garbage analysis*. Melbourne.

14. Klingbeil, M. (2000) *Working document of biodegradable waste management*. Brussels, European Commission.

15. Marsh, K. (1991) 'Effective management of food packaging: from production to disposal [IFT scientific status summary]', *Food Tech*. Institute of food technologists, 45(5): 225–234.

16. Hunt, R. G., Sellers, V. R., Frankalin, W. E., Nelson, J. M., Rathje, W. L. and Hughes, W. W. (1990) *Estimates of the volume of MSW and selected components in trash cans and land fills.* Report prepared by The garbage project and Franklins Assn. Ltd. for the Council for solid waste solutions. Tucson, Ariz.

17. Indice Environnemental, (2014) *Les produits porteurs de l'Indice environnemental*. Available at: http://www.indice-environnemental.fr/les_produits/produit_w?id=60 (Accessed: 1 June 2014)

18. Bez, J. and Heyde, G. M. (1998) 'Waste treatment in product specific lifc cycle inventories, an approach of material-related modelling', part II: sanitary landfill. *Int. J. LCA*. (3): 100–105.

19. Finnveden, G., Albertsson, A-C., Berendson, J., Eriksson, E., Höglund, L. O., Karlsson, S., et al. (1995) 'Solid waste treatment within the framework of life-cycle assessment', *J. Cleaner Prod*. (3): 189–199.

20. EFIB. European Forum for Industrial Biotechnology and the Biobased Economy. (2013) 'Interview with P&G on biobased packaging'. Available at: http://efibforum.com/pg-on-the-future-of-plant-pet.aspx (Accessed: 20 May 2012)

21. Hockensmith, D. (2010) 'P&G outlines broad sustainability plans'. *Plastics News*. 22(30): 23.

22. Rossy, A., Jones, P. T., Geysen, D. and Bienge, K. (2010) 'Sustainable Materials Management for Europe, from efficiency to effectiveness'.

23. Wegst, U. G. K., and Ashby, M. F. (2004) 'The mechanical efficiency of natural materials', *Philosophical Magazine*, 84(21), 2167-2186.

24. Ashby, M. F. and Johnson, K. (2013) *Materials and design: the art and science of material selection in product design*. Butterworth-Heinemann.

25. Ashby, M. F., Shercliff. H. and Cebon, D. (2013) *Materials: engineering, science, processing and design*. Butterworth-Heinemann.

26. Granta Design (2016) CES EduPack. Cambridge, England.

27. MatWeb (2016) Available at: http://www.matweb.com/ (Accessed: 1 November 2015)

28. Checkland, P. B. (1981) *Systems thinking, systems practice*. J. Wiley

29. Checkland, P. B. (1988) 'Information systems and systems thinking: time to unite', *International Journal of Information Management*. Elsevier, 8(4): 239–248.

30. Hall, A. D. (1962) *A methodology for systems engineering*. Van Nostrand.

31. Ulrich, W. (1983) *Critical heuristics of social planning: A new approach to practical philosophy.*

32. Lovins, A. B., Lovins, L. H., and Hawken, P. (1999). ‘A road map for natural capitalism’, *Harvard business review*, 77, 145-161.

33. Freeman, C. (1996) ‘The greening of technology and models of innovation’, *Technological Forecasting and Social Change*. North-Holland, 53(1): 27–39. Available at: DOI:10.1016/0040-1625(96)00060-1 (Accessed: 25 August 2016)

34. Pearce, D. W. and Turner, R. K. (1990) *Economics of natural resources and the environment.* JHU Press.

35. MacArthur E. (2013) ‘Towards the circular economy’, *Journal of Industrial Ecology*.

36. Klemmer, P., Lehr, U. and Loebbe, K. (1999) ‘Environmental Innovation’, Volume 3 of publications from a Joint Project on Innovation Impacts of Environmental Policy Instruments. Synthesis Report of a project commissioned by the German Ministry of Research and Technology, Analytica-Verlag, Berlin.

37. Rennings, K. (2000) ‘Redefining innovation — eco-innovation research and the contribution from ecological economics’, *Ecological Economics*. 32(2): 319–332. Available at: DOI:10.1016/S0921-8009(99)00112-3

38. Young, G. (2010) ‘Design thinking and sustainability’, *Zumio Meaningful Innovation*. 61(0): 1–27.

39. Buchanan, R. (1992) ‘Wicked problems in design thinking’, *Design issues*. JSTOR, 8(2): 5–21.

40. McDonough, W. and Braungart, M. (2002) *Remaking the way we make things: Cradle to cradle*. New York: North Point Press. ISBN. 1224942886: 104.

41. Li, G., Sarazin, P., Orts, W. J., Imam, S. H. and Favis, B. D. (2011) ‘Biodegradation of thermoplastic starch and its blends with poly (lactic acid) and polyethylene: influence of morphology’, *Macromolecular chemistry and physics*. Wiley Online Library, 212(11): 1147–1154.

42. Bledzki, A. K. K. and Jaszkiewicz, A. (2010) ‘Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres – A comparative study to PP’, *Composites Science and Technology*. Elsevier Ltd, 70(12): 1687-1696. Available at: DOI:http://dx.doi.org/10.10 16/j.compscitech.2010.06.005

43. Huda, M. S., Mohanty, A. K., Drzal, L. T., Schut, E. and Misra, M. (2005) ‘Green composites from recycled cellulose and poly (lactic acid): Physico-mechanical and morphological properties evaluation’, *Journal of Materials Science*. Springer, 40(16): 4221–4229.

44. Schut, J. H. (2007) ‘Foamed PLA Shows promise in biodegradable meat trays’, *Plastics Technology*, 53(12): 39–43.

45. Takagi, H., Kako, S., Kusano, K. And Ousaka, A. (2007) 'Thermal conductivity of PLA-bamboo fiber composites', *Advanced Composite Materials*. Taylor & Francis, 16(4): 377–384. Available at: DOI:10.1163/156855107782325186

46. Nourbakhsh, A. and Ashori, A. (2010) 'Wood plastic composites from agro-waste materials: Analysis of mechanical properties', *Bioresource technology*. Elsevier, 101(7): 2525–2528.

47. Tolinski, M. (2011) *Plastics and sustainability: towards a peaceful coexistence between bio-based and fossil fuel-based plastics,* New Jersey: John Wiley & Sons, 53 p.

48. Kowalczyk, M., Piorkowska, E., Kulpinski, P. and Pracella, M. (2011) 'Mechanical and thermal properties of PLA composites with cellulose nanofibers and standard size fibers', *Composites Part A: Applied Science and Manufacturing*, 42(10): 1509–1514. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2011.07.003

49. Mathew, A. P., Oksman, K. and Sain, M. (2005) 'Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC) assesment of PLA composite biodegradability', *Journal of Applied Polymer Science*. Wiley Subscription Services, Inc., A Wiley Company, 97(5): 2014–2025. Available at: DOI:10.1002/app.21779

50. Oksman, K. and Selin, J. F. (2004) 'Plastics and Composites from Polylactic Acid', in: Wallenberger, F. and Weston, N. (eds.) *Natural Fibers, Plastics and Composites*. Springer US, pp. 149–165. Available at: DOI:10.1007/978-1-4419-9050-1_10

51. Rowell, R. M. (1998) 'Property enhanced natural fiber composite materials based on chemical modification', *Science and technology of polymers and advanced materials*. Springer, pp. 717–732.

52. Mohanty, A. K., Misra, M. and Drzal, L. T. (2001) 'Surface modifications of natural fibres and performance of the resulting biocomposites: an overview', *Composite Interfaces*, (8): 313–343.

53. Hu, R. and Lim, J. K. (2007) 'Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites', *Journal of Composite Materials*, 41(13): 1655–1669. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-34347334462&partnerID=40&md5=ff7d5e55b156164dabf8254c047389f7

54. Bisanda, E. and Ansell, M. (1992) 'Properties of sisal-CNSL composites', *Journal of Materials Science,* Kluwer Academic Publishers, 27(6): 1690–1700. Available at: DOI:10.1007/BF00542934

55. Huda, M. S., Drzal, L. T., Mohanty, A.K. and Misra, M. (2008) 'Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (PLA) and kenaf fibers', *Composites Science and Technology.* 68(2): 424-432. Available at: DOI:http://dx.doi.org/10.1016/j.compscitech.2007.06.022

56. Iñiguez-Covarrubias, G., Díaz-Teres, R., Sanjuan-Dueñas, R., Anzaldo-Hernández, J. and Rowell, R. M. (2001) 'Utilization of by-products from the tequila industry. Part 2: potential value of Agave tequilana Weber azul leaves'. *Bioresource technology*, 77(2): 101–108. Available at: DOI:http://dx.doi.org/10.1016/S0960-8524(00)00167-X

57. Íñiguez, G., Valadez, A., Manríquez, R. and Moreno, M. V. (2011) 'Utilization of by-products from the tequila industry', *Revista Internacional de Contaminación Ambiental.* Universidad Nacional Autónoma de México, 27(1): 61–74.

58. Earth Resource Foundation. *Polystyrene Foam Report*. Available at: http://www.earthresource.org/campaigns/capp/capp-styrofoam.html (Accessed: 14 October 2015)

59. Hartmann, M. H. (1998) 'High molecular weight polylactic acid polymers', In: David, L. K. (ed.) *Biopolymers from renewable resources*. Berlin, Germany: Springer, pp. 367–411.

60. Sawyer, D. J. (2003) 'Bioprocessing – no longer a field of dreams', *Macromolecular Symposia*, 201(1): 271–282. Available at: DOI:10.1002/masy.200351130

61. Iñiguez-Covarrubias G., Lange SE., Rowell RM. Utilization of byproducts from the tequila industry: part 1: Agave bagasse as a raw material for animal feeding and fiberboard production. Bioresource technology. 2001; 77(1): 25–32. Available at: DOI:http://dx.doi.org/10.1016/S0960-8524(00)00137-1

62. Oksman, K., Skrifvars, M. and Selin, J. F. F. (2003) 'Natural fibres as reinforcement in polylactic acid (PLA) composites', *Eco-Composites*, 63(9): 1317–1324. Available at: DOI:http://dx.doi.org/10.1016/S0266-3538(03)00103-9

63. Hassan, E. (2012) 'Plant fibers reinforced poly(lactic) acid (Pla) as green composites : Review', *International journal of engineering science and technology*, 4(10): 4429–4439.

64. Kaw, A. K. (2005) *Mechanics of composite materials*. New York: CRC press, 490 p. Available at: DOI:10.1016/j.fsigen.2011.07.001

65. Adamson, A. W. and Gast, A. P. (1997) *Physical chemistry of surfaces*. New York: Interscience publishers.

66. Saheb, D. N., Jog, J. P., Nabi-Saheb, D. and Jog, J. P. (1999) 'Natural fiber polymer composites : a review', *Advances in polymer technology*, 18(4): 351–363. Available at: DOI:10.1002/(SICI)1098-2329(199924)18

67. Mohanty, A. K., Misraa, M. and Hinrichsen, G. (2004) *Biofibres, biodegradable polymers and biocomposites*. Technical University of Berlin, Institute of nonmetallic materials, polymer physics, englische str. 20, d-10587 berlin, germany.

68. Narayan, R. (2006) 'Biobased and biodegradable polymer materials: rationale, drivers, and technology exemplars', *American Chemical*

Society Symposium. Available at: http://standards.nsf.org/apps/group_public/download.php/5554/Narayan ACS BK Chapter Publication 2005 biobased %26 biodegradable FINAL REVISED.pdf (Accessed: 28 March 2016)

69. Joshi, S. V., Drzal, L. T., Mohanty, A. K. and Arora, S. (2004) ‘Are natural fiber composites environmentally superior to glass fiber reinforced composites?’, *Composites Part A: Applied science and manufacturing*. Elsevier; 35(3): 371–376.

70. Zini, E. and Scandola, M. (2011) ‘Green composites: An overview’, *Polymer Composites*. Wiley Subscription Services, Inc., A Wiley Company, 32(12): 1905–1915. Available at: DOI:10.1002/pc.21224

71. Fowler, P. A., Hughes, J. M. and Elias, R. M. (2006) ‘Biocomposites: technology, environmental credentials and market forces’, *Journal of the science of food and agriculture*, John Wiley & Sons, Ltd., 86(12): 1781–1789. Available at: DOI:10.1002/jsfa.2558

72. Shah, A. A., Hasan, F., Hameed, A. and Ahmed, S. (2008) ‘Biological degradation of plastics: a comprehensive review’, *Biotechnology Advances*. Elsevier, 26(3): 246-265. Available at: DOI:10.1016/j.biotechadv.2007.12.005

73. Gautam SP., Pollution C., Board C., Environment MOF. Bio-degradable Plastics- Impact on Environment CENTRAL POLLUTION CONTROL BOARD. Control. 2009; 2009: 1–46.

74. Gruber, P. and O’Brien, M. (2005) ‘Polylactides ‘NatureWorks® PLA’, *Biopolymers Online*. Wiley-VCH Verlag GmbH & Co. KGaA, Available at: DOI:10.1002/3527600035.bpol4008

75. Spinu, M., Jackson, C., Keating, M. Y. and Gardner, K.H. (1996) ‘Material design in poly(lactic acid) systems: block copolymers, star homo- and copolymers, and stereocomplexes’, *Journal of macromolecular science, Part A.* Taylor & Francis, 33(10): 1497–1530. Available at: DOI:10.1080/10601329608014922

76. Garlotta, D. A, (2001) ‘Literature Review of Poly(Lactic Acid)’, *Journal of Polymers and the Environment*. Kluwer Academic Publishers-Plenum Publishers, 9(2): 63–84. Available at: DOI:10.1023/A:1020200822435

77. Sawyer, D. (2003) ‘Bioprocessing ? no longer a field of dreams’, *Macromolecular Symposia*, Wiley-VCH Verlag, 201(1): 271–282. Available at: DOI:10.1002/masy.200351130

78. Vink, E. T.H., Rábago, K. R., Glassner, D. A. and Gruber, P. R. (2003) ‘Applications of life cycle assessment to NatureWorks^{TM} polylactide (PLA) production’. *Polymer Degradation and Stability*, 80(3): 403–419. Available at: DOI:http://dx.doi.org/10.1016/S0141-3910(02)00372-5

79. The Ellen MacArthur foundation, (2016) *The new plastics economy: Rethinking the future of plastics*. Ellen MacArthur Foundation, 120.

80. Perepelkin, K. E. (2002) ‘Polylactide fibres: fabrication, properties, use,

prospects: a review', *Fibre chemistry.* Kluwer academic publishers-plenum publishers, 34(2): 85-100. Available at: DOI:10.1023/A:10163599 25976

81. Zhang, J. F. and Sun, X. (2004) 'Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride. Biomacromolecules', *American chemical society* 5(4): 1446–1451. Available at: DOI:10.1021/bm0400022

82. Mohanty, A. K., Misra, M. and Drzal, L. T. (2002) 'Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world', *Journal of polymers and the environment.* Kluwer Academic Publishers-Plenum Publishers, 10(1-2): 19–26. Available at: DOI:10.1023/A:1021013921916

83. Pradhan, R., Misra, M., Erickson, L. and Mohanty, A. (2010) 'Compostability and biodegradation study of PLA–wheat straw and PLA–soy straw based green composites in simulated composting bioreactor', *Bioresource technology*, 101(21): 8489–8491. Available at: DOI:http://dx.doi.org/10.1016/j.biortech.2010.06.053

84. Kale, G., Auras, R. and Singh, S. P. (2006) 'Degradation of commercial biodegradable packages under real composting and ambient exposure conditions', *Journal of polymers and the environment.* Kluwer Academic Publishers-Plenum Publishers, 14(3): 317–334. Available at: DOI:10.1007/s10924-006-0015-6

85. Kale, G., Auras, R., Singh, S. P. and Narayan R. (2007) 'Biodegradability of polylactide *bottles in real and simulated composting conditions', Polymer Testing*. 26(8): 1049–1061. Available at: DOI:http://dx.doi.org/10.1016/j.polymertesting.2007.07.006

86. Rudeekit, Y., Numnoi, J., Tajan, M., Chaiwutthinan, P. and Leejarkpai, T. (2008) 'Determining biodegradability of polylactic acid under different environments', *J Metals Mater Min*., 18(2): 83–87.

87. Ho, K., Pometto, III A., Gadea-Rivas, A., Briceño, J. and Rojas, A. (1999) 'Degradation of polylactic acid (pla) plastic in Costa Rican soil and Iowa State University compost rows', *journal of environmental polymer degradation*. kluwer academic publishers-plenum publishers, 7(4): 173–177. available at: doi:10.1023/a:1022874530586 (Accessed: 27 November 2015)

88. Sinclair, R. G. (1996) 'The case for polylactic acid as a commodity packaging plastic', *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*. Taylor & Francis; 1996; 33(5): 585–597. Available at: DOI:10.1080/10601329608010880

89. Siracusa, V., Rocculi, P., Romani, S. and Rosa, M. D. (2008) 'Biodegradable polymers for food packaging: a review', *Trends in Food Science & Technology*. Elsevier, 19(12): 634–643. Available at: DOI:10.1016/j.tifs.2008.07.003

90. Bos, H. L., Meesters, K. P., Conijn, S. G., Corré, W. J., & Patel, M. K.

(2012). Accounting for the constrained availability of land: A comparison of bio-based ethanol, polyethylene, and PLA with regard to non-renewable energy use and land use. *Biofuels, Bioproducts and Biorefining*, *6*(2), 146-158.

91. Sutivisedsak, N., Cheng, H. N., Dowd, M. K., Selling, G. W. and Biswas, A. (2012) ‘Evaluation of cotton by-products as fillers for poly(lactic acid) and low density polyethylene’, *Industrial Crops and Products*, 36(1): 127–134. Available at: DOI:http://dx.doi.org/10.1016/j.indcrop.2011.08.016

92. Plackett, D., Løgstrup-Andersen, T., Batsberg-Pedersen, W. and Nielsen L. (2003) ‘Biodegradable composites based on l-polylactide and jute fibres’, *Composites Science and Technology*, 63(9): 1287–1296. Available at: DOI:10.1016/S0266-3538(03)00100-3

93. Gassan, J. and Bledzki, A. K. (1999) ‘Possibilities for improving the mechanical properties of jute/epoxy composites by alkali treatment of fibres’, *Composites Science and Technology,* 59(9): 1303–1309. Available at: DOI:http://dx.doi.org/10.1016/S0266-3538(98)00169-9

94. Zini, E., Baiardo, M., Armelao, L., Scandola, M. ‘Biodegradable polyesters reinforced with surface-modified vegetable fibers’, *Macromolecular bioscience.* Wiley-vch verlag, 4(3): 286–295. Available at: DOI:10.1002/mabi.200300120

95. Bogren, K. M., Gamstedt, E. K., Neagu, R. C., AÅkerholm, M. and LindstroÖm, M. (2006) ‘Dynamic–mechanical properties of wood–fiber reinforced polylactide: experimental characterization and micromechanical modeling’, *Journal of thermoplastic composite materials*. 19(6): 613–637. Available at: DOI:10.1177/0892705706067480

96. Masirek, R., Kulinski, Z., Chionna, D., Piorkowska, E. and Pracella, M. (2007) ‘Composites of poly (L-lactide) with hemp fibers: Morphology and thermal and mechanical properties’, *Journal of Applied Polymer Science*. Wiley Online Library; 2007; 105(1): 255–268.

97. Pan, P., Zhu, B., Kai, W., Serizawa, S., Iji, M. and Inoue, Y. (2007) ‘Crystallization behavior and mechanical properties of bio-based green composites based on poly (L-lactide) and kenaf fiber’, *Journal of Applied Polymer Science*. Wiley Online Library, 105(3): 1511–1520.

98. Lee, S. H. and Wang, S. (2006) ‘Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent’, *Composites Part A: Applied Science and Manufacturing*, 37(1): 80–91. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2005.04.015

99. Stamboulis , A., Baillie, C. A., Peijs, T. (2001) Effects of environmental conditions on mechanical and physical properties of flax fibers. Composites Part A: Applied Science and Manufacturing. 2001; 32(8): 1105–1115. Available at: DOI:10.1016/S1359-835X(01)00032-X

100. Baillie, C. (2005) *Green composites: Polymer composites*.

101. Kollman, F. F. P., and Côté, W. A. (1968). *Principles of wood science and technology: solid wood*. Allen & Unwin.

102. Kestur, G. S., Flores-Sahagun, T. H. S., Dos Santos, L.P., Dos Santos, J., Mazzaro, I. and Mikowski, A. (2013) ‘Characterization of blue Agave bagasse fibers of Mexico’, *Composites Part A: Applied Science and Manufacturing*. Elsevier Ltd., 45(0): 153–161. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2012.09.001

103. Mwaikambo, L. Y. and Ansell, M. P.(2002) ‘Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization’, *Journal of Applied Polymer Science*. Wiley Subscription Services, Inc., A Wiley Company, 84(12): 2222–2234. Available at: DOI:10.1002/app.10460

104. White, N. M. and Ansell, M. P. (1983) ‘Straw-reinforced polyester composites’, *Journal of Materials Science.* Kluwer Academic Publishers, 18(5): 1549–1556. Available at: DOI:10.1007/BF01111977

105. Akin, D. (2010) ‘What are natural fibres? : Chemistry of natural fibres’, in: Müssig, J. (ed.) *Industrial applications of natural fibres: structure, properties and technical applications*, John Wiley & Sons, pp. 13–21.

106. Klemm, D., Philip, B., Heinze, T., Heinze, U., Wagenknecht, W. Klemm, D., et al. (1998) ‘Text Book of Comprehensive Cellulose Chemistry, Volume 1, Fundamentals and Analytical Methods’, Weinheim, Germany: Wiley-VCH.

107. Baker, C. A. (1997) ‘The fundamentals of papermaking materials’, in: Baker, C. F. (ed.) *The Fundamentals of Papermaking Materials,* Transactions of the 11th Fundamental Research Symposium. Cambridge: Pira Internationals, p. 1097.

108. Hiesh, Y. L., Thompson, J. and Miller, A. (1996) ‘Water wetting and retention of cotton assemblies as affected by alkaline and bleaching treatment’, *Textile Research Journal,* (66): 456.

109. Ribitsch, V., Stana-Kleinschek, K. and Jeler, S. (1996) ‘The influence of classical and enzymatic treatment on the surface change of cellulose fibres’, *Colloid and Polymer Science*, 4: 388–394.

110. Yao, F., Wu, Q., Lei, Y., Guo, W. and Xu, Y. (2008) ‘Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis’, *Polymer Degradation and Stability*, 93(1): 90–98. Available at: DOI:10.1016/j.polymdegradstab.2007.10.012

111. Monteiro, S. N., Calado, V., Rodriguez, R. J. S. and Margem, F. M. (2012) ‘Thermogravimetric stability of polymer composites reinforced with less common lignocellulosic fibers - An overview’, *Journal of Materials Research and Technology*. Elsevier, 1(2): 117–126. Available at: DOI:10.1016/S2238-7854(12)70021-2

112. De Paiva, J. M. F. and Frollini, E. (2006) ‘Unmodified and modified surface sisal fibers as reinforcement of phenolic and lignophenolic matrices composites: Thermal analyses of fibers and composites’,

Macromolecular Materials and Engineering, 291(4): 405–417. Available at: DOI:10.1002/mame.200500334

113. Mohanty, A. K., Patnaik, S., Singh, B. C. and Misra, M. (1989) ‘Graft copolymerization of acrylonitrile onto acetylated jute fibers’, *Journal of Applied Polymer Science*, 37(5): 1171–1181. Available at: DOI:10.1002/app.1989.070370502

114. John, M. J. and Anandjiwala, R. D. (2008) ‘Recent developments in chemical modification and characterization of natural fiber-reinforced composites’, *Polymer Composites*. Wiley Subscription Services, Inc., A Wiley Company, 29(2): 187–207. Available at: DOI:10.1002/pc.20461

115. Winfield, A. G. (1979) ‘Jute reinforced polyester, project for UNIDO, Govt of India’. *Plastic and Rubber International*, 4: 23.

