INSTITUTO POLITÉCNICO NACIONAL

Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional Unidad Oaxaca

Tesis

"Materiales biocompuestos basados en almidón de maíz termoplástico reforzados con fibras de hoja de *Agave salmiana*"

"Biocomposite materials based on thermoplastic maize starch reinforced with *Agave salmiana* leaf fiber"

Que para obtener el grado de:

Doctor en Ciencias en Conservación y Aprovechamiento de Recursos Naturales

Presenta

Alicia Reyes Samilpa

Director de Tesis:

Dr. Miguel Chávez Gutiérrez

Santa Cruz Xoxocotlán, Oaxaca, México Junio de 2021

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SECRETARIA DE INVESTIGACIÓN Y POSGRADO

ACTA DE REGISTRO DE TEMA DE TESIS
Y DESIGNACIÓN DE DIRECTOR DE TESIS

Ciudad de México, 10 de junio del 2021

El Colegio de Profesores de Posgrado de **CIIDIR UNIDAD OAXACA** en su Sesión
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1.- Se designa al aspirante el tema de tesis titulado:

"Materiales biocompuestos basados en almidón de maíz termoplástico reforzados con fibras de hoja de *Agave salmiana*"

Objetivo general del trabajo de tesis:

Desarrollo y obtención de materiales bio-compuestos de matriz polimérica y fibras naturales, así como la caracterización de propiedades de los compósitos obtenidos al estar expuestos a distintos factores ambientales

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3.- El Trabajo de investigación base para el desarrollo de la tesis será elaborado por el alumno en:

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"Materiales biocompuestos basados en almidón de maíz termoplástico reforzados con fibras de hoja de *Agave salmiana*"

del (la) alumno (a):

Apellido Paterno:	Reyes	Apellido Materno:	Samilpa	Nombre (s):	Alicia

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CARTA CESIÓN DE DERECHOS

En la Ciudad de Oaxaca de Juárez el día 31 del mes de mayo el año 2021, la que suscribe **Reyes Samilpa Alicia** alumna del Programa de **Doctorado en Ciencias en Conservación y Aprovechamiento de Recursos Naturales** con número de registro **A170363**, adscrita a Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional Unidad Oaxaca, manifiesta que es autora intelectual del presente trabajo de Tesis bajo la dirección del **Dr. Miguel Chávez Gutiérrez** y cede los derechos del trabajo titulado: **"Materiales biocompuestos basados en almidón de maíz termoplástico reforzados con fibras de hoja de *Agave Salmiana*"** al Instituto Politécnico Nacional para su difusión, con fines académicos y de investigación.

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Dedication

To my mom:

My rock, my inspiration, and my friend

Thank you for your love, sense of humor, time, support, caring, and your words of wisdom

Content

Abbreviations and acronyms

Abbreviation/acronym	Definition
3D	Three-dimensional
α_m	Coefficient of thermal expansion
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared
C=O	Carbonyl group
CaCO3	Calcium carbonate
CC^+	Calcium carbonate (particles)
C-H	Hydrocarbon group
CH_2	Methylene
C-O-C	Ether group
CTE	Coefficient of thermal expansion
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetry
FAO	Food and Agriculture Organization
FESEM	Field Emission Electron Microscopy
FTIR	Fourier-Transform Infrared Spectroscopy
GLM	Generalized Linear Model
H-bonds	Hydrogen bonds
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear low-density polyethylene
LMDPE	Linear Medium Density Polyethylene
LSD	Least Significant Difference
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NEP	Not specified (used by FAO in Spanish)
ns	Not specified
OH	Hydroxide
ORL^+	Old roasted leaf fibers
PE	Polyethylene
PHB	Poly(3-hydroxybutyrate
PLA	Polylactic acid
PP	Polypropylene
PPgMA	Polypropylene grafted with maleic anhydride
PS	Polystyrene
RPM	Revolution per minute
SEM	Scanning Electron Microscopy
Tg	Glass transition temperature

TGA	Thermogravimetric Analysis
TMA	Thermomechanical analysis
TPS*	Thermoplastic starch
TPS/YRL10**	Thermoplastic starch from maize reinforced with 10 wt% of young raw leaf fibers
TPS/YRL20**	Thermoplastic starch from maize reinforced with 20 wt% of young raw leaf fibers
TPS/YRL30**	Thermoplastic starch from maize reinforced with 30 wt% of young raw leaf fibers
TPS/ORL10**	Thermoplastic starch from maize reinforced with 10 wt% of old roasted leaf fibers
TPS/ORL20**	Thermoplastic starch from maize reinforced with 20 wt% of old roasted leaf fibers
TPS/ORL30**	Thermoplastic starch from maize reinforced with 30 wt% of old roasted leaf fibers
TPS/F***	Thermoplastic starch from maize reinforced with agave fibers
TPS/F/CC3***	Thermoplastic starch from maize reinforced with agave fibers and 3 wt% of calcium carbonate particles
TPS/F/CC5***	Thermoplastic starch from maize reinforced with agave fibers and 5 wt% of calcium carbonate particles
TPS/F/CC7***	Thermoplastic starch from maize reinforced with agave fibers and 7 wt% of calcium carbonate particles
XRD	X-ray diffraction analysis
YRL[+]	Young raw leaf fibers

[+] Acronyms used in chapter 1 for purposes of this investigation

* Thermoplastic starch in general; and maize starch moisturized with 20 wt% of water and plasticized with 20 wt% of glycerol, for purposes of this investigation

** Formulations based on maize starch moisturized with 20 wt% of water and plasticized with 20 wt% of glycerol. Acronyms used in chapter 1 for purposes of this investigation

*** Formulations based on maize starch moisture with 20 wt% of water, plasticized with 20 wt% of glycerol, and reinforced with 20 wt% of *Agave salmiana* fibers from young raw leaves. Acronyms used in chapter 2 for purposes of this investigation.

Resumen

Esta tesis consta de tres capítulos redactados como manuscritos. El primer manuscrito es una revisión bibliográfica enfocada en las propiedades morfológicas y estructurales de distintas especies del genero *Agave* y la relevancia y el efecto de la incorporación de estas fibras como fase de refuerzo en materiales compósitos. Los principales objetivos de obtener estos materiales son disminuir el impacto ambiental causado por la acumulación de materiales derivados del petróleo en los vertederos, reducir los costos de producción, proporcionar valor agregado a los residuos derivados de diferentes actividades económicas y promover la conservación de los recursos naturales. La selección de una planta de agave para obtener fibras que se utilizaran en el desarrollo de biocompósitos depende de la disponibilidad del recurso, y más recientemente de los residuos generados durante la explotación de dichas especies. El segundo manuscrito corresponde a la primera etapa experimental de este estudio, en el cual utilizamos las hojas de *Agave salmiana* –un importante residuo agrícola de la industria del mezcal y el pulque– como fuente de fibras lignocelulósicas para reforzar almidón de maíz termoplástico usando los métodos de extrusión e inyección. Evaluamos los distintos factores que influyen en las propiedades físicas, mecánicas, térmicas y termomecánicas de dichos materiales: la madurez de las hojas y si éstas recibieron o no un tratamiento previo al tallado manual para obtener la fibra, el efecto de diferentes contenidos de fibra en los biocompuestos, y las condiciones ambientales a las que se expusieron los materiales obtenidos. La madurez de la hoja no mostró diferencias significativas entre las propiedades de las fibras, ni de sus respectivos biocompósitos, particularmente en las propiedades mecánicas y térmicas. El aumento del contenido de fibra mejoró las propiedades mecánicas y termomecánicas de los biocompósitos. El efecto de utilizar fibras obtenidas de hojas con diferente madurez como refuerzo de almidón termoplástico se vio reflejado en las propiedades mecánicas y termomecánicas de los biocompósitos, particularmente al ser expuestos a distintos factores ambientales. El tercer manuscrito corresponde a la segunda etapa experimental, en la cual utilizamos las conchas residuales de *Chicoreus erythrostomus* también conocido como caracol rosado chino –un abundante residuo pesquero acumulado principalmente en las costas de Baja California Sur– para obtener partículas de carbonato de calcio que fueron usadas como tercera fase del biocompósito basado en almidón de maíz termoplástico reforzado con 20 wt% de fibras de las hojas jóvenes y crudas de *A. salmiana*. La adición de carbonato de calcio mejoró las condiciones en el proceso de extrusión, la estabilidad térmica y dimensional y la respuesta a la absorción de agua en los compuestos. Con este estudio demostramos que se pueden utilizar residuos agrícolas y pesqueros como materiales de refuerzo y de relleno en el desarrollo de biocompósitos, abriendo la posibilidad de su uso en la economía circular. Finalmente, demostramos que estos biocompuestos, como muchos otros en la literatura, son adecuados para aplicaciones que implican la exposición a diversos factores ambientales, como el envasado de alimentos, geometrías estructurales e incluso fragmentos de crecimiento de corales.

Abstract

This thesis consists of three chapters written as manuscripts. The first manuscript is a bibliographic review focused in the morphological and structural properties of fibers obtained from different species from the *Agave* genus and the relevance and the effect of incorporating these fibers as reinforcing phase in composite materials. The main objectives of obtaining such materials are: to diminish the environmental impact caused by the accumulation of oil-based materials in landfills, to lower the costs of production, to provide value added to wastes derived from different economic activities, and to promote the conservation of the natural resources used. The selection of the agave plant to obtain fibers that will be used in the fabrication of biocomposites depends on the availability of the resource, and more recently on the residues generated during the exploitation of such species. The second manuscript is a research paper accepted for publication and corresponds to the first laboratory stage, in which we used the leaves of *Agave salmiana* –an important agricultural waste from the mezcal and pulque industry– as a source of lignocellulosic fiber to reinforce thermoplastic maize starch using the extrusion and injection methods. We evaluated different factors affecting the morphological, mechanical, thermal, and thermomechanical properties of such materials: the maturity stage of the leaves and the treatment they received regarding the traditional process to obtain the fiber, the effect of different fiber content in the biocomposites, the environmental conditions to which the biocomposites were exposed, and the addition of a filler to the biocomposites as a third phase, varying also the content of the filler. The maturity of the leaf showed small differences between the properties of the fibers, and of their respective biocomposites as well, particularly in the mechanical and thermal properties. The mechanical and thermomechanical properties improved with the increase in the fiber content. The effect of using fibers from leaves with different maturity as reinforcement in thermoplastic starch was exhibited in the mechanical and thermomechanical properties of biocomposites, particularly when they were exposed to different environmental factors. In the third manuscript corresponding to the second experimental stage, we used the residual shells of *Chicoreus erythrostomus*, also known as pink *Murex* snail –an abundant fishery waste accumulated as piles on the coasts of Baja California Sur, Mexico– to obtain calcium carbonate particles that were used as a third phase in the biocomposite based on thermoplastic maize starch reinforced with 20 wt% of young raw leaves fiber from *A. salmiana*. The addition of calcium carbonate enhanced the conditions of the extrusion process, the dimension and thermal stability, and the response to water absorption of the composites. With this study we proved that agricultural and fishery wastes can be used as reinforcement and filler materials in the production of biocomposites, opening the possibility for those involved in the same economic activities or similar to create circular economy within their communities. We also proved that biocomposites based on different natural resources can be processed by common means, achieving especially good thermomechanical properties. Finally, we demonstrated that these biocomposites, as many others in the literature, are suitable for applications involving the exposure to diverse environmental factors, such as food packaging, structural geometries, and even coral growth fragments.

Introduction

Biodegradable plastics and biocomposite development arisen in the decade of 1980 as a response to the concerning of the great amount of solid residues accumulated in landfills and oceans (Panigrahi, et al., 2007; Kim & Netravali, 2010; Gao, et al., 2019). Among these residues petroleum-based polymers are considered as pollutants mainly because of their non-biodegradable nature and the non-renewable sources depletion their production represents (Kim & Netravali, 2010; Sahari & Sapuan, 2011). The large amounts of agricultural residues annually produced also have pollutant effects in the air and in the quality of the soil, however, they can be harnessed as an important source of biomass (Sahari & Sapuan, 2011).

In Mexico several species from the *Agave* genus are used in the production of alcoholic beverages, such as *A. tequilana* to produce the distilled tequila and *A. salmiana* for the distilled mezcal and the fermented pulque. During the production of these beverages by-products as bagasse and residual leaves are generated, and remained exposed to the environment as contaminants. Some studies have characterized and used the bagasse fibers from *A. tequilana* as reinforcing material for polymers, mainly polyolefins (Sanjuan-Raygoza & Jasso-Gastinel, 2009; Leduc, et al., 2008; Pulido, et al., 2014). However, there is a lack regarding the research related to using the residual *Agave salmiana* leaves generated from the pulque and mezcal production. Although this leaves are considered as an agro-waste (Jiménez-Muñóz, et al., 2016), they represent an important source to obtain quality fiber with potential to be used as reinforcing material in the polymeric composite materials production.

Therefore, the main objective of this thesis was to obtain biocomposites from natural resources and evaluate the effect of using diverse content of *Agave salmiana* fibers from leaves with different age on the properties of biocomposites based on thermoplastic maize

starch. In order to achieve the main objective, specific objectives were set: i) to evaluate the morphological, thermal, thermomechanical, and mechanical properties of the biocomposites, as well as characterize their functional groups in function of two ages of the leaves, and three different contents of fiber; ii) to study the changes in the biocomposites exposed to UV radiation, temperature, moisture, and salt-water immersion; and iii) to evaluate the properties of the biocomposite that exhibited better performance to the environmental exposure by the effect of adding different content of filler as a third phase.

The present work is structured in three chapters written as manuscripts related to the importance of harnessing *Agave salmiana* fibers in composite materials. In the first chapter "*Agave fibers from different species reinforcing polymeric composites and hybrid materials: A review*" the state of art and the background of general characteristics of hard fibers, with special emphasis in agave fibers, and the generalities of polymeric composite materials developed over the last five years using these type of fibers is explored. In the second chapter "*Accelerated aging effect in physical and thermo-mechanical properties of maize starch biocomposites reinforced with Agave salmiana fibers from different leaf ages*" the results presented correspond to the first experimental stage that covered the first and second specific objectives. The third and final chapter "*Hybrid composites based on thermoplastic starch and agricultural and marine wastes for 3d printing filaments*" presents the results of the second experimental stage corresponding to the third specific objective.

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Chapter 1

Fibers from different agave species reinforcing bio-based composites: A review

Alicia Reyes Samilpa and Miguel C. Gutiérrez

Manuscript to be send to Polymer Composites (JCR, Q1, IF= 2.265)

Chapter I: Fibers from different agave species reinforcing bio-based composites: A review

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Keywords: agave species, polymeric matrix, lignocellulosic fiber, composite processes, leaf fiber, bagasse fiber, biopolymers

Abstract

In the present work, general information concerning fibers from different agave species and their use in the production of polymeric reinforced materials has been compiled. The aspects of the agave fiber reviewed include physical properties and chemical composition, common obtaining processes, and agave species used to obtain fibers from their leaves and core. Regarding the polymeric reinforced composite materials, this review focused mainly on biodegradable and natural-based polymers, major manufacturing processes, and general properties of the obtained biocomposites.

Over the last decade, the most commonly used species for this purpose has been *Agave sisalana*, a globally known plant used to obtain the textile fiber sisal. Recently, there has been a notable increasing interest in the by-products of species used for other original purposes like the production of alcoholic beverages, specifically in *A. tequilana*, to harness the residual bagasse fibers obtained from the core of the plant. Moreover, the use of the ornamental species *A. amaricana* as a source of novel fibrous materials is worth mentioning, as well as *A. angustifolia,* and *A. marginata* in lower frequency. Availability, biodegradability, lightness, and high mechanical and thermal properties are some advantages of fabricating composite materials with these hard fibers. By contrast, the principal drawback of using agave fibers is their hydrophilic nature, which affects negatively in the adhesion with several hydrophobic polymers as well as the water absorption response. However, agave fibers can be subjected to chemical treatments to reverse their hydrophilicity, improving their compatibility with diverse polymeric matrixes, extending their applications beyond the textile industry.

Introduction

A composite material merges two or more traditional materials or phases combining the best properties of each one to obtain an enhanced, multiphase, tailor-made material (Gutiérrez, et al., 2014; Balasubramanian, 2016; Díaz, et al., 2017). Some terms referring to those composite materials made up of at least one component obtained from natural resources have been a topic of discussion for researchers.

In general, biocomposites are materials composed either by a biopolymer matrix, or natural fibers as filler or reinforcing agent, (Ho, et al., 2012; Díaz, et al., 2017), representing an

alternative for the use of petroleum-based polymers (Logié, et al., 2018) or synthetic fibers (Sánchez, et al., 2020), respectively. Authors like Averous & Boquillon (2004), Kim & Netravali (2010) and Zuccarello & Marannano (2018), stated that for a material to be considered as a biocomposite, it should be composed of both natural-biodegradable polymeric matrix and fiber reinforcement. This is in agreement with Sapuan and Yusoff (2015), who pointed that composites based on natural fibers reinforcing synthetic polymers cannot be considered as a totally environmental benign material.

Another term used to define these materials is eco-composite, which, according to Bogoeva-Gaceva et al. (2007) involves materials with environmental and ecological advantages, when compared to the traditional ones, and can be composed either by natural fiber, or by a biopolymer matrix, or both.

Finally, another type of composite materials are the hybrid composites, which comprise the individual properties of two or more materials, including the inherent advantages and disadvantages of the individual components (Edhirej, et al., 2017). The most common hybrids combine two reinforcing materials, typically fibers, in one polymeric matrix (Prasad, et al., 2018; Yusoff, et al., 2016; Edhirej, et al., 2017; Martín-del Campo, et al., 2020).

Biocomposites are designed and developed to solve three major environmental problems: i) to decrease and eventually to replace the production of petroleum-based materials; ii) to provide usefulness for waste and by-products derived from different industries like agriculture; and iii) to reduce the accumulation of non-biodegradable plastic residues in landfills (Panigrahi, et al., 2007; Kim & Netravali, 2010; Sahari & Sapuan, 2011; Ho, et al., 2012). Thus, the use of biodegradable polymers, biopolymers, and natural plant fibers

promotes a solution to these environmental problems (Schlemmer, et al., 2010; Sahari & Sapuan, 2011; Singha & Rana, 2012; Zamri, et al., 2016; Sánchez, et al., 2020).

Among the different types of composites, polymer matrix reinforced with fibers composites are the most remarkable due to the ease of production, low-density, and high specific properties the fiber confers to the polymer used (Gutiérrez, et al., 2014; Zamri, et al., 2016; Sánchez, et al., 2020). The production of both natural and synthetic fiber-reinforced polymers (FRP) has gradually replaced synthetic and petroleum-based materials (Zamri, et al., 2016), and at present, they are considered as highly promising materials (Balakrishnan, et al., 2016).

Besides the high specific properties, such as stiffness, impact strength, flexibility, and modulus, and low density, the use of natural fibers as reinforcing agent in biocomposites is also due to their environmental and economical characteristics, since they are highly available and renewable, nonabrasive, ease of processing, and they represent a low-cost production compared to synthetic fibers, the latest especially due to lignocellulosic fibers can be obtained from agricultural waste (Akil, et al., 2014; Zamri, et al., 2016; Karakus, et al., 2016; Li, et al., 2020).

Plant fibers or lignocellulosic fibers can be classified considering the amount of cells they have, their softness or stiffness, the purpose of their utilization, or the vegetal organ they are obtained from. The latter is an accurate and commonly used classification, hence, fibers produced in seeds, stems, leaves, and fruits have different properties (Zimniewska & Wladyka-Przybylak, 2016). In this regard, Cruz-Ramos (1986) classified the most commercial fibers based on their characteristics and origin in three groups: i) soft fibers from the seeds, ii) bast fibers from the stem, and iii) hard fibers from the leaves.

