COMPREHENSIVE UTILIZATION OF THE BAGASSE RESIDUE AS A SOURCE OF FIBERS FOR MANUFACTURING PACKAGING PAPERS AND BIOCOMPOSITES

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10th June of 2017

Ana María Jiménez Serna

"I declare that this thesis has not been presented to qualify for a degree, either in the same way or with variations, in this or any other university" Art 82 Advanced Training Regime."

Firma

Ana Mª. Jiménez S.

Dedicated to my sister

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PUBLICATIONS

The present PhD thesis is based on the following publications:

AM Jiménez, FX Espinach, et al., (2016). **Tensile Strength Assessment of Injection-Molded High Yield Sugarcane Bagasse-Reinforced Polypropylene**. Bioresources, 11 (3), 6346-6361. DOI: 10.15376/biores.11.3.6346-6361.

AM Jiménez, FX Espinach, et al., (2016). **Starch-Based Biopolymer Reinforced with High Yield Fibers from Sugarcane Bagasse as a Technical and Environmentally Friendly Alternative to High Density Polyethylene**. Bioresources, 11 (4), 9856-9868. DOI: 10.15376/biores.11.4.9856-9868.

AM Jiménez, M Delgado-Agular, et al., (2017). **Sugarcane Bagasse Reinforced Composites: Studies on the Young's Modulus and Macro- and Micro-Mechanics.** Bioresources, 12 (2), 3630-3655. DOI: 10.15376/biores.12.2.3618-3629.

M Delgado-Aguilar, I González, AM Jiménez, et al., (2016). **Cellulose Nanofibers Modified with Alkyl Ketene Dimer for Oil Absorbent Aerogels**. Cellulose Chemistry Technology, 50 (3-4), 369-375. http://hdl.handle.net/10256/13946.

AM Jiménez, Quim Tarrés, et al., (2017). **High-yield bagasse pulp for the production of brown-line packaging papers: meeting paper demand and requirements.** Submitted.

CONTENT

FIGURE INDEX

TABLE INDEX

RESUMEN

Esta investigación busca desarrollar diferentes materiales utilizando residuo agroindustrial de bagazo de caña de azúcar para la producción de papel de embalaje, materiales compuestos y celulosa nanofibrilada. El estudio se establece bajo el principio "generar el mínimo residuo a partir de un subresiduo", de forma que los procesos de transformación del bagazo presenten el máximo rendimiento posible.

La presente tesis se presenta como compendio de cinco artículos que, todos ellos, cubren las temáticas expuestas anteriormente: papel de embalaje, materiales compuestos y nanofibras de celulosa.

El primer artículo muestra la viabilidad técnica de utilizar el residuo de bagazo como materia prima para la producción de papeles de embalaje de línea marrón. Para ello, se realizó un estudio de producción de distintas pulpas con el propósito de obtener el máximo rendimiento durante el proceso de cocción y un nivel de propiedades similar a los que presentan los papeles *testliner*. Asimismo, se contempló la combinación de las suspensiones producidas con suspensiones recicladas de papel de embalaje, reduciendo así la cantidad de papel recuperado a utilizar y, por ende, incrementando la vida útil del papel.

El bloque central de la tesis versa sobre la producción y caracterización de materiales compuestos tanto de polipropileno como almidón termoplástico reforzados con fibras de bagazo de alto rendimiento. En ambos casos se estudió la interfase fibra-matriz y, en el caso de los basados en matriz de origen fósil, se utilizó un agente de acoplamiento (MAPP) para promover las interacciones entre las fibras y la matriz. Los tipos de fibra que se prepararon fueron mecánicas, termomecánicas, químico-termomecánicas y, finalmente, serrín de residuo de bagazo. Se determinaron propiedades a tracción y se evaluó el comportamiento de los materiales compuestos desde un punto de vista macro y micromecánico. En ambos casos, la utilización del bagazo como refuerzo en materiales termoplásticos resultó satisfactoria, pues las propiedades originales de la matriz fueron significativamente mejoradas. Asimismo, la utilización de las fibras de bagazo con matrices de almidón termoplástico, matriz biodegradable, dio lugar a materiales compuestos termoplásticos totalmente bio-basados y biodegradables.

Finalmente, en la línea del aprovechamiento integral del residuo, se prepararon nanofibras de celulosa utilizando bagazo como materia prima. Se compararon dos tipos de nanofibras de celulosa radicalmente distintas, unas obtenidas mediante oxidación catalizada por TEMPO y otras obtenidas por procesos totalmente mecánicos. Dichas nanofibras fueron utilizadas para la fabricación de aerogeles modificados con dímero de alquil ceteno (AKD) para su utilizacón como absorbentes de aceite en medios acuosos. Se obtuvieron resultados satisfactorios tanto en condiciones estáticas como dinámicas, pues a medida que se incrementó el grado de hidrofobización, la capacidad de retención de aceite respecto a la de agua fue mayor.

En definitiva, la presente tesis muestra la valorización del residuo agroindustrial sujeto de estudio en distintos sectores, siendo algunos maduros (producción de papel y materiales compuestos) y otro de elevado valor añadido (aerogeles). Asimismo, los procesos utilizados en todas las etapas persiguieron el máximo aprovechamiento de la materia prima, promoviendo así el principio mencionado al inicio de este resumen.

Palabras clave: Caña de azúcar, bagazo, papel de embalaje, materiales compuestos, nanofibras de celulosa.

ABSTRACT

The present study aims to develop different materials using sugarcane bagasse agroindustrial waste as raw material for the production of packaging paper, composites, and cellulose nanofibers. This study is established under the principle “from a residue, minimum residue”, meaning that processing of bagasse should have the highest yield as possible.

This Thesis is presented as a compendium of five articles that, all of them, cover the mentioned above subjects: packaging paper, composites and cellulose nanofibers.

The first papers show the technical feasibility of using sugarcane bagasse residue as raw material for the production of brown-line packaging papers. For that, different pulps were produced with the purpose of obtaining the highest possible yield during the digestion process and a level of properties similar to that of test liner papers. In addition, the combination of the produced pulps with recycled test liner pulp was also explored, reducing thus the amount of recovered paper and, further, increasing the life span of paper.

The central part of this Thesis is about the production and characterization of composites made of polypropylene and thermoplastic starch reinforced with high yield bagasse fibers. IN both cases, the interphase fiber-matrix was studied and, in the case of those fossil-based, MAPP coupling agent was used to further promote the interactions between the fibers and the matrix. The types of fibers were mechanical, thermomechanical, chemical-thermomechanical and, finally, bagasse residue sawdust. Tensile properties were determined and composites behavior was assessed from a macro and micromechanical point of view. In both cases, the use of bagasse fibers as reinforcement in thermoplastic composites was satisfactory, thus the neat properties of the matrices were significantly improved. Moreover, the use of the obtained fibers as reinforcement of thermoplastic starch, which is biodegradable, let to thermoplastic composite materials fully bio-based and biodegradable.

Finally, following with the full exploitation of the residue, cellulose nanofibers from bagasse were prepared. Two types of cellulose nanofibers were compared: TEMPO-oxidized cellulose nanofibers and, on the other hand, nanofibers obtained by fully mechanical methods. Such nanofibers were used for the production of aerogels modified with alkyl ketene dimer (AKD) for their further use as oil absorbents. Good results were obtained both in static and dynamic conditions, thus as hydrophobization degree was increased, oil absorption capacity was significantly improved.

Overall, this Thesis shows the valorization of an agroindustrial residue in several industrial sectors, either mature (papermaking and composites) or those with high value-added (cellulose nanofibers). In addition, all the processes pursued the highest exploitation of the raw material, promoting thus the mentioned above principle.