116. George, J., Sreekala, M. S. and Thomas, S. (2001) ‘A review on interface modification and characterization of natural fiber reinforced plastic composites’, *Polymer Engineering & Science*. Wiley Subscription Services, Inc., A Wiley Company, 41(9): 1471–1485. Available at: DOI:10.1002/pen.10846

117. Li, X., Tabil, L. G. and Panigrahi, S. (2007) ‘Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review’, *Journal of Polymers and the Environment*. Kluwer academic publishers-Plenum publishers, 15(1): 25–33. Available at: DOI:10.1007/s10924-006-0042-3

118. Bledzki, A. K. and Gassan, J. (1998) ‘Natural Fiber Reinforced Plastics’. in: Cheremisinoff, N. P. (ed.) *Handbook of Engineer Polymeric Materials*. New York: Marcel Dekker Inc., pp. 787–810.

119. Zeronian, S. H., Kawabata, H. and Alger, K. W. (1990) ‘Factors affecting the tensile properties of nonmercerized and mercerized cotton fibers’, *Textile Research Journal*, 60(3): 179–183.

120. Semsarzadeh, M. A. (1986) ‘Fiber matrix interactions in jute reinforced polyester resin’, *Polymer Composites*, 7(2): 23–25.

121. Semsarzadeh, M. A., Abdol, R. L. and Hamid, M. (1984) ‘Jute reinforced polyester structures’, *Polymer composites*, 5(2): 141–142.

122. Ray, P. K., Chakravarty, A. C. and Bandyopadhyay, S. B. (1976) ‘Fine structure and mechanical properties of jute differently dried after retting’, *Journal of applied polymer science*, 20(7): 1765–1767.

123. Rowell, C. V. (1932) *388.561*: Process for decorticating vegetable fibre and the manufacture of products therefrom. United Kingdom.

124. Bismarck, A., Mohanty, A. K., Aranberri-Askargorta, I., Czapla, S., Misra, M., Hinrichsen, G., et al. (2001) ‘Surface characterization of natural fibers; surface properties and the water up-take behavior of modified sisal and coir fibers’, *Green Chemistry*. Royal Society of Chemistry, 3(2): 100–107.

125. Bledzki, A. K. A., Mamun, A. A. A., Lucka-Gabor, M. and Gutowski, V. S.

(2008) ‘The effects of acetylation on properties of flax fibre and its polypropylene composites’, *Express Polym Lett*., 2(6): 413–422. Available at: DOI:10.3144/expresspolymlett.2008.50 (Accessed: 27 November 2015)

126. Liu, F. P., Wolcott, M. P., Gardner, D. J. and Rials, G. T. (1994) ‘Characterization of the interface between cellulose fibers and a thermoplastic matrix’, *Journal of Composite Interfaces*, (2): 419–432.

127. Paul, A., Joseph, K., Thomas, S. and Thorna, S. (1997) ‘Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibers’, *Composites Science and Technology,* 57(1): 67-79. Available at: DOI:http://dx.doi.org/10.1016/S0266-3538(96)00109-1

128. Rong, M. Z., Zhang, M. Q., Liu, Y., Yang, G. C. and Zeng, H. M. (2001) ‘The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites’, *Composites Science and Technology*, 61(10): 1437-1447. Available at: DOI:http://dx.doi.org/10.1016/S0266-3538(01)00046-X

129. Sreekala, M. S., Kumaran, M. G. and Thomas, S. (1997) ‘Oil palm fibers: Morphology, chemical composition, surface modification, and mechanical properties’, *Journal of Applied Polymer Science*. John Wiley & Sons, Inc., 66(5): 821-835. Available at: DOI:10.1002/(SICI)1097-4628(19971031)66:5<821::AID-APP2>3.0.CO;2-X

130. Tserki, V., Zafeiropoulos, N. E., Simon, F. and Panayiotou, C. (2005) ‘A study of the effect of acetylation and propionylation surface treatments on natural fibres’, *ACMC/SAMPE Conference on Marine Composites (MarComp) 2003*, pp. 1110-1118. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2005.01.004

131. Zafeiropoulos, N. E., Williams, D. R., Baillie, C. A. and Matthews, F. L. (2002) ‘Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part I. Development and investigation of surface treatments’, *Composites Part A: Applied Science and Manufacturing*, 33(8): 1083-1093. Available at: DOI:http://dx.doi.org/10.1016/S1359-835X(02)00082-9

132. Herrera-Franco, P. J. J. and Valadez-González, A. (2005) ‘A study of the mechanical properties of short natural-fiber reinforced composites’, *Composites Part B: Engineering*, 36(8): 597–608. Available at: DOI:http://dx.doi.org/10.1016/j.compositesb.2005.04.001

133. Sgriccia, N., Hawley, M. C. C. and Misra, M. (2008) ‘Characterization of natural fiber surfaces and natural fiber composites’, *Composites Part A: Applied Science and Manufacturing*, 39(10): 1632–1637. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2008.07.007

134. Wang, Y., Tong, B., Hou, S., Li, M. and Shen, C. (2011) ‘Transcrystallization behavior at the poly(lactic acid)/sisal fibre biocomposite interface’, *Composites Part A: Applied Science and*

Manufacturing. Elsevier Ltd., 42(1): 66–74. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2010.10.006

135. Islam, M. S. S., Pickering, K. L. L. and Foreman, N. J. J. (2010) ‘Influence of alkali treatment on the interfacial and physico-mechanical properties of industrial hemp fibre reinforced polylactic acid composites’, *Composites Part A: Applied Science and Manufacturing*. Elsevier Ltd., 41(5): 596-603. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa. 2010.01.006

136. Jacob, M., Thomas, S. and Varughese, K. T. T. (2004) ‘Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites’, *Composites Science and Technology*, 64(7–8): 955–965. Available at: DOI:http://dx.doi.org/10.1016/S0266-3538(03)00261-6

137. Mylsamy, K. and Rajendran, I. (2011) ‘Influence of alkali treatment and fibre length on mechanical properties of short Agave fibre reinforced epoxy composites’, *Materials & Design*. Elsevier Ltd., 32(8–9): 4629–4640. Available at: DOI:http://dx.doi.org/10.1016/j.matdes.2011.04.029

138. Shanks, R. A., Hodzic, A. and Ridderhof, D. (2006) ‘Composites of poly(lactic acid) with flax fibers modified by interstitial polymerization’, *Journal of Applied Polymer Science*, 101(6): 3620–3629. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-33748324642&partnerID=40&md5=1c73255ebd7b1c38e0b63452819fe245

139. Tokoro, R., Vu, D. M., Okubo, K., Tanaka, T., Fujii, T. and Fujiura, T. (2008) ‘How to improve mechanical properties of polylactic acid with bamboo fibers’, *Journal of Materials Science*, 43(2): 775–787. Available at:http://www.scopus.com/inward/record.url?eid=2-s2.0-37249020116&partnerID=40&md5=2910b0488008230a4daeef50d7a2ac9d

140. Brühlmann, F., Leupin, M., Erismann, K. H. and Fiechter, A. (2000) ‘Enzymatic degumming of ramie bast fibers’, *Journal of Biotechnology*, 76(1): 43-50. Available at: DOI:http://dx.doi.org/10.1016/S0168-1656(99)00175-3

141. Hallila, T., Maijala, P., Vuorinen, J. and Viikari, L. (2013) ‘Enzymatic pretreatment of seed flax-and polylactide-commingled nonwovens for composite processing’, *Journal of Thermoplastic Composite Materials.* SAGE Publications.

142. Islam, M. S., Church, J. S. and Miao, M. (2011) ‘Effect of removing polypropylene fibre surface finishes on mechanical performance of kenaf/polypropylene composites’, *Composites Part A: Applied Science and Manufacturing*, 42(11): 1687–1693. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2011.07.023

143. Niaz, A., Malik, Q. J., Muhammad, S., Shamim, T. and Asghar, S. (2011) ‘Bioscouring of cellulosic textiles’. *Coloration Technology*. Wiley Online Library, 127(4): 211–216. Available at: DOI:10.1111/j.1478-4408.2011.00292.x

144. Ouajai, S. and Shanks, R. (2005) ‘Morphology and structure of hemp

fibre after bioscouring', *Macromolecular Bioscience.* Wiley-vch Verlag, 5(2): 124–134. Available at: DOI:10.1002/mabi.200400151

145. Rho, D., Yang, J. and Lorrain, M. (2008) 'Processing of flax fibers for biocomposites using a thermostable pectate lyase', *Proceedings of the International Conference on Flax and Other Bast Plants*. pp. 201–210.

146. Mohanty, A. K., Khan, M. A. and Hinrichsen, G. (2000) 'Influence of chemical surface modification on the properties of biodegradable jute fabrics—polyester amide composites', *Composites Part A: Applied Science and Manufacturing*, 31(2): 143–150. Available at: DOI:http://dx.doi.org/10.1016/S1359-835X(99)00057-3

147. Ouajai, S. and Shanks, R. A. (2009) 'Biocomposites of cellulose acetate butyrate with modified hemp cellulose fibres'. *Macromolecular materials and engineering*. Wiley-vch Verlag, 294(3): 213–221. Available at: DOI:10.1002/mame.200800266

148. Novozymes, (2014) 'Novozymes at work' Available at: http://www.novozymes.com/en/about-us/brochures/documents/enzymes_at_work.pdf

149. Zafeiropoulos, N. E., Baillie, C. A. and Hodgkinson, J. M. (2002) 'Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part II. The effect of surface treatments on the interface', *Composites Part A: Applied Science and Manufacturing*, 33(9): 1185–1190. Available at: DOI:10.1016/S1359-835X(02)00088-X

150. Davis, S. C., Dohleman F. G. and Long S. P. (2011) 'The global potential for Agave as a biofuel feedstock'. *GCB Bioenergy*. Blackwell Publishing Ltd; 2011; 3(1): 68–78. Available at: DOI:10.1111/j.1757-1707.2010.01077.x

151. Cruz, C. and Alvarez-Jacobs, J. (1992) 'Production of tequila from Agave: historical influences and contemporary processes'. *The alcohol textbook: a reference for the beverage, fuel and industrial alcohol industries* (3rd ed.), Nottingham University Press, Alltech Inc., 225–241.

152. Consejo Regulador del Tequila. (2014) 'Consumo de Agave para Tequila y Tequila 100% de Agave', Available at: http://www.crt.org.mx/EstadisticasCRTweb/ (Accessed: 1 March 2014)

153. Tyson, J. A. (2014) 'Mundo Cuervo Tours - Tequila, Jalisco, Mexico', Available at: http://www.tequilasource.com/mundocuervo/pics/Agave-hearts-ovens_7507_r2.jpg

154. Bessadok, A., Marais, S., Roudesli, S., Lixon, C. and Métayer, M. (2008) 'Influence of chemical modifications on water-sorption and mechanical properties of Agave fibres', *Composites Part A: Applied Science and Manufacturing*, 39(1): 29-45. Availableat:DOI:http://dx.doi.org/10.1016/j.compositesa.2007.09.007

155. Karana E. Materials selection in design: From research to education. the

1st International Symposium for Design Education Researchers, Paris, France, Cumulus Association and DRS. 2011.

156. Mangan, A. T. (1997). By-product synergy: a strategy for sustainable development.

157. Baillie, C. (Ed.). (2005). Green composites: polymer composites and the environment. CRC Press.

158. Peijs, T. (2002). Composites turn green. Department of Materials, Queen Mary, University of London.

159. Kuruppalil, Z. (2011). Green plastics: an emerging alternative for petroleum-based plastics. *International Journal of Engineering Research & Innovation*, *3*(1), 59-64.

160. Buenrostro, O. and Bocco, G. (2003) 'Solid waste management in municipalities in Mexico: goals and perspectives', *Resources, Conservation and Recycling*, 39(3): 251–263. Available at: DOI:10.1016/S0921-3449(03)00031-4

161. Bhuiyan, N. (2011) 'A Framework for successful new product development'. *Journal of Industrial Engineering and Management*, 4(4): 746–770.

162. Tartakowski, Z. (2010). Recycling of packaging multilayer films: New materials for technical products. *Resources, Conservation and Recycling*, *55*(2), 167-170.

163. Bartneck, C., & Rauterberg, M. (2007) 'HCI reality—an 'Unreal Tournament?', *International Journal of Human-Computer Studies*, 65(8), 737-743.

164. United Nations General Assembly (2005) '2005 World Summit Outcome'. *Resolution A/60/1*, adopted by the General Assembly on 15 September 2005.

165. Lovins, L. H., Lovins, A., & Hawken, P. (2007). *Natural capitalism*. Little, Brown.

166. Doss H. (2014) 'Design Thinking In Healthcare: One Step At A Time', *Forbes.* Available at: http://www.forbes.com/sites/henrydoss/2014/05/23/design-thinking-in-healthcare-one-step-at-a-time/#dbab5b1628d7 (Accessed: 29 August 2016).

167. Best, K. (2006) *Design management: managing design strategy, process and implementation*. AVA publishing.

168. Brown, T. and Wyatt, J. (2015) *Design thinking for social innovation*. Annual Review of Policy Design. 3(1): 1–10.

169. Brown, T. (2009) *Change by design*. Collins Business.

170. Institute of Design at Stanford (2009) *Bootcamp bootleg*. Stanford, California: Institute of Design at Stanford, Available at: https://dschool.stanford.edu/wp-content/uploads/2011/03/BootcampBootleg2010v2SLIM.pdf (Accessed: 29 August 2016)

171. Plattner, H., Meinel, C., Weinberg, U. (2009) *Design-thinking*. Springer.

172. Frog Design. (2016) *Market Research & Technology Tools*, frog design, Available at: http://www.frogdesign.com/services/tools.html (Accessed: 28 August 2016).

173. IDEO (2016) *About IDEO*, IDEO. Available at: https://www.ideo.com/about/ (Accessed: 28 August 2016).

174. Design council (2007) *A study of the design process*.

175. Rhea, D. (2005). Bringing Clarity to the “Fuzzy Front End”, A predictable Process for Innovation, Design Research. 145–154.

176. Koen, P. A., Ajamian, G. M., Boyce, S., Clamen, A., Fisher, E., Fountoulakis, S., et al. (2012) Fuzzy front end: effective methods, tools, and techniques. The PDMA toolbook. 1: 5–35.

177. Fiksel, J., Fiksel, J. R. (1996) *Design for environment: creating eco-efficient products and processes*. McGraw-Hill Professional Publishing.

178. Fiksel, J. (2011) *Design for environment: A guide to sustainable product development.* 2nd edition. New York: McGraw-Hill.

179. Cooper, A., Reimann, R., Cronin, D. and Noessel, C. (2014) *About face: the essentials of interaction design*. John Wiley & Sons.

180. Kumar, V. (2012) *101 design methods: A structured approach for driving innovation in your organization*. John Wiley & Sons.

181. Buzan, T. and Buzan, B. (1996) *The mind map book: how to use radiant thinking to maximize your brain’s untapped potential*. Plume.

182. Ogilvie, T. and Liedtka, J. (2011) *Designing for growth: A design thinking toolkit for managers*. Columbia University Press.

183. Pugh, S. (1991) *Total design: integrated methods for successful product engineering.* Addison-Wesley Wokingham.

184. Hoornweg, D. and Bhada-Tata, P. (2012) ‘What a Waste: A Global Review of Solid Waste Management’, *Urban Development Series*; knowledge papers no.15, World Bank. 2012; : 116. Available at: DOI:10.1111/febs.13058

185. Davis, G., & Song, J. H. (2006). Biodegradable packaging based on raw materials from crops and their impact on waste management. *Industrial crops and products*, *23*(2), 147-161.

186. Mohanty, A. K., Misra, M. and Hinrichsen, G. (2000) ‘Biofibres, biodegradable polymers and biocomposites: An overview’. *Macromolecular Materials and Engineering*. Wiley-vch Verlag GmbH; 276-277(1): 1–24. Available at: DOI:10.1002/(SICI)1439-2054(20000301)276:1<1::AID-MAME1>3.0.CO;2-W

187. Baley, C. (2002). Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase. *Composites Part A: Applied Science and Manufacturing*, *33*(7), 939-948.

188. Garkhail, S. K., Heijenrath, R. W. H., & Peijs, T. (2000). Mechanical properties of natural-fibre-mat-reinforced thermoplastics based on flax fibres and polypropylene. *Applied Composite Materials*, *7*(5-6), 351-372.

189. Park, J. M., Quang, S. T., Hwang, B. S., & DeVries, K. L. (2006). Interfacial evaluation of modified Jute and Hemp fibers/polypropylene (PP)-maleic anhydride polypropylene copolymers (PP-MAPP) composites using micromechanical technique and nondestructive acoustic emission. *Composites Science and Technology*, *66*(15), 2686-2699.

190. Keller, A. (2003) 'Compounding and mechanical properties of biodegradable hemp fibre composites', *Eco-Composites,* 63(9):1307-1316. Available at: DOI:http://dx.doi.org/10.1016/S0266-3538(03)00102-7

191. Li, Y., Pickering, K. L. and Farrell, R. L. (2009) 'Determination of interfacial shear strength of white rot fungi treated hemp fibre reinforced polypropylene', *Composites Science and Technology*. Elsevier Ltd., 69(7-8): 1165-1171. Available at: DOI:http://dx.doi.org/10.1016/j.compscitech.2009.02.018

192. Ouajai, S. and Shanks, R. A. A. (2005) 'Composition, structure and thermal degradation of hemp cellulose after chemical treatments', *Polymer Degradation and Stability*, 89(2): 327–335. Available at: DOI:http://dx.doi.org/10.1016/j.polymdegradstab.2005.01.016

193. Bogren, K. M., Gamstedt, E. K., Neagu, R. C., AAkerholm, M. and LindstroOm, M. (2006) 'Dynamic-mechanical properties of wood-fiber reinforced polylactide: experimental characterization and micromechanical modeling', *Journal of Thermoplastic Composite Materials,*19(6): 613–637. Available at: DOI:10.1177/0892705706067480

194. Bisanda, E. and Ansell, M. (1991) 'The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites'. *Composites Science and Technology*, 41(2): 165–178. Available at: DOI:http://dx.doi.org/10.1016/0266-3538(91)90026-L

195. Silva, F., Chawla, N. and Filho, R. (2008) 'Tensile behavior of high performance natural (sisal) fibers', *Composites Science and Technology*. Elsevier Ltd., 68(15-16): 3438-3443. Available at: DOI:http://dx.doi.org/10.1016/j.compscitech.2008.10.001

196. Majeed, K., Jawaid, M., Hassan, A., Abu-Bakar, A., Abdul-Khalil H., Salema, A., et al. (2013) 'Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites', *Materials & Design*. 46(0): 391-410. Available at: DOI:http://dx.doi.org/10.1016/j.matdes.2012.10.044

197. Pickering, K., Sreekumar, P. and Thomas, S. (2008) 'Properties and performance of natural-fibre composites'. *Properties and Performance of Natural-Fibre Composites.* Elsevier, 67-126 p. Available at: DOI:10.1533/9781845694593.1.67

198. Johansson, C., Bras, J., Mondragon, I., Nechita, P. (2012) 'Renewable

fibers and bio-based materials for packaging applications - a review of recent developments', *BioResources*, 7(2): 2506–2552.

199. Atchison, J. E. (1976) 'Agricultural residues and other nonwood plant fibers', *Science*, (191): 768–772.

200. Staniforth, A. R. (1979) 'Straw for pulping, paper and board', in: Staniforth, A. R. (ed.) *Cereal straw*. Oxford: Clarendon Press, 116–123.

201. Mwaikambo, L. and Ansell, M. (2006) 'Mechanical properties of alkali treated plant fibres and their potential as reinforcement materials II. Sisal fibres', *Journal of Materials Science*. Kluwer Academic Publishers, 41(8): 2497–2508. Available at: DOI:10.1007/s10853-006-5075-4

202. Focher, B., Marzetti, A., Marsano, E., Conio, G., Tealdi, A., Cosani, A., et al. (1998) 'Regenerated and graft copolymer fibers from steam-exploded wheat straw: Characterization and properties'. *Journal of Applied Polymer Science,* 67(6): 961-974. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-0032492053&partnerID=40&md5=20b932ee432c032d1d3c779dcc19acdf

203. Gollapalli, L. E., Dale, B. E., Rivers, D. M. (2002) 'Predicting digestibility of ammonia fiber explosion (AFEX)-treated rice straw', *Applied Biochemistry and Biotechnology - Part A Enzyme Engineering and Biotechnology*, 98-100: 23-35. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-0036240360&partnerID=40&md5=427aeb52c43f5e69db9acbdbcec43da1

204. Tilby, S. E. (1971) *Method and apparatus for processing sugarcane*. Google Patents, Available at: http://www.google.com/patents/US3567511

205. Kulkarni, A. G., Satyanarayana, K. G., Rohatgi, P. K. and Vijayan, K. (1983) 'Mechanical properties of banana fibres (Musa sepientum)', *Journal of Materials Science*, 18(8): 2290–2296. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-0020799530&partnerID=40&md5=0d9b1261a909ec2d14a906e0bf517a51

206. Mukherjee, P. S. and Satyanarayana, K. G. (1986) 'An empirical evaluation of structure-property relationships in natural fibres and their fracture behaviour', *Journal of Materials Science*. Kluwer Academic Publishers, 21(12): 4162–4168. Available at: DOI:10.1007/BF01106524

207. Geethamma, V. G., Mathew, K. T., Lakshminarayanan, R., and Thomas, S. (1998) 'Composite of short coir fibres and natural rubber: effect of chemical modification, loading and orientation of fibre', *Polymer*, 39(6-7), 1483-1491.

208. Karade, S. R. (2010) 'Cement-bonded composites from lignocellulosic wastes', *Construction and Building Materials*. Elsevier, 24(8): 1323–1330.

209. Murray, G. (1997) Handbook of materials selection for engineering applications. CRC Press.

210. Yueping, W., Ge, W., Haitao, C., Genlin, T., Zheng, L., Feng, X. Q. and

Xushan, G. (2010). ‘Structures of bamboo fiber for textiles’, *Textile research journal*, 80(4), 334-343.

211. Bledzki, A. K., Reihmane, S. and Gassan, J. (1996) ‘Properties and modification methods for vegetable fibers for natural fiber composites’, *Journal of Applied Polymer Science*. Wiley Online Library, 59(8): 1329–1336.

212. Rowell, R. M. (2008) ‘Natural fibres: types and properties’, in: Pickering, K. L. (ed.) *Properties and Performance of Natural-Fibre Composites*. Cambridge, England: Woodhead Publishing Limited pp. 3–66.

213. Ibrahim, M. M., Dufresne, A., El-Zawawy, W. K. and Agblevor, F. A. (2010) ‘Banana fibers and microfibrils as lignocellulosic reinforcements in polymer composites’, *Carbohydrate Polymers*. Elsevier, 81(4): 811–819.

214. Cordeiro, N., Belgacem, M. N., Torres, I. C. and Moura, J. C. (2004) ‘Chemical composition and pulping of banana pseudo-stems’, *Industrial Crops and Products*, 19(2): 147–154. Available at: DOI:http://dx.doi.org/10.1016/j.indcrop.2003.09.001

215. Pillai, M. S. and Vasudev, R. (2001) ‘Application of coir in agricultural textiles’, *International Seminar on Technical Textiles*, Mumbai, India, p. 3.