Although there is scarce and former information about the advantages of hard fibers over soft fibers, most of the production of soft fibers is intended for the textile industry due to their physical properties (Cruz-Ramos, 1986). Also, compared to other fibers, hard fibers are more resistant to the effects of microorganisms (Mastache, 1971) because of the presence of lignin (Velásquez, et al., 2016). Dizbay-Onat et al. (2017) compared between bast (hemp, flax) and leaf fibers (sisal) as precursors for activated carbon adsorbent materials, founding that bast fibers decompose at lower temperatures compared to hard or leaf fibers.

Regarding natural fiber-reinforced composites, the most frequently used fibers for such purpose are: soft fiber as cotton; bast fibers as flax, hemp, jute, kenaf, and ramie; hard fibers as banana or abaca, curauá, henequen, phormium, piassava, pineapple, palm, sansevieria, and sisal; fruit fiber as coir and kapok; and grass and reed fiber as bamboo (Ho, et al., 2012; Costa, et al., 2018; Akil, et al., 2014; Karakus, et al., 2016; Prasad, et al., 2018; Gutiérrez, et al., 2014; Li, et al., 2020).

Several review studies summarize the major fabrication processes, the improvement of mechanical properties, drawbacks, and possible applications of composites based on both natural and synthetic polymers reinforced with natural fibers (Azwa, et al., 2013; Gurunathan, et al., 2015; Dicker, et al., 2013; Mohanty, et al., 2018). Other studies review different aspects concerning specific natural fibers used as reinforcing phase in biocomposites: Sorieul et al. (2016) described in detail the chemical composition and the structural arrangement of wood fibers, as well as compiled information including definitions and biological origin, extraction processes, physical properties, and treatments to use these fibers in wood polymer composites; Kalia et al. (2009) investigated the effects on the surface –related to the adhesion with polymer matrix– and the mechanical properties of natural fibers

subjected to chemical pretreatments such as mercerization, acetylation, etherification, benzoylation, graft copolymerization, and acrylation, as well as the application of peroxide, silane coupling agent, permanganate, sodium chlorite, plasma, and isocyanate. Yahaya et al. (2018) gathered the characteristics of kenaf (*Hibiscus cannabinus*) fibers and their effect in the physical, mechanical, and thermal properties of synthetic fibre hybrid composites, as well as the major fabrication methods; Senthilkumar et al. (2018) investigated the effects of using sisal (*Agave sisalana*) fibers as reinforcing material in the mechanical properties of thermoplastics and thermoset polymers, and the limitations and applications of implementing these lightweight structural materials in the construction industry.

Even though there are plenty agave species that represent an important source of fiber, to the knowledge of the authors, there is a lack of studies compiling information about polymers reinforced specifically with agave fibers. Thus, this review focuses on the current state and the relevance concerning agave fiber over the last five years about the following issues: i) the agave species commonly used to obtain fiber which is further used as filler and as reinforcing phase for composite and hybrid materials; ii) the polymers used as matrix in these materials, and the techniques used to fabricate agave reinforced polymeric composites; and iii) general properties and applications of such materials. To compile the information regarding the three objectives mentioned, only research articles were considered, while other types of publications, such as article reviews or books, were used only to complement general information and as context background.

1. Hard fibers

Some physical and anatomical characteristics of plant fibers are related to the organ from which they are extracted –stem or core, leaves, fruits, or roots– and are classified according to their physical and chemical properties (i. e. length and content of cellulose and lignin, respectively) in soft, hard, and short fibers. These features define the applications for the fibers, such as textiles and fabrics, paper production, household goods, or other industrial products (Simpson & Conner-Ogorzaly, 1995; FAO, 2014; Maiti, 1995; Dewey, 1941). Also, the properties of the fibers depend essentially on the maturity of the plant from which they are collected as well as the process to obtain them (Mohanty, et al., 2005).

Within lignocellulosic fibers, the so-called hard fibers are those which are obtained from the leaves of some monocotyledon plants (Robles, 2002), with multicellular structure, rough texture, and partially flexible, due to the presence of lignin and hemicellulose (McKenna, et al., 2004), being *Musa textilis* and *Agave sisalana* the two species most produced to obtain hard fibers over the world.

In Figure 1, the world production of the three major crops of hard fibers over the last 60 years is shown, and the data suggest that the demand for sisal crop is mainly for the production of hard fibers to fabricate textiles and fabrics, and the crops of several other agave species for the production of hard fibers and alcoholic beverages.

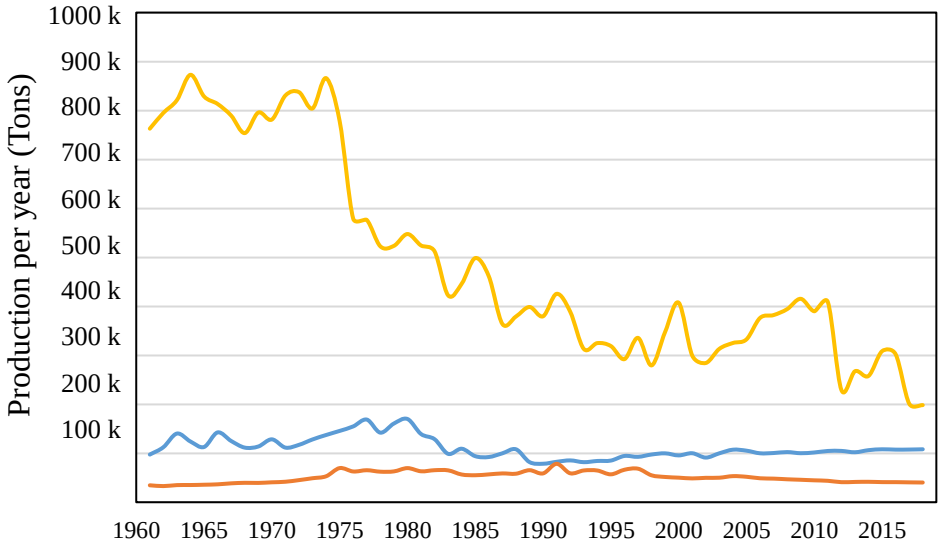

Figure 1. Top three lignocellulosic fibers worldwide production over 60 years: Sisal (—); abaca (—); agave fiber (—). Elaborated by Reyes-Samilpa with information from FAO (2019).

According to the Food and Agricultural Organization (FAO, 2019), the major plant fibers produced in Mexico can be classified into two groups: i) agave fibers NEP (not specified) that includes pita floja (*Agave foetida*), ixtle or lechuguilla (*A. lechuguilla*), cantala or maguey fiber (*A. cantala*), pita (*A. americana*), and henequen from El Salvador or letona (*A. letonae*); and ii) sisal fiber (*A. sisalana*) including henequen fiber (*A. fourcroydes*). Vietnam, Brazil, and Canada are the major producers of hard fibers in the world, but is Brazil which increasing production has been more constant since the 1970s, as shown in Figure 2.

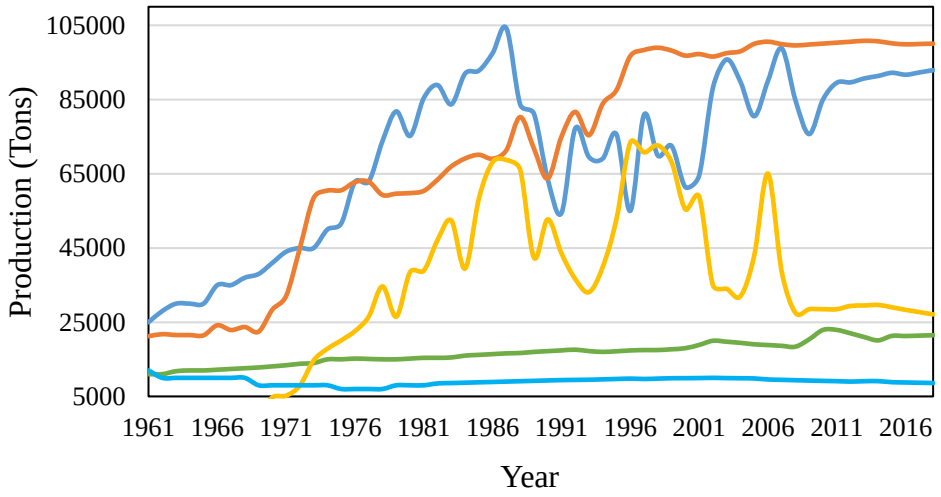

Figure 2. Top five world producers of hard fibers over 60 years: Vietnam (—); Brazil (—); Ethiopia (—); Canada (—); Tanzania (—). Elaborated by Reyes-Samilpa with information from FAO (2019).

1.1. Composition of hard fibers

Lignocellulosic fibers are essentially composites themselves, since cellulosic microfibrils are immersed in a lignin matrix (Cruz-Ramos, 1986). The major plant fibers components, with the exception of cotton fibers, are cellulose, hemicellulose (polysaccharides), lignin (polyphenol), pectin, wax, and substances soluble in water, being the first three the responsible for the fibers' physical properties (Bledzki & Gassan, 1999; Bondaris, et al., 2017). Some items such as species, age of the plant, origin region, and weather can define the amount of cellulose and lignin and, therefore, the physical-mechanical properties of vegetable fibers (Mohanty, et al., 2005). Within a bundle of fiber each cell is connected by a middle lamella, which consists of lignin and hemicellulose (Alves, et al., 2013); the structural arrangement of cellulose, consisting of rigid cells and lignin, defines the stiffness and strength

of the fibers (Cazaurang-Martínez, et al., 1991). Cellulose and hemicellulose polysaccharides are produced during the biological synthesis of the cell wall, simultaneously with the lignification process that occurs when lignin fills the spaces within the polysaccharides fibers, cementing them (Mohanty et al. 2005).

John & Thomas (2008) described the cell wall of a fiber as a non-homogenous membrane, since a single fibril consists of a complex structure built by layers. The first layer is a primary cell wall which is developed during the cell growth. Within the primary wall is the secondary wall which, in turn, consists of three layers, being the middle layer the thickest one, and which determines the mechanical properties of the fiber. The long chain of cellulose molecules constituting the cellular microfibrils helicoidally arranged is found in the middle layer.

The major component of plant fibers is cellulose, a linear polymer consisting of molecular chains of β-1-4-glucosidic oriented in the direction of the fiber with an approximate 10 000 degree of polymerization (Bledzki & Gassan, 1999). Usually, the chemical structure of cellulose in different plant fibers is the same, however, the degree of polymerization has variations depending on the type of fiber (Bledzki & Gassan, 1999; Mohanty, et al., 2005). The structure of cellulose presents two types of regions: high ordered, forming crystalline regions, and low ordered, forming amorphous regions. Inside of the crystalline region there are hydroxyl groups which confers to the cellulose its hydrophilic character (Bledzki & Gassan, 1999); these groups can form hydrogen bonds between parallel chains and reduce water absorption (Sreekala, et al., 2002). They exist as microfibrills and are responsible to provide mechanical strength to the fiber or fiber bundle (John & Thomas, 2008).

Another important component of hard fibers is lignin, which is a complex and amorphous structured polymer. Lignin is a hydrocarbon with high molecular weight, high carbon content, and low hydrogen content, and presents aliphatic and aromatic constituents. The exact structure of the lignin –which depends on the botanical origin and the extraction method– is still uncertain because it has multiple structural units which are seldom regular repeated. However, some associated groups such as methoxyl, hydroxyl, and carboxyl are recognized (Mohanty, et al., 2005; Lu & John, 2010; John & Thomas, 2008). Each structural unit has five hydroxyl groups, five methoxyl, and is completely hydrophobic. Lignin confers rigidity to the wall of the vegetable cell fibers and protects the cellulose from microorganisms degradation (John & Thomas, 2008).

The third polymer contained in lignocellulosic fibers is hemicellulose. This is a group of polysaccharides that form a branched linear structure non-crystalline, with 50 to 3000 polymerization degrees. It contains 5-6 types of sugars as glucuronoarabinoxylans, xyloglucans, galactomannan, galactoglucomannan, glucomannan, mix bounded glucans, and arabinogalactans (Velásquez, et al., 2016; Bledzki & Gassan, 1999; Sorieul, et al., 2016). Hemicelluloses are present in the primary and secondary cell walls, mostly distributed between cellulose and lignin, with hydrophilic character, and because of its heterogeneity and complexity are considered as a single entity (Sorieul, et al., 2016). The name given is a misnomer and is not a derivative of cellulose (John & Thomas, 2008; Choi, et al., 2008). Therefore, the cellulose microfibrils are coated with hemicellulose and in turn are embedded in a matrix cementing of hemicellulose, lignin, and sometimes pectin, making a cross-linked structure (John & Thomas, 2008; Velásquez, et al., 2016; Mohanty, et al., 2005).

Hemicelluloses are polysaccharides composed by sugar, glucose, xylose, galactose, arabinose, and mannose. Compared to cellulose, hemicelluloses have lower degree of polymerization and lower mechanical contribution to the fiber. However, hemicelluloses provide the binding effect between microfibrils, providing them structural reinforcement (Razali, et al., 2015). In Figure 3, the representation of the cell walls and the cellulose microfibrils arrangement within a bundle of agave fiber is shown.

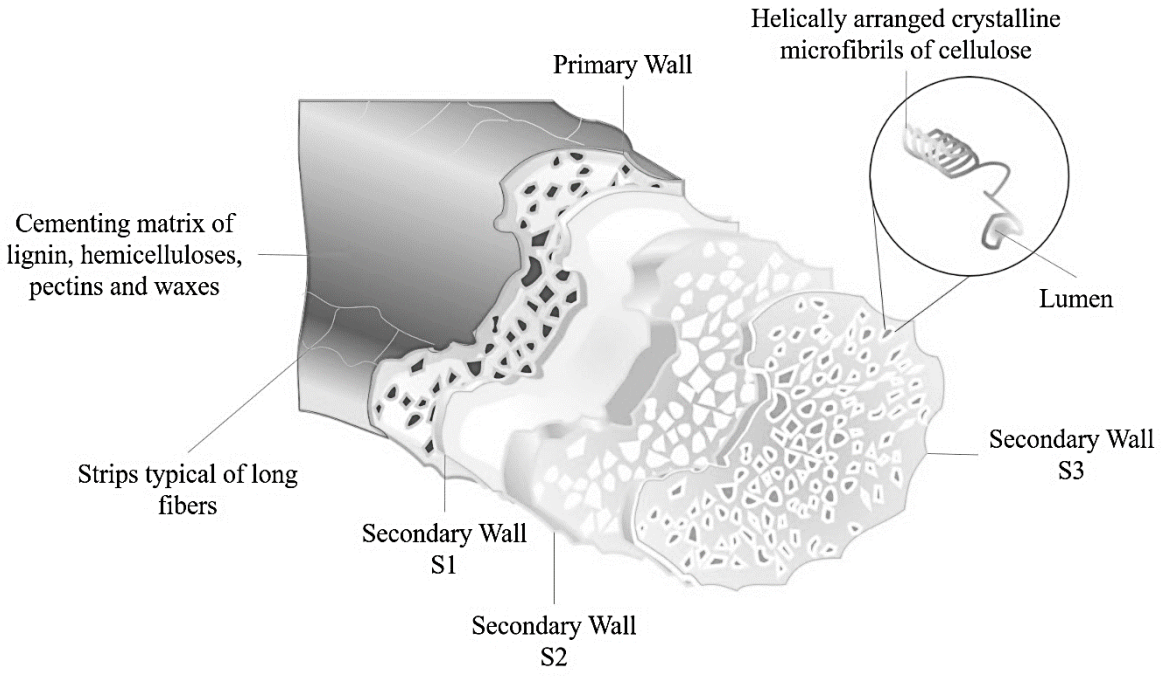

Figure 3. Scheme of the agave fiber structure and composition. Elaborated by Alicia Reyes with information based on the micrographs form Alves et al. (2013) and Kalia et al. (2009).

2. Agave fiber

The lignocellulosic fibers obtained from several *Agave* species are often used to textile and artisan purposes, mainly being cantala (*Agave cantala*), henequen (*A. fourcroydes*), ixtle (*A.*

salmiana y *A. mapisaga*), lechuguilla (*A. lechuguilla*), letona (*A. letonae*), sisal (*A. sisalana*) and zapupe (*A. zapupe*). The fiber known as izote or samandoca palm (*Yucca carnerosana*) is also included in this classification (McLaughlin & Schuck, 1991; Valenzuela-Zapata, et al., 2011).

Pérez-Zavala et al (2020) estimated that during the production of tequila in the period of 2015-2019 around 5 168 200 tons of *Agave tequilana* leaves were wasted, however the analogue information of other agave species used in pulque and mezcal production is yet unknown. Commercial agave fibers account represents around the three percent of the fresh weight of the leaf (Mukherjee & Satyanarayana, 1984; León, 2000) of *Agave sisalana*, which, with an approximate weight of 600 g, 3% fiber, which are around 1000 fibers can be obtained. However, different authors have registered fiber yields in other species of *Agave* fiber producers expressed in a productive context. López (2008) recorded that 104 kg of green leaves of *Agave angustifolia* can provide 5.12 kg of dry fiber. Meanwhile, Martínez (2015) registered in *A. lechuguilla* that 85 kg of the cogollo, that are the youngest leaves of the plant, can provide about 5.6 kg of dry fiber.

2.1. Morphology and composition of agave fibers

Variations of lignocellulosic concentration in agave fibers depends on the plant species they were obtained from, being cellulose the major component content (Jiménez-Muñóz, et al., 2016). Henequen and sisal has the greater content of cellulose (around 60 to 78%), and *Agave salmiana* fiber the lowest (49%) as reported to different authors (Table 1).

Table 1. Chemical composition of the fibers obtained from different *Agave* species

***Agave* species**	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Author**
A. americana L.	68 a 80	15	5 a 17	Mylsamy, (2011); Hulle et al. (2015)
A. angustifolia	65	23	6.5	Teli & Jadhav (2017)
A. cantala	64.23	9.45	5.91	{Ubaidillah, 2016 #2})
A. fourcroydes	60 a 78	4 a 28	8 a 13	Fajardo et al. (2013)
A. lechuguilla	17	17	7	Carmona et al. (2017)
A. salmiana	49	Not specified	8	Naranjo et al. (2016)
A. sisalana	66 a 78	10 a 14	10 a 14	Mohanty et al. (2005)
A. sisalana variegata	69.3	19.4	7.6	Athijayamani et al. (2016)
A. tequilana	64.8	5.1	15.9	Iñiguez (2001b)

In general, the morphology of plant fibers is very similar, only differing in quantity of fibrous cells, size of the primary and secondary cell walls, and cross section area (Alves, et al., 2013). After extraction, fibers obtained from different species of Agave are arranged in beams of elementary fibers, joined together by waxy and sticky substances (Msahli & Drean, 2005).

Cruz-Ramos (1986) described the ultimate fiber of hard fibers as the rigid cellulosic material immersed in a soft matrix of lignin. Msahli et al., (2006) described *Agave americana* L. ultimate fibers as long technical fibers, usually hard, rigid and coarse in texture, with 24 µm average diameter and 1 to 7.5 mm average length. According to the Great Soviet Encyclopedia (1970) an ultimate or elementary fiber is a natural textile fiber that cannot be divided longitudinally without destroying the structure and that can be used to produce fashion yarns and textiles (Figure 4).