Keywords: Sugarcane, bagasse, testliner paper, composite materials, cellulose nanofibers.

1. INTRODUCTION

Nowadays the demand of cellulosic fibers has increased significantly and the available surfaces in the globe cannot meet all the current necessities (Nibedita et al., 2012). The alternatives that arise pass through the incorporation of more secondary fibers (today they represent 54% of the mass of paper produced), to use more mineral fillers (eg. calcium carbonate), increase the yield of available resources, decrease weights but retaining the properties and, of course, the use of alternative fibers from agricultural and forestry residues or agro-industrial wastes.

Sugar cane is in these days the most important raw material for the production of ethanol in tropical and subtropical countries. This biofuel production generates very large quantities of agricultural or agroindustrial waste (Mesa et al., 2016) that are used for energy production and for producing fibers for papermaking (Mesa et al., 2016).

The sugarcane bagasse is a lignocellulosic material consisting mainly of cellulose, hemicellulose, and lignin. It is obtained as a by-product or agroindustrial residue in the mills, after extraction of the cane juice and represents approximately 25% and 40% of the processed material.

The vast majority of this residue is used to produce low-performance fibers (around 35%) once the pith has been removed from the bagasse, the lignin and the fibers have been bleached. The result is that 65% of subresidue is produced from an agroindustrial residue.

This study seeks the integral use of pith and fibers of the bagasse, to obtain sawdust, mechanical pulps (MP), thermo-mechanical pulps (TMP) and chemo-thermo-mechanical pulps (CTMP) with yields equal to or greater than 80% relative to raw material (agroindustrial bagasse residue). Another new aspect that arises is the manufacturer of NFC from bagasse fibers and their incorporation into the paper suspensions and biocomposites in order to increase their physical-mechanical properties.

The obtained materials have market share in the manufacture of compounds and especially in the production of biodegradable matrices derived from petroleum so that they can be incorporated in typical papers made from virgin fibers. Its addition can also be made as a single component or mixed with virgin, secondary, fillers, etc

Currently, most of the paper cardboard casing is made from recycled paper. The market for recycled paper has an economic, logistical and organizational potential as powerful as that of virgin pulps from wood. The fluting paper goes to the market via the processing and conversion into a corrugated paper to be incorporated as cardboard.

It is commonly accepted that biopolymers and bio fibers have the potential to replace or reduce the consumption of petroleum-based plastics. The thermoplastic starch (TPS) is considered one of the most promising biopolymers for industrial-scale applications, and in recent decades this has received considerable attention from the scientific world (John and Thomas, 2008; Belhassen et al., 2009; Cañigueral et al., 2009; Smith and Gross, 2012; Espinach et al., 2015). In recent years some companies have begun the production and marketing of various biodegradable based starch polymers, the use of these polymers mixed with vegetable fibers gives them an eco-friendly character with the environment (Faruk et al., 2012).

The nano-fibrillated cellulose (NFC) has attracted great attention recently due to their interesting intrinsic properties such as high surface area, low density, high tensile strength, transparency and functionalization (Siró and Plackett, 2010; Vallejos et al., 2016). Moreover, has to consider the characteristics of cellulose such as its wide availability, biodegradability, biocompatibility, etc. All these properties make CNFs suitable for application in areas such as aerogels manufacturing, hydrogels, nano papers and membranes with important barrier properties (Henrikson et al., 2008; Österberg et al., 2013; Sehaqui et al., 2010; Zimmermann et al., 2004; Chun et al., 2011; Delgado-Aguilar, et al., 2015); besides, the nanometric dimensions and high resistance appropriated for materials with applications in the manufacture of new nano compounds. Very recently, studies have been published where the feasibility of the implementation of CNF in mass as a reinforcing agent of papermaking pulps has been demonstrated (González et al., 2012; Gonzáles et al., 2013; Ahola et al., 2008; Taipale et al., 2010).

2. THEORETICAL FOUNDATIONS AND STATE OF THE ART

2.1. Sugarcane

Sugarcane is one of the most important crops in the world and it is cultivated in more than 100 countries (White, Catallo and Legendre, 2011). Even though the cane is cultivated for the sugar production, the current focus on sustainable energy and environmental practices have to lead the products derived from the sugarcane to be the basis of Biorefinery with a wide range of applications (Moncada, El-Halwagi, and Cardona, 2013).

Sugar cane is composed mainly of sucrose, fiber, and water, in the proportions of 12%, 15%, and 70%, respectively (Wong Sak Hoi and Martincigh, 2013). The others constituents are other sugars (glucose and fructose), inorganic materials, nitrogenous substances, gums, waxes and organic acids (Chen and Chou, 1993).

Sugarcane is grown in a very wide range of tropical and subtropical countries but the largest producers are from Latin America and Southern and Eastern Asia, as shown in *Figure 1*.

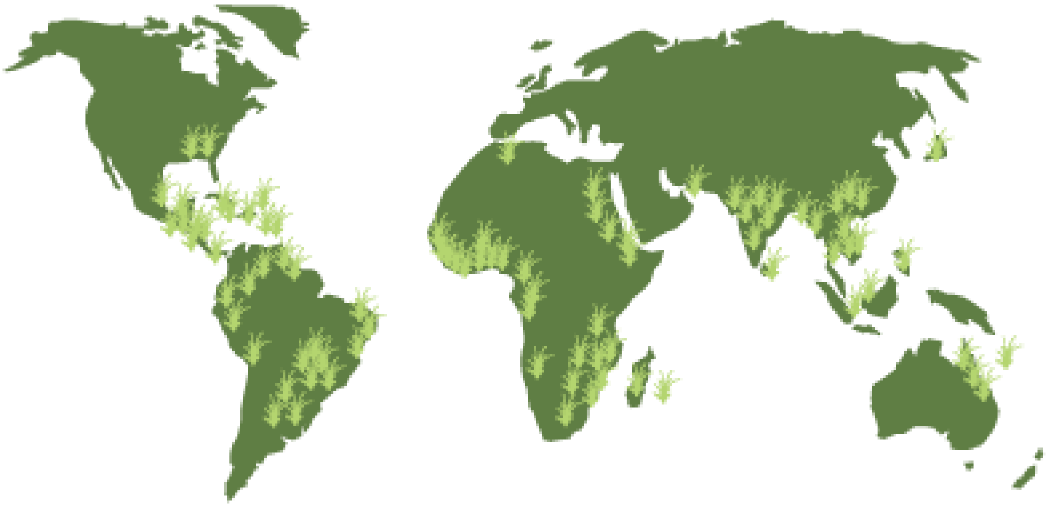

Figure 1*:* Sugarcane producing countries (UNICA and ApexBrasil, 2015)**.**

In 2013, the worldwide production of sugar cane was 1,558 millions of metric tons. Figure 2 indicates the main producers and their sugarcane production.