216. Georgopoulos, S. T., Tarantili, P. A., Avgerinos, E., Andreopoulos, A. G. and Koukios, E. G. (2005) ‘Thermoplastic polymers reinforced with fibrous agricultural residues’, *Special Issue on Chemical Modification of Polymers* 90(2): 303-312. Available at: DOI:http://dx.doi.org/10.1016/j.polymdegradstab.2005.02.020

217. Ludueña, L., Fasce, D., Alvarez, V. A. and Stefani, P. M. (2011) ‘Nanocellulose from rice husk following alkaline treatment to remove silica’. *BioResources*, 6(2): 1440–1453.

218. Lim, S. K., Son, T. W., Lee, D. W., Park, B. K. and Cho, K. M. (2001) ‘Novel regenerated cellulose fibers from rice straw’, *Journal of Applied Polymer Science,* 82(7): 1705–1708. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-0035860940&partnerID=40&md5=10c5c5839f30b52e2422efc9d9e46e22

219. Han, J. C. (1998) ‘Properties of noonwood fibres’, *Proceedings of the Korean Society of Wood Science and Technology Annual Meeting*, Seoul, Korea. The Korean Society of Wood Science and Technology, pp. 3–12.

220. Gressel, J. and Zilberstein, A. (2003) ‘Let them eat (GM) straw’, *Trends in biotechnology*, 21(12): 525-530. Available at: DOI:http://dx.doi.org/10.1016/j.tibtech.2003.10.007

221. Needham, L. (2014) ‘Agave tequilana farm’, Available at: http://plantworlds.com/Agave_tequilana_farm.html

222. Rasband, W. S. (2007) ‘ImageJ’, *US National Institutes of Health*. http://rsb. info. nih. gov/ij/(1997-2007).

223. Ilankeeran, P. K., Mohite, P. M. and Kamle, S. (2012) ‘Axial Tensile

Testing of Single Fibres', *Modern Mechanical Engineering*. Scientific Research Publishing, 151-156. Available at: DOI:10.4236/mme.2012.24020

224. ASTM (1989) ASTM Standard D 3379 - 75, Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single-Filament Materials. 1-5 p. Available at: DOI:10.1520/D3379-75R89E01

225. Thomason, J. L. and Carruthers, J. (2012) 'Natural Fibre Cross Sectional Area, Its Variability and Effects on the Determination of Fibre Properties', *Journal of Biobased Materials and Bioenergy.* American Scientific Publishers, 6(4): 424-430. Available at: http://www.ingentaconnect.com/content/asp/jbmb/2012/00000006/00000004/art00011 (Accessed: 27 November 2015)

226. Fengel, D. and Wegener, G. (1983) *Wood: chemistry, ultrastructure, reactions*. Walter de Gruyter.

227. Akin, D. E. (2010) Chemistry of plant fibres. Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications. John Wiley & Sons, 10: 13.

228. Trochim, W. M. K. and Donnelly, J. P. (2006) *The research methods knowledge base.* Third Edit. Cincinnati: OH: Atomic Dog Publishing.

229. George, D. (2011) *SPSS for windows step by step: A simple study guide and reference*, 17.0 update, 10/e. Pearson Education India.

230. Kazayawoko, M., Balatinecz, J. J., Woodhams, R. T. and Sodhi, R. N. (1998) 'X-ray photoelectron spectroscopy of lignocellulosic materials treated with malea ted polypropylenes', *Journal of wood chemistry and technology*. Taylor & Francis, 18(1): 1–26.

231. Kim, J. T. and Netravali, A. N. (2010) 'Mercerization of sisal fibers: Effect of tension on mechanical properties of sisal fiber and fiber-reinforced composites', *Composites Part A: Applied Science and Manufacturing.* Elsevier Ltd, 41(9): 1245-1252. Available at: DOI:10.1016/j.compositesa.2010.05.007

232. FAO (2016) *Future Fibres: Sisal*. Available at: http://www.fao.org/economic/futurefibres/fibres/sisal/en/ (Accessed: 22 January 2016)

233. Karmaker, A. C. and Youngquist, J. A. (1996) 'Injection molding of polypropylene reinforced with short jute fibers', *Journal of Applied Polymer Science.* New York, Wiley, 62(8): 1147–1151.

234. Bledzki, A. K. and Gassan, J. (1999) 'Composites reinforced with cellulose based fibres', *Progress in Polymer Science*, 24(2): 221–274. Available at: DOI:http://dx.doi.org/10.1016/S0079-6700(98)00018-5

235. Gauthier, R., Joly, C., Coupas, A. C., Gauthier, H. and Escoubes, M. (1998) 'Interfaces in polyolefin/cellulosic fiber composites: chemical coupling, morphology, correlation with adhesion and aging in moisture', *Polymer Composites*. Wiley Online Library, 19(3): 287–300.

236. Rowell, R. M., Sanadi, A. R., Caulfield, D. F. and Jacobson, R. E. (1997)

‘Utilization of natural fibers in plastic composites: problems and opportunities’, *Lignocellulosic-Plastic Composites*, 23–51. Available at: http://www.fpl.fs.fed.us/documnts/pdf1997/rowel97d.pdf

237. Akin, D. E. (2010). Chemistry of plant fibres. *Industrial applications of natural fibres: Structure, properties and technical applications*, 13-22.

238. Matoba, Y. (1985) *Lectures on Mercerization* (1)-(13). Senshoku nouhau no rironka (The theorisation of dyeing know-how).

239. Van de Weyenberg, I., Ivens, J., De Coster, A., Kino, B., Baetens, E. and Verpoest, I. (2003) ‘Influence of processing and chemical treatment of flax fibres on their composites’, *Composites Science and Technology*. Elsevier, 63(9): 1241–1246.

240. Sharma, H. S. S., Faughey, G. and Lyons, G. (1999) ‘Comparison of physical, chemical, and thermal characteristics of water-, dew-, and enzyme-retted flax fibers’, *Journal of Applied Polymer Science*. Wiley Online Library, 74(1): 139–143.

241. Fakin, D., Golob, V., Kleinschek, K. S. and Le Marechal, A. M. (2006) ‘Sorption properties of flax fibers depending on pretreatment processes and their environmental impact’, *Textile research journal*. Sage Publications; 2006; 76(6): 448–454.

242. DiFrancia, C., Ward, T. C. and Claus, R. O. (1996) ‘The single-fibre pull-out test. 1: Review and interpretation’, *Composites Part A: Applied Science and Manufacturing*. Elsevier, 27(8): 597–612. Available at: DOI:10.1016/1359-835X(95)00069-E

243. Morlin, B. and Czigany, T. (2012) ‘Cylinder test: Development of a new microbond method’, *Polymer Testing*. Elsevier Ltd., 31(1): 164–170. Available at: DOI:http://dx.doi.org/10.1016/j.polymertesting.2011.10.007

244. Piggott, M. R. (1993) ‘The single-fibre pull-out method: its advantages, interpretation and experimental realization’, *Composite Interfaces*. Taylor & Francis, 1(3): 211–223.

245. Ramanathan, T., Bismarck, A., Schulz, E. and Subramanian, K. (2001) ‘The use of a single-fibre pull-out test to investigate the influence of acidic and basic surface groups on carbon fibres on the adhesion to poly (phenylene sulfide) and matrix-morphology-dependent fracture behaviour’, *Composites Science and Technology.* Elsevier, 61(12): 1703–1710. Available at: DOI:10.1016/S0266-3538(01)00069-0

246. Sydenstricker, T. H. D., Mochnaz, S. and Amico, S. C. (2003) ‘Pull-out and other evaluations in sisal-reinforced polyester biocomposites’, *Polymer Testing.* Elsevier, 22(4): 375–380. Available at: DOI:10.1016/S0142-9418(02)00116-2

247. Weibull W. (1939) *A statistical theory of the strength of materials*. Ingeniors Vetenskaps Akademien

248. Roy, A., Chakraborty, S., Kundu, S. P., Basak, R. K., Majumder, S. B., & Adhikari, B. (2012). Improvement in mechanical properties of jute fibres

through mild alkali treatment as demonstrated by utilisation of the Weibull distribution model. *Bioresource technology*, *107*, 222-228.

249. Sawpan, M. A., Pickering, K. L. and Fernyhough, A. (2011) ‘Effect of fibre treatments on interfacial shear strength of hemp fibre reinforced polylactide and unsaturated polyester composites’, *Composites Part A: Applied Science and Manufacturing.* Elsevier Ltd., 42(9): 1189–1196. Available at: DOI:http://dx.doi.org/10.1016/j.compositesa.2011.05.003

250. De Rosa, I. M., Kenny, J. M., Puglia, D., Santulli, C. and Sarasini, F. (2010) ‘Morphological, thermal and mechanical characterization of okra (Abelmoschus esculentus) fibres as potential reinforcement in polymer composites’, *Composites Science and Technology.* Elsevier Ltd., 70(1): 116–122. Available at: DOI:10.1016/j.compscitech.2009.09.013

251. Stevens, E. S. (2002) *Green plastics.* Princeton: Princeton University Press.

252. Garkhail, S. K., Heijenrath, R. W. H. and Peijs, T. (2000) ‘Mechanical Properties of Natural-Fibre-Mat- Reinforced Thermoplastics based on Flax Fibres and Polypropylene’, *Applied Composite Materials.* Kluwer Academic Publishers, 7(5-6): 351–372. Available at: DOI:10.1023/A:1026590124038

253. Cao, Y., Shibata, S. and Fukumoto, I. (2006) ‘Mechanical properties of biodegradable composites reinforced with bagasse fibre before and after alkali treatments’, *Composites Part A: Applied Science and Manufacturing.* 37(3): 423-429. Available at: DOI:10.1016/j.compositesa. 2005.05.045 (Accessed: 28 November 2015)

254. Hill, C. A., Khalil, H. P. and Hale, M. D. (1998) ‘A study of the potential of acetylation to improve the properties of plant fibres’, *Industrial Crops and Products.* Elsevier, 8(1): 53–63.

255. Pickering, K. L., Beckermann, G. W., Alam, S. N. and Forema, N. J. (2007) ‘Optimising industrial hemp fibre for composites’, *Composites Part A: Applied Science and Manufacturing*. Elsevier, 38(2): 461–468.

256. Van de Weyenberg, I., Truong, T. C., Vangrimde, B., and Verpoest, I. (2006) ‘Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment’, *Composites Part A: Applied Science and Manufacturing,* 37(9), 1368-1376.

257. Valadez-Gonzalez, A., Cervantes-Uc, J. M., Olayo, R. and Herrera-Franco, P. J. (1999) ‘Chemical modification of henequen fibers with an organosilane coupling agent’, *Composites Part B: Engineering.* Elsevier, 30(3): 321–331.

258. Fortunati, E., Puglia, D., Monti, M., Santulli, C., Maniruzzaman, M., Foresti, M. L., et al. (2013) ‘Okra (Abelmoschus esculentus) Fibre Based PLA Composites: Mechanical Behaviour and Biodegradation’, *Journal of Polymers and the Environment,* 21(3): 726–737. Available at: DOI:10.1007/s10924-013-0571-5

259. Serizawa, S., Inoue, K. and Iji, M. (2006) ‘Kenaf-fiber-reinforced poly(lactic acid) used for electronic products’, *Journal of Applied Polymer Science.* Wiley Subscription Services, Inc., A Wiley Company, 100(1): 618–624. Available at: DOI:10.1002/app.23377

260. Song, Y., Liu, J., Chen, S., Zheng, Y., Ruan, S., and Bin, Y. (2013) ‘Mechanical properties of poly (lactic acid)/hemp fiber composites prepared with a novel method’, *Journal of Polymers and the Environment,* 21(4), 1117-1127.

261. Teixeira, E. D. M., Lotti, C., Corrêa, A. C., Teodoro, K. B., Marconcini, J. M., and Mattoso, L. H. (2011) ‘Thermoplastic corn starch reinforced with cotton cellulose nanofibers’*, Journal of applied polymer science*, 120(4), 2428-2433.

262. Hietala, M., Rollo, P., Kekäläinen, K., Oksman, K. (2014) ‘Extrusion processing of green biocomposites: Compounding, fibrillation efficiency, and fiber dispersion’, *Journal of Applied Polymer Science*. Wiley Online Library, 131(6).

263. Gamon, G., Evon, P. and Rigal, L. (2013) ‘Twin-screw extrusion impact on natural fibre morphology and material properties in poly(lactic acid) based biocomposites’, *Industrial Crops and Products*, 46: 173–185. Available at: DOI:10.1016/j.indcrop.2013.01.026

264. Oksman, K., Mathew, A. P. and Sain, M. (2009) ‘Novel bionanocomposites: Processing, properties and potential applications’, *Plastics, Rubber and Composites*, 38(9/10): 396–404.

265. Oksman, K., Mathew, A. P., Bondeson, D. and Kvien, I. (2006) ‘Manufacturing process of cellulose whiskers/polylactic acid nanocomposites’, *Composites science and technology*. Elsevier, 66(15): 2776–2784.

266. Oksman, K., Mathew, A. P., Långström, R., Nyström, B. and Joseph, K. (2009) ‘The influence of fibre microstructure on fibre breakage and mechanical properties of natural fibre reinforced polypropylene’, *Composites Science and Technology.* 69(11): 1847–1853. Available at: DOI:10.1016/j.compscitech.2009.03.020

267. Mehan, M. L. and Schadler, L. S. (2000) ‘Micromechanical behavior of short-fiber polymer composites’, *Composites Science and Technology*, 60(7): 1013–1026. Available at: DOI:10.1016/S0266-3538(99)00194-3 (Accessed: 17 February 2016)

268. Ibrahim, N. A., Yunus, W. M., Othman, M., Abdan, K. and Hadithon, K. A. (2009) ‘Poly (Lactic Acid)(PLA)-reinforced Kenaf Bast Fibers Composites: The Effect of Triacetin’, *Journal of reinforced plastics and composites.* SAGE Publications.

269. Rana, A. K., Mitra, B. C. and Banerjee, A. N. (1999) ‘Short jute fiber-reinforced polypropylene composites: Dynamic mechanical study’, *Journal of Applied Polymer Science*. Wiley Online Library, 71(4): 531–539.

270. Graupner, N., Herrmann, A. S. and Müssig, J. (2009) ‘Natural and man-made cellulose fibre-reinforced poly(lactic acid) (PLA) composites: An overview about mechanical characteristics and application areas’, *Composites Part A: Applied Science and Manufacturing.* Elsevier Ltd; 2009; 40(6-7): 810-821. Available at: DOI:http://dx.doi.org/10.1016/j.com positesa.2009.04.003

271. Huda, M. S., Drzal, L. T., Misra, M. and Mohanty, A. K. (2006) ‘Wood-fiber-reinforced poly (lactic acid) composites: evaluation of the physicomechanical and morphological properties’, *Journal of Applied Polymer Science.* Wiley Online Library, 102(5): 4856–4869.

272. Mascia, L. (1974) *The role of additives in plastics*. Edward Arnold.

273. Chatterjee, A. M., Price, E. E. and Newman, S. (1975) ‘Heterogeneous Nucleation of Crystallization of High Polymers from the Melt. I. Substrate-Induced Morphologies’, *Journal of Polymer Science Part B: Polymer Physics*, 13: 2369–2383.

274. Piemonte, V., Sabatini, S. and Gironi, F. (2013) ‘Chemical Recycling of PLA: A Great Opportunity Towards the Sustainable Development?’ *Journal of Polymers and the Environment*, 21(3): 640–647. Available at: DOI:10.1007/s10924-013-0608-9

275. Jacobsen, S., Fritz, H. G., Degée, P., Dubois, P. and Jérôme, R. (1999) ‘Polylactide (PLA)?a new way of production’, *Polymer Engineering & Science*. Wiley Subscription Services, Inc., A Wiley Company, 39(7): 1311–1319. Available at: DOI:10.1002/pen.11518

276. Nampoothiri, K. M., Nair, N. R., and John, R. P. (2010) ‘An overview of the recent developments in polylactide (PLA) research’, *Bioresource technology*, 101(22), 8493-8501.

277. Bajpai, P. K., Singh, I. and Madaan, J. (2012) ‘Development and characterization of PLA-based green composites: A review’, *Journal of Thermoplastic Composite Material,* 27(1): 52–81. Available at: DOI:10.1177/0892705712439571

278. John, M. J. and Thomas, S. (2008) ‘Biofibres and biocomposites’, *Carbohydrate Polymers*, 71(3): 343–364. Available at: DOI:http://dx.doi.org/10.1016/j.carbpol.2007.05.040

279. Lawrence, C. and Collier, B. (2005) ‘Biodegradable and Sustainable Fibres’, *Biodegradable and Sustainable Fibres*, 343-366 p. Available at: DOI:10.1533/9781845690991.343

280. Rwawiire, S., Tomkova, B., Militky, J., Jabbar, A., Kale, B. M. (2015) ‘Development of a biocomposite based on green epoxy polymer and natural cellulose fabric (bark cloth) for automotive instrument panel applications’, *Composites Part B: Engineering,* 81: 149–157. Available at: DOI:10.1016/j.compositesb.2015.06.021

281. AL-Oqla, F. M. and Sapuan, S. M. (2014) ‘Natural fiber reinforced polymer composites in industrial applications: feasibility of date palm

fibers for sustainable automotive industry', *Journal of Cleaner Production*. Elsevier Ltd., 66(0): 347-354. Available at: DOI:http://dx.doi.org/10.1016/j.jclepro.2013.10.050

282. Tanmay, P., Jason, H., James, P., RheTech Inc, and Whitmorem, L. M. I., (2013) 'Bio-waste composites: A comparative study of polypropylene compounds reinforced with waste agricultural residue', *Presented at the Global Plastics Environmental Conference (GPEC 2013).*

283. Netravali, A. N. and Chabba, S. (2003) 'Composites get greener', *Materials* Today, 4(6): 22–29. Available at: DOI:10.1016/S1369-7021(03)00427-9

284. Ho, M., Wang, H., Lee, J., Ho, C., Lau, K., Leng, J., et al. (2012) 'Critical factors on manufacturing processes of natural fibre composites', *Composites Part B*. Elsevier Ltd., 8(8): 3549–3562. Available at: DOI:10.1016/j.compositesb.2011.10.001

285. Taha, I. and Ziegmann, G. (2006) 'A Comparison of Mechanical Properties of Natural Fiber Filled Biodegradable and Polyolefin Polymers', *Journal of Composite Materials*, 40(21): 1933–1946. Available at: DOI:10.1177/0021998306061304

286. Rowell, R. M., and Rowell, J. (1996). *Paper and composites from agro-based resources*. CRC press, 7-427 p.

287. Alemdar, A. and Sain, M. (2008) 'Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties', *Composites Science and Technology,* 68(2): 557–565. Available at: DOI:http://dx.doi.org/10.1016/j.compscitech.2007.05.044

288. Bernal, C,. Ramírez, M. and Villalvazo, N. (2014) 'Recycling Agave Bagasse of the Tequila Industry', *Advances in Chemical Engineering and Science*. Scientific Research Publishing.

289. Lilholt, H. and Lawthe, J. M. (2000) *Natural Organic Fibers*. Edts P (ed.) Elsevier Science Ltd.

290. Garkhail. S., Meurs, E., Van de Beld, T. and Peijs, T. (1999) 'Thermoplastic composites based on biopolymers and natural fibres' *ICCM 12 (12Th International Conference on Composite Materials).* Paris, paper n°1175.

291. Ouagne, P., Bizet, L., Baley, C. and Bréard, J. (2010) 'Analysis of the film-stacking processing parameters for PLLA/flax fiber biocomposites', *Journal of Composite Materials*. Sage Publications, 44(10): 1201–1215.

292. Bax, B. and Müssig, J. (2008) 'Impact and tensile properties of PLA/Cordenka and PLA/flax composites', *Composites Science and Technology*, 68(7): 1601-1607. Available at: DOI:10.1016/j.compscitech.2008.01.004

293. Jiang, L., Zhang, J. and Wolcott, M. P. (2007) 'Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms', *Polymer*.

48(26): 7632–7644. Available at: DOI:10.1016/j.polymer.2007.11.001

294. Scott, G. (1999) *Polymers and the Environment*. Royal Society of Chemistry.

295. INEGI. (2011) *Censo Nacional de Gobiernos Municipales y Delegacionales*. Mexico.

296. SEDESOL. (2012) *Dirección General de Equipamiento e Infraestructura en Zonas Urbano-Marginadas*, Mexico.

297. Patel, M. (2003) 'Cumulative energy demand (CED) and cumulative CO2 emissions for products of the organic chemical industry', *Energy*, 28(7): 721-740. Available at: https://econpapers.repec.org/RePEc:eee:energy:v:28:y:2003:i:7:p:721-740

298. Tukker, A. (2002) *Plastics waste: feedstock recycling, chemical recycling and incineration.* iSmithers Rapra Publishing.

299. Moreno, S. (2012) *Residuos sólidos urbanos en México*. Reporte CESOP No. 51.

300. Ojeda-Benitez, S. and Beraud-Lozano, J. (2003) 'The municipal solid waste cycle in Mexico: final disposal', *Resources, Conservation and Recycling*, 39(3): 239–250. Available at: DOI:10.1016/S0921-3449(03)00030-2

301. Le Duigou, A., Davies, P. and Baley, C. (2010) 'Analyse du cycle de vie d'un biocomposite', *Matériaux & Techniques*, 98(2): 143–150. Available at: DOI:10.1051/mattech/2010021 (Accessed: 19 September 2016)

302. Mohanty, A. K., Misra, M., Drzal, L.T. (2005) *Natural fibers, biopolymers, and biocomposites*. CRC Press.

303. Faaij, A. (2006). Modern biomass conversion technologies*. Mitigation and adaptation strategies for global change*, 343–375. Available at: DOI:10.1007/s11027-005-9004-7

304. Panoutsou, C., Eleftheriadis, J. and Nikolaou, A. (2009) 'Biomass supply in EU27 from 2010 to 2030', *Energy Policy,* 37(12): 5675–5686. Available at: DOI:10.1016/j.enpol.2009.08.032

305. DEFRA (2014) *Energy from Waste A guide to the debate.* Department for Environment Food & Rural Affairs. 2014. Available at: https://www.gov.uk/government/publications/energy-from-waste-a-guide-to-the-debate

306. Żenkiewicz, M., Richert, J., Rytlewski, P., Moraczewski, K., Stepczyńska, M. and Karasiewicz, T. (2009) 'Characterisation of multi-extruded poly (lactic acid)', *Polymer Testing.* Elsevier, 28(4): 412–418.

307. Lea, W. R. (1996) 'Plastic incineration versus recycling: a comparison of energy and landfill cost savings', *Journal of Hazardous Materials*. Elsevier, 47(1): 295–302. Available at: DOI:10.1016/0304-3894(95)00117-4

308. Soroudi, A. and Jakubowicz, I. (2013) 'Recycling of bioplastics, their

blends and biocomposites: A review', *European Polymer Journal*. Elsevier Ltd, 49(10): 2839-2858. Available at: DOI:10.1016/j.eurpolymj.2013.07.025

309. Piemonte, V. (2011) 'Bioplastic wastes: the best final disposition for energy saving', *Journal of Polymers and the Environment*. Springer, 19(4): 988–994.

310. Mahalle, L., Alemdar, A., Mihai, M. and Legros, N. (2014) 'A cradle-to-gate life cycle assessment of wood fibre-reinforced polylactic acid (PLA) and polylactic acid/thermoplastic starch (PLA/TPS) biocomposites', *The International Journal of Life Cycle Assessment*, 19(6): 1305–1315. Available at: DOI:10.1007/s11367-014-0731-4

311. Beg, M. and Pickering, K. (2007) 'Recycling and its effects on the physical and mechanical properties of wood fibre reinforced polypropylene composites', *Key Engineering Materials*. Trans Tech Publ., 497–500.

312. Rao, S., Bhattacharyya, D., Jayaraman, K. and Fernyhough, A. (2009) 'Manufacturing and recycling of sisal-polypropylene composites', *Polymers & polymer composites*. Smithers Rapra Technology Limited; 2009; 17(8): 467.