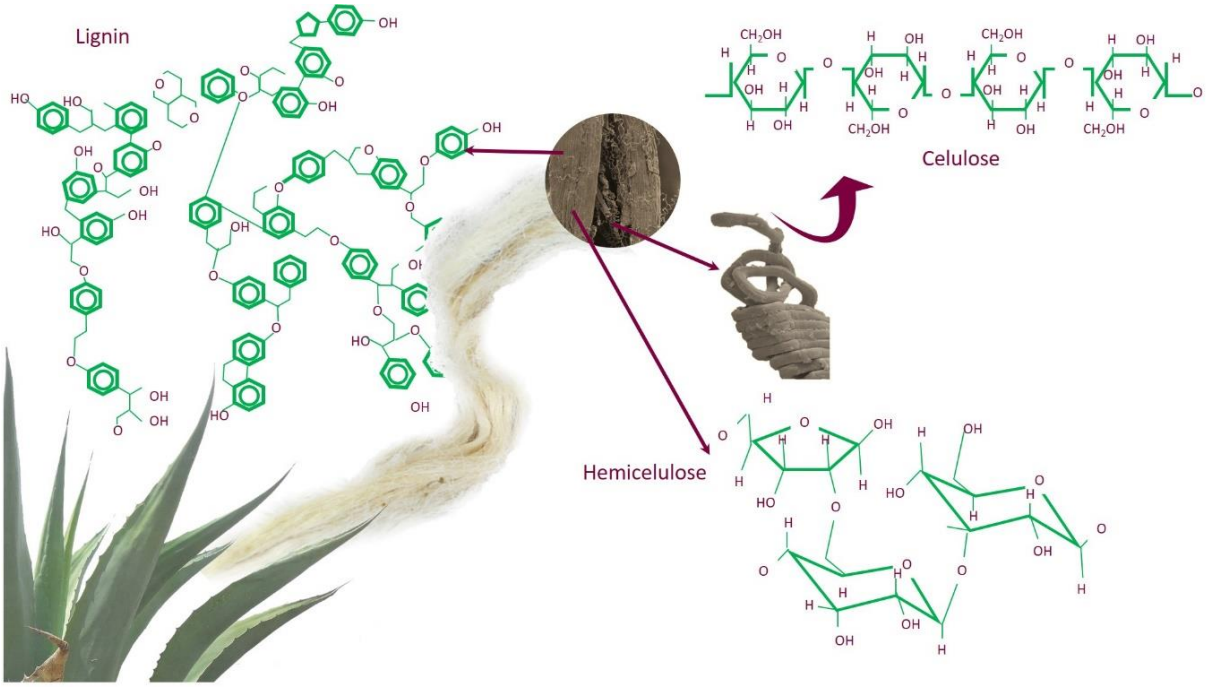

Figure 4. Scheme of *Agave* fibers: fiber emerging from the leaf amd micrograph showing cellulose microfibrills covered by a matrix of lignin and hemicelluloses, and the structures of cellulose, hemicellulose and lignin. Elaborated by Alicia Reyes with original photographs and micrographs.

Some authors have observed and described different aspects of the individual fibers structure from several species of *Agave* using the Scanning electron microscopy (SEM). This is one of the most used techniques to observe individual fibers more detailed and its morphology fracture (Bunsell, et al., 2018).

Teli & Jadhav (2017) indicate that the process of obtaining fibers from *Agave angustifolia* influences in the lignin and hemicellulose layer surrounding cellulose microfibrils, since the extraction with retting method employs water and physical and biological process. Maiti and Garza de la Riba (1992) observed that the high permeability on lechuguilla (Agave lechuguilla) fibers are due to the microfibrils that constitute them.

Cazaurang-Martínez et al., (1991) pointed out that lignin matrix cements stiff cellulosic fibers within a single sisal fiber (*Agave fourcroydes*) and mechanical properties of fibers are based on the structural arrangement of each cellulosic fiber. Wilson & Hamilton (1986) explain that large cellulose cells are microscopic filaments or microfibrils parallel joined together with both crystalline and amorphous regions molecular alignment in some areas of these microfibrils. Choi et al., (2008) showed that the surface of the henequen is soft due to wax, pectin and primary cell wall surround the fibers.

In the cross section of a single sisal fiber (*Agave sisalana*) He & Li., (2007) observed that it is consisting of 100 to 200 tracheids or microtubes; each tracheid is surrounded by other five to seven neighboring tracheids and are separated by a middle lamella. Bismarck et al., (2001) analyzed the morphology of raw and surface modified *Agave sisalana* fibers with different treatments and found small particles attached in the granular surface of raw fibers, that are feasible to be waxy and fatty substances.

Stripes located in the length of the fibers can be observed as Msahli et al., (2005) established to be distinctive to long vegetable fibers. All micrographs shown in Figure 5 were obtained from fibers without chemical treatments, in some cases only to observe their morphology, and in others to analyze the effects of chemical treatments on the fiber surfaces.

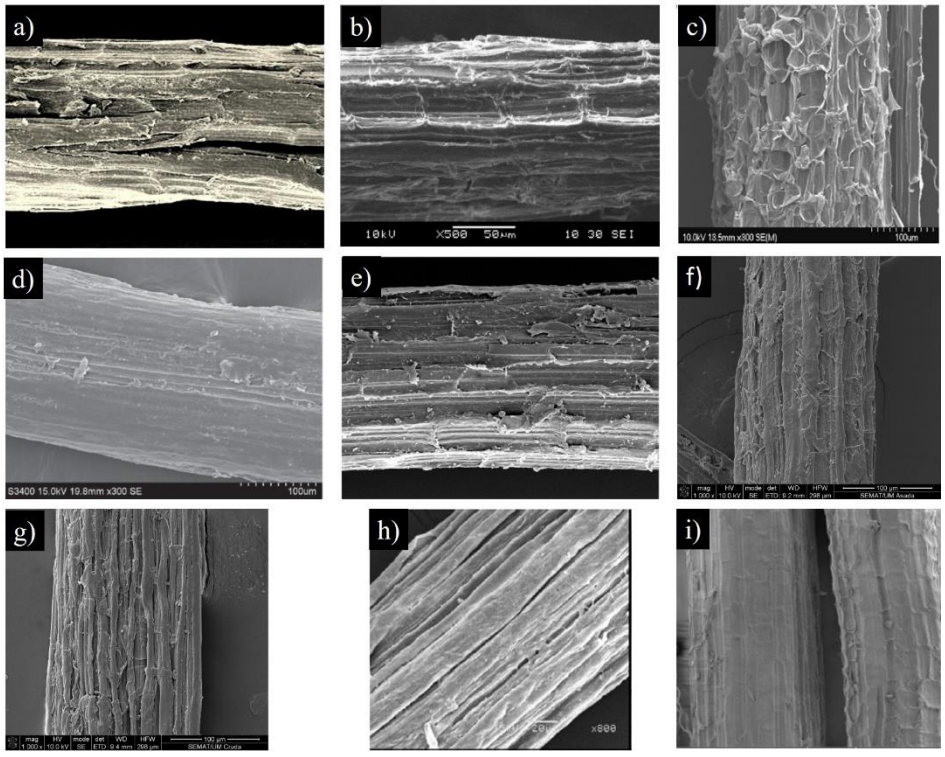

Figure 5. Surface structure of different agave fibers: a) *Agave americana* L. (Hulle, et al., 2015); b) *A. angustifolia* (Teli & Jadhav, 2017); c) *A. fourcroydes* (Choi, et al., 2008); d) *A. lechuguilla* (Kicińska-Jakubowska, et al., 2012); e) *A. sisalana* (Bismarck, et al., 2001); f) *A. salmiana* from roasted leaf (autor's original image); g) *A. salmiana* from raw leaf (author's original image); h) *A. tequilana* (Alanis, 2012); i) *A. furcraea* (Guzmán, et al., 2018).

2.2. Fiber extraction methods

In this section of the review, the most common process of obtaining agave fiber are described. It is worth to mention that the agave fibers used in several of the reviewed works were commercially supplied, hence, a detailed description of the process used to obtain such fibers was not provided. The methods described below are classified according to the organ of the agave plant from which the fiber is obtained in order to maintain the focus in these species of the present investigation. The description of obtaining the bagasse fibers is presented first, since the they are obtained from few agave species, and the process to obtain this type of fiber is implied in the production of alcoholic products. Then, a more extensive description of the major processes used to obtain leaf fibers is explained, since there are broader techniques as well as species used to such purpose.

Different methods and techniques to obtain fiber from agave plants are used. The selection of such processes depends on many factors, such as the organs from which the fiber is extracted, the primary application of those organ, the quality wanted of the final fibers, and the technology available. For example, the technique used to obtain the fiber located in the plant's core –which is originally harnessed for alcoholic beverages– is completely different from those techniques to obtain fiber from the leaves of agave that are exclusively harvested for textile applications. Lignocellulosic fibers can be obtained by mechanical, chemical, or biological methods (El Oudiani, et al., 2017), or a combination of them, and the method applied affects the fine structure and influences the physical properties of the fibers (Sorieul, et al., 2016; El Oudiani, et al., 2017; Ortega, et al., 2019).

2.2.1. Bagasse fiber obtaining process

There is no a specific name for the process of obtaining the fiber from the core of an agave plant, because the bagasse is a by-product from the tequila and mezcal –distilled beverages, production in Mexico. The main commercial purpose of this organ is to extract the sugars (glucose and fructose) contained in the core by cooking it to hydrolyze natural polysaccharides (Pérez-Zavala, et al., 2020). Although the residual bagasse fibers most commonly obtained by this process are from *Agave tequilana* (Iñiguez-Covarrubias, et al., 2001a; Pech-Cohuo, et al., 2018), other authors have also described a similar process to obtain and harness bagasse fiber from other species used in the mezcal production like *A. angustifolia* (Hidalgo-Reyes, et al., 2015) and *A. salmiana* (Naranjo, et al., 2016). The first stage of the process is the selection of the plant according to its maturity, an important factor of sugar content in the core (Escamilla-Treviño, 2012) which is around seven to ten years (Langhorst, et al., 2019; Pérez-Zavala, et al., 2020). The second step is to harvest the core by cutting off all the leaves from the plant. The third step is to subject the core into a crushing-cooking process to extract all the sugars concentered in this organ of the plant, and continue the production of the beverage by fermenting the core and eventually distilling the product (Iñiguez-Covarrubias, et al., 2001a; Girones, et al., 2017; Pech-Cohuo, et al., 2018; Pérez-Zavala, et al., 2020). Since the core also contains primarily fibrovascular bundles (Iñiguez-Covarrubias, et al., 2001a) the final residue is the so-called bagasse, an important source of fibrous material (Hidalgo-Reyes, et al., 2015; Naranjo, et al., 2016; Pech-Cohuo, et al., 2018; Langhorst, et al., 2019; Escamilla-Treviño, 2012; Pérez-Zavala, et al., 2020).

Iñiguez-Covarrubias et al. (2001a) described the use of depithers –devices specialized in the separation of the fiber from the core of an agave plant, varying in size and form depending

on the scale of fiber recollection. For large scale production, a mechanical fiber-pith separator with a cylinder of 2.65 m in length and 60 cm of diameter specifically fabricated for this purpose was used. For a smaller production they used a small metal cylindrical depither, similar to a hammer mill, equipped with a circular sieve. There is no trace of using manual techniques to obtain fibers from the core in the works investigated.

2.2.2. Leaf fiber obtaining process

Manual scraping

This is a popular technique consisting of two major steps to separate the fiber bundles contained in the leaves of the agave plant from the epidermis and parenchymal material. First, the most voluminous part of the leaf is beaten preferable with a wooden mallet to avoid cutting the fibers. Next, one transversal half of the leaf is scraped with a knife until the fibers are realized from the parenchymal material, and then the other half is scraped. This technique has been used and described by several authors for different agave species like *A. sisalana*, *A. marginata, A. angustifolia* and *A. salmiana* (Alves, et al., 2013; Zuccarello & Scaffaro, 2017; Thirumalaisamy & Pavayee Subramani, 2018; Reyes-Samilpa, et al., 2020). According to the ASTM D 123 – 03 Standard Terminology Relating to Textiles, other terms applied to refer this process and its variations are decortication, decorticating process, and scotching. Prior to the manual scraping –as well as to the mechanical scraping process– the tip and marginal thorns should be removed from each leaf as a safety procedure and to facilitate the process (Ortega, et al., 2019; Vivekanandan & Sakthivel, 2019; Mansouri, et al., 2020).

Mechanical scraping

This process usually replaces manual scrapping when time reduction in process is desired and is carried out in different mechanical devices, commonly known as decorticators (Hulle, et al., 2015). Alves et al. (2013) used a rotating wheel with blunt knives to obtain leaf fibers from *A. sisalana*; Hulle et al. (2015) described in detail the process to obtain *A. americana* leaf fibers. The leaves are fed into fluted rollers while the stripping drum is crushing and beating out the parenchymal material, separating it from the fibers. They also observed that depending on the model of the device, a whole leaf can be scraped at once, or the process is performed in two stages by scraping the leaf in halves, as in the manual method. Ortega et al. (2019) and Vivekanandan & Sakthivel (2019) also used this method to obtain leaf fibers from *Agave americana*.

Another mechanical process reported is calendering –which, according to the Encyclopedia Britannica (2007) consists of passing a material, commonly a continuous sheet of paper or fabric, through heated rolls called calenders– was carried out by El Oudiani (2017) using leaves from *A. americana* previously hydrolyzed to separate the fibers from the cementitious substances of the leaf.

Although the mechanical techniques represent an efficient process in terms of time, usually the fibers resulting are more roughened and present more residues of lignin, hemicelluloses, and waxes added to their surface, comparing to other methods (Hulle, et al., 2015).

Biological methods

Retting and burying are the most common biological processes to obtain fiber from the leaves of agave plants. The principle of this techniques involves microbial activity to degrade the cementitious substances contained in the leaf induced by the presence of moisture and a warm temperature (Hulle, et al., 2015; Mansouri, et al., 2020).

According to the ASTM D 123 (2019) a partial biological or chemical decomposition of pectins and other non-fibrous matter covering the fiber occurs during the retting process facilitating the removal of the fibers. The process of water retting is applied to leaves and stems to obtain hard and bast fibers, respectively. This technique consists on immersing the plant organ of interest in water bodies such as ponds, rivers, or tanks, in a time period up to three weeks in which the microbes consume the non-fibrous matter without damaging the cellulose fibers and the leaf or the stem softens (Hulle, et al., 2015). The water retting time period depends on the evolution of the degradation progress and varies from species to species, the organ processed, and even the age of the organ. Mylsamy & Rajendran (2011) subjected *Agave americana* leaves to water retting for two weeks, meanwile Teli & Jadhav (2016) performed this process for 15 days to obtain fiber from mature leaves of *A. angustifolia*.

The other biological technique consists in burying the leaves in soil for several days and even months, time period in which the microorganisms in the soil, along with the effect of sun and moisture or rain promotes the decomposing microbial activity of non-fibrous matter of the plant organ (Mansouri, et al., 2020). Bezazi et al. (2014) carried out this process for *A. americana* leaves by buried them under the soil at 30 cm and 40 cm deep for three months, meanwhile Mansouri et al. (2020) buried *A. americana* leaves at 30 cm deep in the soil for

45 days, recording the weather temperature in the morning and in the evening. By performing both biological techniques the fibers can be easily separated from the parenchymal matter (Hulle, et al., 2015; Mansouri, et al., 2020) since the natural matrix of the leaves is totally bio-degraded (Bezazi, et al., 2014).

3. Agave species used to obtain fiber as reinforcement materials

Until 2015 most of the fiber reinforced composites were produced using glass fiber, specifically, 95% of this type of composites (Li, et al., 2020). However, in recent years the interest of using natural plant fibers as reinforcing material have been increasing due to economic, ecological, and mechanical advantages they represent comparing to synthetic fibers.

The overview of the literature implies that over the last four decades, sisal (*Agave sisalana*) and henequen (*A. fourcroydes*) have been the fibers most commonly used as fillers and as reinforcing agents in composites using either petroleum-based polymers or biodegradable polymers as matrixes (Bisanda & Ansell, 1992; Joseph, et al., 1999; Valadez-Gonzalez, et al., 1999; Rahman, 2009; Kim & Netravali, 2010; Barreto, et al., 2011; May-Pat, et al., 2013; Senthilkumar, et al., 2018). In a more detailed review, we found that fibers obtained from several unexplored agave species have also been used in the fabrication of composites.

In Figure 6, the trend of the research papers related to composites using agave fibers as reinforcement is shown, it is notable that from 2015 to date the relevance of these fibers have emerged in this particular research area.

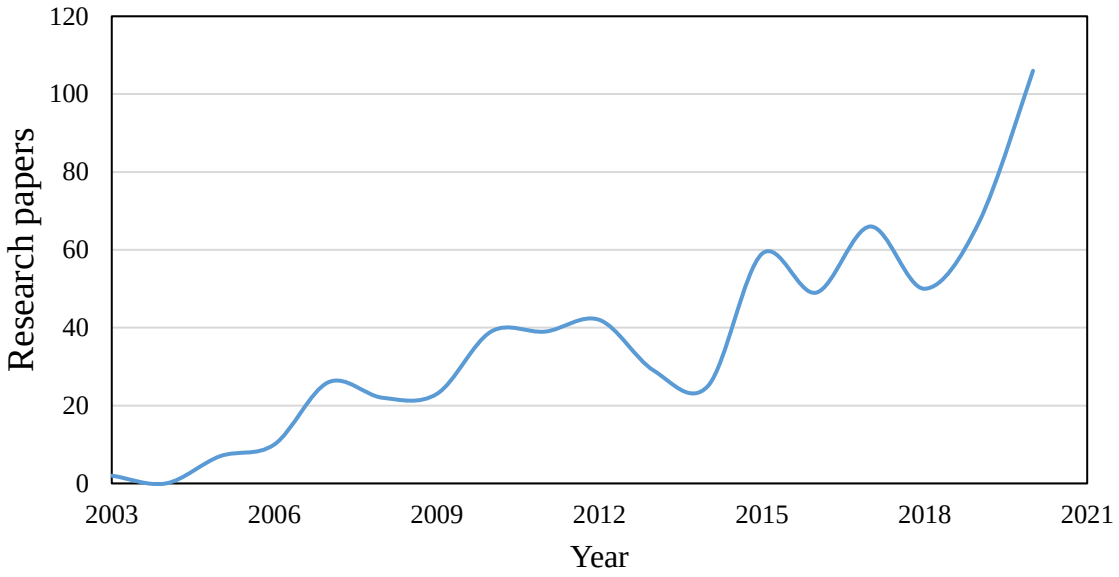

Figure 6. Relevance over the last 18 years of items related to the keywords "Agave fiber composites". Elaborated by Reyes-Samilpa with data from WorldWideScience.org, 2021.

Agave sisalana and *A. fourcroydes* are the two most important commercial species as source to obtain the so-called sisal and henequen fiber, respectively, for textile applications; whereas *A. lechuguilla* remains in a lower production scale to obtain lechuguilla fiber (León, 2000; Li, et al., 2000; Mayorga, et al., 2004; Silva-Santos, et al., 2009). However, over the last years, researchers have been interested in other agave species to obtain fiber for the production of composites for different reasons (i. e. as plague control) as is the case of *A. americana*, a potential fiber producer species usually used only as an ornamental plant (Msahli & Drean, 2005; Mylsamy, 2011), that, in some regions is considered as a plague (Ortega, et al., 2019).

In Mexico the two major plant species involved in the distilled beverages production tequila and mezcal are *Agave tequilana* and *A. salmiana*, respectively, due to their high productivity and wide distribution around the country (Martinez-Salvador, et al., 2012; García-Moya, et al., 2011). However, the leaves and the cores of both species are rarely harnessed to obtain fiber, thus these organs remains in the fields as an agro-waste, but it has been stated that when large amounts of such by-products are illegally dumped in agricultural fields, negative changes in soil fertility and environmental pollution by leachate might occur (Binoj & Bibin, 2018).