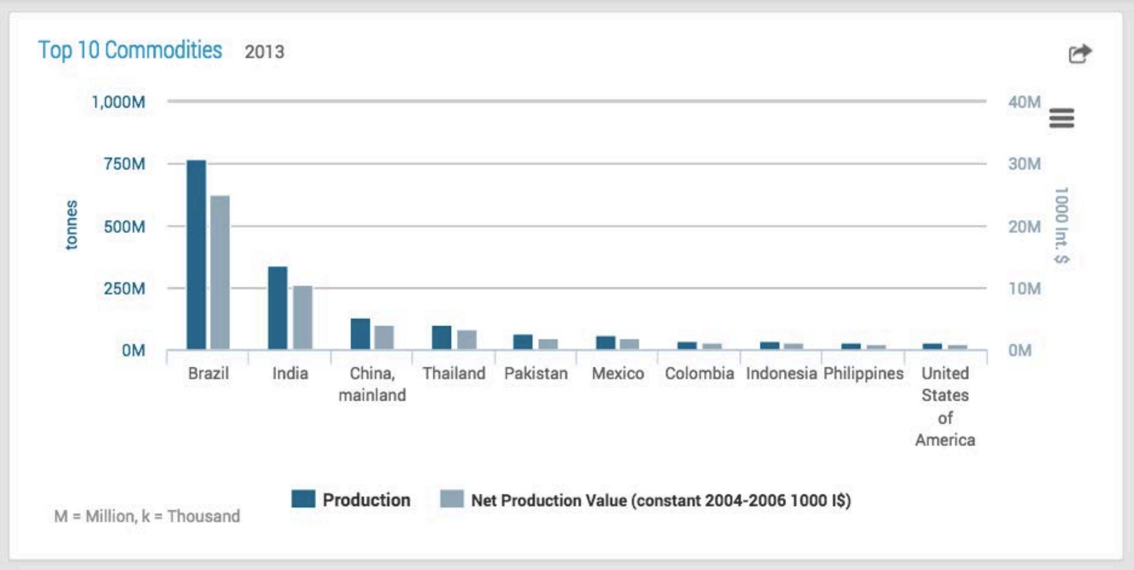

Figure 2: Major producing countries (FAO, Food, and Agriculture Organization of the United Nations, 2015)

Brazil is the leading producer of sugar cane in the world and it ranks first with 48.28% of the world production, India is the second producer with 21.45%, China with 8.06%, Thailand with 6.29%, Pakistan with 4.01%, Mexico with 3.85%, Colombia with 2.19%, Indonesia with 2.12% and the Philippines and the United States with values lower than 2%.

Sugarcane mills are factories that process sugarcane to obtain raw or white sugar and molasses. Sugar industries are agro based industries and produce bagasse in large quantity which will be available in large quantity for paper production (Pathak, Ray, Großmann, and Kleinert, 2015). Raw sugar mills are located close to sugar cane fields because sugar cane deteriorates within 24 hours of harvest (Kim and Day, 2010). Figure 3 shows the process of sugarcane manufacturing.

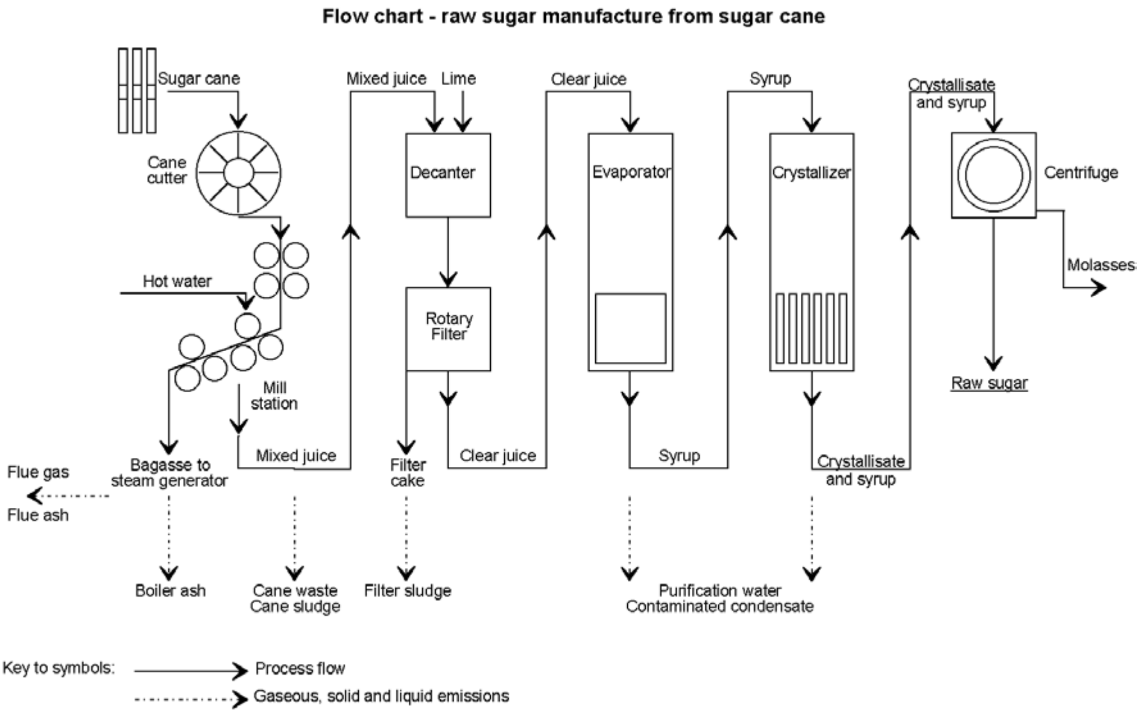

Figure 3*:* Sugarcane manufacturing (Chen and Chou, 1993)

The five main byproducts of the sugarcane industry are ash, filter cake, molasses, vinasse (or waste water) and bagasse.

- *Ash*: it is often generated during the energy cogeneration process in bagasse boilers and can be applied as fertilizer in agricultural activities
- *Filter sludge:* it is an organic waste from the mill's filtration process where the juice is extracted in rotary filters. The cake is commonly employed as fertilizer, but it can also be applied to produce biogas via anaerobic digestion processes (Contreras et al., 2009).
- *Molasses:* it is a by-product of the centrifugation process during sugar production that can be used as animal food or as a resource for ethanol production (Chauhan, Chaudhary, and Kumar, 2011).
- Waste water or Vinasse: it is a coproduct of the alcohol distillation process that can be used with the filter cake to produce biogas or be recycled to the field as fertilizer in a fertigation form (Ometto et al., 2009).
- *Bagasse:* it is the most important solid by-product from sugarcane, generated during the sugarcane juice extraction process (Kiatkittipong, Wongsuchoto, and Pavasant, 2009). Typically, the moisture content of bagasse is 40–50% and its major chemical components are cellulose (30.0%), hemicelluloses (23%) and lignin (22%). It represents around half of the sugarcane matter and is strongly intermeshed in lignocelluloses (Lopes et al., 2014)

From the sugarcane crop is obtained sugar, ethanol and byproducts bagasse, filter cake, vinasses, and others); a part of the cane is washed to remove mineral impurities. An extraction system separates the juice, which contains sucrose, from the fiber (bagasse). For sugar production, the juice is cleaned (settling and filter-press, whereby the filter cake is removed), concentrated and crystallized. Part of non-crystallized sugars and impurities (molasses) are separated (de Carvalho et al., 2005). Then it is centrifuged and dried.

2.1.1. Vegetal structure

Sugarcane is a tropical perennial grass, belonging to the gender of *Saccharum*. Although sugarcane thrives in humid climates with an average temperature between 21°C and 35°C, sugarcane can be grown in many areas of the southern United States, Colombia, Brazil, India, China and other countries.