313. Hermann, B. G., Debeer, L., De Wilde, B., Blok, K. and Patel, M. K. (2011) 'To compost or not to compost: Carbon and energy footprints of biodegradable materials' waste treatment. Polymer Degradation and Stability', 96(6): 1159-1171. Available at: DOI:10.1016/j.polymdegradstab.2010.12.026

314. Alexander, M. (1994). Biodegradation and Bioremediation Academic Press Inc. San Diego, California, 267, 269.

315. Babatunde, A. E. (2016) *Energy Recovery from a New Bio-composite Material*. MSc thesis. Cranfield University.

316. Gonzalez, C. and Morales, J. J. (2002) 'Hard times or promising future for composting in Mexico?', *BioCycle*. JG Press, 43(2): 74–75.

317. Way, C., Dean, K., Wu, D. Y. and Palombo, E. (2012) 'Biodegradation of sequentially surface treated lignocellulose reinforced polylactic acid composites: Carbon dioxide evolution and morphology', *Polymer Degradation and Stability*, 97(3): 430–438. Available at: DOI:10.1016/j.polymdegradstab.2011.11.013

318. Agarwal, M., Koelling, K. W. and Chalmers, J. J. (1998) 'Characterization of the degradation of polylactic acid polymer in a solid substrate environment', *Biotechnology progress*. Wiley Online Library, 14(3): 517–526.

319. Koppejan, J. and Van Loo, S. (2002) *Handbook of Biomass Combustion and Cofiring*, IEA Bioenergy Task 32: Biomass Combustion and Cofiring.

320. Van den Broek, R., Faaij, A. and Van Wijk, A. (1996) 'Biomass combustion for power generation', *Biomass and Bioenergy*. Elsevier,

11(4): 271–281.

321. Wilén, C., Moilanen, A. and Kurkela, E. (1996) *Biomass feedstock analyses*. Espoo.

322. Zevenhoven, R., Karlsson, M., Hupa, M. and Frankenhaeuser, M. (1997) ‘Combustion and Gasification Properties of Plastics Particles’, *Journal of the Air & Waste Management Association*. Taylor & Francis; 1 August 1997; 47(8): 861-870. Available at: DOI:10.1080/10473289.1997.10464461

323. Courtemanche, B. and Levendis, Y. A. (1998) ‘A laboratory study on the NO, NO2, SO2, CO and CO2 emissions from the combustion of pulverized coal, municipal waste plastics and tires’, *Fuel*. Elsevier, 77(3): 183–196. Available at: DOI:10.1016/S0016-2361(97)00191-9 (Accessed: 6 July 2016)

324. Martín-Gullón, I., Esperanza, M. and Font, R. (2001) ‘Kinetic model for the pyrolysis and combustion of poly-(ethylene terephthalate) (PET)’, *Journal of Analytical and Applied Pyrolysis*, 58: 635–650. Available at: DOI:10.1016/S0165-2370(00)00141-8

325. Finell, M., Xiong, S., Olsson, R. (2006) *Multifunktionell industrihampa för norra Sverige* [Multifunctional industrial hemp for Northern Sweden] BTK-report 2006. Umeå, Sweden.

326. Miles, T. R., Miles, Jr T. R., Baxter, L. L., Bryers, R. W., Jenkins, B. M. and Oden, L. L. (1995) ‘Alkali deposits found in biomass power plants: A preliminary investigation of their extent and nature’. Volume 1. National Renewable Energy Lab.California Univ., Davis, C.

327. Iyer, P. V. R., Rao, T. R., Grover, P. D. and Singh, N. P. (1997) ‘Biomass Thermo-chemical Characterization’. revised se. Delhi, India: Indian Institute of Technology.

328. Lin, K. S., Wang, H. P., Lin, C. J. and Juch, C. (1998) ‘A process development for gasification of rice husk’, *Fuel processing technology.* Elsevier; 1998; 55(3): 185–192.

329. DEFRA (2013) *Incineration of Municipal Solid Waste*. Available at: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/221036/pb13889-incineration-municipal-waste.pdf

330. Valdez-Vazquez, I., Acevedo-Benítez, J. A. and Hernández-Santiago, C. (2010) ‘Distribution and potential of bioenergy resources from agricultural activities in Mexico’, *Renewable and Sustainable Energy Reviews*, 14(7): 2147–2153. Available at: DOI:10.1016/j.rser.2010.03.034

331. OLADE (2000) *Energy and Sustainable Development in Latin America and the Caribbean: Guidelines for the formulation of energy policies.* Latin-American Energy Organization.

332. Johnson, T. M., Alatorre, C., Romo, Z. and Liu, F. (2009) ‘Low-carbon development for Mexico’, *World Bank Publications*.

333. Pradhan, R., Misra, M., Erickson, L. and Mohanty, A. (2010)

‘Compostability and biodegradation study of PLA-wheat straw and PLA-soy straw based green composites in simulated composting bioreactor’, *Bioresource Technology.* Elsevier Ltd, 101(21): 8489–8491. Available at: DOI:10.1016/j.biortech.2010.06.053

334. Shogren, R. L., Doane, W. M., Garlotta, D., Lawton, J. W. and Willett, J. L. (2003) ‘Biodegradation of starch/polylactic acid/poly(hydroxyester-ether) composite bars in soil’, *Polymer Degradation and Stability*, 79(3): 405–411. Available at: DOI:10.1016/S0141-3910(02)00356-7

335. Kolstad, J. J., Vink, E. T., De Wilde, B., & Debeer, L. (2012) ‘Assessment of anaerobic degradation of Ingeo™ polylactides under accelerated landfill conditions’, *Polymer Degradation and Stability*, 97(7), 1131-1141.

336. Monroy, O., Famá, G., Meraz, M., Montoya, L. and Macarie, H. (2000) ‘Anaerobic digestion for wastewater treatment in Mexico: state of the technology’, *Water Research*, 34(6): 1803–1816. Available at: DOI:10.1016/S0043-1354(99)00301-2

337. Cruz, F. B. D. L., and Barlaz, M. A. (2010). Estimation of waste component-specific landfill decay rates using laboratory-scale decomposition data. *Environmental science & technology*, 44(12), 4722-4728.

338. Buffiere, P., Loisel, D., Bernet, N. and Delgenes, J. P. (2006) ‘Towards new indicators for the prediction of solid waste anaerobic digestion properties’, *Water Science and Technology*. IWA Publishing, 53(8): 233–241.

339. Turick, C. E., Peck, M. W., Chynoweth, D. P., Jerger, D. E., White, E.H., Zsuffa, L., et al. (1991) ‘Methane fermentation of woody biomass’, *Bioresource technology*. Elsevier, 37(2): 141–147.

340. Tong, X., Smith, LH., McCarty, P. L. (1990) ‘Methane fermentation of selected lignocellulosic materials’, Biomass. Elsevier, 21(4): 239–255.

341. Frank, J. R., Smith W. H. (1988) ‘Methane from Biomass: A Systems Approach’, *Elsevier Applied Science*.

342. Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J. L., Guwy, A. J., et al. (2009) ‘Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays’, *Water science and technology*. IWA Publishing, 59(5): 927–934.

343. Palmowski, L. and Muller, J. (1999) ‘Influence of comminution of biogenic materials on their bioavailability’. *Muell Abfall*, 31(6): 368–372.

344. Fan, L. T., Lee, Y. H. and Gharpuray, M. M. (1982) ‘The nature of lignocellulosics and their pretreatments for enzymatic hydrolysis’, *Microbial reactions*. Springer, 157–187.

345. Jeanne-Espinosa, R. (2016) *New material degradation enhancement by enzymatic pre-treatments*. MSc thesis. Cranfield University.

346. Lee, S. H., Kim, I. Y., Song, W. S. (2014) ‘Biodegradation of polylactic acid (PLA) fibers using different enzymes’, *Macromolecular Research*.

Springer, 22(6): 657–663.

347. APHA/AWWA/WEF(1999) *Standard Methods for the Examination of Water and Wastewater.* Standard Methods. 541.

348. Lettinga, G., and Van Haandel, A. C. (1993) *Anaerobic digestion for energy production and environmental protection.* 817-839.

349. Lay, J. J., Li Y. Y., Noike, T. (1997) ‘Influences of pH and moisture content on the methane production in high-solids sludge digestion’, *Water Research*. Elsevier, 31(6): 1518–1524.

350. Kolstad, J. J., Vink, E. T. H., De Wilde, B. and Debeer, L. (2012) ‘Assessment of anaerobic degradation of Ingeo^{TM} polylactides under accelerated landfill conditions’, *Polymer Degradation and Stability*, 97(7): 1131–1141. Available at: DOI:10.1016/j.polymdegradstab.2012.04.003

351. Yagi, H., Ninomiya, F., Funabashi, M. and Kunioka, M. (2009) ‘Anaerobic biodegradation tests of poly (lactic acid) and polycaprolactone using new evaluation system for methane fermentation in anaerobic sludge’, *Polymer Degradation and Stability*. Elsevier Ltd, 94(9): 1397–1404. Available at: DOI:10.1016/j.polymdegradstab.2009.05.012

352. Yesiller, N. and Hanson, J. L. (2003) Analysis of temperatures at a municipal solid waste landfill.

353. Vaverková, M. and Adamcová, D. (2015) ‘Long-term temperature monitoring of a municipal solid waste landfill’, *Polish Journal of Environmental Studies*, 24(3).

354. Mata-Alvarez, J., Macé, S. and Llabrés, P. (2000) ‘Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives’, *Bioresource Technology*, 74(1): 3–16. Available at: DOI:10.1016/S0960-8524(00)00023-7

355. De Baere, L. A., Devocht, M., Van Assche, P. and Verstraete, W. (1984) ‘Influence of high NaCl and NH 4 Cl salt levels on methanogenic associations. *Water Research*. Elsevier, 18(5): 543–548.

356. Björkqvist, S., Fröling, M., Härelind-Ingelsten, H. and Petersson, G. (1998) ‘Hydrocarbons in biogas from household solid waste’, *Environmental technology.* Taylor & Francis, 19(6): 639–642.

357. Baldasano, J. M. and Soriano, C. (2000) ‘Emission of greenhouse gases from anaerobic digestion processes: comparison with other municipal solid waste treatments’, *Water science and technology*. IWA Publishing, 41(3): 275–282.

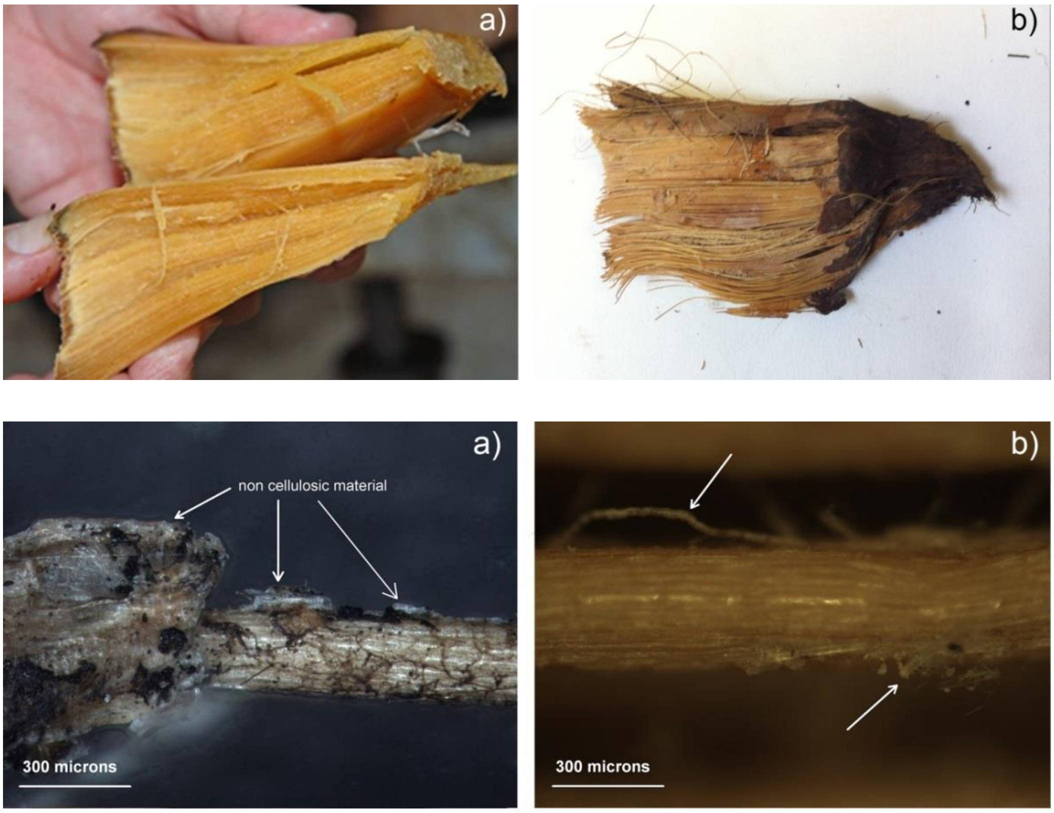
358. Pier, P. A. and Kelly, J. M. (1997) ‘Measured and estimated methane and carbon dioxide emissions from sawdust waste in the Tennessee Valley under alternative management strategies’, *Bioresource technology*. Elsevier; 1997; 61(3): 213–220.

359. Bhamra, T., Lilley, D. and Tang, T. (2008) ‘Sustainable use: changing consumer behaviour through product design’, *Changing the Change: Design Visions, Proposals and Tools*, Turin, 2008, Proceedings.

360. Barlaz, M. A., Chanton, J. P. and Green, R. B. (2009) ‘Controls on landfill gas collection efficiency: instantaneous and lifetime performance’, *Journal of the Air & Waste Management Association*. Taylor & Francis, 59(12): 1399–1404.

12 APPENDICES

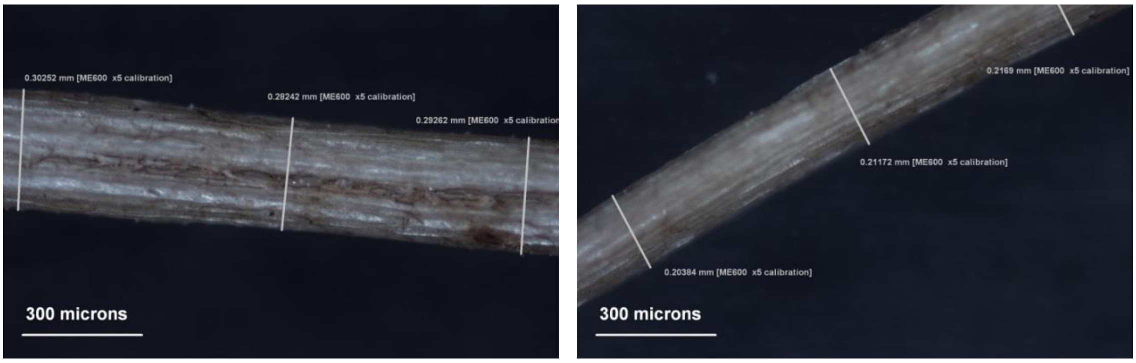
Appendix A Bagasse Characterization



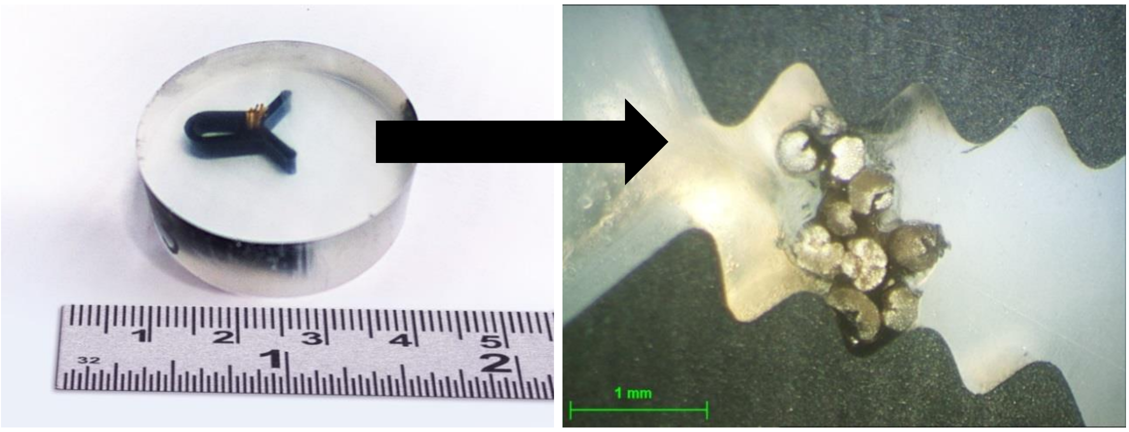
Figure_Apx A-1. *Agave tequilana* bagasse and fibres as received. a) Longitudinal micrograph from *Agave tequilana* bagasse showing remaining bark attached to the fibre bundle. b) Longitudinal section from a bundle of *Agave tequilana* fibres showing partially loose fibres.

Appendix B Cross sectional area measurement

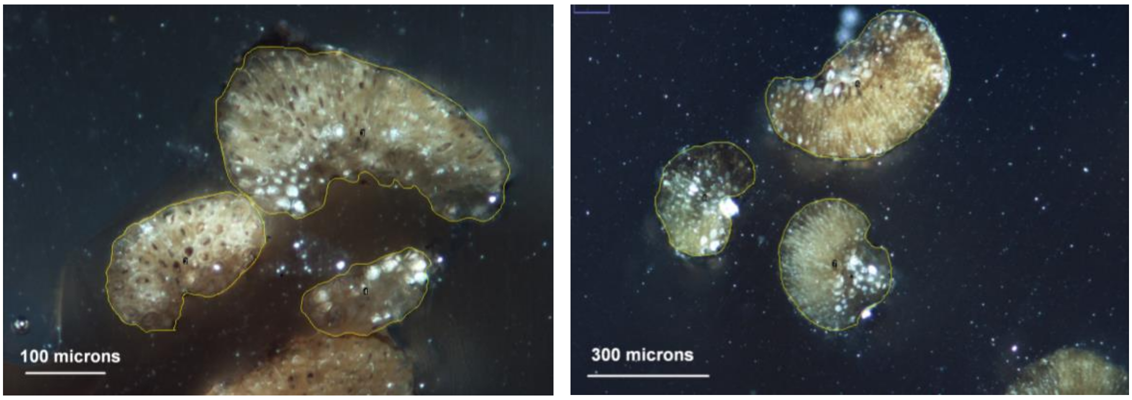
The embedded samples were prepared for microscopy by grinding them down to a fine finish using progressively finer grinding papers (120, 1200, and 2400 grade). Fibre cross sections were then photographed under the microscope at 50x magnification. Samples were repeatedly ground, polished and photographed, in 2 mm steps, following the above procedure, to give ten CSA measurements along a 20 mm length of fibre. Each fibre micrograph was traced using Image J analysis software to find the CSA.



Figure_Apx B-1. Traditional diameter dimension by planimetering.

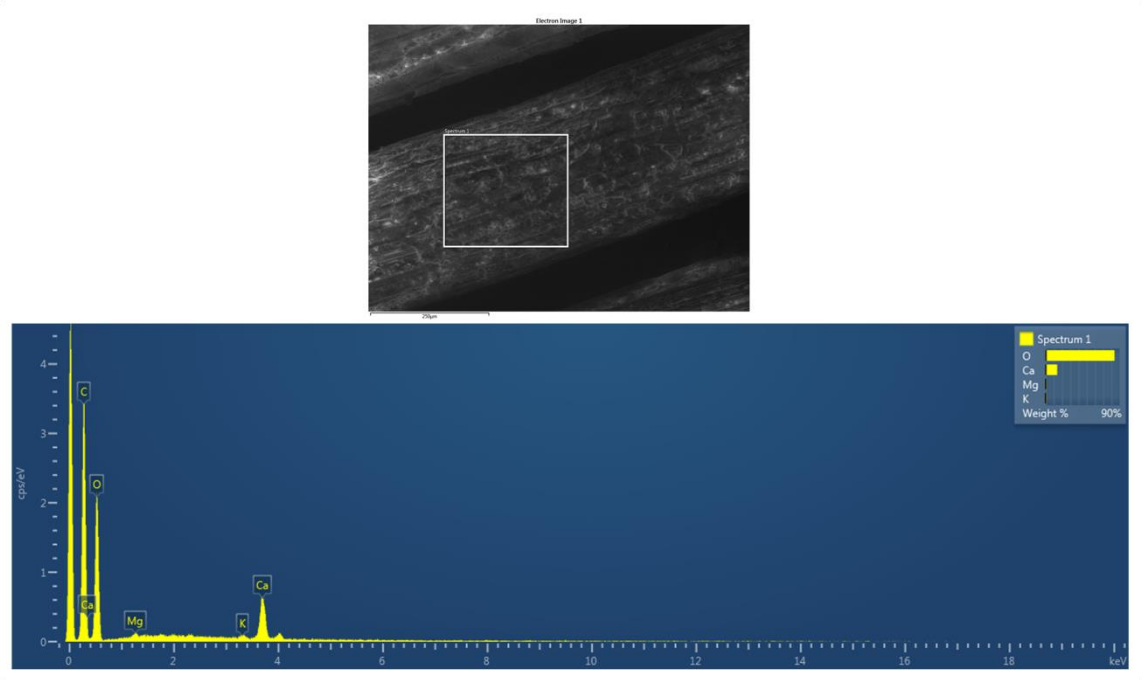


Figure_Apx B-2. Sample preparation for microscopy and CSA measurement.

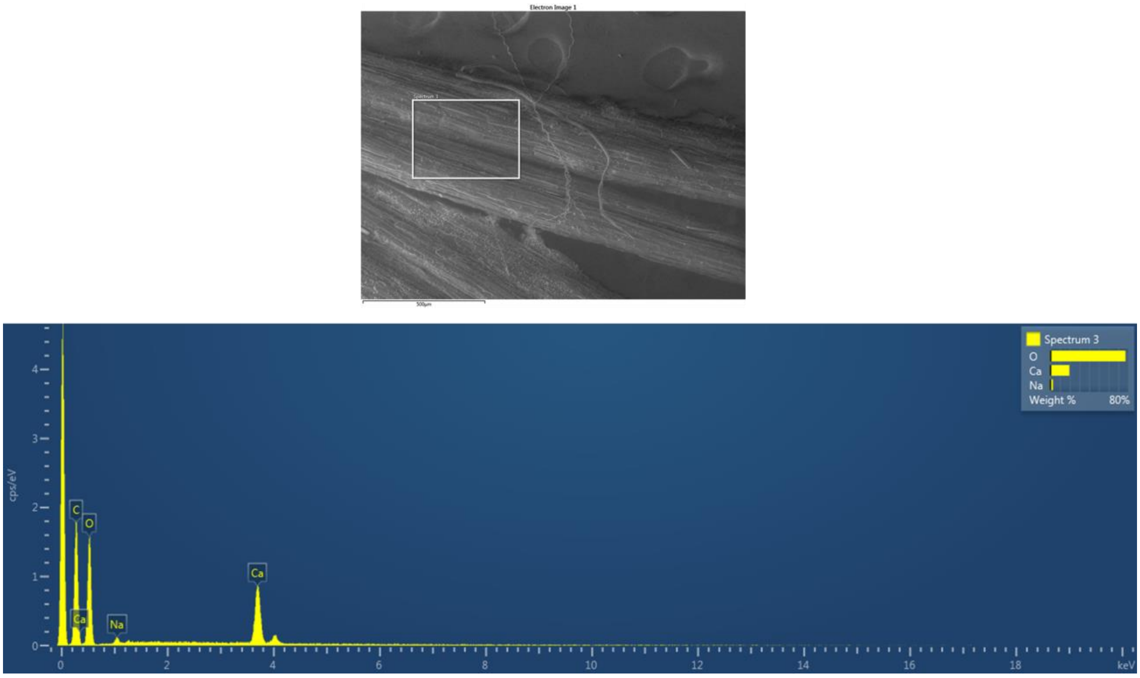


Figure_Apx B-3. Image data processing using Image J.