A rough-fibrous residue –known as bagasse– from the core of the plant is generated during the production process of the beverages mentioned above, and has been recently getting the attention of researchers for different applications: *A. tequilana* bagasse has been frequently used as reinforcing and filler material in the production of composites (González-López, et al., 2020; Huerta-Cardoso, et al., 2020; Robledo-Ortíz, et al., 2020a; Robledo-Ortíz, et al., 2020b; Smith, et al., 2020; Vázquez Fletes, et al., 2020; Martín-del Campo, et al., 2020). In this context, the fiber of *A. tequilana* is usually obtained from the core of the plant, however Binoj & Bibin (2018) evaluated the leaf fibers of this species as reinforcing material. In the case of *A. salmiana*, its bagasse has been harnessed as source of biofuels and as absorption material of heavy metals (Láinez, et al., 2018; Velázquez-Jiménez, et al., 2013), but neither its leaf fiber nor its bagasse have been yet explored in composites materials.

Similar situation has been observed for other agave species like *A. marginata*, an unexplored species as reinforcing material until Zuccarello and Scaffaro (2017) and Zuccarello and Zingales (2017) used it to reinforce green epoxy resin and PLA and compared them with composites reinforced with sisal fiber, finding enhanced mechanical properties with those of

A. marginata. Guzmán et al., (2018) evaluated the effect of alkali treatment on the mechanical and morphological properties of *A. furcraea* fibers to proposed them as reinforcing material for further composites applications (Table 2).

Table 2. Trend of agave species as source to obtain fiber for reinforcement purposes.

Agave species	**2020**	**2019**	**2018**	**2017**	**2016**
A. tequilana Weber var. Azul	8	3,1	4	3	2
A. americana	1	4		1	1*
A. sisalana	1	1	3	1, 1*, 1+	1,1*
A. marginata				1*, 1+	
A. fourcroydes			1		
A. angustifolia			1	1	
A. cantala			1		2

Note: Numbers with the same figure in the same year indicates that those polymers were used to obtain a blend.

3.1. Biodegradable polymeric matrixes reinforced with agave fiber

There is a discussion around what can be considered a biocomposite: one posture suggests that it can be integrated by at least one biodegradable component or obtained from renewable resources (Ho, et al., 2012; Díaz, et al., 2017). The opposite posture states that all of its components should be from renewable resources and biodegradable (Averous & Boquillon,

2004; Kim & Netravali, 2010; Sapuan & Bin Yusoff, 2015). Regardless these different postures, there are several studies about composites based on both biodegradable and non-biodegradable polymeric matrices reinforced with plant fibers, and more accurately, with agave fibers. As shown in Table 3, most of the matrices are non-biodegradable polymers such as Low Density Polyethylene (LDPE), epoxy resin, or Polypropylene (PP), and have a hydrophobic nature which may hinder a proper interface with the agave fibers due to their hydrophilic character (Barreto, et al., 2011). Also, since agave fibers have a high lignin content if compared with other plant fibers, some chemical modifications, like alkali treatment or mercerization, have been applied to their surface in order to enhance the adhesion of the fiber to the polymeric matrix (Vilaseca, et al., 2007), however the use of NaOH should be discarded as a green process, due to the significant environmental pollution it involves (Zuccarello & Zingales, 2017).

Petroleum-based polymers also known as polyolefins, comprise a large group of non-biodegradable thermoplastics and thermoset resins, polyurethans, and insaturated polyesthers (Kim & Netravali, 2010), and they were not approached in this work. However, in the field of composite materials, the term of "partially degradable biocomposites" is given to materials of petroleum-based polymers reinforced and/or filled with natural fibers (Kim & Netravali, 2010; Sahari & Sapuan, 2011).

Li et al. (2020) compiled information about the processes, mechanical properties, applications, and life-cycle analysis of natural fibers reinforcing the three most commonly used thermoplastics as polymeric matrixes in composites, such as polypropylene (PP), polyethylene (PE), and polylactic acid (PLA). They included general information about several fibers within the classification of bast, leaf, seed, and fruit fibers.

3.1.1. Biopolymers

Polymers derived from natural resources used as matrix in biocomposites are also known as biopolymers or bio-based green polymers (Mohanty, et al., 2018). Torres-Tello et al. (2017) classified the biopolymers in three groups: i) natural polymers; ii) polymers obtained from natural monomers; and iii) polymers derived from microbial fermentation. Within the most common examples of these biopolymers are starch and cellulose-based, polylactic acid, and polyhydroxyburyte, respectively. Thermoplastic starch (TPS) and polylactic acid (PLA) have been widely studied as polymeric matrix to obtain fully-green natural fiber-reinforced composites.

Starch is a semicrystalline polysaccharide, and is the main energy reserve in higher plants, meaning a carbohydrate existing in form of discrete granules composed by two glucopyranose homopolymers with different structures: amylose and amylopectin (Figure 7). Amylose is a linear structured polymer consisting of repeated D-glucose units linked by α-D 1:4 bonds. Although the main chain of amylopectin consists in D-glucose units linked by α-D 1:4, but also contains short chains linked by α-D 1:6 bonds to the main chain, which results in a branched structure (Bello, 2000; Jiang & Zhang, 2013; Cuevas, 2017).

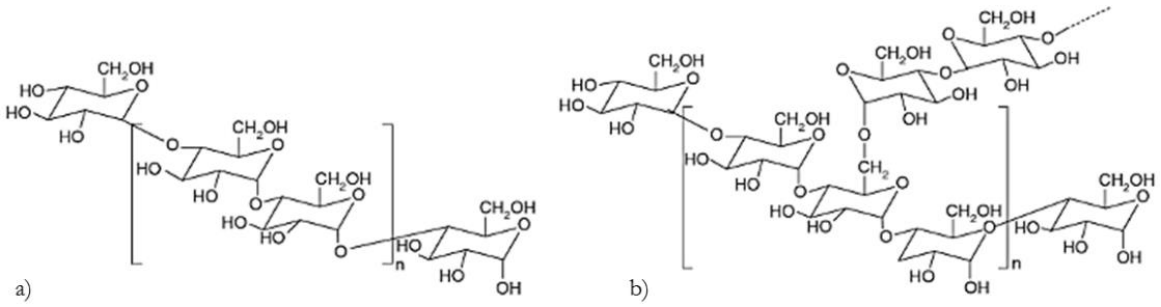

Figure 7. Structure of the homologue polymers composing a starch granule: a) amylose; b) amylopectin (Carvalho, 2011).

Starch is obtained by isolating the granules from different important commercial crops (Gómez-Aldapa, et al., 2020), being the most popular, maize in tempered and subtropical zones, cassava and banana in tropical environments, rice in inundated areas and potatoes in cold climates (Carvalho, 2012).

The starch granules can be turned into a thermoplastic material through a gelatinization process. In this process, the grains disrupt and lost their crystalline arranged structure through plasticizers, and shear and heat application (Jiang & Zhang, 2013). The role of plasticizers is to decrease the melting temperature of the starch (Gao, et al., 2019) by separating the free volume between the molecules and decreasing the interaction between them (de Graaf, et al., 2003). The resultant material can be melted or processed by the extrusion method, and is called thermoplastic starch (TPS) (Jiang & Zhang, 2013).

PLA is one of the most biodegradable plastics produced in the world (Djukić-Vuković, et al., 2019) and it can be obtained by fermenting different natural resources or biomass products and wastes such as corn starch, sugar cane, and biomass waste to lactic acid (Yusoff, et al.,

2016; Gómez-Aldapa, et al., 2020; Nofar, et al., 2019). PLA has been implemented in several studies of composites reinforced with different types of agave fibers, mainly with *A. tequilana* fiber (Huerta-Cardoso, et al., 2020; Robledo-Ortíz, et al., 2020b; González-López, et al., 2019; Samouh, et al., 2019; Zuccarello & Zingales, 2017; Cisneros-López, et al., 2018).

In Table 3, the fabrication of agave fiber-reinforced composites includes synthetic polymers, natural polymers and biodegradable polymers of both thermoplastics and thermoset polymeric matrixes.

Table 3. Polymers used as matrix phase in agave fiber-reinforced composites.

Polymeric matrix	**2020**	**2019**	**2018**	**2017**	**2016**
LDPE	1*			1•	1
PLA	3	1	2	1, 1*, 1+	
Epoxy resin	1	2	3	1, 1*, 1+, 1☆	
Polyester resin	1	2			2
LLDPE	1	1+			
PHB	1				
LMDPE	1				1
PP		1,1+		1•	1
HDPE		1+			
PE		1	1		
PS	1*	1			
TPS		1	2		
Polyester resin			1		

Polymeric matrix	2020	2019	2018	2017	2016
Phenolic resin			1		
Polyamid resin				1☆	
Polyhydroxyburyte/ hydroxyvalerate				1	
Natural rubber latex				1	
Polyfurfuryl alcohol				1	1

Note: Numbers with the same figure in the same year indicates that those polymers were used to obtain a blend.

3.2. Major fabrication processes

Polymer-based composites can be processed by injection molding, extrusion, and rotational molding. The typical temperatures to process cellulose-based materials range from 180°C up to 240°C considering a glass transition temperature (Tg) range from 140°C to 190°C (Sahari & Sapuan, 2011).

Although there was no particular preferred fabrication technique to produce composites or hybrid materials using agave fibers in the research works analyzed (Table 4), nor a clear relation between methods and type of agave fiber, it can be observed that thermoset polymers like epoxy and polyester resins were found to be fabricated with only two techniques: compression molding (Binoj & Bibin, 2018; Zuccarello & Marannano, 2018) and hand lay-up (Karthik, et al., 2019; Mbeche & Omara, 2020). Whereas both petroleum-based and biodegradable thermoplastic polymers were found to be fabricated using different techniques and even mixing between them. However, the two major process are compression molding –

mainly applied for the production of laminated composites– (Binoj & Bibin, 2018; Ortega, et al., 2019; Vega-Hernández, et al., 2019; Lomelí-Ramírez, et al., 2018), and extrusion or extrusion/injection (Huerta-Cardoso, et al., 2020; González-López, et al., 2020; Smith, et al., 2020; Martín-del Campo, et al., 2020; Langhorst, et al., 2019; Samouh, et al., 2019). Other techniques like rotational molding have been recently explored by Robledo-Ortíz et al. (2020a)a, Robledo-Ortíz et al. (2020b)b, Vázquez Fletes et al (2020), González-López et al. (2019), and Cisneros et al. (2018).

Table 4. Fabrication techniques commonly used to produce agave fiber-reinforced composites.

Method	**2020**	**2019**	**2018**	**2017**	**2016**
Extrusion	1,1*	1	1+	1•	
Compression molding	1,1*	3,1+	2*,1+,1	1*, 1+, 1•, 1	2
Hand lay-up	1	2,1+	2*,1	1*, 1, 1•, 2	2
Extrusion/ injection	2	2	1	1	
Rotational molding	3	1	1	1+	1
Thermo-compression			1	1	
Casting			1		
Vacuum			1		1

Note: Numbers with the same figure in the same year indicates combined techniques.

3.3. Properties and applications of agave composites

A general characterization and evaluation of the properties of composite materials reinforced with agave fiber includes the mechanical, morphological, and thermal properties, together with the identification of their functional groups, and their water absorption performance, as shown in Figure 8. Within the works evaluating mechanical properties, tensile strength was the only one recurrent. Then, flexural and impact are common stresses assessed, and only two works evaluated the stress of the agave composites by effect of compression.

It was observed that in 23 of the 43 works reviewed, chemical treatments were applied to the fibers in order to reduce or remove lignin content, and to improve the surface of the fibers and therefore, to enhance the interfacial adhesion with the polymeric matrix. Reducing and removing the lignin from the surface of the fibers affects directly the mechanical and thermal properties of the composites (Soriano Corral, et al., 2016; Motaung, et al., 2016; Ibrahim, et al., 2016; Cisneros-López, et al., 2016; Geethika & Rao, 2017; Webo, et al., 2018; González-López, et al., 2019; Jain, et al., 2019; Martín-del Campo, et al., 2020; Robledo-Ortíz, et al., 2020a). It is worth to mention that in half of these works the fibers from *Agave tequilana* were chemically treated, probably because fibers from the core are more lignified, however a study that compares the chemical composition between leaf fibers and core fibers from the same plant was not found.

By contrast, although a clear objective of using agave fiber without any surface treatment was not identified, Annandarajah et al. (2019) aimed to determine if agave raw fiber could effectively enhance the mechanical properties of composites based on Linear low-density polyethylene (LLDPE), High Density Polyethylene (HDPE), and Polypropylene (PP); and

Vega-Hernández et al. (2019) aimed to reduce the production of residues during the grafting processes of lignocellulosic fiber.

According to Balakrishnan et al. (2016) the properties of the fiber are related to the maturity of the plant, which represents an important aspect to consider when using natural plant fibers in the production of composites. Razali et al. (2015) observed this correlation in the roselle fiber, and also confirmed that the chemical content of cellulose, hemicellulose, lignin, and ashes in the plant fiber varies depending on the age of the plant, for example, as the plant matures the content of cellulose in the fiber gradually decreases. Nevertheless, only the work of Zuccarello & Zingales (2017) considered the maturity of the plant as factor affecting the properties of the fiber. They analyzed the influence of the fiber leaves from *Agave marginata* and *A. sisalana* having 1, 2, 3, 4, and 5 years old in composites for semi-structural and structural applications, and concluded that the strength increased about 25% and the stiffness increased 50% if comparing 1 fiber with 5 years old fiber.

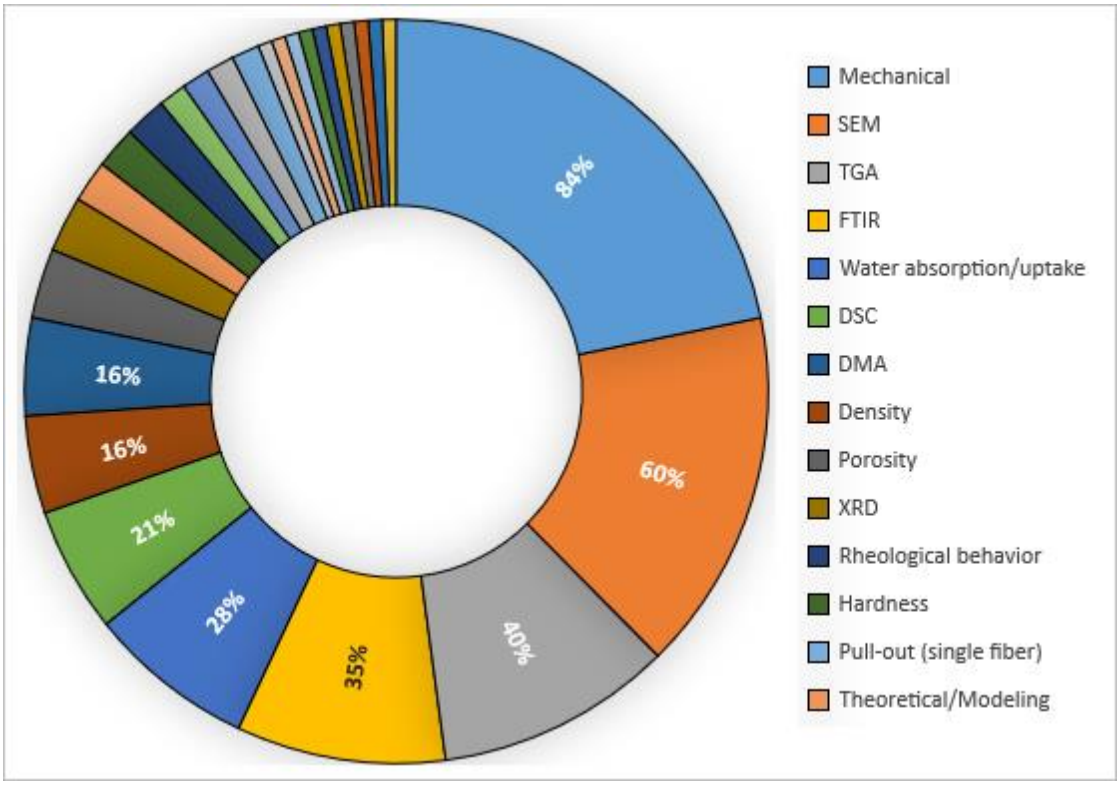

Figure 8. Properties evaluated on agave fibers reinforced composites, biocomposites and hybrid materials. Works using theoretical models evalualed mechanical properties, such as tensile and flexural strength and stiffness. SEM= Scanning Electron Microscopy; TGA= Thermogravimetric Analysis; FTIR= Fourier-Transform Infrared Spectroscopy; DSC= Differential Scanning Calorimetry; DMA= Dinamic Mecanichal Analysis; XRD= X-ray diffraction analysis. Elaborated by Reyes-Samilpa.

In general, the objectives of developing most of the agave-reinforced composites and biocomposites were varied, and among the most frequent was to obtain an alternative to oil-based materials (Huerta-Cardoso, et al., 2020) as well as biodegradable and sustainable composite materials (Pech-Cohuo, et al., 2018; Robledo-Ortíz, et al., 2020a), reduce production costs (Torres-Tello, et al., 2017; Robledo-Ortíz, et al., 2020b; Smith, et al., 2020), find uses to by-products or agricultural wastes (Torres-Tello, et al., 2017; Lomelí-Ramírez,

et al., 2018; Sanchez-Olivares, et al., 2019; Smith, et al., 2020; Huerta-Cardoso, et al., 2020; Ortega, et al., 2019), or to use agave fibers from barely known species as reinforcing material in different polymeric matrixes (Ubaidillah, et al., 2016; Bakri, et al., 2017; Zuccarello & Zingales, 2017; Zuccarello & Scaffaro, 2017; Maulana, et al., 2018; Chandrabakty, et al., 2018), few studies focused the production on specific applications. For example, (Smith, et al., 2020) evaluated the effect of adding *Agave tequilana* fibers to Poly(3-hydroxybutyrate) or PHB, a brittle but non-toxic polymer, to obtain a biodegradable alternative for food packaging. They found that adding 25% of *A. tequilana* fiber treated with organic peroxide improved the mechanical properties of the PHB while a green composite can be produce, if compared to other polymers or compatibilizer treatments.

In the study of Langhorst et al. (2019), the intention of producing a composite based on polypropylene PP and PP grafted with maleic anhydride (PPgMA) using *Agave tequilana* fibers obtained by two different heating processes as reinforcement was to apply the obtained composite in automotive components produced in Mexico. They found that differences in heat treatments of agave fibers lead to differences in thermal stability of the fibers, but not in the thermal and mechanical properties nor in the crystallinity of the composites. They concluded that additional treatment modifications and future studies must be performed to evaluate these composites for the application aimed.

In the research carried out by Teklay et al. (2017) a textile application was assessed by comparing the absorption and mechanical properties (tensile and stitch tear strength) of composites based on resin and natural rubber latex containing leather scrap reinforced and the effect of adding different plant fibers, including sisal fibers. They found that using sisal fiber improves the tensile strength of the composites, especially when using resin at dry

conditions if compared to material control, and composites reinforced with enset, hibiscus, jute, and palm. Regarding the stitch tear strength composites with sisal fiber ranked the third best performance but only when natural rubber latex was used. Composites based on the both studied polymers reinforced with sisal fiber presented high values of water absorption. They concluded that composites containing 40% of sisal fiber are among the ones that exhibited the best mechanical properties, the fibers were well embedded in both polymeric matrixes as confirmed by SEM, and also showed a smooth low-porosity surface, which make these materials suitable for textile purposes, particularly in the production of footwear.

Díaz-Batista et al. (2018) elaborated structural profiles made of HDPE reinforced with henequen by the extrusion method and evaluated the mechanical properties in function of the angle –0, 45, and 90°– in which the profile is stressed. Since henequen fibers have a high aspect ratio during the composite extrusion process they adopt a traverse position to the direction they are forced to flow through the die of the extruder, leading to enhance mechanical properties at 90° which corresponds to the structural charge surface of the profile. They conclude that these profiles are suitable to manufacture containers, packaging, and pallets.