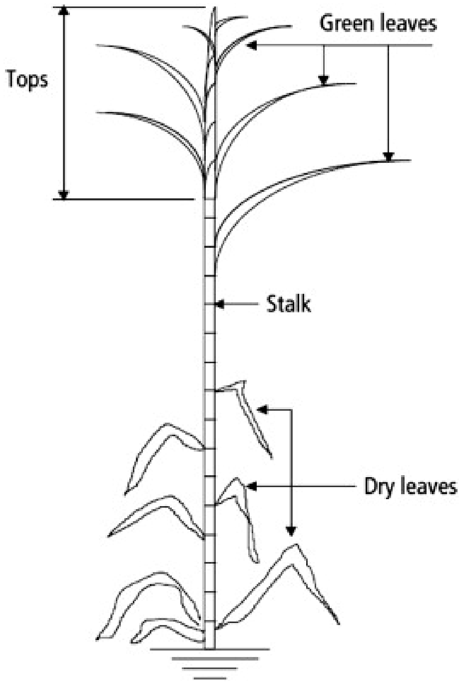

Figure 4*:* Cane plant parts (Seabra et al., 2010)

Each ton of sugarcane stalk contains about 150 kg of dry sugars such as sucrose and it is used for the production of sugar and ethanol, 125 kg of dry bagasse fiber is to be used to generate heat and electricity for the manufacturing of sugarcane. The tops and leaves represent the remaining material, which is burned in the field after the mechanical harvesting or used to generate heat and electricity (Seabra et al., 2010).

2.1.2. Sugarcane bagasse

Sugarcane bagasse is a by-product from the extraction of sugarcane, which is rich in two carbohydrate polymers (cellulose and hemicellulose or xylans) and lignin. Hemicellulose and cellulose are composed of monomeric sugars, that can be converted into fermentable sugars by enzymatic hydrolysis. Lignin, a complex of three-dimensional polymer network structure, surrounds the cellulose and hemicellulose, preventing their degradation while contributing to their mechanical strength (Hongdan, Shaohua, and Shubin, 2013).

Bagasse, which is a complex material, is one of the main products of the industry of sugarcane. It contains approximately 50% cellulose, 25% hemicellulose and 25% lignin. Due to its abundant availability, which can serve as an ideal microbial process for the production of value-added products substrate (Pandey et al., 2000). In the fibrous fraction, not everything is usable because there are other non-fibrous materials such as vascular vessels, parenchyma, tissue fibers, among others. The chemical analysis of the fiber fraction and pith fraction is listed in Table1.

Table 1*:* Chemical analysis of fiber and pith sugarcane bagasse fractions

Analysis	**Integral Bagasse (%)**	**Fiber Fraction (%)**	**Pith Fraction (%)**
Cellulose	45.0	47.7	41.2
Pentosans	25.0	25.0	25.0
Klason Lignin	20.7	19.0	21.7
Ethanol-Benzene Extractives	2.7	2.4	29.0
Hot Water Extractives	4.1	3.4	4.3
Cold Water Extractives	2.2	2.2	3.0
NaOH (1%) Extractives	34.9	32.0	36.0
Ash	2.6	1.4	5.5

(Sanjuán et al., 2001)

2.1.3. Application of bagasse

Many research efforts have explored the use of bagasse as a renewable power generation source and for the production of bio-based materials. In Table 2 some applications of sugarcane bagasse are compiled.

Table 2*:* Applications of bagasse

Field	Application	Authors
As a fuel	Electricity	(Akhtar et al., 2011; Alves et al., 2015; Santos, Ely, Szklo and Magrini, 2016)
	Charcoal Briquettes	Teixeira, Pena and Miguel, 2010
	Biogas	Hwu and Cai, 2010; Liu et al., 2015
	Ethanol	Capecchi et al., 2015; de Cassia et al., 2016; Mesa et al., 2016
Fibrous products	Bleached and Unbleached pulps	Andrade and Colodette, 2014; Hassan et al., 2015; Khristova et al., 2006; Nie et al., 2015
	Fiber Board	Doost-Hosseini, Taghiyari, and Elyasi, 2014
	Paper	Hassan et al., 2015
Miscellaneous	Furfural	Iryani et al., 2013; Mesa et al., 2014
	Nanofibrillated Cellulose	(Bhattacharya, Germinario, and Winter, 2008; Ghaderi, Mousavi, Yousefi, and Labbafi, 2014; Zhang et al., 2016)
	Xylitol	(Kamat et al., 2013; Prakash et al., 2011; Rao et al., 2006)
	Composites	(Hajiha and Sain, 2015)
	Activated Carbon	(Gonçalves, Pereira, and Veit, 2016)
	Fertilizer	(Parthasarathy and Pradhan, 1982)
	Animal feed	(Abdel-Aziz et al., 2015)
	Concrete	(Bahurudeen et al., 2015; Rerkpiboon et al., 2015; Sua-iam and Makul, 2013)
	Soil amendment	(Meunchang et al., 2005; Mohee et al., 2015)

In the last years, the efficient utilization of agro-industrial residues, including sugarcane bagasse it has grown. Several processes and products have been reported using sugarcane bagasse as raw material, the most important, in the industry, is the production of pulp and paper, and bioethanol; other applications are electricity generation and fermentation products (Pandey et al., 2000).

The applications of the bagasse residue used in the present work are focused on three sectors mainly: i) use as raw material in papermaking; (Ii) use as a reinforcement in composite materials; and (iii) bagasse as a raw material for the production of nanofibers and their possible applications in advanced sectors.

2.2. Papermaking

2.2.1. General aspects

Paper is a flexible material used for writing, packaging and a variety of specialized purposes. Paper consists of a net of pulp fibers (typically wood or other vegetable fibers), usually formed from an aqueous suspension on a screen, and is held together by hydrogen bonds. The paper may also contain a variety of additives and fillers (Biermann, 1996a; Mutjé et al., 2005).

The basic components of the paper are the fibers. A fiber is a tubular or cylindrical element, obtained from plant matter containing cellulose as the main constituent. The properties of pulp fibers determine many of the characteristics of the final paper and have been described (Biermann, 1996b; González et al., 2013).

Paper is used in printing operations, packaging and others, making it a material of high demand in the market. Due to the current concern about the environment, the paper from wood becomes an object of deforestation (Masrol, Ibrahim, and Adnan, 2015).

2.2.2. Pulping

There are two types of pulping processes: Mechanical (including the mechanical and thermomechanical pulps) and chemical (including the Chemo-thermomechanical pulp). Thus, chemical pulping methods rely on the effect of chemicals to separate fibers, whereas mechanical pulping methods rely completely on physical action. The more that chemicals are involved, the lower the yield and lignin content since chemical action degrades and solubilizes components of the wood, especially lignin and hemicelluloses (Biermann, 1996a) (Pèlach et al., 2012).

Mechanical Pulp (MP):

Mechanical pulp is produced by using only mechanical attrition to pulp lignocellulosic materials. Light colored, non-resinous softwoods and some hardwoods are often the fiber source. The total yield is about 90-98%. Mechanical pulps are characterized by high yield, high bulk, high stiffness, and low cost. They have low strength since the lignin interferes with hydrogen bonding between fibers when the paper sheet is produced.

The use of mechanical pulps is confined mainly to non-permanent papers like newsprint and catalog paper (Biermann, 1996b).

In contrast to chemical pulping, mechanical pulping preserves virtually all of the biomass components in the water insoluble fraction, resulting in good overall carbohydrate recovery but also high lignin retention (Chandra et al., 2016).

Thermo Mechanical Pulp (TMP):

TMP process involves chips disintegration between revolving metal disks or plates (in a rotor) to further steam treatment. The pulp yield is 91-95%.

Solubilization of wood components makes biochemical oxygen demand levels relatively high in mill effluents. If the steaming temperature is too high, then the surface of the fibers becomes coated with lignin, that interferes with the formation of hydrogen bonding. This results in a weak and dark paper (Biermann, 1996b).