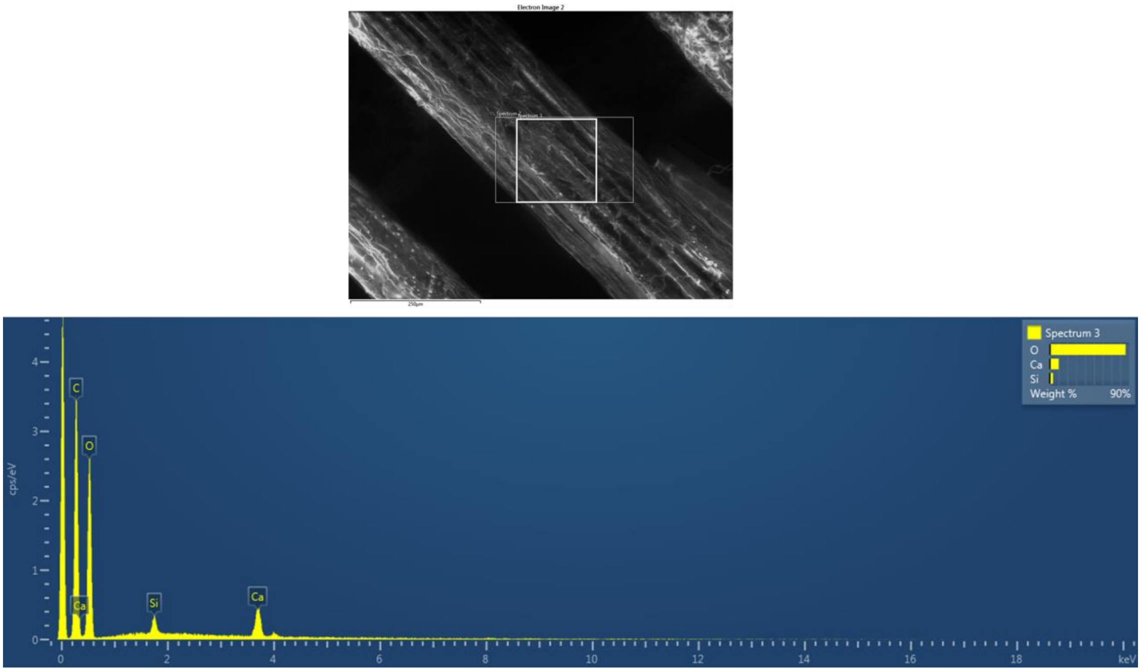
Appendix C Elemental analysis



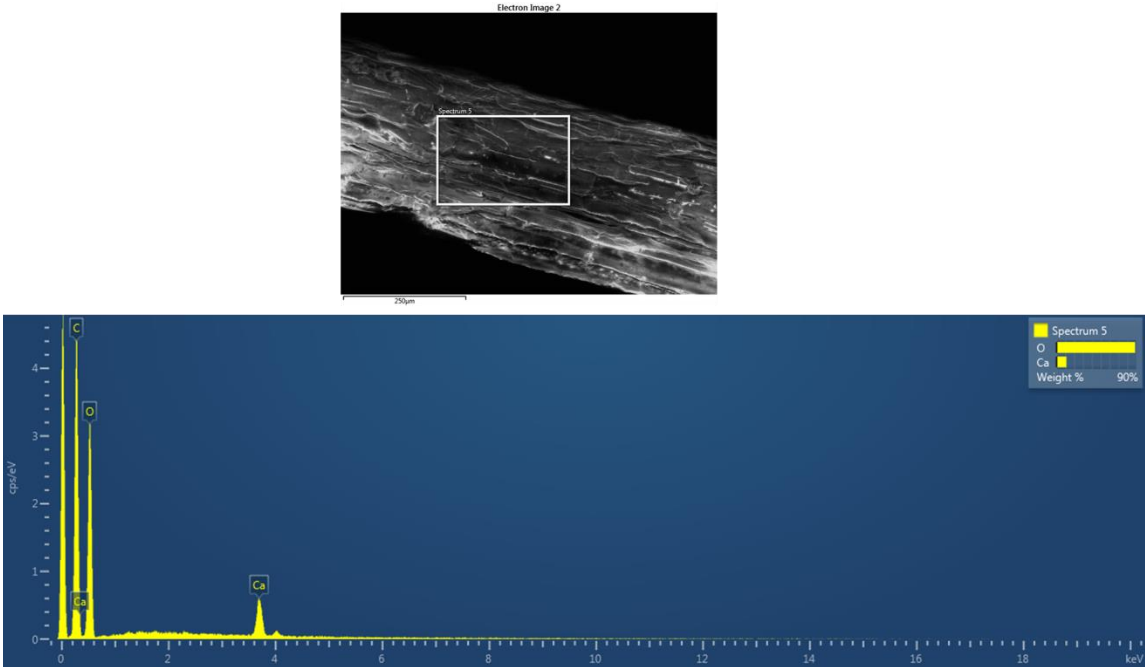
Figure_Apx C- 1 X-ray spectrum of untreated *Agave tequilana* fibre.



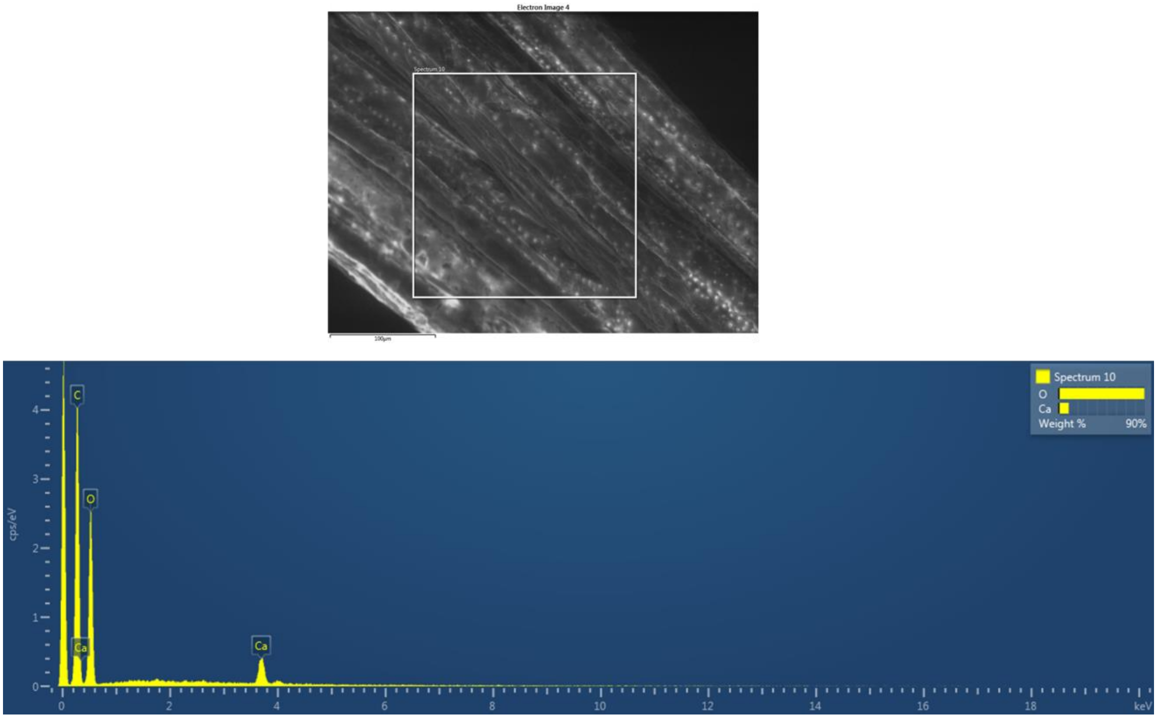
Figure_Apx C- 2 X-ray spectrum of alkali treated *Agave tequilana* fibre.



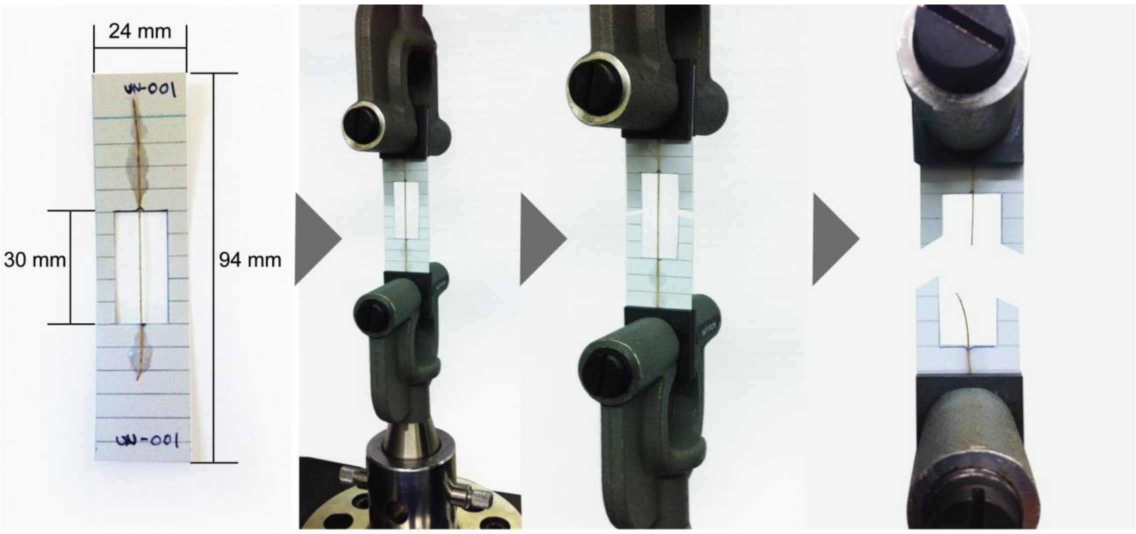
Figure_Apx C- 3 X-ray spectrum of silane-treated *Agave tequilana* fibre.



Figure_Apx C- 4 X-ray spectrum of enzyme treated *Agave tequilana* fibre.

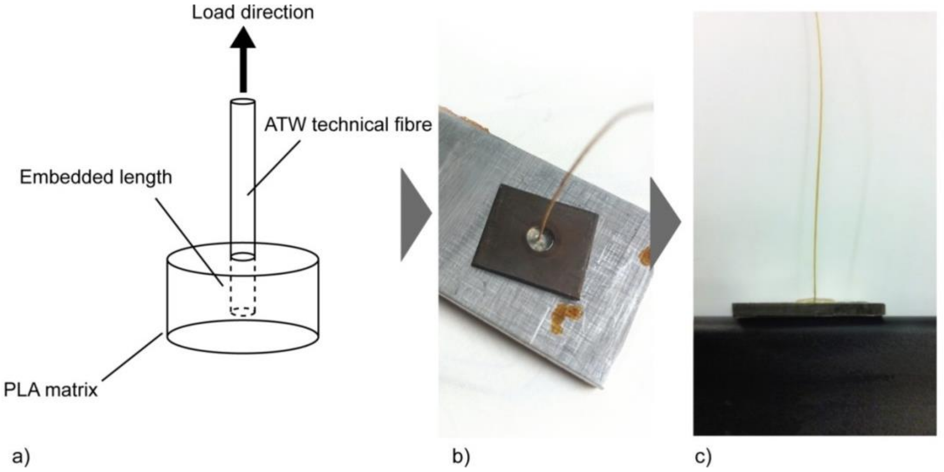


Figure_Apx C- 5 X-ray spectrum of acetylated *Agave tequilana* fibre.



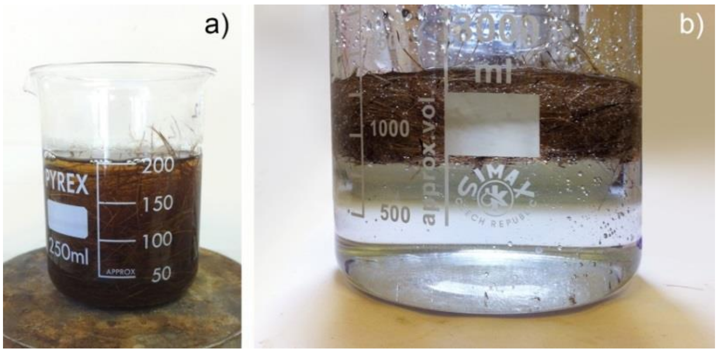
a) b) c) d)

Figure_Apx C-1. Single fibre tensile test. a) Tensile test specimen. b) Mounting tab. c) Mounting tab cut out. c) Fibre failure.



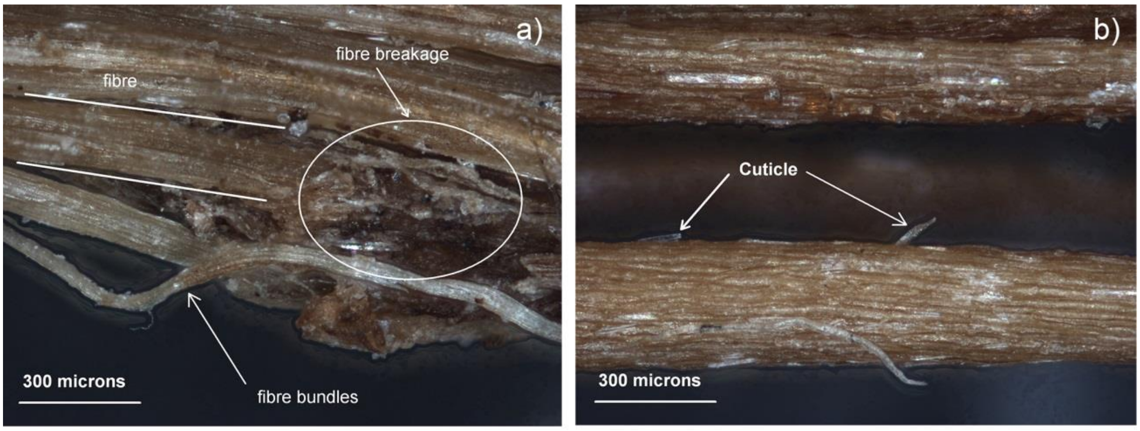
Figure_Apx C-2. Pull-out test specimens. a) Schematic view of pull-out specimen. b) Pull-out specimen. c) Lateral view of pull-out specimen.

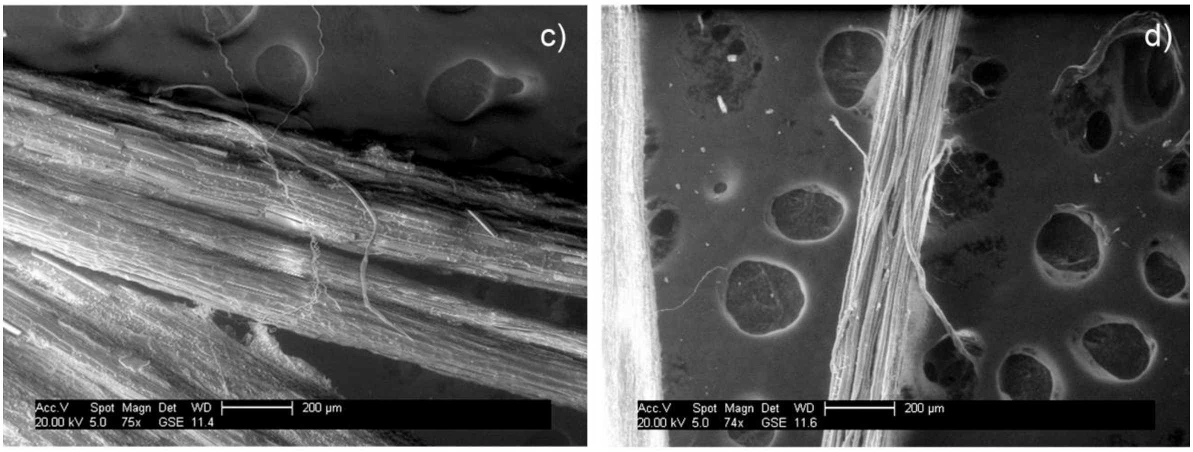
Appendix D Surface Treatments



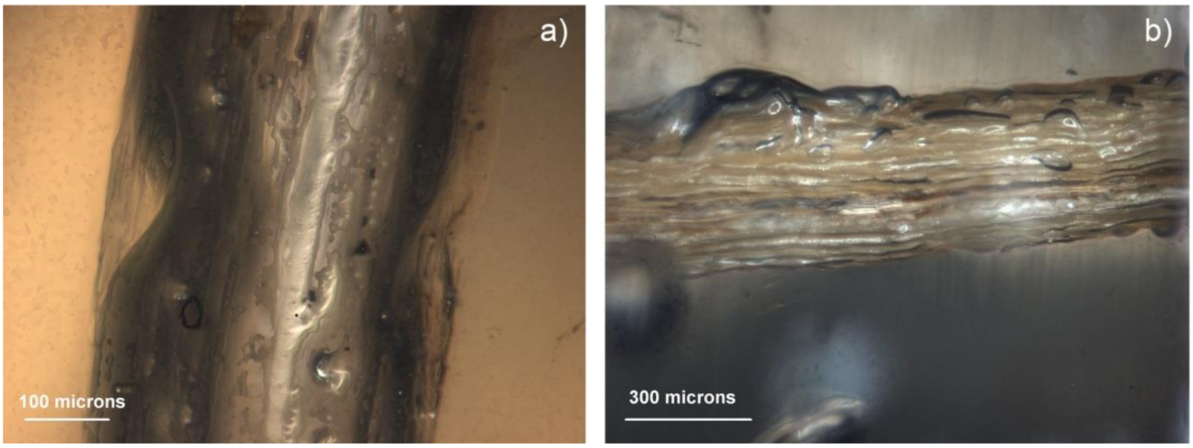
Figure_Apx D-1. Hydrophilic and hydrophobic *Agave tequilana* fibres. a) untreated *Agave tequilana* fibres in water bath. b) *Agave tequilana* fibres showing hydrophobicity after acetylation.

D.1 Alkali treatment

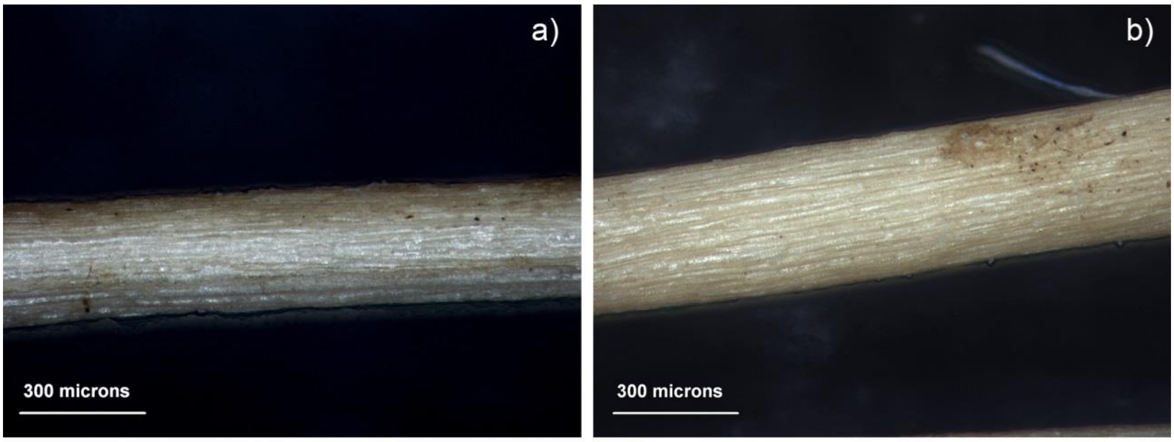


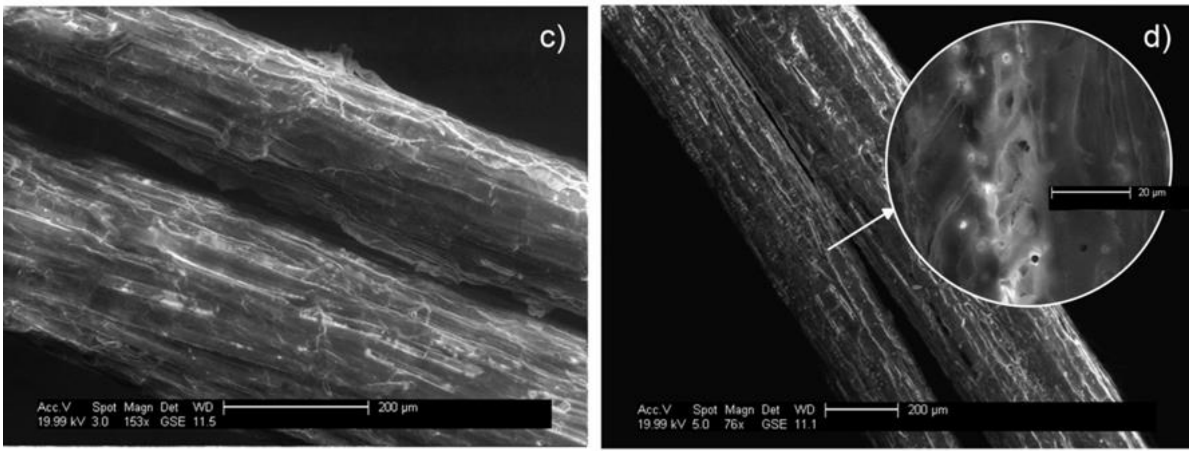


Figure_Apx D-2. Alkali-treated fibres. a) 8%-60. b) 8%-180. c) 8%-60. d) 8%-180

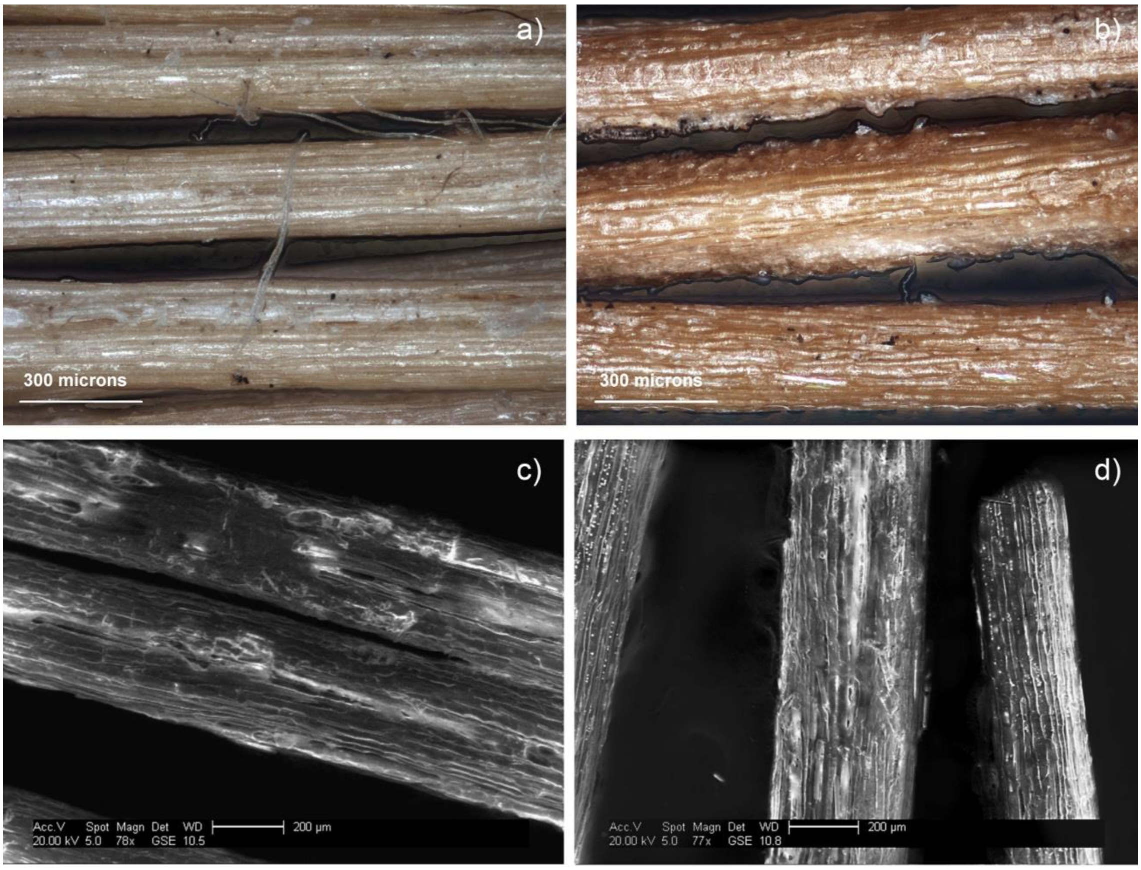


Figure_Apx D-3. Embedded *Agave tequilana* fibres. a) Alkali-treated fibre and b) bioscoured fibre in PLA matrix showing mechanical interlocking at the interface.