Although in the literature reviewed few studies are focused in specific applications, in essence the utilization of natural plant fiber-reinforced composites with similar properties to the materials mentioned in this study are feasible to be replied in agave-reinforced composites, considering the respective methodologies and processes. Common applications of polymers reinforced with plant fibers are food packaging, structural components, aerospace and automotive parts, and biomedical devices and fixtures as compiled and described by Mohanty et al. (2018), Ngo et al. (2018), and Li et al. (2020).

Conclusions

The relevance of using agave fibers as a reinforcing material in the production of composites is increasing, especially when the use of a particular species solves environmental problems like the accumulation of agro-wastes as in the case of *A. tequilana* or the plant is considered as invasive as in the case of *A. americana*. Although the factor determining the selection of using one species or another is unclear, it may depend on the geographical area on which the researching is being carried out, since Agavaceae is a worldwide distributed family.

As fibers originated in plants from the same family, agave fibers obtained from different species share similarities in their properties, such as surface morphology, cross section area, structural arrangement, and cellulose content. However, many biological factors such as the age of the plant, the organ from which the fibers were obtained, and the weather and soil conditions of the plant growth affects the mechanical properties of the agave fibers, and thus, their performance as reinforcing material.

One of the major drawbacks of agave fibers is their hydrophilic nature, that can be minimized with chemical treatments that reduce the content of lignin and hemicellulose in the fibers, improving their interaction with many hydrophobic polymers. However, in many studies fibers without chemical treatment are preferred to evaluate them as a novel fibrous material, and also because of economic and environmental concerning, since chemical treatments elevate the production costs, and undesired and pollutant residues might be generated.

Regarding the polymeric matrixes reinforced with agave fibers, there was observed a highly diversity of polymers used, from polyolefins to synthetic and bio-based polymers. However,

there was also observed that PLA and epoxy resins are the most commonly matrixes used, probably because their commercial availability and their ease of processing.

Concerning the processes, it was observed that compression molding and hand lay-up are the methods most frequently used which is consistent to the type of matrixes preferred. Both methods are completely feasible and are also compatible with textile composites produced by matting and waving techniques.

The production of composites using agave fibers represents an alternative for oil-based materials, promotes the use and conservation of natural resources, and provides added value to agroindustrial wastes. And, because of their structural, functional, biocompatible, and biodegradable properties, agave composites are feasible to be used in architectural and building applications, in the aerospace and automotive industries, as well as in biomedical devices, and food packaging.

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Chapter 2

Accelerated aging effect in physical and thermo-mechanical properties of maize starch biocomposites reinforced with *Agave salmiana* fibers from different leaf ages

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Accelerated Aging Effect in Physical and Thermo-mechanical Properties of Maize Starch Biocomposites Reinforced with *Agave Salmiana* Fibers from Different Leaf Ages

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Abstract: In this study, lignocellulosic fibers from *Agave salmiana* –an important socio-economical species endemic to Mexico– were used to reinforce thermoplastic maize starch (TPS). Fibers from young raw leaves (YRL) and old roasted leaves (ORL) were obtained according to the traditional methods used by small producers. The formulations of biocomposites were obtained varying the content of both types of fiber and processed by extrusion and injection molding. Morphological, structural, mechanical, thermal, and thermomechanical properties of biocomposites were evaluated. To use the hydrophilicity of these materials as an advantage in unexplored applications, biocomposites behavior under degradative tests such as accelerated aging and salt water immersion was evaluated. The processes of heating the old leaves partially removed the lignin and hemicellulose layer from the fibers, which led to a better interaction fiber-matrix, as confirmed by FESEM, ATR-FTIR, and TGA. Biocomposites with 30 wt% of YRL fiber reported the highest values of tensile strength and Young's modulus when compared to ORL biocomposites and with TPS. Accelerated aging exposure affected mainly the thermomechanical properties of TPS and confirmed the reinforcing effect of the fibers due to the thermal and mechanical stability they provided to the matrix, especially when 20 wt% of fiber was added. This was also observed when biocomposites were immersed in salt water solution. Using *Agave salmiana* fiber obtained from different leaf ages by traditional methods in the production of biocomposites promotes the complete harnessing of this species and represents a possibility to small producers in Mexico to introduce circular economy in their communities.

Keywords: Thermoplastic starch, Hard fiber, Biocomposites, Extrusion, Injection molding, Accelerated weathering

Introduction

The environmental problems caused by the disposal of large volumes of plastics, along with the depletion of petroleum stocks, have prompted an increasing interest in the design of new environment-friendly materials [1]. The use of raw materials from renewable natural resources and from agro-wastes promotes the use of green composites [2].

Poly(lactic acid), rubber, soy protein, and starch are polymers used as an alternative to the production of composites based on non-biodegradable materials [3]. Starch is a polysaccharide with thermoplastic behavior when water or glycerol is added under shear forces and continuous heat [4]. This polysaccharide can be obtained from cassava, maize, potato, among others, and has been widely studied and used as a polymeric matrix in the production of biocomposites [5-7] because of its low cost and availability [8].

The addition of natural fibers to thermoplastic starch increases its mechanical properties and thermal stability [9]. Plant fibers present several advantages over synthetic fibers, such as abundance, renewability, sustainability, biodegradability, low density or lightness, high specific properties, and low production costs [3,5]. Fiber with low lignin and hemicellulose content on the surface creates a strong interfacial bonding, improving the response of biocomposites to accelerated aging, as observed by Islam *et al.* [10] in PLA reinforced with alkali-treated hemp fibers. The accelerated aging technique is used to reproduce the weathering effects on materials exposed to sunlight, moisture, or dew, under controlled conditions on laboratory accelerated exposure devices [11].

Hard fibers can be obtained from the leaves of different agave species and represent a significant source for textile and artisan products. The most commercial agave species used to obtain hard fibers used to reinforce different polymers, mainly polyolefins, are sisal (*Agave sisalana*) [2,12-14], henequen (*A. fourcroydes*) [15-17], and fiber from *A. americana* [18-20]. Other studies have evaluated the fibers from by-products –mostly bagasse– of the tequila (*A. tequilana*) production as reinforcing material [21,22].

Another socio-economical relevant agave species in Mexico is *A. salmiana*, which is endemic to Mexico and widely distributed over the country [23], especially in arid and semi-arid zones of the north-central region [24,25], with poor soil conditions [26], and is potentially resistant to

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climate change [27]. The major economic relevance of this species is the production of the distilled "mezcal" and fermented "pulque" beverages [25-28]. To obtain these products only the core of the agave plant is harnessed and the leaves –with different stages of maturity– are discarded [28], left in the fields [26], and considered an agro-industrial waste in several regions of the country [9].

In a smaller productive scale the leaves with different maturity stages of *A. salmiana* represent a source to obtain high-quality textile fiber, which is an important economic activity for artisan producers and their families, especially in one region of central Mexico named the Mezquital Valley, Hidalgo [29], and occasionally in some localities of Jalisco and Mexico City [25]. These fibers are obtained only by artisanal methods, which vary depending on the age of the leaf: when young leaves are used, they are manually scraped at raw to obtain the fiber, and when mature and old leaves are used, a roasting process is applied to the leaves prior the manual scraping process. The use of these fibers in industries different from textiles represents an opportunity to small producers to initiate circular economy in their communities.

As mentioned, the leaf fiber of *A. salmiana* is barely known at large productive scale and has not been reported as a reinforcing agent for composite materials. Therefore, the aim of this work was to evaluate *A. salmiana* fibers obtained by two traditional methods, according to the age of the leaf, as the reinforcing phase in biocomposites based on thermoplastic maize starch. Biocomposites were exposed to two types of degradative tests: the first was an accelerated aging technique and the second a long immersion test in salt water, to observe their degradation behavior in different environmental contexts and to use their hydrophilic nature as an advantage in unexplored, short-live, biodegradable applications, such as the design of artificial substrate tiles for coral reef restoration, given that the materials currently used are contaminant as the concrete or petroleum based plastics [30].

Experimental

Materials

Agave salmiana var. *Xa'mni* fiber was obtained by traditional method from the Mezquital Valley, Hidalgo, Mexico. Leaves with two different maturity stages were used to obtain the fiber: young leaves (3-4 years), and old leaves (around 8 years). Maize starch was supplied by Sigma-Aldrich, and glycerol was purchased from ACS Fermont. In order to remove parenchyma remnants from the fiber, washing powder (with linear alkylbenzene sulfonate as active ingredient and proteolytic enzyme), sugarcane white vinegar (with 5 % acidity), and tap water were used. Purified drinking water was used to moisten the maize starch.

Obtaining and Processing the *Agave Salmiana* Fibers

The first stage of the traditional process is to obtain the agave fiber from young leaves by manual scraping. This technique consists in separating the fiber beams from the parenchymal tissue of the leaf by beating the base of each leaf with a wooden mallet. Then, the agave leaf is pressed against a wooden board fixed in the soil with a wooden rod knife, scraping with up-and-down movements to remove the fibers from the parenchymal tissue.

As old leaves contain a higher amount of parenchymal tissue, they are roasted in a domestic wood fire at up to 400 ^{o}C to soften and moisten them to easily remove the fiber [31-33]. After this process, the leaves remained covered with a cotton blanket for three days, and then, the fiber was obtained by manual scraping.

Fiber Processing

To soften YRL fibers, they were immersed in a solution of 1:2:20, detergent, sugarcane white vinegar, and tap water, for 5 hours or overnight, depending on the time elapsed since the scraping process. In contrast, ORL fibers were soaked for three days in a mix of 1:10, corn meal and tap water. Afterwards, both YRL and ORL fibers were rinsed, drained and dried under an outdoor shade. Then, to remove minor fibers and particle traces, the fibers were carded.

After the preparation process, fibers were cut into segments of 2 cm long and then milled in a Fritsch Cutting Mill Pulverisette 19 (Idar-Oberstein, Germany) –with tungsten V blades– using 250 µm sieves. Then, these short fibers were passed through three W. S. Tyler ASTM E-11 stainless steel sieves (No. 200, 100, and 50) to obtain a length range within 75±5 µm to 300±14 µm. Finally, the resulting fibers were placed in 10×15 cm aluminum foil trays and dried in an oven (Arsa AR-290D, Jalisco, México) at 60 °C±2 °C for 24 h.

Biocomposite Production

To produce the biocomposites, 10, 20, and 30 wt% of YRL and ORL fiber contents were separately added (Table 1) to the maize starch that was previously moisturized with 20 % of purified water, manually stirred for 10 minutes, and rested for 24 h in hermetically sealed plastic bags. Then, 20 % of glycerol was added to each formulation and manually stirred for 10 minutes before extrusion. Thermoplastic maize starch (TPS) without fiber was used as control material. After this, the extrusion and injection processes were performed. The extrusion was carried out in a DSM Xplore MC-5 micro compounder (Geleen, Netherlands) with double conical screw with the following parameters: 90 °C at the three heating zones of the barrel; screw rotation speed of 100 RPM at the feed and processing areas. The injection was performed in a micro injection moulder DSM Xplore IM 5.5 (Geleen, Netherlands) with the following parameters: 95 °C in the heating barrel, 35 °C in the injection mold with 10 bar of pressure. The dimensions of the samples were established according to the type V of the ASTM D638 Standard Test Method for Tensile Properties

Table 1. Experimental design of polymeric matrix and biocomposite formulations

Sample ID	Maize starch (wt%)	Water (wt%)	Glycerol (wt%)	ORL fiber (wt%)	YRL fiber (wt%)
TPS	60	20	20	-	-
TPS/YRL10	60	20	20	-	10
TPS/YRL20	60	20	20	-	20
TPS/YRL30	60	20	20	-	30
TPS/ORL10	60	20	20	10	-
TPS/ORL20	60	20	20	20	-
TPS/ORL30	60	20	20	30	-

of Plastics.

Morphological Analysis

The morphological surfaces of YRL and ORL fiber and biocomposites were analyzed by Field Emission Electron Microscopy (FESEM) using a NOVA 200 Nano SEM from the FEI Company (Oregon, USA) at 10 kV of acceleration voltage. Samples were fractured with liquid nitrogen on their transversal area and coated with a layer of Au/Pd film (20 nm thickness and 80:20 wt%). The magnification range was from 500 and 5000×.

Fourier Transform Infrared (ATR-FTIR) Spectroscopy

Spectra of the fibers and the composites were obtained using an IRAffinity-1S, SHIMADZU FTIR spectrophotometer (Kyoto, Japan) with an ATR accessory. ATR-FTIR spectra of the samples were recorded in the range of 4000-400 cm^{-1}, with 45 scans and at a spectral resolution of 8 cm^{-1}. Scale in the fiber spectra was normalized.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed on an STA 449 F3 from NETZSCH Q500 (Bavaria, Germany) using aluminum pans. The weight of the specimens was 5±2 mg. The TGA trace was obtained in a temperature range of 25-600 ºC, at a heating rate of 10 °C/min under a dynamic nitrogen atmosphere with a flow rate of 10 m*l*/min.

Thermomechanical Analysis (TMA)

Thermomechanical tests were performed in a TMA Q400 from TA Instruments (Delaware, USA). First, the equipment was calibrated under the ASTM E2113-04 Standard Test Method for Length Change Calibration of Thermomechanical Analyzers. Samples were prepared according to the ASTM E 831-14 Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis. To calculate the coefficient of thermal expansion (CTE) and glass transition temperature (Tg), the TMA was adjusted to the macro-expansion mode with an applied force of 0.02 N, and a temperature ramp from 0 °C to 100 °C with a rate speed of 5 °C/min. Samples were heated from 5 °C to 41 °C to calculate their CTE and to observe their behavior in a temperature of 23 °C±5 °C. Once obtained the curve of temperatures, the onset, midpoint, and endpoint temperatures of the Tg transitions were calculated using the tangents drawn on the displacement curve, considering the midpoint as Tg.

Mechanical Characterization

Tensile tests were performed using a Universal Testing Machine HOUNSFIELD H10KS (Surrey, UK) at room temperature (25 °C) with a constant speed of 5 mm/min, a load range of 50 N, an extension range of 50 mm, and a gauge length of 40 mm. The tests were performed according to ASTM D638.

Accelerated Aging

This experiment was conducted in an accelerated weathering tester QUV/spray from Q-Lab (Arizona, USA). Samples were exposed to a period of 500 h, as reported by Islam *et al.* [10], with 12 h of alternated condensation and UV radiation cycles. The condensation cycle was performed for 4 h at 50 °C using laboratory distilled water, while the irradiation cycle was for 8 h at 60 °C. An Ultra-Violet A [UVA] 340 lamp at 0.76 W/m^2 was used for irradiation exposure.

Immersion Test

The ASTM D570-98 Standard Test Method for Water Absorption of Plastics was performed to evaluate the behavior of the biocomposites immersed in salt water. For this test, three samples of 9.7×9.7±0.1 mm from each formulation were used. A salt water solution was prepared with 1000 m*l* of distilled water, 33.3 g of NaCl and 0.1 m*l* of NaOH to simulate seawater conditions of 33 ppm of salinity and 8.2 pH [34]. Each sample was placed in a 20 m*l* glass vial completely covered with the salt water solution for 30 days, following the step 7.4 Long Term Immersion of the ASTM D570-98.

In order to evaluate the best performance among the biocomposites, a Generalized Linear Model (GLM) with a Least Significant Difference (LSD) Fisher test was recorded. Then, to predict the behavior of the biocomposites during a longer period of immersion, a Linear Regression Model was performed. Statistical analysis were done in InfoStat [35].

Results and Discussion

Morphological Analysis

FESEM images of YRL and ORL are shown in Figure 1 at different magnifications to analyze and compare their surface morphology. Typical properties of hard agave fibers are observed in Figure 1(a), 1(c), 1(f), and 1(h), including the

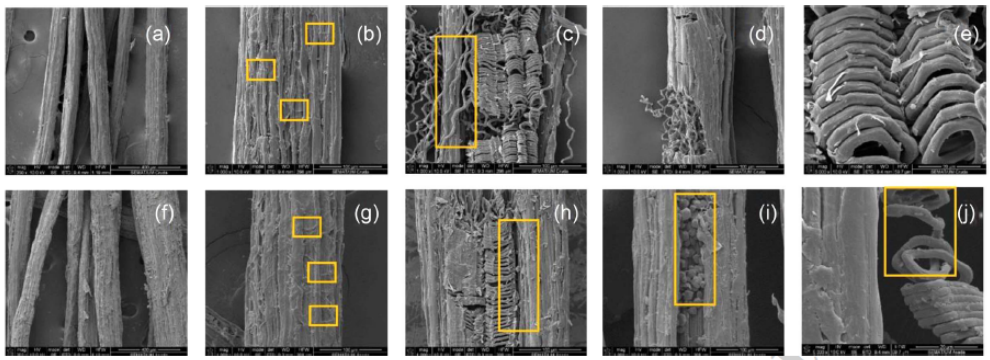

Figure 1. FESEM images of *Agave salmiana* fibers with different magnifications. From (a) to (e): YRL fiber; from (f) to (j): ORL fiber.

cementing substances lignin, hemicellulose and pectin that hold together the elementary fibers or cellulose microfibers; cellulose helicoidally arranged chains (Figure 1(c), 1(d), 1(e), 1(h) and 1(j)) as observed by John and Thomas [36]; and lines located along the fibers (Figure 1(b) and Figure 1(g)), distinctive to long lignocellulosic fibers [37].

Some residual fats or waxes remain in the fiber after the extraction process, especially if no chemical treatment has been carried out, due to the fiber beam containing some of these particles, as can be seen in Figure 1(i). This was also observed by Bismarck *et al*. [38]. They found small particles attached in the granular surface of raw *Agave sisalana* fibers, possibly waxy and fatty substances not soluble in water without a previous treatment such as alkali [39].

Teli and Jadhav [40] stated that the mechanical process used to obtain *Agave angustifolia* fiber influences the layer of lignin and hemicellulose surrounding the cellulose microfibrils, given that the retting extraction also involves a chemical process. This suggests that, in addition to the maturity effect of the fibers, the differences between ORL and YRL fiber observed in their morphological surface, such as an apparent thicker layer of lignin (Figure 1(g)) and the presence of residues (Figure 1(i)) in ORL fiber, could be attributed to the washing treatment YRL fiber received after the scraping process, resulting in a slimmer and more defined layer of lignin and hemicellulose covering the cellulose microfibrils (1(b)).

In Figure 2 the fiber-matrix interface is shown. A homogeneous interaction fiber-matrix was obtained, especially with 20 and 30 wt% of YRL content (Figure 2(b) and 2(c)). Some fractures appeared in the matrix, possibly as an effect of liquid nitrogen fracturing (Figure 2(g) and 2(j)). Micrographs with 5000× magnification show that the presence of lignin and hemicellulose impairs the interaction fiber-matrix, by creating micro-pores in the fiber (Figure 2(l)), as stated by Sreekala *et al*. [41]. The pull-out effect is more evident in TPS/ORL30 biocomposite (Figure 2(i)). This indicates a lower interaction fiber-matrix if compared with all TPS/YRL biocomposites, where gaps surrounding the YRL fiber are smaller and less frequent.

Fourier Transform Infrared (ATR-FTIR) Spectroscopy

In Figure 3 the spectra of YRL and ORL are shown. In general, a broad and well defined band at 3300 cm^{-1} is related to the hydroxyl group stretching vibration typical of polysaccharides such as cellulose, lignin and hemicellulose [42,43]. This band can also be attributed to inter- and intra-molecular hydrogen bonds of the cellulose [40,44,45]. Although a significant change in length or definition between the bands of the two types of fiber was not observable, the signal for YRL was found at 3332 cm^{-1} while in ORL shifted to 3279 cm^{-1}. According to the study made by Poletto *et al*. [45] of four different wood fibers the shifting to lower values suggests an increase in strength of the hydrogen-bonding, specifically within the frequency of 3432-3277 cm^{-1} which corresponds to inter and intramolecular changes in the H-bonds contained in cellulose. One possible explanation could be that the roasting pretreatment applied to ORL fibers might have affected the consistency of the lignin and hemicellulose matrix, leading to stronger H-bonds on their cellulose chains if compared to YRL fibers.