Chemo-Thermo Mechanical Pulp (CTMP):

CTMP is a chemo-mechanical process that is similar to the TMP process with the exception that the fibers are first pretreated with relatively small amounts (about 2% on dry wood) of sodium sulfite or sodium hydroxide under elevated temperature and pressure prior refining.

The chemomechanical pulping process consists of two stages with yields of 85-95%. A particularly mild chemical treatment is followed by a drastic mechanical action. The original lignin structure and content is preserved, but extractives and small amounts of hemicellulose are removed (Biermann, 1996b; Mutjé et al., 2005; Moral et al., 2016).

2.2.3. Paper properties

The peer-reviewed standards of TAPPI, an ANSI-certified standards development organization, ensure that products comply with best practices recognized in the pulp and paper industry.

Table 3 shows the TAPPI standards used for the characterization of the fibers, pulp, and paper made in this study.

Table 3*:* TAPPI Standard description

Test media	Analysis	Tappi Standard No.	Description

Fiber	Organic Extractives	T-264-om-97	Determining the amount of solvent-soluble, nonvolatile material in pulp
	Hot Water Extractives	T-207-om-93	Determining the hot water soluble materials in pulp
	Klason Lignin	T-207-om-88	Determining the acid-insoluble lignin of pulp
	Ash	T-211-om-93	Determining ashes expressed as the percentage of residue remaining after dry oxidation of pulp
	Kappa Number	T-236-om-85	Determining the residual lignin content of the fibers
Pulp	Schopper Riegler Degree	T-227-om-94	Give a measure of the rate at which a dilute suspension of pulp may be drained
Paper	Breaking Length	T-404-om-87	Determining the force per unit width required to break a specimen
	Burst Index	T-403-om-85	Determining the maximum hydrostatic pressure required to rupture the sample by constantly increasing the pressure applied through a rubber diaphragm
	Tear Index	T-414-om-88	Determining the ability of the paper to withstand any tearing force when it is subjected to
	Gurley Porosity	T-460-om-11	Determining the resistance to the passage of air, when a pressure difference exists between two sides of paper
	Scott Bond	T-569-om-09	Determining the ability of the product to resist splitting when a tensile load is applied through the paper´s thickness in the direction of the sheet

The paper properties are used to characterize the papers in pulp mills, seeking to enhance specific parameters required by the client (Ek, 2009; Aguado et al., 2016). In this context, among the most important ones are the strength properties of the raw material and must be mentioned that the softwood fibers are stronger than hardwoods;

this also applies to binding forces of the material.

2.2.4. Bagasse for papermaking

Paper production from bagasse is a process found in industrial plants in countries such as India, China, Colombia, Iran, Thailand and Argentina (Andrade and Colodette, 2014). Bagasse pulping is performed by a well-known process using soda chemical pulping, in a pressurized reactor (Khristova et al., 2006), to produce pulp with physical and mechanical properties that are suitable for printing and writing papers as well as for tissues and fluting paper (Biermann, 1996a).

Andrade, et al., (2014) characterized the sugarcane bagasse in two main fractions: pith and depithed bagasse (fiber fraction), and evaluated the potential of the depithed for the production of dissolving grade pulps. The depithed bagasse was chemically characterized and converted into a brown pulp of two different extents of de-lignification degrees (kappa 16.9 and 9.2) by the pre-hydrolysis soda process, which consists of bagasse treatment with hot water (15 min at 180 °C) followed by conventional soda pulping. The resulting pulps were fully bleached by the O-D-(EP)-D-P sequence and evaluated for their main dissolving pulp characteristics. The contents of cellulose, hemicelluloses and lignin in the pith and depithed bagasse varied significantly. For example, the lignin S:G: H of the pith and depithed bagasse were 1.0:1.6:1.8 and 1.0:2.1:2.0, respectively. The pre-hydrolysis pretreatment terminated at pH 3.4 and removed 29% of the depithed bagasse weight. The pre-hydrolysis soda process improves the xylan removal but decreases pulp yield. The bleached pulps showed similar glucans (~95%), xylans (~5.0%), ash (~0.4%), silica (~0.15%) and α-cellulose content (~92%) regardless of kappa number (Andrade and Colodette, 2014).

Pathak, et al., (2015) evaluated energy efficient mechanical pulping potential of bagasse using TMP, CTMP, and ECTMP (Energy efficient Chemo-Thermo Mechanical Pulping) pulping methodology with electron irradiation pretreatment. It is evident from the results that more than 50% energy saving potential of irradiation pre-treatment was achieved. The authors describe, In ECTMP, bagasse was irradiated with 15 kGy and 30 kGy doses and after that irradiated bagasse was processed analogously to CTMP trials. The analysis of results shows that it is possible to produce bagasse pulp with high yield and energy efficient through a high energy electron the pretreatment. Results of irradiation show that specific energy consumption of bagasse refining was significantly reduced. This was attributed to easier fiber separation due to structural and chemical changes in the raw material. It has been observed that irradiation pretreatment of bagasse had reduced the specific energy consumption more than 50%. Considering the importance of energy efficiency during mechanical pulping operations, it is expected that the approach of pre-irradiation can be implemented for other raw materials as a solution to address the issue of high specific energy consumption in mechanical pulping/refining (Pathak et al., 2015).

Cordeiro, et al., (2013) studied the effects of hot water pre-extraction of depithed bagasse on the soda pulping and surface properties. The conditions of hot water pre-extraction were: maximum temperature 170 °C, heat-up time 90 min, time at maximum temperature 10 min, and solid to liquor ratio (S:L) 1:8. Consequently, the pre-extracted and un-extracted bagasse chips were subjected to soda pulping at 160 °C for 1 h with 11, 14 and 17% active alkali charge and an S:L of 1:5. The results showed that the hot water pre-extraction increased bagasse surface texture porosity by hemicellulose degradation. Therefore, the de-lignification was faster for pulping of pre-extracted samples. At a certain charge of alkali, pre-extracted samples showed higher screened yield and lower Kappa number. For instance, at 17% alkali charge, pre-extracted bagasse gave 11.3% higher pulp yield compared with the un-extracted ones. Inverse gas chromatography (IGC) results showed that the hot water pre-extraction changed the active sites on the bagasse surface, decreasing the dispersive energy and the basicity character, and affected the particle morphology. The pulping process decreased the hydrophobicity and the basicity of the bagasse surface. The surfaces of un-extracted and pre-extracted bagasse pulps had similar properties but different morphology. The pulps present higher surface area and permeability with more reactive capacity (Cordeiro et al., 2013).

Sheikhi, et al., (2013) evaluated the properties of fluting paper made with a mix of bagasse and recycled pulp. The conditions of the cooking process were: 15% of NaOH, 170ºC and 15 min in a pressurized reactor for bagasse raw material. The hand sheets are made according to TAPPI T 205 sp-02; for bagasse hand sheets the tensile strength of 43.60 N.m/g, burst index of 2.63 kPa.m2/g, tear index 5.47 mN.m2/g were obtained (Sheikhi et al., 2013).

Fernandez and García (1996) obtained a high yield of pulps from bagasse (Chemo-mechanical pulps and chemo-thermomechanical pulps) according to the following conditions: low investments costs, low production cost, no contaminants and good printing and strength properties. The bagasse pulp was excellent for printing paper and magazine newsprint, wrapping paper, light boards, wax-based paper for the food industry and corrugating paper. Chemomechanical pulps are brighter than the mechanical pulps, though the brightness is 50-60 ISO units for chemo-mechanical pulps and 47.9 g/m^2 of the tensile index were founded (Fernandez and García, 1996).