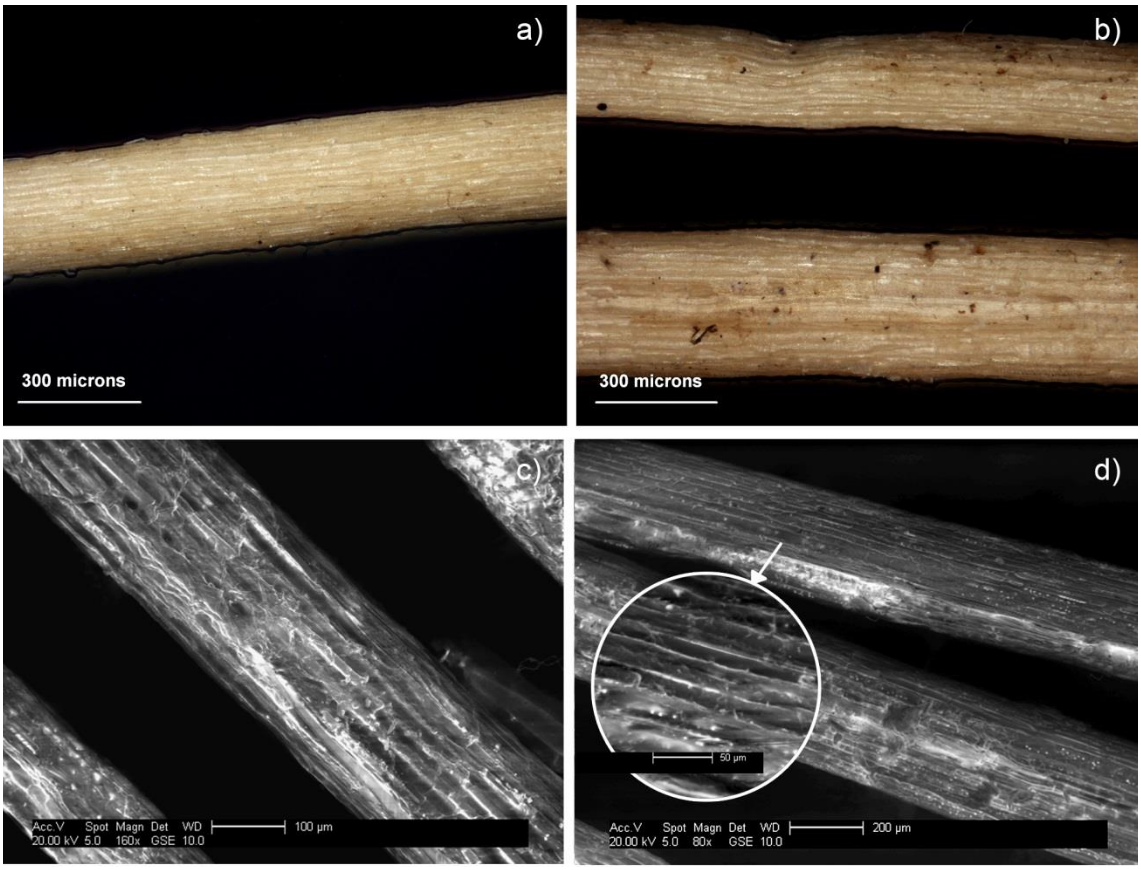




Figure_Apx D-4. Acetylated *Agave tequilana* fibres. a) 30%-60 min b) 50%-60 min c) 30%-60 d) 50%-60.

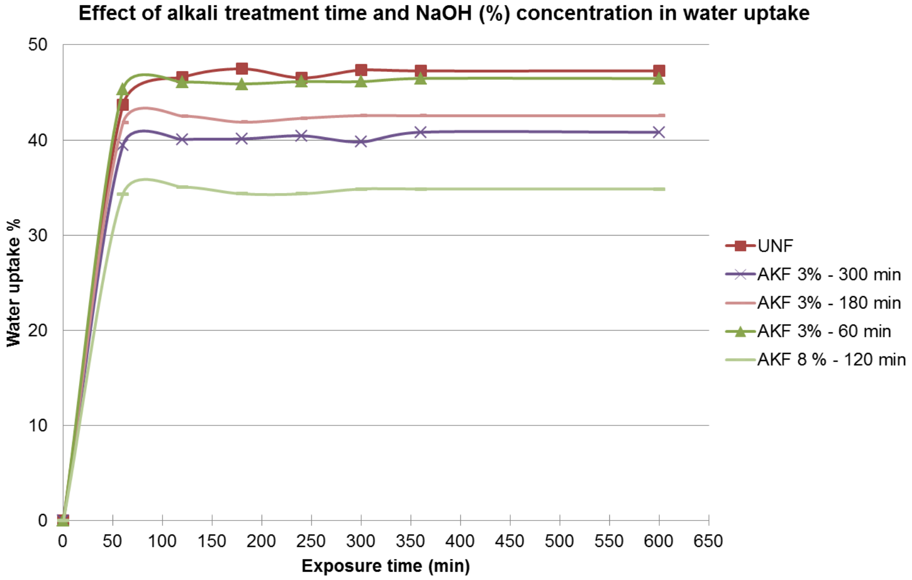


Figure_Apx D-5. Pectate lyase treated fibres. a) 2%-60 min b) 0.4% -60 min c) 2%-60 min d) 0.4%-60 min

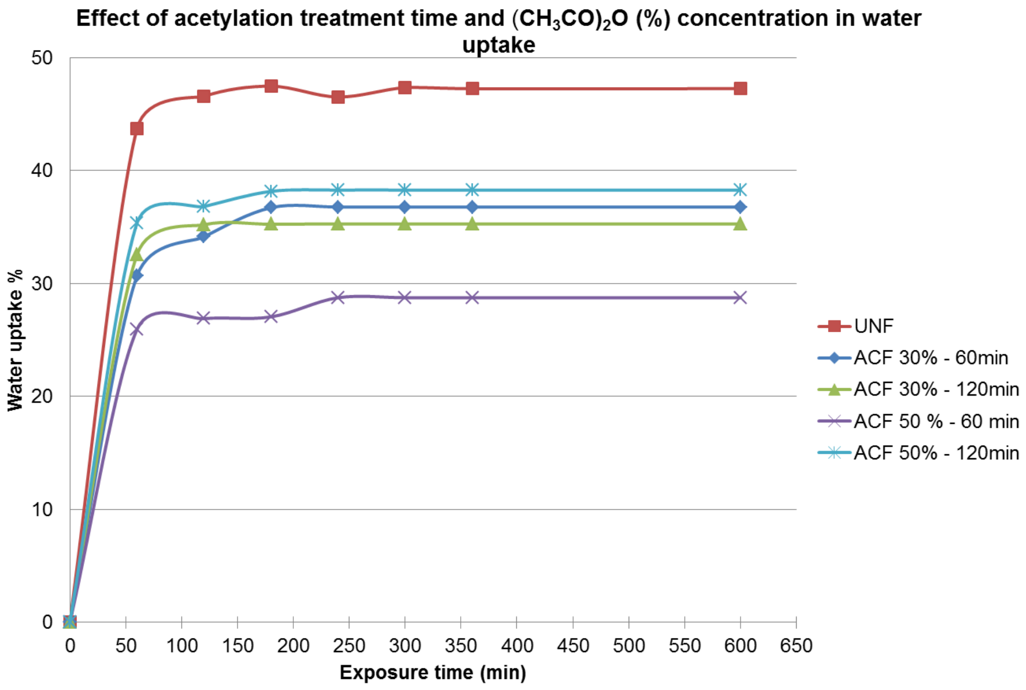


Figure_Apx D-6. Silane-treated fibres. a) 10%-240 min b) 3%-60 min c) 10%-240 min. d) 3%- 60 min

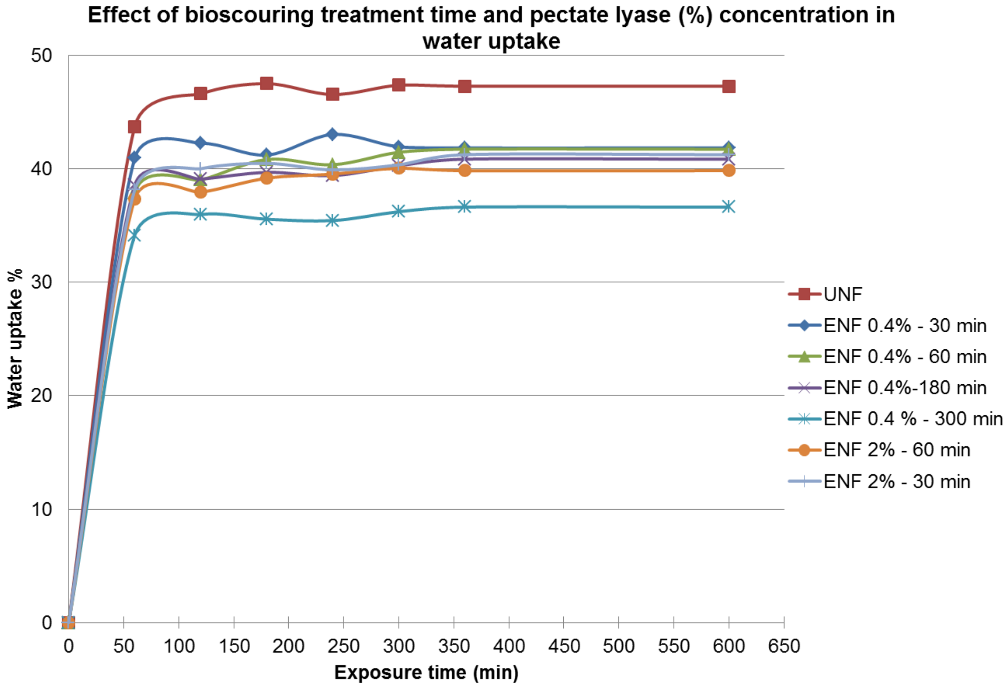
D.2 EFFECT OF FIBRE TREATMENTS



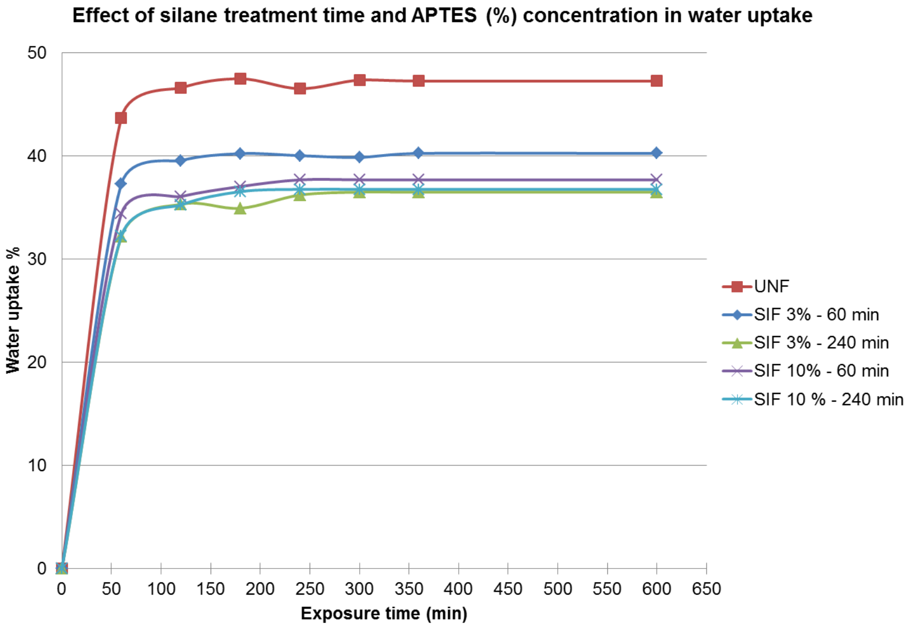
Figure_Apx D-7. Alkali treatment effect in water uptake.



Figure_Apx D-8. Acetylation treatment effect in water uptake.

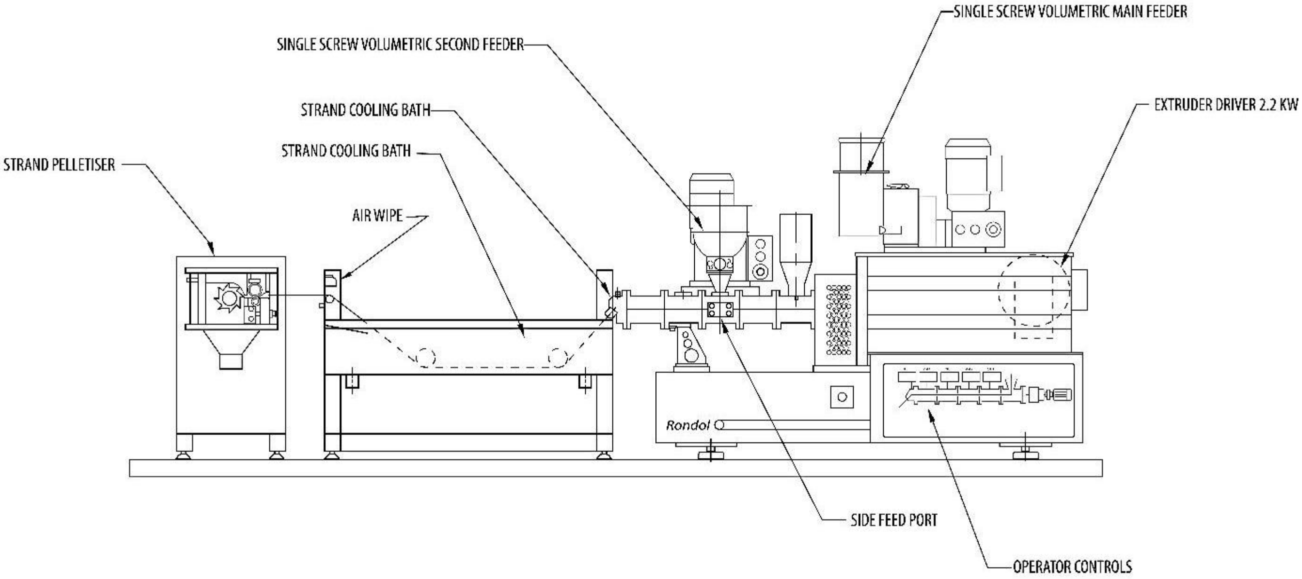


Figure_Apx D-9. Bioscouring treatment effect in water uptake.

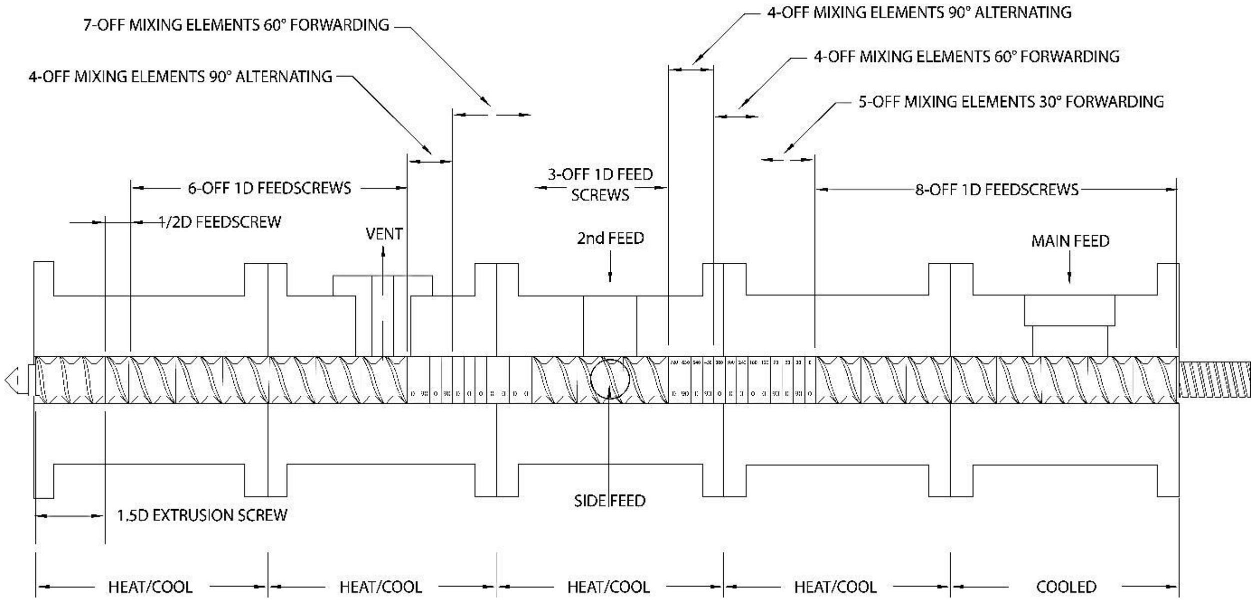


Figure_Apx D-10. Silane treatment effect in water uptake.

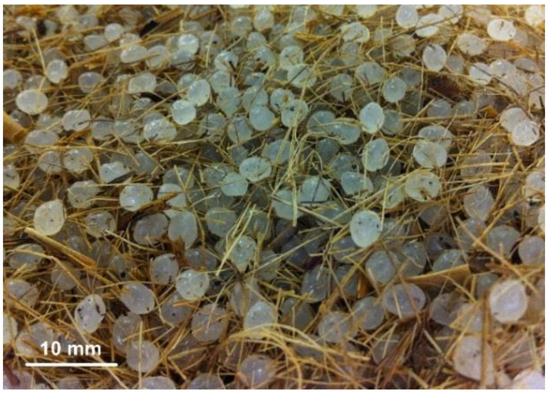
Appendix E Extrusion



Figure_Apx E-1. Rondol Twin-screw extruder diagram with cooling bath and pelletizer used for ATF/PLA compounding.



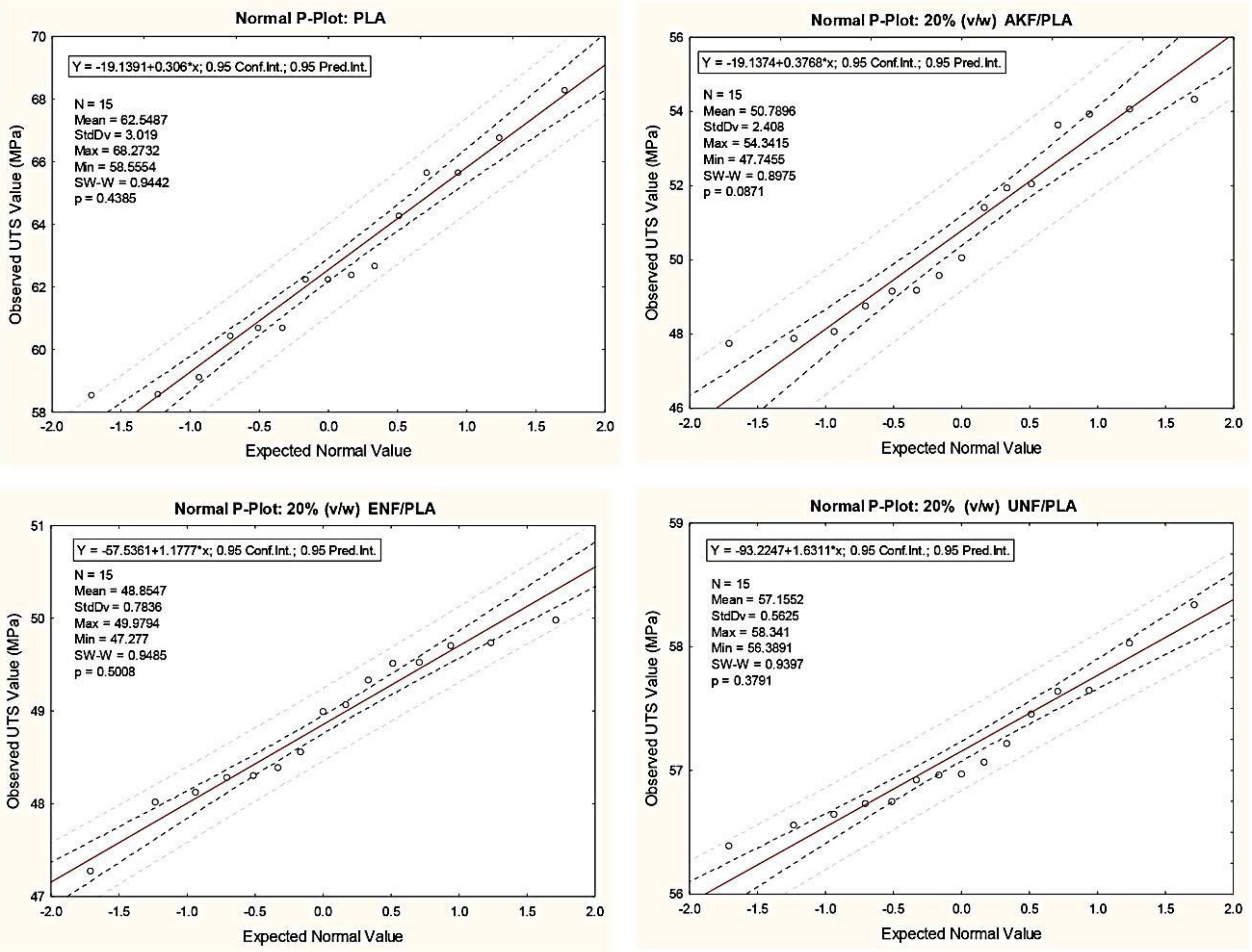
Figure_Apx E-2. Extruder's elements configuration used during ATF/PLA compounding.