All the following signals appeared in both YRL and ORL fibers. The band at 2920 cm^{-1} is generally associated with the asymmetrical C-H stretching vibration of cellulose and hemicellulose [42]. At 1728 cm^{-1}, the stretching vibration of the internal double bonds in C=O from hemicellulose, lignin, pectin, and waxes appeared [40,42,46-48]. The aromatic C=C stretching bonds typical of lignin are observed at 1604 cm^{-1} [40] and at 1507 cm^{-1} [42].

The band at 1424 cm^{-1} corresponds to the in-plain bending HCH,OCH vibration of the cellulose [42], and it can be associated to its crystalline structure [44] and to aromatic skeletal vibrations [49]. However, if the band is close to 1460 cm^{-1}, it is attributed to the bending and stretching of C-H and C-O groups, respectively, present in lignin and carbohydrates of the fiber [50]. The signal at 1368 cm^{-1} is

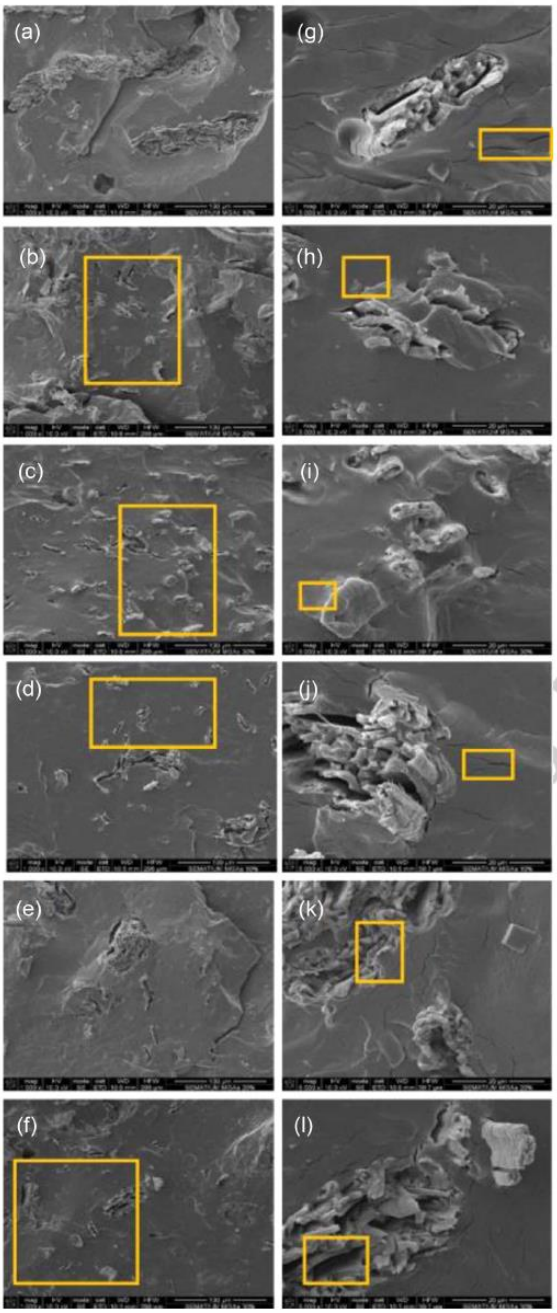

Figure 2. Micrographs of the fiber-matrix interface obtained by FESEM. Left column at 1000× magnification, right column at 5000× magnification. (a) and (g) TPS/YRL10, (b) and (h) TPS/YRL20, (c) and (i) TPS/YRL30; (d) and (j) TPS/ORL10, (e) and (k) TPS/ORL20, and (f) and (l) TPS/ORL30.

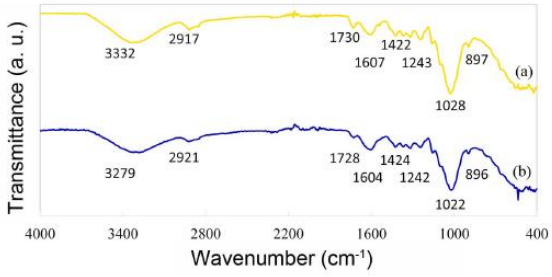

Figure 3. ATR-FTIR spectra of *Agave salmiana* var *Xa'mni* fibers; (a) YRL fiber and (b) ORL fiber.

related to the CH in-plain bending vibration of the cellulose and hemicellulose [42].

The rocking vibration of CH_2 of the cellulose can be observed at 1317 cm^{-1} [42].

At 1243 cm^{-1}, symmetric stretching of C=O and G (guaiacyl) ring of lignin [42,49]. At around 1020 and 1030 cm^{-1}, a wide peak corresponding to the symmetric C-O stretching of lignin appears [51]. Peaks found at 897 and 896 cm^{-1} are attributed to β-glucoside linkage of cellulose and hemicellulose [46]; these peaks are also related to the amorphous region in cellulose [44].

In spite Dai and Fan [42] and Hospodarova *et al.* [44] stated that signal at 1603 cm^{-1} shifting up to 1623-1633 cm^{-1} is related to the OH bend of absorbed water in cellulose, this was not the case for either of the fibers. Given the old leaves were roasted, the esters of the fibers were hydrolyzed and broke down into acids and alcohols decreasing the content of lignin and hemicellulose that covers the cellulose microfibrils of ORL fiber. Hydroxyl groups of the cellulose crystalline region create hydrogen bonds with parallel chains, reducing the absorption of water [41], as observed in ORL fiber with the cellulose microfibrils more exposed than in YRL fiber.

In Fogure 4 typical signals of thermoplastic starch can be observed. The strong broad band at 3286 cm^{-1} is attributed to the stretching vibration of hydroxyl groups derived from the hydrogen bonding of starch [52,5]. The signal at 2927 cm^{-1} corresponds to the C-H stretching and at 1649 cm^{-1} it is associated to bound water [52], which is consistent with the hydrophilic nature of starch. The bending vibration of C-H and C-O typical of aromatic rings was observed at 1338 cm^{-1} [53]. The band found at 1417 cm^{-1} is attributed to the presence of glycerol in the material [52]. At 1149 cm^{-1}, the C-O stretching of typical functional groups of starch and glycerol were found. The C-O bending vibration at 1078 cm^{-1} suggests a strong hydrogen bonding interaction of OH groups [53,54], and the O-C stretching of anhydroglucose ring occurred at 995 cm^{-1} [5].

For biocomposites, a variation in the intensity of signals

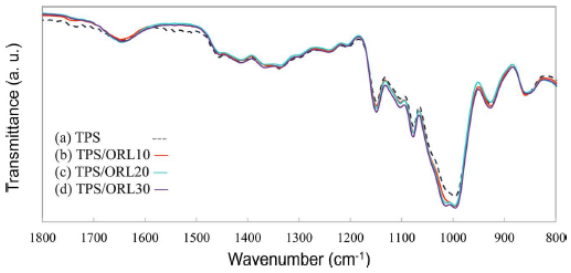

Figure 4. ATR-FTIR spectra of thermoplastic maize starch and biocomposites reinforced with 10, 20, and 30 wt% of old leaf fiber before accelerated weathering: TPS (a); TPS/ORL10 (b); TPS/ORL20 (c); TPS/ORL30 (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

related to lignin at 1730 and 1245 cm^{-1} was expected to be observed as the content of the fiber increased or as different fiber age was used. However, all the signals of aromatic rings typical of lignin completely overlapped with the functional groups of starch.

All the biocomposites spectra (Figure 4) exhibited an absorption band in the range of 3300 cm^{-1}, which can be attributed to different modes of stretching of the O-H bond, typical of the cellulose structure, and a slight shift occurred if compared with TPS. The presence of the two absorption bands at 2920 and 2850 cm^{-1} may be caused by the presence of pectin, waxes, and esters containing methyl and methylene groups. The bands at 1240 and 1160 cm^{-1}, as well as the bands at 1020 cm^{-1}, can be assigned to C=O, C-H, C-O-C, and C-O deformation or the stretching of the vibrations of different groups in the carbohydrates. A peak near 1100 cm^{-1} corresponds also to C-O-C stretching vibrations of cellulose [45,55]. A shift can be observed at 1078 cm^{-1} as the fiber content increases, which is an indicator of improved interaction between components [54].

The spectra of the biocomposites either before accelerated weathering or with 500 h of exposure display no shifting, which reveals their capacity to withstand UV radiation. Similarly, a peak at around 1730 cm^{-1} related to the stretching vibration of C=O proves the permanence of hemicellulose, lignin, and pectin even after accelerated weathering.

Thermogravimetric Analysis (TGA)

TGA curves of YRL and ORL are shown in Figure 5. The thermograms of the fibers showed that the drop in mass occurred in two stages: the first stage observed from the beginning of the test up to 90 and 85 °C for YRL and ORL fibers, respectively, corresponds to the loss of absorbed moisture –including chemisorbed water and/or intermolecularly H-bonded water [56] on the surface of both fibers. The difference in the degradation temperature of the fibers at this initial stage could be related to the results reported in section 3.2 concerning the H-bonding strength of the cellulose, which increased in ORL fibers as the frequency of their OH stretching band at around 3300 cm^{-1} decreased, according to the stipulated by Poletto *et al.* [45] in wood fibers.

The second stage of mass loss registered occurred from 180 °C to 380 °C. This can be attributed to the thermal decomposition of hemicellulose and the rupture of the glycoside link of the cellulose molecule [13]. The presence of a drop at around 270 °C in the thermogram of ORL fiber highlights the decomposition of the hemicellulose, which occurred in a range of 250-300 °C in an inert atmosphere [57]. This may reveal a non-uniform content of hemicellulose in the fiber caused by the pretreatment the fiber received. The mass loss observed as a flat tailing section of the TGA curve in the range of 350-500 °C is attributed to the degradation of lignin [57].

The firewood temperature in which the old leaves were

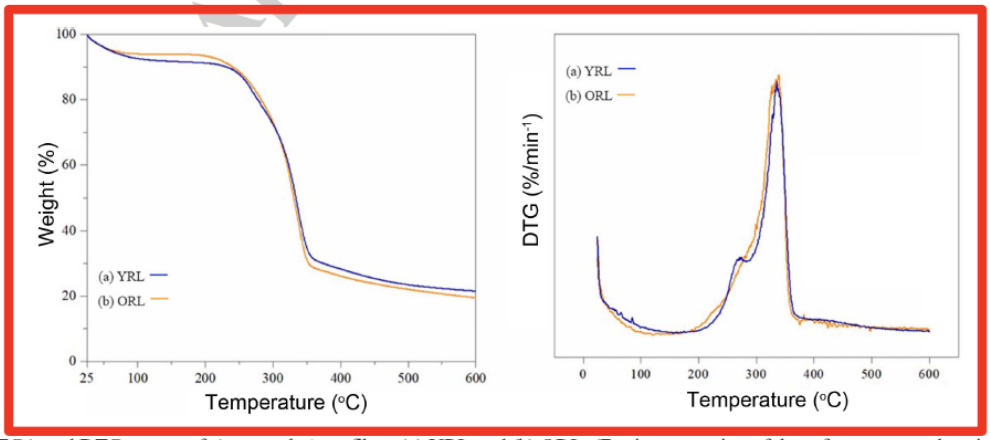

Figure 5. TGA and DTG curves of *Agave salmiana* fiber; (a) YRL and (b) ORL. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

roasted is unknown, since it was an artisanal process. However, a similar technique was described by Caballero *et al.* [33] to obtain fiber from the leaves of *Agave angustifolia* Haw. In their work, they cooked the leaves in a stone oven, and they observed that while the oven temperature reached up to 467 °C, leaves reached only up to 70 °C. The temperature reached by the leaves may explain why lignin –which degrades in a range from 200 to 700 °C [12]– was partially removed from ORL fibers.

TGA curves of TPS and biocomposites are shown in Figure 6. The thermal degradation curves of biocomposites indicate higher thermal resistance than those of neat fibers (Figure 5). The degradation of biocomposites occurs in two stages, the first one takes place at 230-380 °C and is associated with the degradation of non-cellulosic components (pectin and hemicelluloses), with the major component of fibers (cellulose), and the matrix. The second stage, with a slight slope at around 350-600 °C, is attributed to the degradation of lignin [55]. Biocomposites before accelerated aging exhibited a steep slope in their first loss, which occurred at 100 °C due to phased evaporation of absorbed and bound water in the matrix. This step was prolonged up to 200 °C where the migration of glycerol occurs [6].

The major mass loss occurred within 210-400 °C for the different biocomposites. In comparison to the fiber thermograms (Figure 6), there was a decrease in the maximum degradation temperature due to the presence of thermoplastic starch. As a particular feature of plasticizers, glycerol changed the structure of the starch by breaking its intermolecular or intramolecular hydrogen bonds, increasing its plasticity by reducing the intermolecular interactions within the starch chains.

TPS/ORL biocomposites were closer to the stable behavior of TPS at the beginning of the thermo-degradation. However, at around 480 °C these biocomposites were more stable than TPS as an effect of the lignocellulosic content of fibers. By contrast, broader and steeper drops were observed for biocomposites with 500 h of accelerated weathering, particularly in TPS/ORL. This difference indicates that the UV radiation and simulated dew directly affected not only the plasticizers of the TPS, as observed in the first drop, but also the fibers, as shown in the final drop of TPS/ORL biocomposites, where temperatures corresponding to lignin degradation produced almost 15 % of mass loss.

The accelerated weathering exposure significantly affected the specimens of TPS, which started their physical deterioration before the 500 h of accelerated weathering. All the TPS specimens exhibited fractures in the grips area of the sample, and considerable bending in the testing area; therefore, thermogravimetric, thermomechanical, and mechanical characterization of this material was not performed because of the damages in the testing area. However, the addition of agave fiber to the TPS supports their performance as reinforcing material by improving the physical and mechanical properties of the polymeric matrix; hence, biocomposites with 500 h of accelerated weathering were able to be characterized.

The effect of plasticization, coupled with the degradation temperatures of glycerol at 213 °C and starch at 309 °C, increased the vulnerability of the biocomposites to the heat

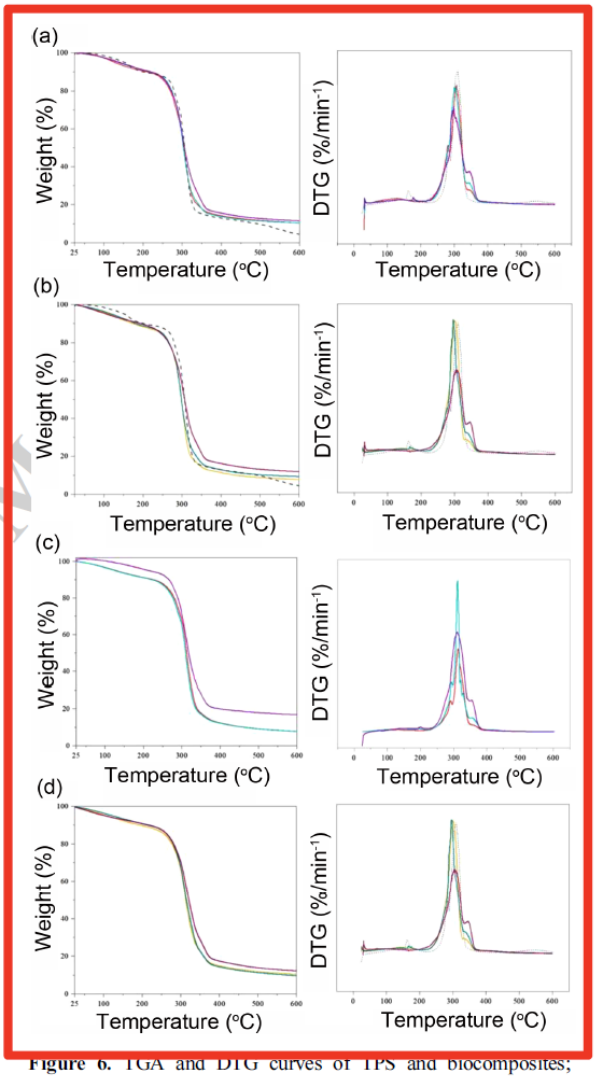

Figure 6. TGA and DTG curves of TPS and biocomposites; (a) TPS (- -), TPS/ORL10 (—), TPS/ORL20 (—), TPS/ORL30 (—), (b) TPS (- -), TPS/YRL10 (—), TPS/YRL20 (—), TPS/YRL30 (—), (c) accelerated aging effect on TPS/ORL10 (—), TPS/ORL20 (—), TPS/ORL30 (—), and (d) accelerated aging effect on TPS/YRL10 (—), TPS/YRL20 (—), TPS/YRL30 (—). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

causing notable degradation of the matrix. This degradation was observed in the first peak of the TGA curves, with maximum degradation temperatures occurring at 300 ºC and 309 ºC for samples before accelerated weathering and with 500 h of accelerated weathering, respectively. Then, the degradation of agave fibers was observed in the second peak at around 350 °C. Similar results were obtained by Islam *et al.* [10], who observed that fibers started to tear off from the eroding PLA matrix as an effect of the UV-radiation application.

This is consistent with the TGA curves that showed that increasing fiber content increases the thermal stability of thermoplastic maize starch, particularly in biocomposites containing 30 wt% of YRL fiber, which had a higher thermal resistance once the material burned off as illustrated in Fiugre 6.

Thermomechanical Analysis (TMA)

In Table 2 the thermomechanical properties variations of the biocomposites are observed regarding the type of the fiber (YRL and ORL), the content of the fiber (10, 20, and 30 wt%), and the accelerated weathering exposure time.

TPS samples registered a Tg of 48 ºC, which is in agreement with the temperature verified by Versino *et al.* [58]. This low value of Tg occurs since the function of the plasticizer is to increase the mobility of the polymer chains creating free volume [59]. Inversely, the incorporation of fiber increased the Tg of the polymeric matrix, indicating a good interaction fiber-matrix. This may be explained by the interaction between hydrophilic cellulose microfibrils –due to a low presence of lignin and hemicellulose in the fiber– and the absorbed water in the starch, allowing the migration of glycerol from the matrix to the fibers. The migration of water molecules also occurs when the small hydrophilic molecule of glycerol is inserted between the adjacent polymeric chains of the starch [60]. As observed by Gutiérrez *et al.* [61], increasing the filler decreases the chains mobility within the polymeric matrix, especially when treated fibers are added, since they exhibit stronger interfacial bonding when compared to pristine fibers. This effect is observed in biocomposites reinforced up to 20 wt% of both YRL and ORL fiber, possibly because the free volume can only be occupied at an optimum amount of reinforcing material, hence, adding a higher amount of fiber will decrease the molecular fiber-matrix interaction, as observed by Dorado *et al.* [62] in corn starch/silica nanocomposites.

In addition, the presence of the fibers affecting the thermal stability of the polymeric matrix can be observed in the CTE results. TPS and biocomposites with 10 and 20 wt% of fiber content exhibit slight changes in their thermal stability. However, a further increase (30 wt%) of YRL and ORL fibers decreased by 19 % and 33 % the CTE values, respectively, confirming the retaining effect on the polymeric chains expansion induced by the fiber. These differences are caused by the hydrogen bonds generated between the hydroxyl groups of the fiber and the TPS, which confirms a better interaction fiber-matrix in this biocomposite. This higher thermal dimensional stability of biocomposites was also observed by Gutiérrez *et al.* [61] when increasing curauá fibers content to reinforce cellulose acetate, particularly when fibers were chemically treated.