Samariha and Khakifirooz (2011) studied the properties of dephited sugarcane bagasse with a Neutral Sulphite Semi Chemical Pulping (NSSC). The fiber was treated with 20% of Na2SO3 and NaHCO3 for 30 minutes at 170ºC, obtaining a yield of 74.95%, after a refined process. Properties obtained include Freeness of 345 mL, Tensile index of 59.06 N.m/g^2, Breaking length of 6.02 km, Tear index of 74 mN.m2/g and Burst index of 3.5 kPa.m^2/g (Samariha and Khakifirooz, 2011).

2.3. Composite materials

2.3.1. General aspects

Polymer composites are defined as a combination of two or more materials, which present significantly distinct physical and chemical features, for instance, any reinforcement or filler into a polymer matrix (Nourbakhsh and Kouhpayehzadeh, 2009) (Oliver-Ortega et al., 2016). Synthetic fibers and lignocellulosic fibers may be used as fillers.

The composite material has two components: the filler and the matrix. In the case of the filler, the use of natural fibers in plastic matrix leads to many benefits such as low volumetric cost, increase heat deflection temperature, increase of stiffness of thermoplastics and improvement of fiber surface appearance (Karim et al., 2013) (Espinach et al., 2015).

The lignocellulosic fibers present desirable properties, such as low density, low cost, abundance, and renewability (Nourbakhsh and Kouhpayehzadeh, 2009; Granda et al., 2016).

Consequently, natural fibers such as wood, jute, kenaf, hemp, sisal, rice husk, sugarcane bagasse, have been successfully used to improve the mechanical properties of plastic composites (de Carvalho Neto et al., 2014; Reixach et al., 2015).

Polymer matrix composites are very strong and lightweight materials. These materials consist of many strong fibers surrounded by a polymer matrix. The fibers provide the strength and stiffness to the material and the matrix holds the fibers in place and transfers internal loads between them. The matrix also protects the fibers from the environmental damage. The fiber properties, content, orientation, and arrangement determine the strength of the composite (Karim et al., 2013; Espinach et al., 2016).

2.3.2. Processing of natural-based composite materials

One way of processing of natural fiber thermoplastic composites involves extrusion of the ingredients at melt temperatures followed by shaping operations such as injection molding and thermoforming. Fiber–fiber interactions as well as fiber–matrix interactions play a crucial role in determining the properties of such composites. Many times, it is observed that these fibers do not function as an effective reinforcement system due to poor adhesion at the fiber-matrix interface. Cellulose fibers also tend to aggregate and therefore the fibers do not disperse well in a hydrophobic polymer matrix and thus pose difficulties in achieving a uniform distribution of fiber in the matrix. The surface characteristics of the reinforcing fiber are important in the transferring of stress from the matrix to the fiber. The pretreatment of the fiber with suitable additives prior to processing leads to good dispersion and significantly improved mechanical properties of the composites. The properties of the composites are also influenced by the processing parameters in the case of thermoplastic composites (Saheb et al., 1999; López et al., 2013).

The incorporation of cellulosic fibers in thermoplastics often leads to poor dispersion of the fibers due to strong interfiber hydrogen bonding, which holds the fibers together. Treatment of the fibers or use of external processing aids can reduce this problem.

Various processing aids/coupling agents such as stearic acid, mineral oil, and maleate ethylene have been used. The concentration of the additive is approximately 1% by weight of fibers. The stearic acid is highly effective in dispersing, reducing fiber-to-fiber interaction. Mineral oil functions as a lubricant that is adsorbed by the fibers and this facilitate the disentanglement of individual fibers (Saheb et al., 1999; Granda et al., 2016).

2.3.3. Properties of natural-based composites

The properties of natural fiber reinforced composites depend on a number of parameters such as volume fraction of the fibers, fiber aspect ratio, fiber–matrix adhesion, stress transfer at the interface, and orientation. Most of the studies on natural fiber composites involve the study of mechanical properties as a function of fiber content, the effect of various treatments of fibers, and the use of external coupling agents (Saheb et al., 1999; Naghmouchi et al., 2015).

Both the matrix and fiber properties are important in improving mechanical properties of the composites. The tensile strength is more sensitive to the matrix properties, whereas the modulus is dependent on the fiber properties. To improve the tensile strength, a strong interface, low-stress concentration, fiber orientation is required whereas fiber concentration, fiber wetting in the matrix phase, and high fiber aspect ratio determines tensile modulus. The aspect ratio is very important for determining the fracture properties. In short fiber-reinforced composites, there exists a critical fiber length that is required to develop its full stressed condition in the polymer matrix. Fiber lengths shorter than this critical length lead to failure due to debonding at the interface at lower load. On the other hand, for fiber lengths greater than the critical length, the fiber is stressed under applied load and thus results in a higher strength of the composite (Saheb et al., 1999; Espinach et al., 2013).

For good impact strength, an optimum bonding level is necessary. The degree of adhesion, fiber pullout, and a mechanism to absorb energy are some of the parameters that can influence the impact strength of a short-fiber-filled composite. The properties mostly vary with composition as per the rule of mixtures and increase linearly with composition. However, it has been observed that this linear dependence on the percentage of fiber content does not hold at a high percentage (80%) of the fiber, probably due to lack of wetting of the fiber surface by the polymer (Saheb et al., 1999; Reixach et al., 2013).

2.3.4. Bagasse as reinforcement fiber in polymeric matrix

The application of Sugarcane bagasse (SCB) in reinforcing low-cost resin composites delineated that manufactured bagasse-polyester composites have a homogeneous structure (Monteiro et al., 1998). However, the composites were of inferior quality given

its high porosity (7.6 ± 1.8%). It was reported that the undesirable high porosity condition could be reduced by increasing the molding pressures and/or mixing temperature (Monteiro et al., 1998). Despite its inferiority, the bagasse-polyester composite showed higher flexural strength at rupture though with poorer mechanical properties compared to other natural fiber composites. The shorter fiber (5 mm) does not allow high stress to be transferred to reinforcement and that contributes to its inferior mechanical properties (Loh et al., 2013).
However, the possible application of the high porosity SCB composite material should also be revealed since porosity may not be a restricting factor that affects performance in certain usages. As an illustration, high porosity may be favorable in medical packaging as it allows gas sterilization. In fact, the possibility of the composite to have similar properties and be applied as the foam-like engineered material would be interesting if explored (Loh et al., 2013).

Investigation Conducted by Mendes and Cestari, (2011) on the utilization of cellulose polarity as a vehicle for receiving and retaining ink, has enabled the use of continuous polymeric matrix (HDPE) highly filled with sugarcane bagasse fiber (SCB) as an ink-absorbing material. They found that: (i) the ground SCB fiber can pass through 20, 40 and 100 mesh sieve as they are small enough to present good dispersion in polymer composite; (ii) dispersion between polymer and filler was fine while shearing occurred during process in Haake mixer; (iii) HDPE burnt and left no residue, showing one-step degradation, while SCB has 3 steps of weight loss due to moisture loss, burn of hemicellulose and cellulose, and lignin degradation; (iv) SCB can increase thermal stability; (v) all composites presented high repellency to distilled water; (vi) when SCB content increased, absorption efficiency of the tested liquids increased; (vii) for 80–20 and 50–50 composites, ink drops did not spread on sheet surface, while for 30–70 composite, ink was completely dried and partially absorbed within 1 hour; (viii) Young modulus decreased when SCB filler content decreased; and (ix) when SCB filler content increased, tensile stress, tensile strain, break strength and break elongation values decreased. Hence, it is shown that triturated SCB can enhance the printability, thermal and mechanical properties of composites in preparing good quality and low-cost printing surfaces and also paper (Loh et al., 2013)

Anggono, et al., (2015) evaluated the improved performance of sugarcane bagasse fibers-polypropylene (PP) composites as a result of alkali treatment done on sugarcane bagasse as reinforcing fibers. The authors carried a treatment with alkali out resulted in a relevant increase of tensile strength of the composite to 229.29MPa at 20/80 fibers/PP weight ratio or an increase of 43% comparing to the composite samples which their fibers were untreated with alkali. The tensile strength of the composite with 25/75 fibers/PP weight ratio increased to 290.30MPa and decreased to 214.17MPa as the fibers/PP weight ratio increased to 30/70. Alkali treated-sugarcane bagasse gave the best reinforcement for composites after 2 hours of treatment which resulted in the excellent fiber-matrix bonding (Anggono et al., 2015).