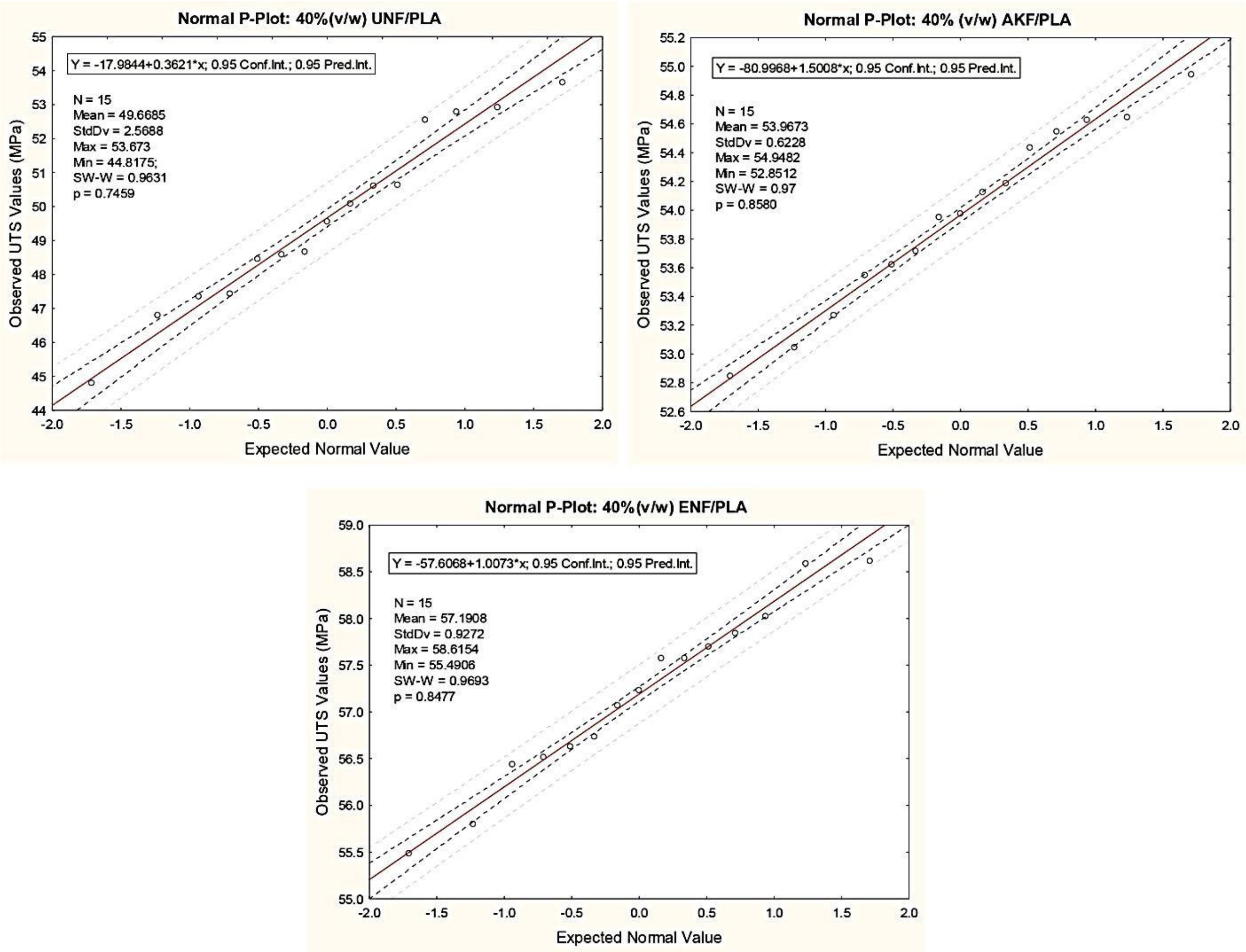
Figure_Apx E-3. *Agave tequilana* fibres and poly(lactic) acid premixing after compounding.

E.1 Composite properties.

E.1.1 Ultimate tensile strength of *Agave tequilana* fibres and poly(lactic) acid bio-based composites and neat poly(lactic) specimens tested.



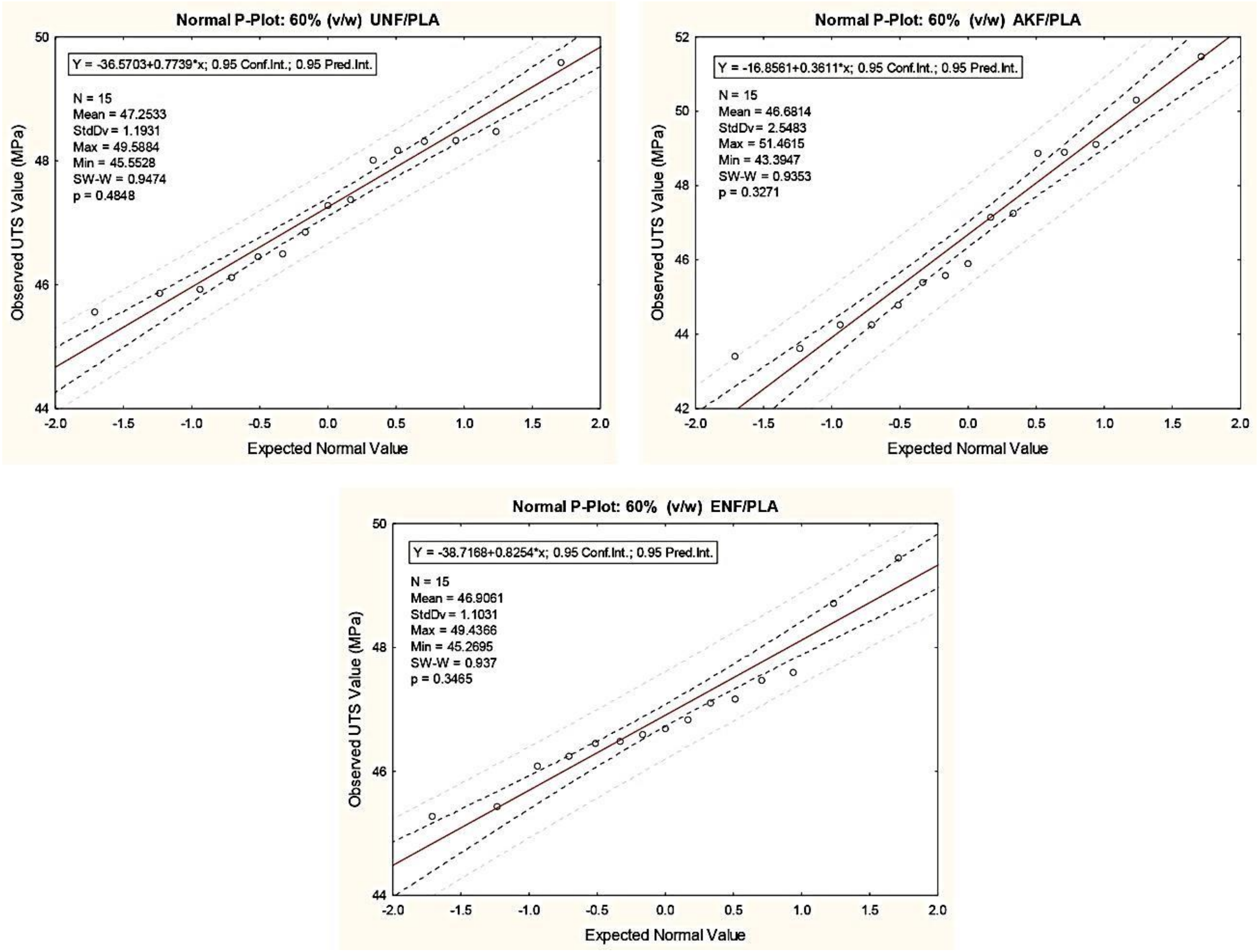
Figure_Apx E-4. Probability plots for ultimate tensile strength of 20% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites and neat PLA specimens tested.



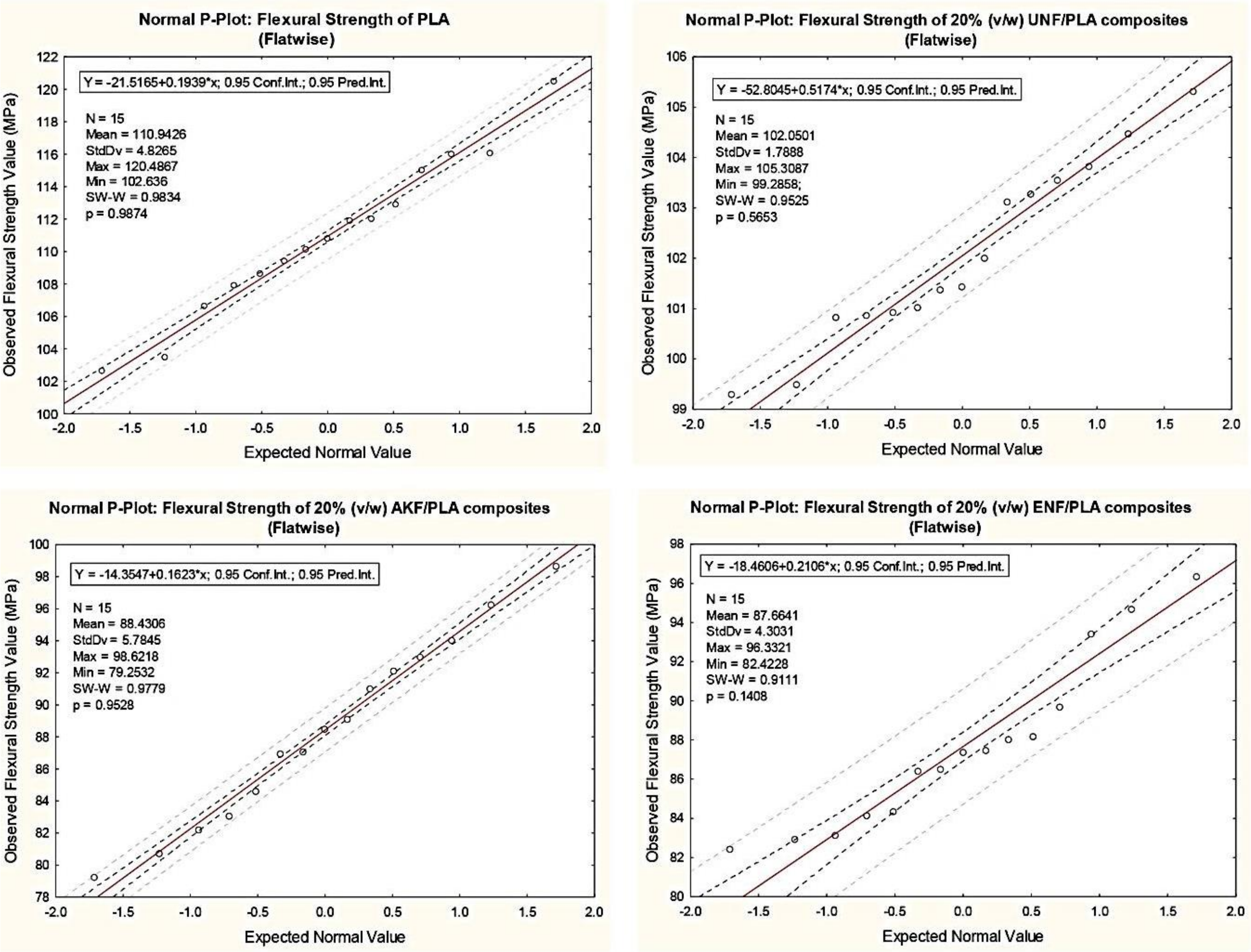
Figure_Apx E-5. Probability plots for ultimate tensile strength of 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested.

Table_Apx E-1. T-test for dependent samples for ultimate tensile strength of 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites.

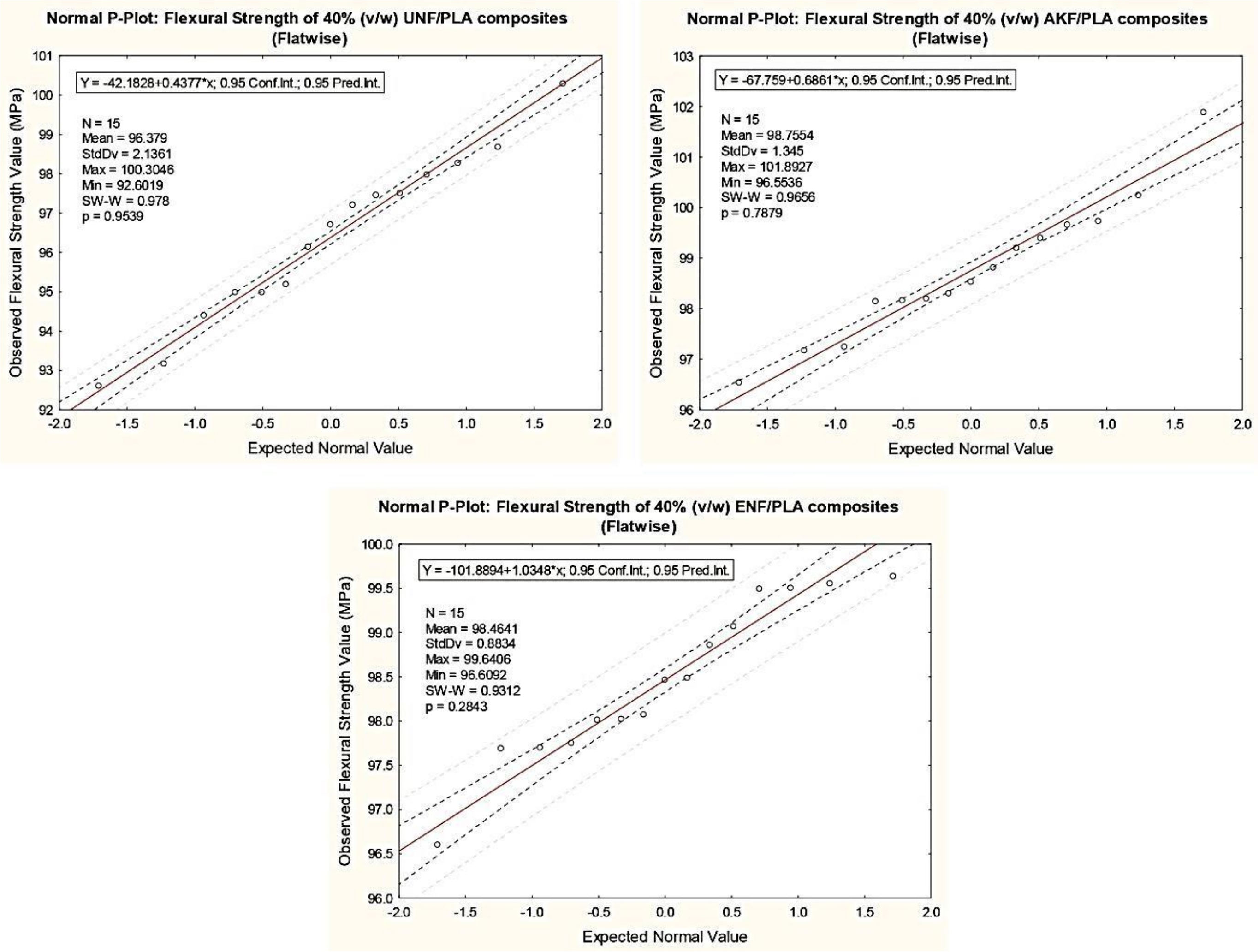
Variable	Marked differences are significant at p < .05000									
	Mean	Std.Dv.	N	Diff.	Std.Dv. (Diff.)	t	df	p	Confidence (-95.00%)	Confidence (+95.00%)
40% AKF	53.97	0.62								
40% UNF	49.67	2.57	15	4.30	2.53	6.59	14	0.000012	2.90	5.70
40% ENF	57.19	0.93								
40% UNF	49.67	2.57	15	7.52	2.81	10.38	14	0.000000	5.97	9.08



Figure_Apx E-6. Probability plots for ultimate tensile strength of 60% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested.



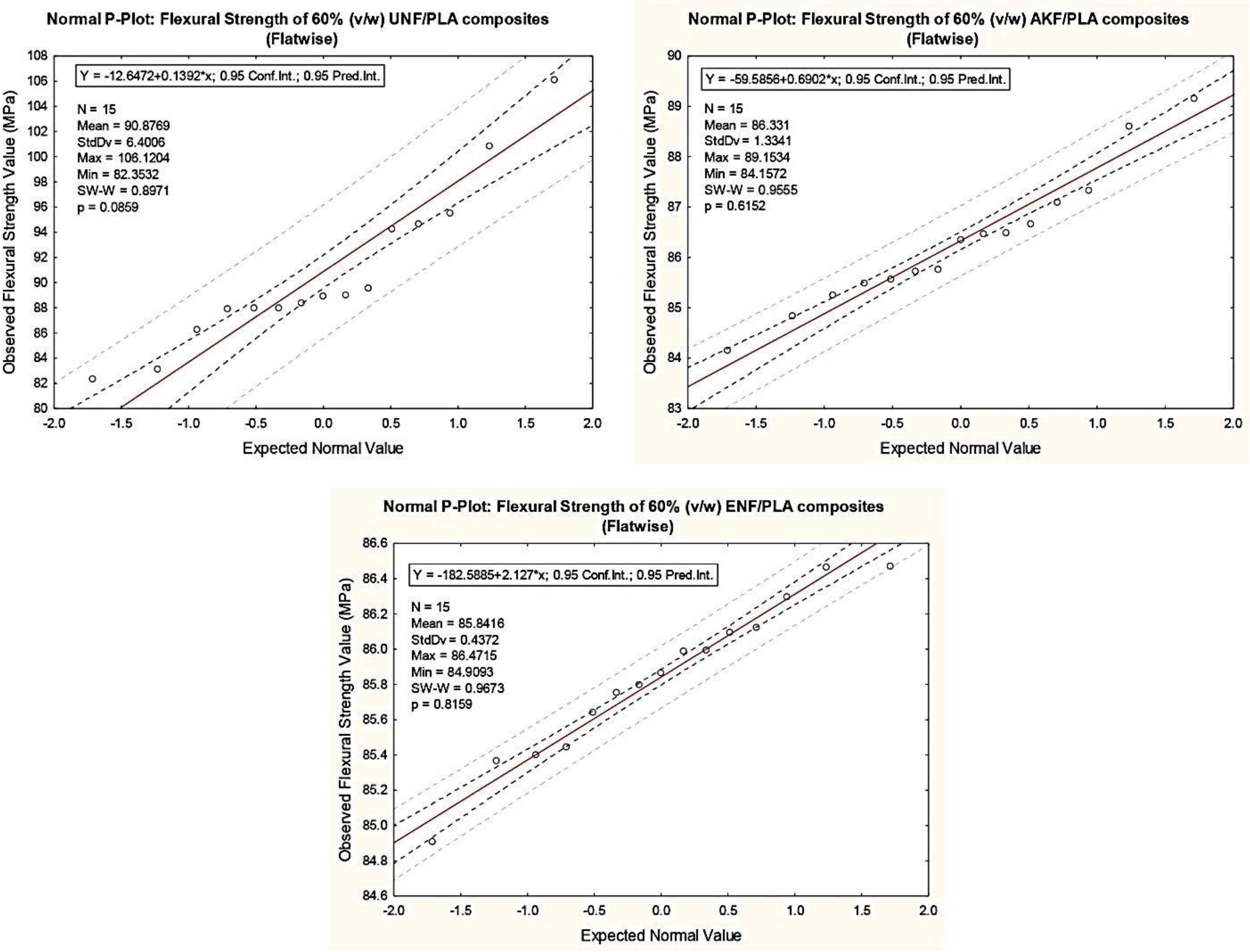
Figure_Apx E-7. Probability plots for flexural strength of 20% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested in flatwise direction.



Figure_Apx E-8. Probability plots for flexural strength of 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested in flatwise direction.

Table_Apx E-2. T-test for dependent samples for flexural strength of 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested in flatwise direction.

Variable	Marked differences are significant at $p < .05000$									
	Mean	Std.Dv.	N	Diff.	Std.Dv. (Diff.)	t	df	p	Confidence (-95.00%)	Confidence (+95.00%)
40% AKF	98.76	1.35								
40% UNF	96.38	2.14	15	2.38	3.03	3.04	14	0.008884	0.70	4.05
40% ENF	98.46	0.88								
40% UNF	96.38	2.14	15	2.09	2.30	3.52	14	0.003410	0.81	3.36



Figure_Apx E-9. Probability plots for flexural strength of 60% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested in flatwise direction.

E.1.2 Moisture and water absorption properties for 40%(v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites.

Table_Apx E-3.T-test for dependent samples of moisture absorption at equilibrium for 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites.

Variable	Marked differences are significant at p < .05000									
	Mean	Std.Dv.	N	Diff.	Std.Dv. (Diff.)	t	df	p	Confidence (-95.00%)	Confidence (+95.00%)
40% AKF	0.417	0.010								
40% UNF	0.397	0.002	3	0.020	0.010	3.39	2	0.077089	-0.005	0.046
40% ENF	0.387	0.003								
40% UNF	0.397	0.002	3	-0.010	0.001	-16.90	2	0.003484	-0.012	-0.007

Table_Apx E-4. T-test for Dependent Samples of water absorption at saturation for 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites.

Variable	Marked differences are significant at p < .05000									
	Mean	Std.Dv.	N	Diff.	Std.Dv. (Diff.)	t	df	p	Confidence (-95.00%)	Confidence (+95.00%)
40% AKF	3.477	0.084								
40% UNF	1.468	0.016	3	2.008	0.098	35.45	2	0.000795	1.765	2.252
40% ENF	1.788	0.022								
40% UNF	1.468	0.016	3	0.319	0.038	14.74	2	0.004570	0.226	0.413

Appendix F Commercial polystyrene properties

Table_Apx F-1. General purpose polystyrene and high impact polystyrene properties

Property	Test Method	Conditions	Units	Value	
				General Purpose Polystyrene [a]	High Impact Polystyrene [b]
Relative Density	ISO 1183		g/cm^3	1.05	<1.13
Water Absorption	ISO 62	23 °C	%	<0.1	<0.1
Tensile Strength at break	ASTM D-638 ISO 527		MPa	45-50	19
Tensile Yield Strength	ASTM D-638 ISO 527-2		MPa	45-50	24
Elongation at break	ASTM D-638 ISO 527		%	3	40
Tensile Modulus of Elasticity	ASTM D-638		MPa	3000-3100	
Flexural Modulus	ASTM D-790 ISO 178		MPa	3000-3240	2300
Flexural Strength at yield	ASTM D-790 ISO 790		MPa	66	22
Unnotched Izod Impact Strength	ASTM D-256 ISO 180a	unnotched	KJ/m^2	7.5*-8.1	
Izod Impact Strength	ISO 180a	notched	KJ/m^2	1.5	8.0
Rockwell Hardness	ASTM D-785		L scale	70*	

Suppliers:

a) High heat crystal polystyrene EA3130 with Food Contact Compliance. Source: http://www.amstyrenics.com/images/Technical-Data-Sheets/GPPS/ea3130.pdf

b) Polystyrene compound 801. Total petrochemicals research Feluy. Source: http://www.totalrefiningchemicals.com/SiteCollectionDocuments/Technical%20Datasheets/801.pdf

*) Polystyrene 1540. Total petrochemicals research Feluy. Source: http://www.totalrefiningchemicals.com/SiteCollectionDocuments/Technical%20Datasheets/1540-AS.pdf

Appendix G Material costs

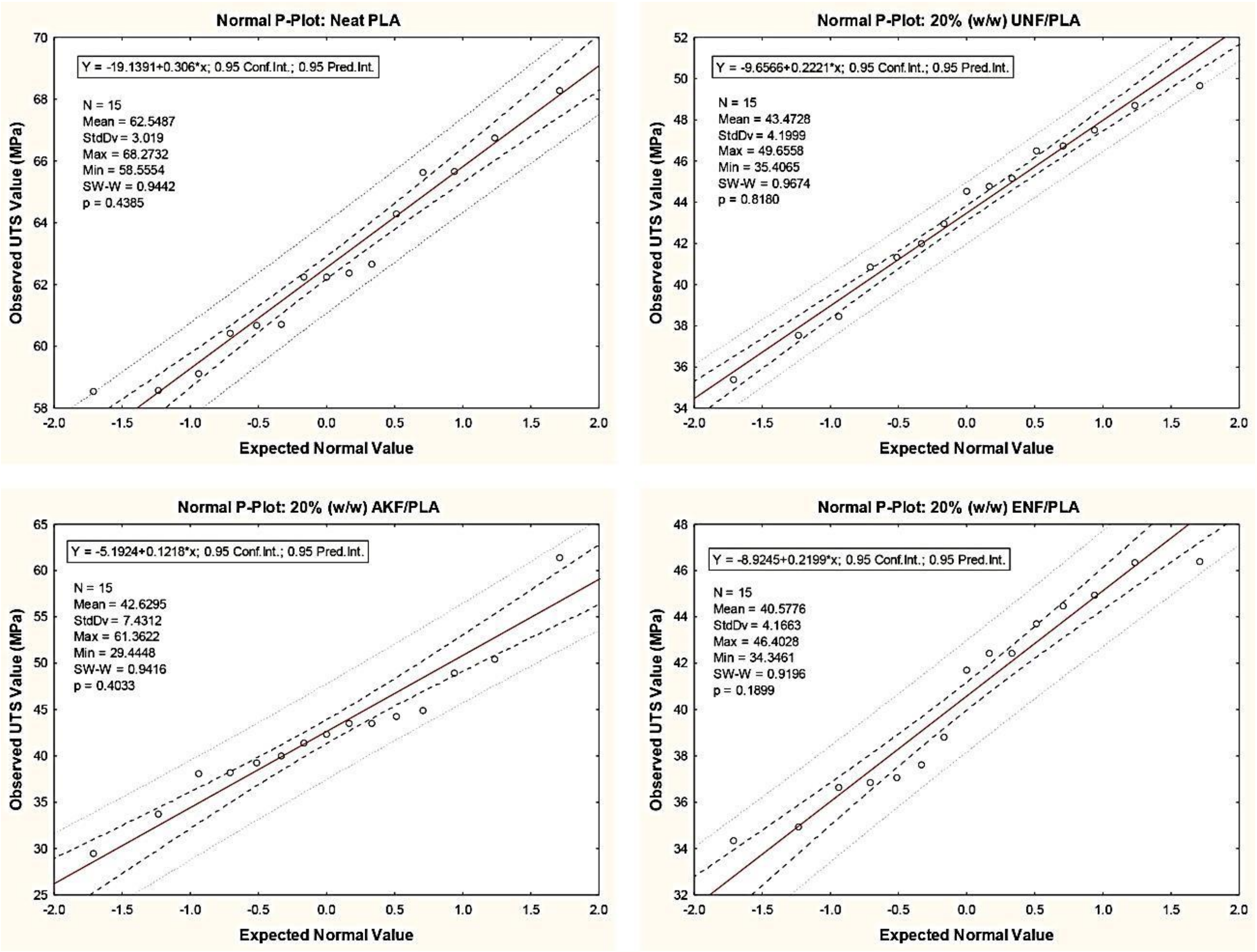
Table_Apx G-1. Costs of materials and reactives used for the composite fabrication.