The degradation of the biocomposites exposed to 500 h of accelerated weathering was uneven, which probably interfered in the determination of thermomechanical properties, especially in TPS/ORL biocomposites, where the pattern of such properties is not as consistent as in TPS/YRL. After the exposure of biocomposites to cycles of UV radiation and moisture, Tg remained similar only in biocomposites reinforced with 20 and 30 wt% of YRL fiber, demonstrating a stable thermal dimension. By contrast, TPS/ORL biocomposites presented significant changes on the Tg values, particularly with 20 wt% of fiber. This result can be related to the heat treatment that old leaves received, providing the fiber a non-uniform surface as observed in FESEM and TGA, which, when compared to TPS/YRL bicomposites, showed a more stable thermal dimension behavior.

Finally, CTE values decreased in all samples exposed to accelerated aging, probably because the reduction in the polymeric chain size of the starch led to a degradation of the fibers exposed, hence, the fiber-matrix interface decreased. Changes in the moisture content of the polymeric matrix are caused by the swelling and shrinkage as the materials were exposed during the accelerated aging [10].

Mechanical Characterization

In Figure 7 mechanical properties obtained by tensile tests of thermoplastic maize starch and biocomposites before

Table 2. Thermomechanical properties of TPS and biocomposites before accelerated weathering and with 500 h of accelerated aging. Glass transition temperature (Tg) and mean coefficient of thermal expansion (CTE mean, am) were calculated at 23 °C±5 °C

Sample	Before accelerated weathering		500 h accelerated weathering	
	Tg (±1 °C)	CTE mean, α_m (µm/(m·°C))	Tg (±1 °C)	CTE mean, α_m (µm/(m·°C))
TPS	48	102±3	nd	nd
TPS/YRL10	52	97±3	64	75±2
TPS/YRL20	69	109±3	68	75±2
TPS/YRL30	66	83±2	67	58±2
TPS/ORL10	57	110±3	82	78±2
TPS/ORL20	76	111±3	58	77±2
TPS/ORL30	64	69±2	73	79±2

nd=not determined.

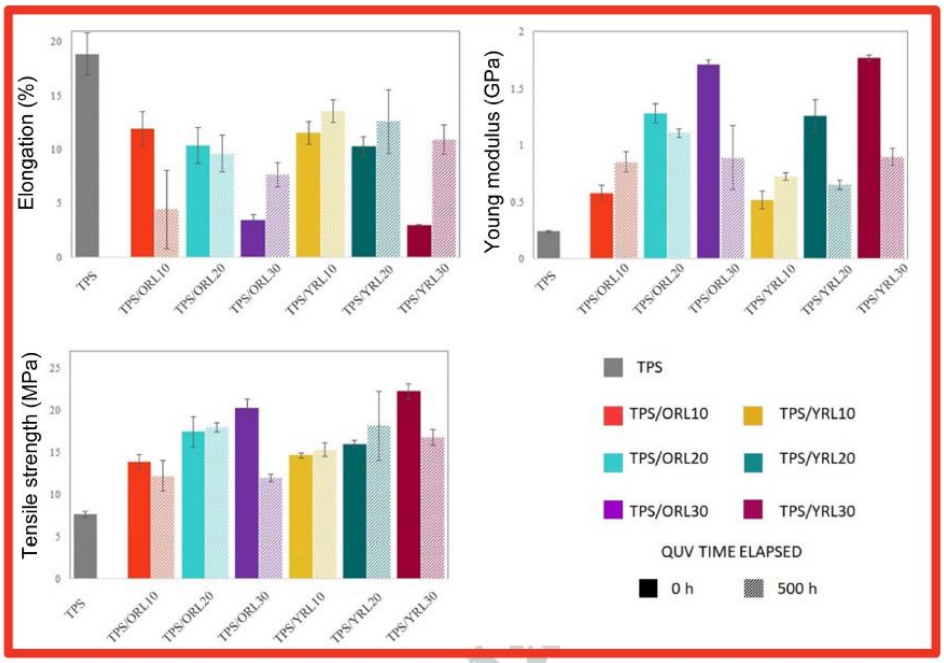

Figure 7. Mechanical properties of biocomposites with accelerated aging exposure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

accelerated weathering and with 500 h of accelerated weathering are shown.

The TPS samples reported the highest elongation value and the lowest tensile strength and Young's modulus compared to materials reinforced with fibers of *Agave salmiana*.

The mechanical properties of biocomposites before accelerated weathering were not influenced by the type of fiber. However, there was an effect due to the content of fiber, at 10 and 20 wt% of both YRL and ORL fiber the elongation was similar, but it decreased when adding 30 wt%, which contributes to increase the mechanical strength of the TPS.

For biocomposites exposed to 500 h of accelerated weathering, an increase in elongation and decrease in tensile strength and modulus was observed, due to the migration of glycerol and the degradation of the fibers, as previously discussed in the thermomechanical and the ATR-FTIR analyses.

In general, the elongation decreases in samples before accelerated aging and increases in those exposed to 500 h. This can be attributed to the higher absorption of water by samples that registered higher degradation of fibers during the accelerated weathering, as observed by Islam *et al.* [10], providing a plasticizing effect. This is in agreement with the values of Tg obtained by thermomechanical analysis for TPS/YRL biocomposites. Also, the degradation of the fibers as an effect of the accelerated weathering exposure contributed to the decrease in the Young's modulus and the tensile

Table 3. Weight loss in biocomposites by the effect of immersion in salt water

Sample	Mean weight (%)				
	Day 1	Day 7	Day 14	Day 21	Day 30
TPS	74.5±0.1	67.3±0.3	58.4±1.0	61.1±3.4	55.9±3.2
TPS/YRL10	80.6±11	69.2±1.1	63.3±4.9	61.9±7.6	54.9±7.1
TPS/YRL20	95.1±3.3	76.0±3.8	75.5±2.5	71.7±1.7	65.3±1.6
TPS/YRL30	129.1±0.2	74.9±4.8	74.3±10.6	53.8±10.7	42.1±17.3
TPS/ORL10	92.4±0.5	77.4±1.4	65.7±0.9	64.7±4.8	52.5±14.6
TPS/ORL20	76.1±1.3	67.7±2.7	59.7±2.4	58.6±2.0	50.4±2.6
TPS/ORL30	104.0±6	74.7±4.8	64.6±3.8	65.1±1.5	52.4±1.3

strength of the biocomposites and to increase the elongation, which almost reached the original value of the TPS samples.

Immersion Test

In Table 3 the weight loss trend of TPS and biocomposites immersed in salt water is shown. As an effect of the long term immersion test, in all biocomposite samples the polymeric matrix was probably the first component dissolved in the water, because the remaining lignin in both types of fibers may inhibit the dissolution of the fibers in water during the time they were immersed. Even though hydroxyl groups can form hydrogen bonds between parallel chains and reduce water absorption [41], samples of biocomposites gained more weight when immersed in salt water if compared with samples of neat TPS, since both the polymeric matrix and the *Agave salmiana* fibers used are hydrophilic materials. Increasing the fiber content probably increases the porosity of the composites and the free volume for absorbing the salt water. This could be an effect of the mechanism of capillary through the microfractures present in the biocomposites surface, as reported by Sreekala *et al*. [41] in palm oil fiber reinforced composites.

A notable weight loss was recorded in TPS/ORL30 biocomposites, losing about 50 % of their initial weight. This result is in agreement with the FESEM images, where the surface of TPS/ORL30 presents protrusions, cracks, and pores that allowed a greater penetration of the water, dissolving the polymeric matrix with ease.

Therefore, biocomposites with 10 and 20 wt% of fiber content are in advantage when compared to further content of reinforcing material since its porosity may trigger the dissolution in water of the biocomposite.

Conclusion

The two types of *Agave salmiana* fiber used to reinforce thermoplastic maize starch led to slight differences in the properties of the biocomposites. The traditional method of heating the old leaves prior to the manual scraping process partially removed the layer of lignin and hemicellulose from the surface of the cellulose microfibrils, as observed in the micrographs of the fibers.

Different properties of thermoplastic maize starch improved when adding the two types of fibers. ORL fiber enhanced the tensile strength and the thermomechanical properties of thermoplastic maize starch when compared to YRL fiber biocomposites, probably because the heat applied to old leaves promoted a slight degradation of the lignin, triggering a good interaction between the hydroxyl groups of the cellulose and the TPS, decreasing the free volume in the interface of the ORL/TPS biocomposites.

By contrast, since YRL fibers were obtained by manual scraping at raw, the changes on their surface derived from mechanical damage only, leaving the layer of lignin and hemicellulose integrated. YRL fibers enhanced the properties of thermoplastic maize starch when subjected to accelerated weathering and salt water immersion, as observed in the thermal dimensional stability and mass stability, respectively.

The use of the two types of fibers evaluated as reinforcing phase in biocomposites is feasible and innovative, promotes the complete harnessing of residual leaves from the alcoholic beverages industry, and represents an opportunity for small producers in Mexico to develop circular economy.

Based on the results of the different tests performed, further uses of the biocomposites obtained in this study should consider the following: if a short time of processing the fibers is desirable, the use of YRL fibers is adequate; for applications demanding mechanical strength and thermal dimensional stability, formulations with 30 wt% of both fibers are recommended. In contrast, if the material is going to be exposed to sunlight, moisture, or dew, but structural mechanical properties are not required, YRL/TPS biocomposites are suitable. Finally, if the material is going to be immersed in conditions similar to marine environment, and considering approximately one month of material life under such conditions, the use of formulations with 20 wt% of both fibers is feasible.

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Chapter 3

Hybrid composites based on thermoplastic starch and agricultural and marine wastes for 3d printing filaments

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HYBRID COMPOSITES BASED ON THERMOPLASTIC STARCH AND AGRICULTURAL AND MARINE WASTES FOR 3D PRINTING FILAMENTS

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Abstract

In this work, 3D printing filaments of hybrid composites based on thermoplastic maize starch reinforced with *Agave salmiana* fiber and calcium carbonate –at three concentrations– as filler were obtained by the extrusion method to be further evaluate as artificial substrate for coral growth in a parallel work. At this first stage, the diameter uniformity, density, and thermomechanical properties of the filaments were analyzed. The filaments were tested in a

3D printer and preliminary results showed that there are two possible aspects that affected the printing process: the uniformity or tolerance margin of the diameter which reached up to 0.15 mm in the TPS filament, and the flexible nature of the TPS composites. These aspects should be modified in order to the filaments be feasible to use in this method processing: 1) a modification to the formulations of the composites, particularly to the polymeric matrix, by changing the current flexible nature of the materials for a rigid one; and 2) evaluate the current formulations performance in a 3D printer equipped with a direct drive system for flexible filaments.

Keywords: agave fiber, murex shell, maize starch, by-products, extrusion, 3D printing

1. Introduction

Coral reefs are natural breakwaters that protect coastal areas and act as shelter to highly-productive biodiversity, providing critical services and goods to around 500 million people. However, coral reefs have been increasingly exposed to several natural and anthropogenic disturbances threatening their survival (Adjeroud, 2017).

A strategy recently used in the restoration of coral reefs is installing artificial structures and substrates, for example lime-rock boulders and concrete mat or modules, however, the use of natural non-invasive materials like calcium carbonate as artificial substrate is preferred (Spieler, 2001). Chou (1997) suggested that materials used for artificial coral substrate containing a surface with both smooth and rough textures provides higher possibilities for diverse organisms to attach and settle. Composites using $CaCO_3$ as filler have been proved

to be feasible in the development of bone substitution and regeneration due to the inert nature and the mechanical strength this inorganic filler presented (Boyjoo, et al., 2014).

The efficiency of attaching coral fragments in experimental fixation units –based on thermoplastic starch reinforced with agave fibers (TPS/F) biocomposites obtained by the extrusion-injection method, was previously evaluated *in situ*. In the first 24 hours the surface of these experimental units was covered by microorganisms at 28.7% (±8.4), suggesting a good coral-biocomposite interaction (Mazaba-Lara, 2019).

Generally, the composition and structure of both fillers and reinforcing agents differ from the matrix, since the latest remains in continuous phase (Mohanty, et al., 2018). The main intention of adding fillers - unlike the use of reinforcing agents- to a polymeric matrix is to cause changes in the thermoplastic properties, like increasing its density or stiffness (Geyssant, 2001), since biopolymers have low softening temperatures and modulus, along with a hydrophilic behavior (Schlemmer, et al., 2010). Recently, another reason to incorporate natural fibers is to lower the cost of the biopolymers production, since they represent an expensive material if compared with traditional petroleum based polymers (Smith, et al., 2020).

Clay, talc, and calcium carbonate are typical mineral filler materials, however there are some alternative sources to obtain natural fillers, such as wastes from processed food, wood, carbon, plant fibers (Mohanty, et al., 2018), eggshells (Jiang, et al., 2018) and even the starch itself (Angellier, et al., 2006; Bogoeva-Gaceva, et al., 2007). Also, the addition of natural fillers contributes to the compatibility with natural polymeric matrices, as thermoplastic starch (Bootklad & Kaewtatip, 2013).

In this work, calcium carbonate particles were added to the TPS/F biocomposites previously evaluated to increase their mechanical properties, and coral attraction and fixation, maintaining a potentially biodegradable character. The present results correspond to the properties of hybrid composite filaments obtained by the extrusion method, as a first stage in the production of textured fixation units that will be obtained by 3D printing.

2. Materials and Methods

2.1 Materials

Long, carded, and washed fiber from *Agave salmiana* leaves were kindly provided by people from the Mezquital Valley, Hidalgo, Mexico. The fiber was obtained by manual-traditional scraping method as described in previous works (Reyes-Samilpa, et al., 2020; Reyes-Samilpa, et al., 2020). Residual pink-mouthed *Murex* shells were obtained from the fishery industry in the coasts of Baja California Sur, Mexico by the team of the Laboratory of Gobernanza y Manejo de Recursos Marinos y Costeros, IPN-CIIDIR Oaxaca. Maize starch was supplied by Sigma-Aldrich, glycerol was purchased from ACS Fermont, and purified drinking water was used to moisten the maize starch.

2.2 Methods

2.2.1 Agave fiber (F) processing

Since *Agave salmiana* fibers can reach around 1000 mm in length, a reduction in size was performed by first manually trimming them with scissors to obtain short fibers up to 20 mm in length, and then by milling these short fibers using in a Fritsch Cutting Mill Pulverisette

19 (Idar-Oberstein, Germany) –with tungsten V blades– using 250 μm sieves. Then, these fibers were passed through three W. S. Tyler ASTM E-11 stainless steel sieves (No. 200, 100, and 50) to obtain a length range within 75 ± 5 μm to 300 ± 14 μm.

2.2.2 Calcium carbonate (CC) processing

The process of obtaining calcium carbonate particles form *Murex* shells was performed in two stages: shredding and milling. Before the first stage shells were rinsed in tap water to eliminate residues and let dried. The shredding stage consisted in reducing the original size of the shells to particles of approximated 2 cm. This reduction was performed using a lab-made hammer miller (patent No. 358266). The material obtained in this first step was passed through a Elvec México sieve No. 16 which corresponds to a grid of 1190 μm. Then, the particles up to 1.9 mm obtained were subjected to a further milling process.

The second stage was performed in a lab-made roller mill using Haldenwanger ceramic jars with a capacity of 1.5 L. 100 g of shredded shells and 25-26 ceramic balls of 20 mm diameter were incorporated into de jar to reach the relation in weight of 8:1 ceramic balls and material. The milling process was carried out for 5 h with a velocity of 494 RPM. The material obtained in this step were passed through three sizes of Mont Inox sieves: No. 200, and 400, corresponding to a grid of 74 and 47 μm, respectively, to use this range as particle size of calcium carbonate.

2.2.3 Thermoplastic starch, biocomposites and hybrid materials obtaining

Thermoplastic starch from maize (TPS) was produced for the control material as follows: to moisturize the maize starch 20% of water was added to the starch and manually stirred for 10 minutes and stored for 24 hours in a re-sealable zipper storage plastic bag prior the extrusion process –this step was the same for composites reinforced with agave fiber, filled with calcium carbonate, and hybrid composites. After this time 20% of glycerol was added to the moisturized starch and manually stirred for 10 minutes. For agave fiber-reinforced TPS composites, 20 wt% of agave fiber was added to the moisturized starch and manually stirred for 5 minutes, and then 20 wt% of glycerol was added and manually stirred for 10 minutes as well.

To obtain the hybrid composite formulations first, 20 wt% of agave fiber was added to the moisturized starch and manually stirred for 5 minutes. After this, the particles of calcium carbonate were added at content of 3, 5 and 7 wt% and manually stirred for 5 minutes. Finally, glycerol at 20 wt% was added to the mix and manually stirred for 10 minutes.

2.2.4 Preparation of biocomposites and hybrid composites filaments for 3D printing

To obtain filaments based on different formulations the extrusion process was performed using a DSM Xplore MC-5 micro compounder (Geleen, Netherlands) with double conical screw with the following parameters: 95 °C at the three heating zones of the barrel; screw rotation speed of 100 RPM at the feed and processing areas, and 5 minutes of material recirculation, these are similar conditions to those reported in a previous work where composites based on TPS and agave fibers varying fiber content and leaf age were obtained

by the extrusion-injection process (Reyes Samilpa, et al., In Press). The extruded filament was directly collected in a plastic coil –originally used for containing commercial PLA. To obtain a continuous filament the coil was manually rotated as the filament was coming out from the extruder. The extrusion parameters and collecting process were the same for all formulations.

2.2.5 Measuring the hybrid composite filaments

Weight, length, and diameter measurements of the filaments were done. Continuous filaments of each formulation were weighted in a BWL 51 Boeco precision balance (Germany), length measured with a Truper Gripper Flexometer (Mexico). The diameter was measured at 20 points along each continuous filament with a MDC-1" MX Mitutoyo Digimatic micrometer (Japan). The density of the continuous filaments was calculated using equation (1):

$$\boldsymbol{\rho = \frac{m}{v} = \frac{m}{S * l} = \frac{m}{(\pi x r^2) * l}} \quad \textbf{(1)}$$

Where ρ is the density expressed in g/cm^3, *m* is the mass and *v* is the volume of the sample, *l* is the length, and *S* is the surface of the sample obtained by multiplying the constant π by *r* which is the radius of the filament.

2.2.6 Water absorption

According to the ASTM D570-98 Standard Test Method for Water Absorption of Plastics to determine the relative rate of water absorption by plastics when immersed, different procedures can be performed varying the time of immersion. Thus, for testing plastics in general the Twenty-Four Hour Immersion should be applied, and for materials having a relatively high rate of absorption the Two-Hour Immersion should be performed. Due to the hydrophilic nature of the thermoplastic starch and to evaluate a possible contribution of the calcium carbonate to lower such characteristic of the TPS, in this work the extruded filaments were tested by the two procedure modes. Samples of ½ inch length were cut out of the continuous filaments, maintaining the original diameter. For each procedure modes filaments from each formulation were placed in individual aluminum recipients filled with 20 ml of purified drinking water and tested in triplicate. The percentage of water absorption (W_a) of the filaments was calculated using equation (2):

$$W_a = \left[\frac{W_t - W_0}{W_0}\right] \times 100\% \quad \textbf{(2)}$$

The water absorption (W_a) of each specimen was calculated according to the initial weight of the sample (W_0) and the weight of the sample immersed at 2 h and 24 h (W_t).

2.2.7 Thermomechanical analysis (TMA)

Thermomechanical tests were performed in a TA Instruments Q400 Analyzer. The samples of the filaments were cut to 20 mm in length. The equipment was calibrated under the ASTM E2113-04 Standard Test Method for Length Change Calibration of Thermomechanical Analyzers. Samples were prepared according to the ASTM E 831-14 Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis. The TMA was adjusted to the penetration mode with an applied force of 0.2 N, and a temperature ramp from 0 °C to 150 °C with a rate speed of 5 °C/min. The glass transition temperature (T_g) of the filaments was calculated using the TA Universal Analysis software. The first limit was placed at the beginning of the observed slope and the second limit at approximately the fall of the observed slope.