Karim et al., (2013) evaluated bagasse fiber reinforced PP composites using the compression-molding method. Raw bagasse was treated with 5% NaOH in order to increase the compatibility between the bagasse fiber with PP matrix. A significant effect of the alkali treatment in physical and mechanical properties was observed. The tensile strength, flexural modulus, and impact strength increased with increase in fiber loading. However, alkali treated fiber composites had better properties compared to raw fiber composites (Karim et al., 2013).

Samariha, et al., (2013) studied the feasibility of using bagasse flour for producing natural fiber-plastic composites based on polypropylene. The authors found that the tensile properties improved, but the impact strength decreased with increase in the bagasse fiber loading from 25 to 45%. The composites treated with MAPP exhibited enhanced mechanical properties, which pointed to an efficient fiber-matrix adhesion. In the study, the optimum fiber content was found to be 45%. A comparison between samples indicated that composites with 25% bagasse fibers had a lower tensile strength (10.74MPa) than the 45% ones (16.97MPa) (Samariha et al., 2013).

Nourbakhsh, et al., (2009) demonstrated the bagasse fiber content had the greatest effect on the mechanical strength of PP/fibers composites. On the basis of the results, the highest mechanical properties of bagasse fiber reinforced composites can be reached with 30% and 40% fiber contents. The notched Izod impact strength composites improved with 10% fiber (Nourbakhsh et al., 2009).

2.4. Other materials

2.4.1. Nanofibrillated Cellulose

The term ‘nanocellulose’ generally refers to cellulosic materials having at least one dimension in the nanometer range (John and Thomas, 2008; Boufi et al., 2016). Nanocellulose can be produced by different methods from various lignocellulosic sources. Recently, considerable interest has been devoted to cellulose nano-fibers because of their low thermal expansion (Fukuzumi et al., 2009), high aspect ratio (Moon et al., 2011) defined as the ratio of length to diameter, strengthening effect and good mechanical and optical properties These nano-fibers can find many applications such as in nanocomposites, paper making, coating additives, security papers, food packaging and gas barriers (Belbekhouche et al., 2011).

The CNF may be manufactured by mechanical and chemical treatments: In mechanical treatments such as high-pressure homogenization, micro fluidization, grinding, high-intensity ultrasonication, and cryo crushing. In chemical treatments such as enzymes, alkaline-acid, ionic liquids, Carboxymethylation, oxidation, sulfonation, acetylation, and silylation (Abdul Khalil et al., 2014; González et al., 2014).

Mandal, et al., (2011) obtained nano cellulose by acid hydrolysis of sugarcane bagasse. Nanocellulose with a reasonable content of cellulose II has been synthesized from waste sugarcane bagasse. It has been obtained in the form of a stable dispersion where the surface anionic charges help to bring forth the necessary stabilization of the nano cellulose. The AFM studies have given supporting evidence for the formation of nano cellulose. This observation has further been corroborated by the DLS studies, which indicate that majority of the hydrolyzed particles lie in the nano range. Nanocellulose and cellulose exhibited identical FTIR spectra quite different from SCB. TG analysis shows that the bagasse starts to degrade earlier than cellulose and the nano cellulose shows an even earlier onset of degradation compared to SCB but leaves the maximum residue within the range of temperatures studied (Mandal et al., 2011).

Hassan, et al., (2015) bleached palm rachis pulp, pretreated with xylanase enzymes, was used for isolation of micro-fibrillated cellulose (MFC) and TEMPO-oxidized MFC (TMFC) by ultrafine grinding. The isolated MFC and TMFC were used at ratios from 2.5% to 20% for improving strength properties of paper sheets prepared from unbeaten softwood and bagasse pulps. The retention of micro-fibrillated cellulose in paper sheets was also estimated. The results showed that MFC or TMFC brought about an increase in density, wet and dry tensile strength, tear resistance, and a decrease in air permeability of paper sheets prepared from unbeaten softwood or bagasse. However, the usual beating of softwood fibers was much more effective in improving strength properties of softwood paper sheets than the addition of micro-fibrillated cellulose. On the other hand, the improvement in strength properties of bagasse paper sheets as a result of MFC or TMFC addition was generally higher than that resulted from the beating of bagasse pulp. Use of TMFC with unbeaten softwood or bagasse fibers resulted generally in better improvement in tensile strength (wet and dry) than in a case of using MFC (Hassan et al., 2015).

The authors obtained the maximum increase in wet tensile strength of bagasse paper sheets was 131% and 438% and was obtained upon addition of 20% of MFC or TMFC, respectively. The increase in wet tensile strength as a result of beating the bagasse fibers was 105%. The addition of the different ratios of MFC to bagasse fibers resulted in an increase in elongation at break of paper sheets; the maximum increase in elongation at break was 38% and 28% and obtained at 10% of MFC and TMFC, respectively. The increase in elongation at break resulted from the beating of bagasse fibers were similar to that noticed as a result of the addition of MFC to bagasse fibers at high ratios (Hassan et al., 2015).

Li, et al., (2012) isolated nano cellulose from sugarcane bagasse by high-pressure homogenization (HPH) in a homogeneous medium. In this study, the nano cellulose from sugarcane bagasse was prepared by high-pressure homogenization coupled with an ionic liquid pretreatment. The HPH process resulted in nano cellulose with a diameter range of 10–20 nm. Chemical morphology and structural analysis of nano cellulose were measured by TEM, IR, XRD, TG and the suspension rheology determined. The nano cellulose exhibited a lower thermal stability and crystallinity, which was attributed to the breakage of hydrogen bonds between celluloses by ionic liquid homogeneous treatment and the high-pressure shearing of HPH. Further studies will explore the applications of this form of nano cellulose (Li et al., 2012).

Mandal, et al., (2014) synthesized nanocomposites from polyvinyl alcohol (PVA) in a linear and cross-linked state using varying proportions of bagasse extracted nano cellulose. These were characterized by tensile, thermal, X-ray diffraction (XRD), moisture vapor transmission rate (MVTR), and morphological studies. Cross-linked PVA and linear PVA nano composite exhibited highest tensile strength at 5 wt.% and 7.5 wt.% of nano cellulose respectively. Thermogravimetric analysis (TGA) studies showed the higher thermal stability of nanocomposite made of cross-linked PVA and nano cellulose with respect to linear PVA and nano cellulose. TEM and AFM studies confirm the formation of nanocomposites while the SEM images show the dispersion of nano cellulose particles in them (Mandal et al., 2014).