Material	Cost	Supplier
Sodium phosphate, monobasic monohydrate, 99+%	£18.00	Fisher Scientific UK LTD
Sodium phosphate, dibasic, 99+%, for analysis, anhydrous	£23.60	Fisher Scientific UK LTD
Sodium hydroxide solution, 50%wt, 1L	£20.80	Fisher Scientific UK LTD
Ingeo biopolymer 2003D 25KG	£87.84	NatureWorks LLC
Bagasse/fibre (by-product)	n/a	Distillery La Fortaleza S.A. de C.V.
Pectate lyase 10mg	$105.00	Prozomix
Labour per hour for treatment of ATF	£6.10 Approx.	

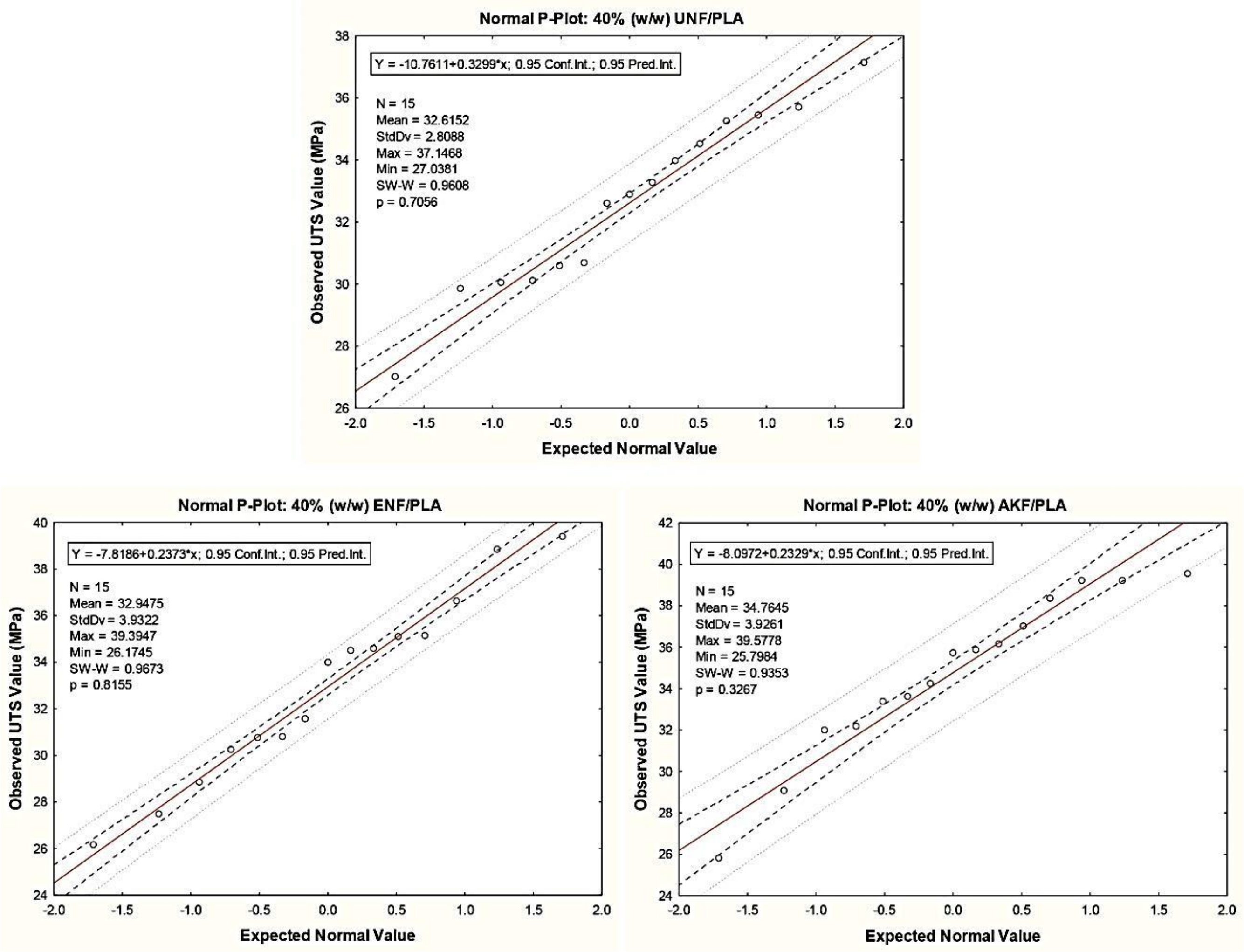
Appendix H Film stacking

H.1 Composite properties.

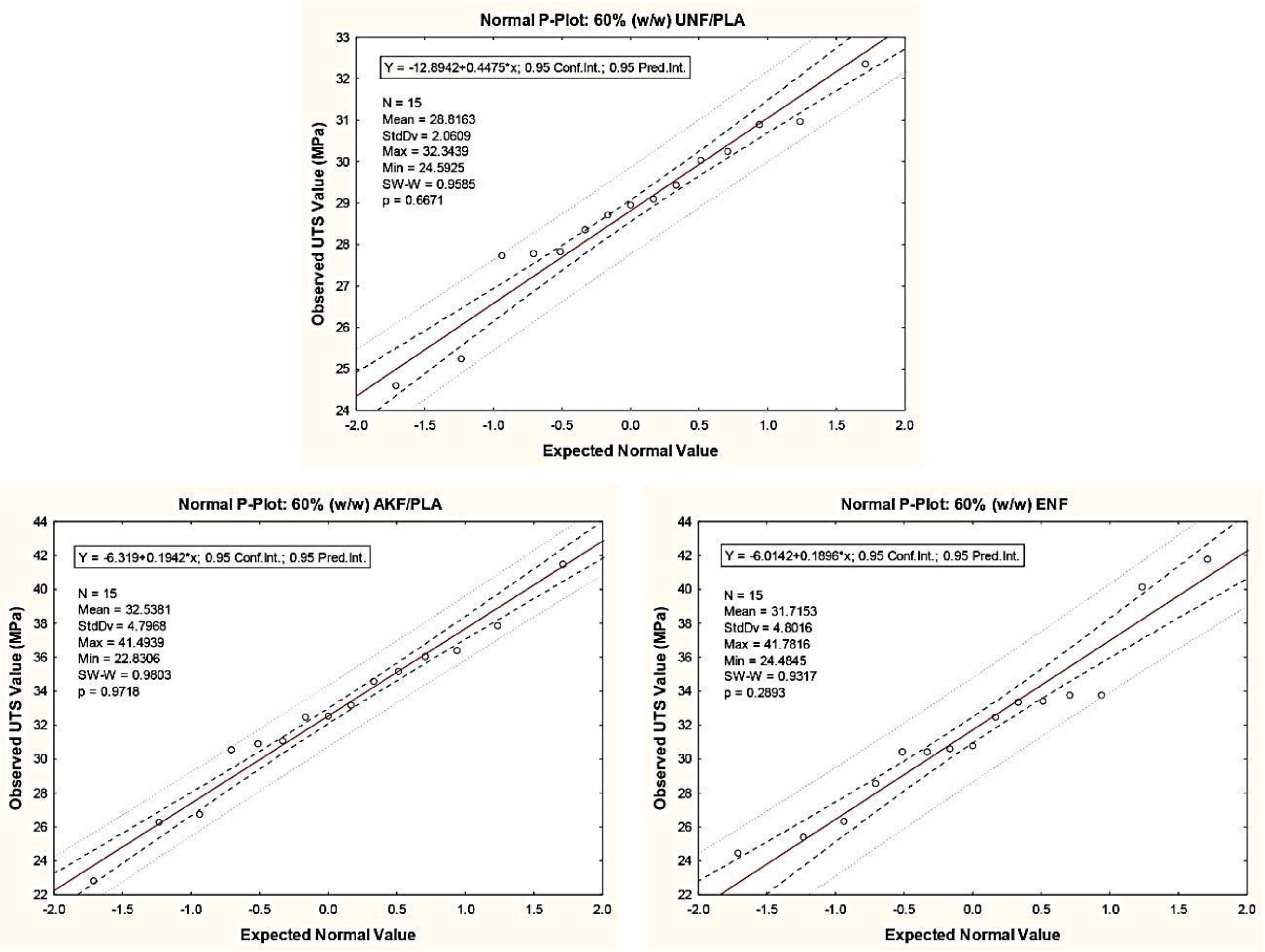
H.1.1 Ultimate tensile strength of ATF/PLA and neat PLA specimens tested.



Figure_Apx H-1. Probability plots for ultimate tensile strength of 20% (w/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites and neat PLA specimens tested.

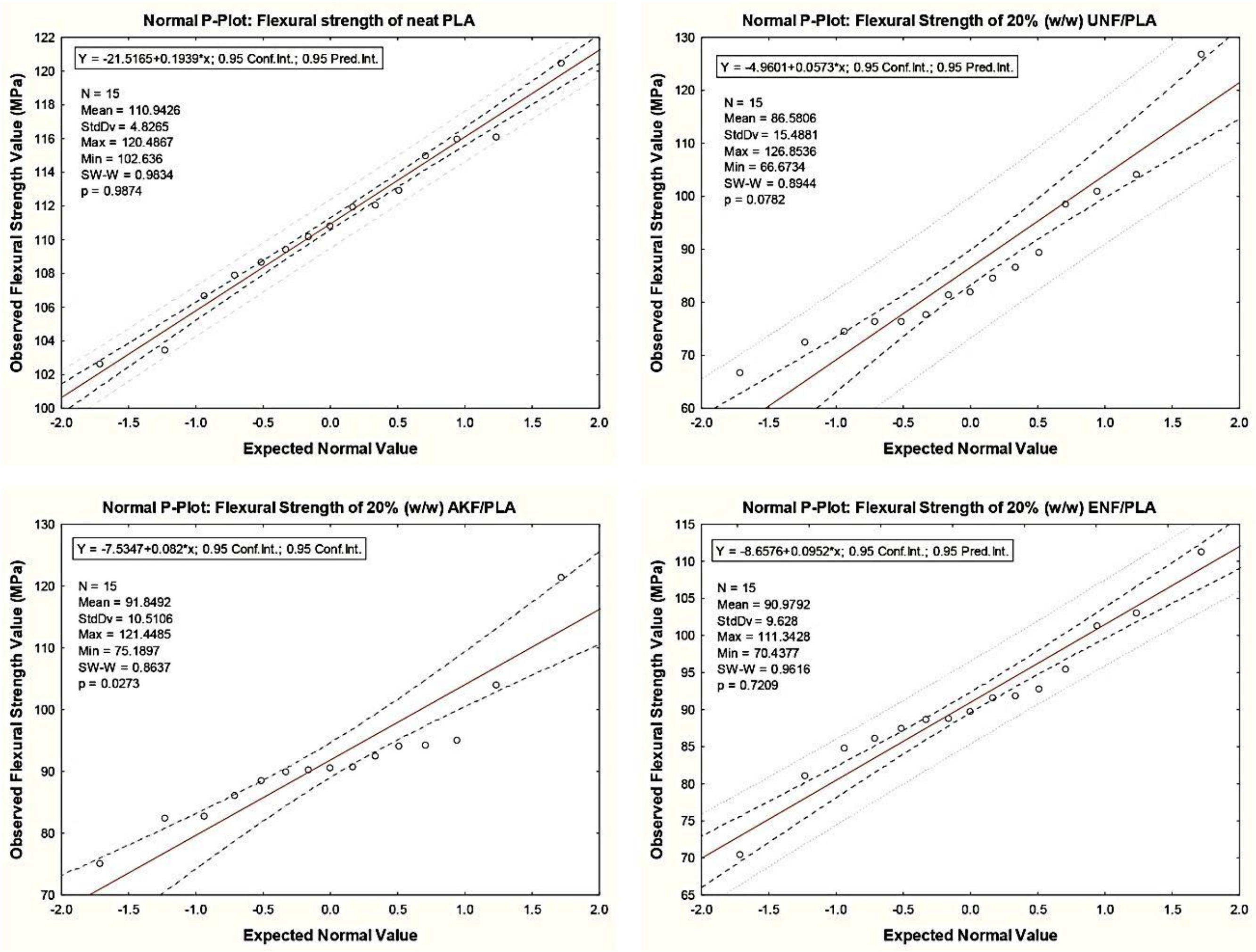


Figure_Apx H-2. Probability plots for ultimate tensile strength of 40% (w/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested.

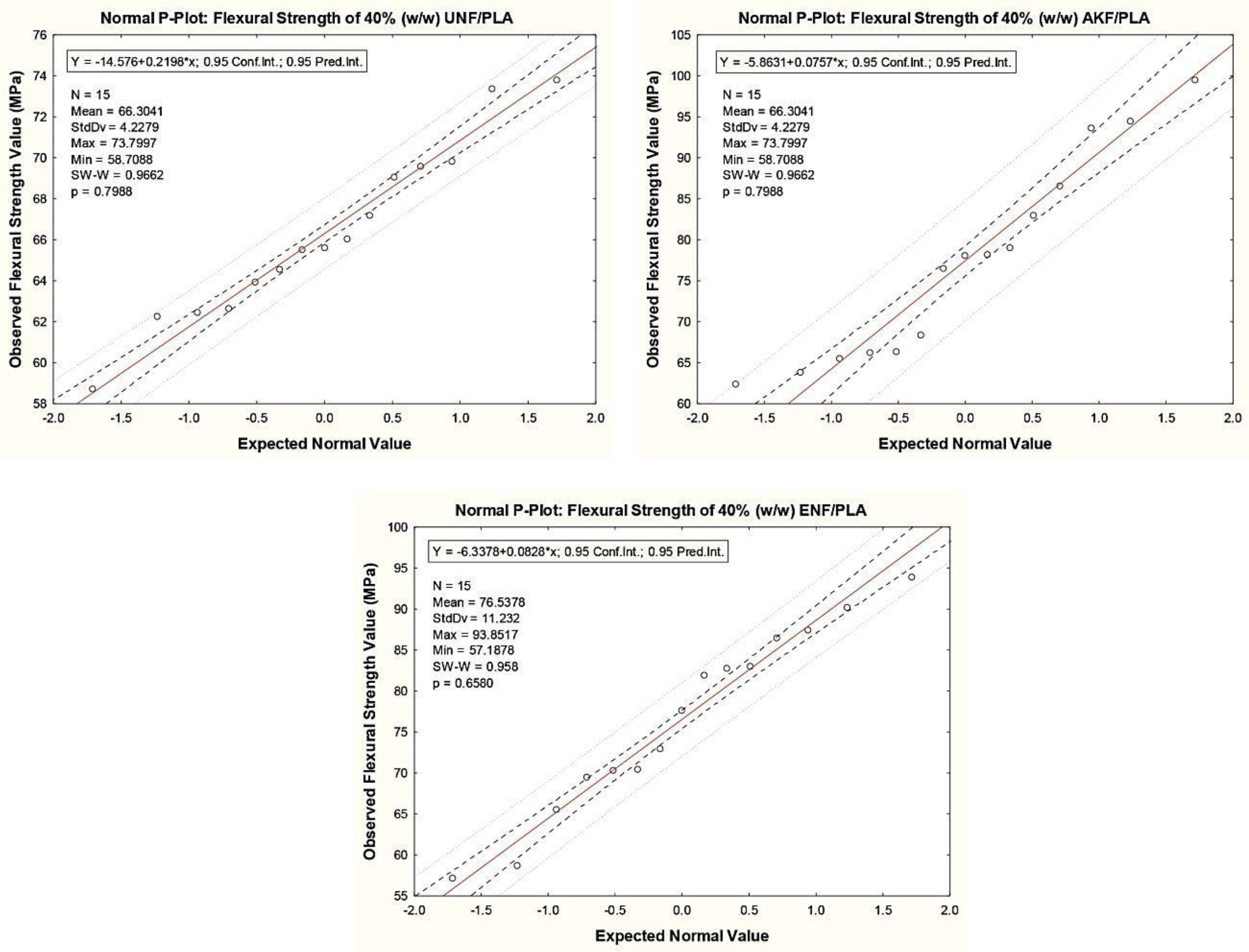


Figure_Apx H-3. Probability plots for ultimate tensile strength of 60% (w/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites specimens tested.

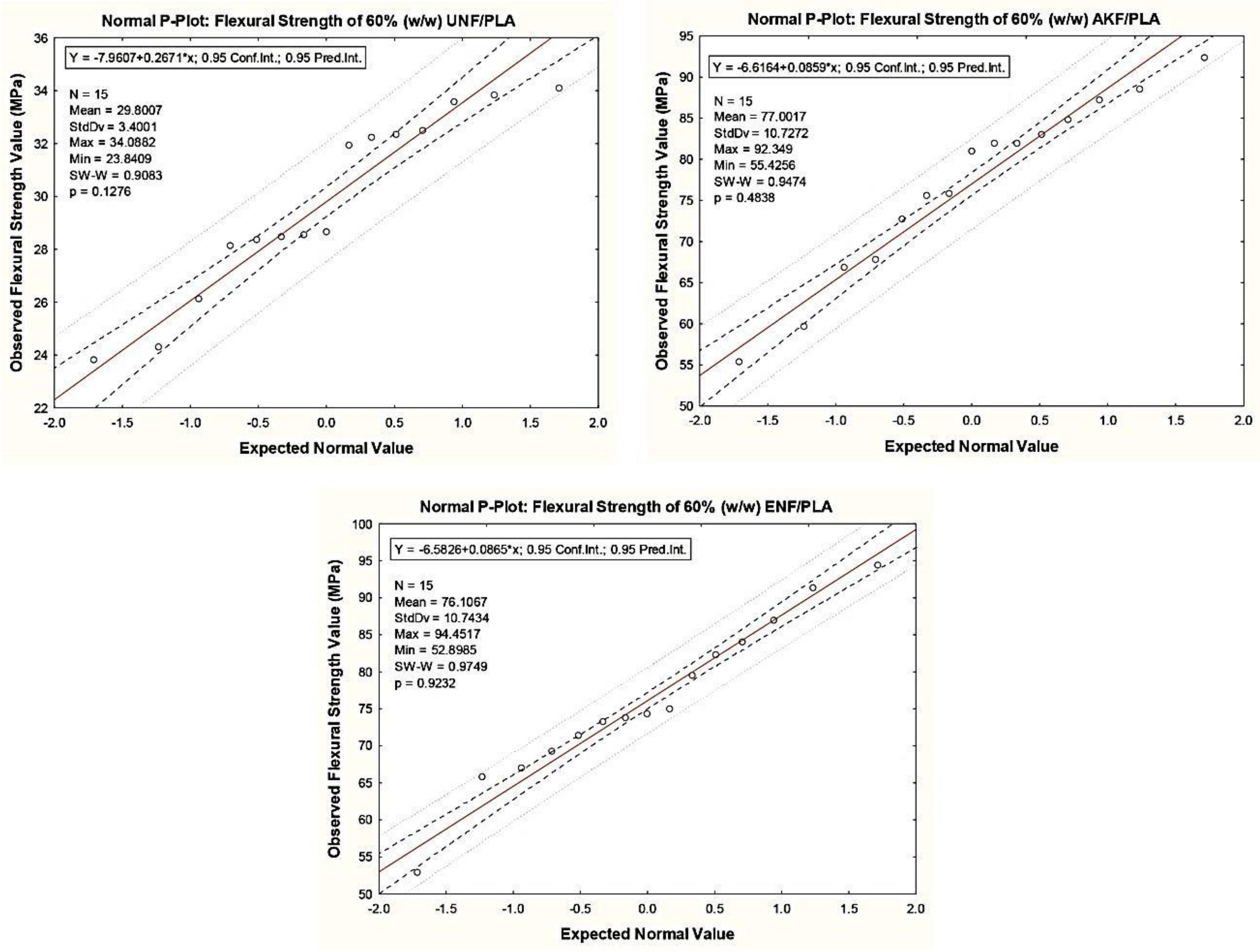
H.1.2 Flexural strength of Agave tequilana fibres and poly(lactic) acid bio-based composites specimens tested.



Figure_Apx H-4. Probability plots for flexural strength of 20% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites and neat PLA specimens tested.



Figure_Apx H-5. Probability plots for flexural strength of 40% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites and neat PLA specimens tested.



Figure_Apx H-6. Probability plots for flexural strength of 60% (v/w) *Agave tequilana* fibres and poly(lactic) acid bio-based composites and neat PLA specimens tested.

Appendix I Biodegradability of *Agave tequilana* fibres and poly(lactic) acid bio-based composites

Table_Apx I-1. One-way anova for untreated and alkali-treated samples

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
UNF 60%	3	42.3	14.1	0.0025
AKF 60%	3	48.1028	16.0343	0.0025

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5.61204	1	5.61204	2244.815	1.1871E-06	7.708647
Within Groups	0.01	4	0.0025			
Total	5.62204	5				

Table_Apx I-2. One-way anova between samples

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
UNF 20%	3	36.175	12.05833	0.0025
UNF 60%	3	42.3	14.1	0.0025
AKF 20%	3	25.35	8.45	0.0025
AKF 60%	3	48.10278	16.03426	0.0025
PLA	3	20.18056	6.726852	0.0025

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	179.1398	4	44.78496	17913.98	3.17E-19	3.47805
Within Groups	0.025	10	0.0025			
Total	179.1648	14				