2.2.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a TGA-DSC 2 Mettler Toledo placing the samples in aluminum pans. The weight of the specimens was 4 ± 1 mg. The TGA trace was obtained in a temperature range of 25-450 °C, at a heating rate of 10 °C/min under a dynamic nitrogen atmosphere with a flow rate of 10 ml/min.

2.2.9 3D Printing evaluation

To evaluate the performance of the extruded filaments, three-dimensional models were drawn in the Adobe AutoCad (2017) software. These geometries were prepared for to 3D printing by setting the parameters in the Ultimaker-Cura 4.4.1 software. The model of the

printer used was the Creality Ender 3X equipped with Bowden system and heat bed. Seven tests were performed varying the parameters concerning to the filaments and the software, and making physical adjustments to the printer.

3. Results and discussion

3.1 Measuring the hybrid composite filaments

In Table 1, the dimensions of the filaments from different formulations are shown. The presence of agave fibers improved the dimension stability of TPS during the extrusion process. Also, increasing the content of calcium carbonate increased the diameter´s uniformity on hybrid filaments, as observed in the reduction of the standard deviation –or diameter tolerance– of the composite and hybrid filaments as the content of CC increased, however, even the TPS/F/CC7 hybrid with 1.73 ± 0.07 mm of diameter did not reached the desirable diameter and tolerance, which is 1.75 ± 0.05 mm as indicated by Dimonie et al (2019) who obtained a tolerance of ± 0.04 mm in filaments based on modified starch and polyvinyl alcohol blends. Calcium carbonate addition improved the extrusion process and provided an apparently smoother surface texture if compared with TPS/F filaments as shown in Figure 1. Moreover, the density of hybrid filaments was reduced by 29-26 % in hybrids with 3 and 5 wt% and 7 wt% respectively, if compared to neat TPS, which is one the main purposes of adding a filler to polymers: to obtain a lightweight material while reducing the material costs (Geyssant, 2001). Similar effect was reported by Morales et al. (2021) in filaments based of recycled polypropylene reinforced with 5 and 10 wt% of rice husk, where the decrease in the density of the composites was attributed to the lower density of the filler fiber compared to the respective polymeric matrix.

Table 1. Diameter, density, and percentage of water absorption of different formulation filaments obtained by the extrusion method.

Formulation	Filament diameter (mm)	Filament density (g/cm^3)	W_a (%)	
			2 h	24 h
TPS	1.82 ± 0.15	2.218	60	59
TPS/F	1.97 ± 0.10	1.953	60	68
TPS/F/CaCO3-3	1.93 ± 0.08	1.586	50	62
TPS/F/CaCO3-5	1.90 ± 0.09	1.567	59	68
TPS/F/CaCO3-7	1.73 ± 0.07	1.647	59	53

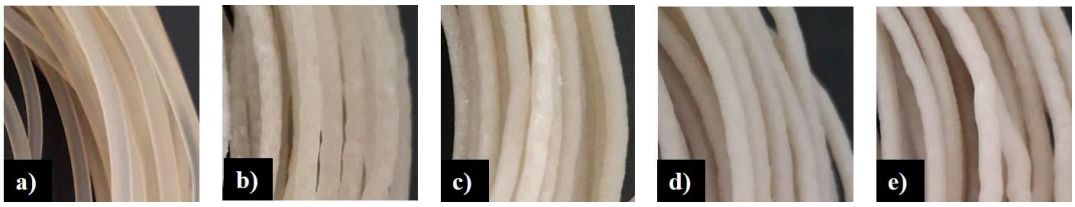

Figure 1. Filaments of different formulations: a) TPS; b) TPS/Fiber; c) Hybrid with 3% of calcium carbonate; d) Hybrid with 5% of calcium carbonate; e) Hybrid with 7% of calcium carbonate.

3.2 Water absorption

In Figure 2, the response in function to the weight of the different formulatons subjected to 2 h and 24 h immersion tests is observed, and the percentage of water absorption calculated

is shown in Table 1. At 2 h of immersion all filaments reached up to 60% and behave similarly between each other, except for the hybrid with 3% of calcium carbonate, which had the lower absorption. At 24 h the TPS samples reached an equilibrium, meanwhile TPS/F composites and hybrids with 3 and 5 wt% of calcium carbonate content increased the absorption if compared to the TPS/F/CC7 hybrid formulation. The later result suggests that higher amounts of calcium carbonate are difficult to dissolve in water, as stated by Geyssant (2001), and, according to Yahaya et al. (2018) hybrid composites have a better response to water absorption. Similar results were obtained by Syafri et al. (2017) in composites based on cassava starch using precipitated calcium carbonate as filler, where they observed that the hidrophobic nature of the CC particles reduced the water vapur absorption of the bioplastic, especially with 10% of CC content, which reached the equilibrium since the 20 h of humidity exposure.

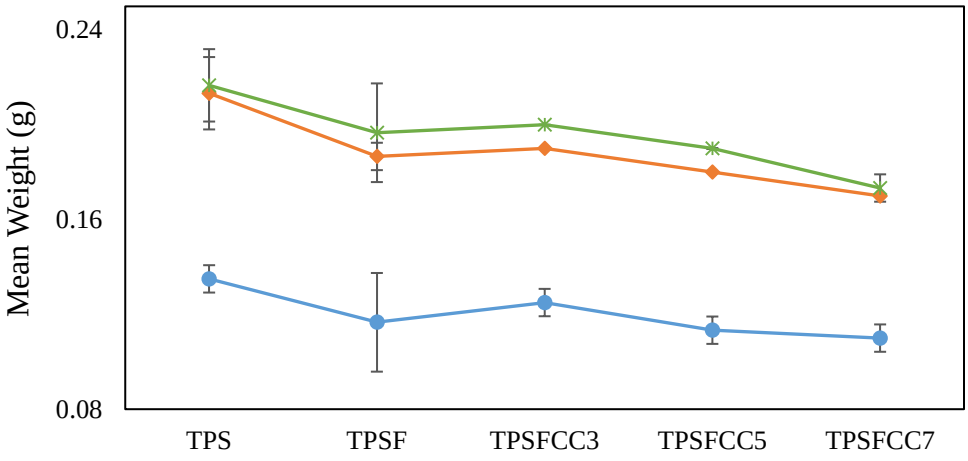

Figure 2. Water absorption response of thermoplastic maize starch (TPS), thermoplastic maize starch reinforced with agave fibers (TPSF), and hybrids based on thermoplastic

starch reinforced with agave fibers and 3, 5, and 7 wt% of calcium carbonate (TPSFCC3, 5, and 7) subjected to immersion tests; 0 h (—●—), 2 h (—◆—), and 24 h (—∗—).

3.3 Thermomechanical properties

In Table 2, the thermomechanical properties of the obtained materials are shown. It can be observed that when agave fibers were added to the TPS the Tg decreased, probably as an effect of the fiber matrix interaction. According to Schlemmer et al. (2010) the effect of low content (i.e. 1, 3, and 5 wt%) of montmorillonite particles within a polymeric matrix restrict the movement of the polymer chains increasing the Tg of the composite, but further content of inorganic fillers results in an adverse effect. Similar results were observed in our hybrid extruded filaments, where the Tg increased when 3 and 5 wt% of calcium carbonate particles were added to the TPS/F, but decreased with 7 wt% of calcium carbonate content. This plasticizing effect can be attributed to hydrogen bonding created between CC and the water molecules contained in the samples as they were exposed to two heating process –during the extrusion and during the thermomechanical analysis– as explained by Jensen et al. (2018) who suggests that the removal of water during a dehydration process produces vacancies in Ca molecules and to a consequently rearrangement of the carbonate ions, were hydrogen bonding occurs mainly between water molecules and carbonate ions.

The coefficient of thermal expansion (CTE) of the TPS increased with incorporation of the agave fiber, resulting in an enhanced thermal stability which is in accordance to a previous work (Reyes Samilpa, et al., In Press). However, the CTE of hybrid materials decreased, particularly when 5 wt% of calcium carbonate was added, lowering about 50% compared to the value of neat TPS. This behavior demonstrates another important function of calcium

carbonate as filler, which is to improve the stability of the final material by reducing the thermal expansion of the polymer (Geyssant, 2001) as a result of the restricted movement of the polymer chains (Schlemmer, et al., 2010). The addition of calcium carbonate particles improves the rheological and the mechanical properties of the polymer matrix (Lin & Chan, 2012; Boyjoo, et al., 2014; Syafri, et al., 2017), which may suggests that in the hybrid filaments obtained in this study, the function of CC particles was also as plasticizer and as nucleating agent between the polymeric matrix and the fibers.

Table 2. Thermomechanical properties of the extruded filaments: thermoplastic maize starch (TPS), thermoplastic maize starch reinforced with agave fibers (TPSF), and hybrids based on thermoplastic starch reinforced with agave fibers and 3, 5, and 7 wt% of calcium carbonate (TPSFCC3, 5, and 7).

	Tg (±1 °C)			**CTE mean, α_m**
Sample	onset	midpoint	endpoint	(μm/(m·°C))
TPS	69	99	108	45 ± 1
TPS/F	60	104	108	126 ± 3
TPS/F/CC3	65	102	107	94 ± 2
TPS/F/CC5	69	107	110	22 ± 0.5
TPS/F/CC7	60	104	108	64 ± 1

3.4 Thermogravimetric analysis (TGA)

In Figure 3, the thermal degradation of the extruded filaments is shown. The curves of the five formulations exhibited a typical weight loss in two stages. For TPS and TPS/F the first one occurred before 280 °C and is attributed to the degradation of the cellulose, pectin, and hemicelluloses contained in the agave fiber, as well as the thermoplastic maize starch, which is consistent to the results obtained in a previous work (Reyes Samilpa, et al., In Press). Regarding to the hybrid composites, they also exhibited the first stage before 280 °C, indicating the degradation of most of the polymeric matrix (Schlemmer, et al., 2010). Formulations with 5 and 7 wt% of calcium carbonate presented a similar behavior between each other, and lower weight loss was observed in the second stage, in which the lignin of the agave fibers remains without degrading. This low weight loss of the hybrids is probably an effect of a good interaction between the hydrophobic groups of the lignin and the $CaCO_3$, and a good dispersion of the filler within the hybrid composites, as similarly observed by Li et al. (2003) in composites of poly(propylene carbonate) filled with 5, 10, 20, and 30 wt% of $CaCO_3$ particles.

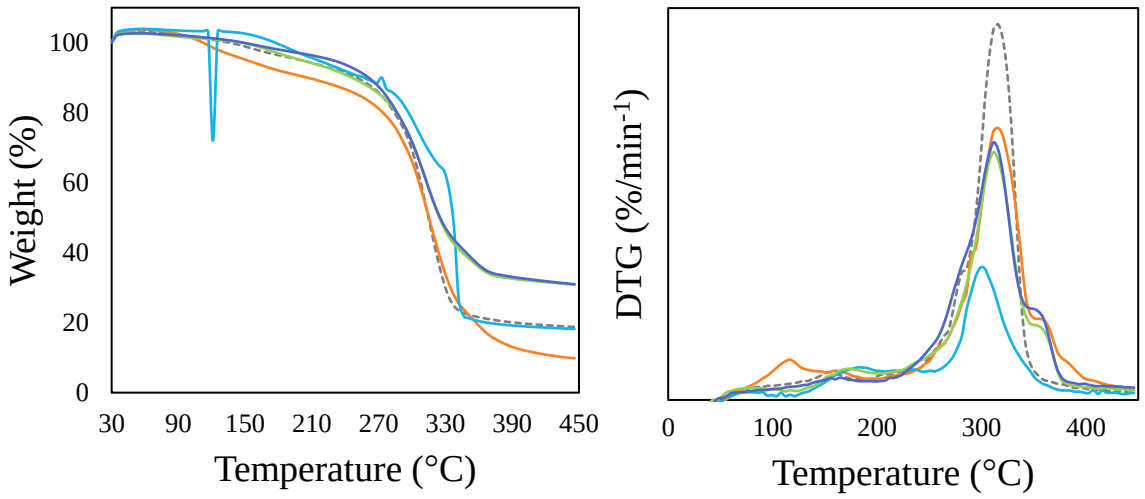

Figure 3. TGA and DTG curves of extruded filaments based on different formulations; TPS (--); TPS/F (—); TPS/F/CC3 (—); TPS/F/CC5 (—); TPS/F/CC7 (—).

3.5 3D Printing evaluation

In Table 3, basic adjustments to 3D printing parameters are shown, according to the work of Dobrosielska et al. (2020). However, additional adjustments were performed (Table 4) due to the changes in basic parameters were not sufficient to achieve the printing. The geometries attempted to print corresponded to the specimens defined in the ASTM E 831-14 Standard Test Method for Linear Thermal Expansion of Solid Materials for thermomechanical analysis. Different modifications concerning the physical properties of the extruded filaments, the printer, and the software were made in order to obtain the samples.

Table 3. Basic adjustments to 3D printing parameters

Basic parameters for sample printing	Test 1	Test 2	Test 3	Test 4
Layer height	0.12 mm	0.12 mm	0.12 mm	0.12 mm
Top layer height	0.12 mm	0.12 mm	0.12 mm	0.12 mm
Shells	2	2	3	3
Top and bottom layers number	7	7	7	7
Infill density	100%	100%	50%	50%
Infill pattern	Grid	Triangles	Triangles	Triangles
Printing speed	40 mm/s	40 mm/s	30 mm/s	30 mm/s
Extruder temperature	100 °C	100 °C	150 °C	180 °C

Filament adjustments

Before introducing any of the obtained filaments into the Bowden system of the 3D printer each filament was introduced and run through a metallic hub provided by the equipment, and when areas with non-uniform and higher diameter of the filament were detected, the excess of material was removed from the surface to make it regular.

Printer adjustments

There are few parameters of the printer that can be changed, and in this preliminary evaluation all of them was adjusted.

The size of the nozzle influences the quality and the time of impression, where a narrow diameter like 0.2 mm is preferable to obtain geometries with high quality of the impression, and broader diameters like 0.8 mm is recommended to obtain impressions in the shortest time. For mechanical pieces and geometries like the ones requested in this study, the best option is to print with 0.4 mm or smaller nozzles.

Another common parameter to consider is the adhesion of the fused material to the bed of impression, especially the first deposition layer. In order to obtain such adhesion, it is recommended to apply an adhesive which can be obtained in different presentations, such as tape or spray. In this case adhesive spray was applied, however, only in one occasion the material was adhered to the bed but not at the first deposition layer but as the hot-end was dropping the material to prepare the impression process.

Software adjustments

The most relevant parameters that can be adjusted from 3D printing the software to improve the quality of the impressions are: nozzle temperature, bed temperature, printing velocity, cooling, and retraction of filament. In this first approach, different temperatures of the nozzle were tested, considering that the processing temperature of the thermoplastic starch is about 100°C, as performed in the extrusion process. It was observed that the mentioned temperature only heated the material, but the material did not flow and remained inside the hot-end, inhibiting the impression. Thus, higher temperatures were tested, obtaining the extrusion of the material at 180°C, but the material extruded was brittle and probably degraded –given

the brownish color and the smell of the material realized. Therefore, the adhesion of the layers was not possible even when the bed was heated up to 60°C which is the recommended temperature.

Table 4. Additional adjustments to different parameters affecting the 3D printing process

	Filament Parameter Adjustment		**Printer Parameter Adjustment**				**Software Parameter Adjustment**		
	Formulation	Diameter	PLA to drive TPS filament into hot-end	Nozzle size (mm)	PTFE tube (Bowden system)	Adhesive spray	Bed temperature	Cooling	Retraction of filament
Test 1 Extruded? No Printed? No	TPS (double extruded)	Irregular	Not applied	0.4 (original)	Applied	Not applied	40°C	On (100%)	On
Test 2 Extruded? No Printed? No	TPS	Regular	Applied	0.6 (new)	Not applied	Applied	55°C	On (50%)	On
Test 3 Extruded? No Printed? No	TPS	Regular	Applied	0.8 (new)	Applied	Applied	60°C	On (100%)	Off
Test 4 Extruded? Yes Printed? No	TPS	Regular	Applied	0.4 (new)	Applied	Applied	60°C	Off	Off
Test 5 Extruded? Yes Printed? No	TPS/CC-7	Regular	Applied	0.4 (new)	Applied	Applied	60°C	Off	Off
Test 6 Extruded? No Printed? No	TPS/F/CC-7	Regular	Not applied	0.4 (new)	Applied	Applied	60°C	Off	Off
Test 7 Extruded? No Printed? No	TPS/F/CC-7	Regular	Applied	0.4 (new)	Applied	Applied	60°C	Off	Off

4. **Conclusions**

The use of waste by-products as reinforcing and filler materials in the production of hybrid biocomposites is not only feasible, but highly recommended to provide alternatives to the use and production of oil-based polymer materials. The addition of *Agave salmiana* fibers and micronized calcium carbonate improved the thermomechanical properties in maize starch as expected. Based on the results obtained, filaments of TPS reinforced with *Agave salmiana* fiber and calcium are suitable to be used in 3D printing process to obtain different three-dimensional samples, adjusting the settings according to the T_s obtained for each formulation.

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General conclusions

Agave salmiana is a plant widely distributed in Mexico, and its major utilization focuses on the fabrication of distilled and fermented products, where the core of the plant is the only organ harnessed, while the leaves are discarded and left in the fields. By contrast, in the region Valle del Mezquital, Hidalgo, Mexico, the fibers from the leaves of *A. salmiana* are obtained by traditional methods exclusively for textile applications, but their use in the production of composite materials has not been reported yet.

The fibers from *Agave salmiana* studied in this doctoral thesis were obtained from the central region of Mexico mentioned by traditional methods, and presented similar properties to fibers from other agave species. With this investigation it has been demonstrated that *A. salmiana* fibers are suitable to be used as the reinforcing phase of polymeric composite materials. This application could promote the utilization of the residual leaves from the alcoholic products as a source of reinforcing fibrous material.

In the first stage of the laboratory work, the extruded and injected biocomposites based on thermoplastic maize starch (TPS) reinforced with *A. salmiana* fibers from young raw leaves (YRL) and from old roasted leaves (ORL) exhibited not significant differences on their morphological, mechanical, thermomechanical, and thermal properties, suggesting that there is no effect of the leaf age or the treatment the fibers received over such properties.

When composites where exposed to environmental conditions, biocomposites with YRL fibers presented better results. The effect of the content of the fiber was more evident in biocomposites with 30 wt% of both types of fibers, which presented enhanced thermal

dimensional stability and mechanical properties. However, the water absorbance of all the formulations needed to be improved.

In the second stage of the laboratory work, the extruded hybrid materials were obtained to enhance the water absorbance of the biocomposites, and to evaluate their performance as filaments for 3D printing. The incorporation of a calcium carbonate particles (CC) to the biocomposites based on TPS and 20 wt% of *Agave salmiana* fiber from young leaves (TPS/F) improved their water absorbance as expected, but also provided better processing conditions of the hybrid materials, and enhanced their thermal degradation and thermal dimensional properties, particularly when 5 and 7 wt% of CC were added. However, the performance of the biocomposites and hybrid materials in the 3D printing process was not as expected, suggesting that improvements in formulations, as well as experimenting in different models of printers have to be explored.

We recommend to applied the obtained biocomposites and hybrid materials in all the same areas and industries that other plant fiber-reinforced composites are being used, such as food packaging, automotive and biomedical devices, as well as in environmental applications like coral growth attachment substrate or fragments.

With the present thesis we demonstrate that residues from different economic activities, such as agriculture and fishery, are highly feasible to be used as a source of fibrous and filler materials and that these residues can be characterized and processed with the same methods used for traditional materials like lignocellulosic fibers, oil-based thermoplastics, and ceramic particles. Finally, the use of agricultural and fishery residues as raw material for composites fabrication represents a possibility for the people involved in those economic sectors to initiate circular economy within their own communities.

Academic Resume

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