Wulandari, et al., (2016) obtained nano cellulose by acid hydrolysis of cellulose. The cellulose used in this study was isolated from sugarcane bagasse, and then it was hydrolyzed by 50% sulfuric acid at 40 °C for 10 minutes. Transmission Electron Microscope (TEM), Particle Size Analyzer (PSA), Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) have characterized Nanocellulose. Analysis of FTIR showed that there was not a new bond, which formed during the hydrolysis process. Based on the TEM analysis, nano cellulose has a spherical morphology with an average diameter of 111 nm and a maximum distribution of 95.9 nm determined by PSA. The XRD analysis showed that the crystallinity degree of nano-cellulose was higher than cellulose in the amount of 76.01% (Wulandari et al., 2016).

3. OBJECTIVES

3.1. General

Evaluate alternatives for the use of agroindustrial bagasse residue in the development of various value-added materials such as fluting paper, composite materials, and nano-fibrillated cellulose.

3.2. Specific

a. Compare the behavior of the pulps from organosolv, soda-anthraquinone and mechanical processes and evaluating their properties in packaging paper.

b. Establish the effect of the refining conditions on the physicomechanical properties of pulps derived from sugarcane bagasse fibers, by improving the wrapping paper type feasibility for use in industry.

c. Develop composite materials using bagasse fibers, previously treated as reinforcing polymeric and biodegradables matrices for further characterization and property evaluation.

d. Evaluate the use of nano-fibrillated cellulose from bagasse fibers de-lignified with chemical, enzymatic or mechanical pre-treatments, for application in mass and the manufacturing of products such as aerogels.

4. PUBLICATIONS

4.1. HIGH-YIELD BAGASSE PULP FOR THE PRODUCTION OF BROWN-LINE PACKAGING PAPERS: MEETING PAPER DEMAND AND REQUIREMENTS

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When paper is recycled, fibers experience irreversible structural damages due to hornification phenomena and the side-effects of mechanical refining. To palliate this, fresh wood fibers are usually added to further improve mechanical properties of paper. However, forest have a finite capacity to supply lignocellulosic resources, and there is the need to look for alternative raw materials from other agricultural or industrial activities. These residues are of great interest due to their low cost and abundance. For this, the aim of the present work is to produce high-yield pulps from sugarcane bagasse residue for the production of brown-line papers, in combination with recycled testliner fibers. It was found that an organosolv treatment leads to high-yield bagasse pulp with properties near to those commonly used for paper production. Several hybrid papers were prepared, looking for a well-balanced combination that could allow the production of testliner paper, meeting demand and technical requirements.

Keywords: bagasse, papermaking, testliner, mechanical properties, organosolv, mechanical refining, hybrid papers

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Introduction

In the beginning of nineties, the raw materials consumption in CEPI area for paper production was about 73 million tonnes, while in 2015, was 104. This increase can be surprising if recent technological advances are taken into account, such as e-readers, smartphones, and some other platforms where press and books can be read. Nonetheless, fiber-based products are gaining interest as potential substitutes of plastic, not for writing and printing substrates, but specially for packaging. Having a look to the total share of woodpulp for paper production in 1991, one can see that it accounted for 51 %, while paper for recycling was about 35 %. Half a century later, woodpulp has lost 10 % of market share, having significantly increased the paper for recycling, concretely in a 10 % (CEPI 2016). Having a look to the referred statistics, one can see that recycling is becoming one of the central parts of papermaking industries, having achieved a recycling rate of 72 % in Europe, according to data from 2015.

This increasing tendency on recycling mainly comes from the need of palliating cellulosic resources consumption, making the paper production more sustainable, together with decreasing basis weights and/or increasing the mineral filler content in paper products (Hubbe 2014). However, recovering the abovementioned statistics (CEPI 2016), the total share of raw materials considered as “pulp other than wood”, is 0.3 %. Under this category, agricultural and agroindustrial residues are included, and it becomes apparent that they are not being successfully exploited.

During recycling, fibers experience structural damages due to mechanical refining and hornification phenomena. This effect is much higher in kraft and sulfite than in high-yield pulps (mechanical and thermomechanical), these last commonly used in newsprint production (Hubbe 2014). To palliate these loses, paper, once redispersed back into water, is usually mechanically refined. This treatment increases the specific surface of fibers, implying more and stronger bonds per volume unit, higher swelling capacity of fibers and, thus, higher mechanical properties of the resulting paper. However, it causes permanent structural damages and increases the amount of fine elements in the pulp suspension, leading to poorer drainability (Delgado-Aguilar et al., 2015b).

Lignocellulosic residues from agriculture and agroindustry are of great interest because their abundance and cost (Pathak et al., 2015). The comprehensive utilization of waste generated by farming crops (corn, sugarcane, rapeseed, soy, etc) can generate sawdust and fibers that could be used for composite materials production and even for paper (Flandez et al., 2012; González et al., 2013; Tarrés et al., 2017; Theng et al., 2015). Concretely, such fibers are of special interest when used in combination with recycled fibers, since they usually present higher mechanical properties and their incorporation does not affect the quality of the suspension, since no structural damages are caused (Moral et al., 2017).

For all the above, the aim of the present work is to produce high-yield pulps from sugarcane bagasse residue for the production of brown-line papers. In addition, the suitability of using the obtained fibers in combination with recycled liner-grade pulps will be studied in terms of physical and mechanical properties of pulps and papers.

Experimental

Materials

Sugarcane bagasse residue was provided by University Pontificia Bolivariana (Colombia) and testliner paper was kindly supplied by Saica S.A. (Spain). All the chemical reagents used during pulping were supplied by ScharLab (Spain), except antraquinone, which was supplied by BASF S.A. (Spain).

Chemical analysis

Bagasse residue was prepared for chemical characterization according to TAPPI standard T257. Samples were dried in an oven at 105°C until constant weight and then, samples were milled and screened (40 mesh) to assure homogeneous particle size.

Once samples were conditioned for chemical characterization, one portion was used for ash content determination (T211). Briefly, 2-gram samples were placed in porcelain crucibles (previously cleaned and dried) and placed in an electric muffle furnace. The initial temperature was 100 °C and temperature was slowly raised until 525 °C to assure sample carbonization without flaming. Crucibles were removed from the furnace when no black particles were observed, indicating that the specimen was completely combusted.

In parallel, samples were submitted to solvent extractives determination (T204). This determination was carried out by Soxhlet extraction using ethanol-toluene mixture as solvent. This was performed to quantify the extractives of the samples and because the next determinations require extractive-free samples. For the determination, extraction thimbles containing 5-gram samples were submitted to Soxhlet extraction for 5 hours in presence of 150 mL of ethanol-toluene. Extract was transferred to a tared dish and dried in an oven at 105 °C until constant weight. A blank determination was also carried out with the solvent used in the test.

Acid-insoluble lignin of the extractive-free samples was determined following the procedure described in TAPPI standard T222. Two samples of 2 grams from each extractive-free sample were placed in 100-mL beakers. Then, 40 mL of cold (10 °C) 72 % sulfuric acid was added to each beaker. This operation was performed gradually under constant stirring and the beaker was placed in a cold water bath to palliate sample heating. Then the beaker was covered with a watch glass and kept in a bath at 20 °C for 2 hours. The material was stirred frequently to ensure complete solution. After this time, the material from the beaker was transferred to a flask containing 400 mL of deionized water, adding more water until achieving a 3 % concentration of sulfuric acid and then boiled for 4 hours. Extra water was added to maintain the total volume. The flask was left inclined overnight to promote lignin precipitation and then the liquid was filtered by a 0.22 µm of pore size nylon membrane, passing through hot water with to remove free acid. Acid-insoluble lignin was then oven dried at 105 °C until constant weight.

Cellulose content was determined by high performance anion exchange chromatography (HPAEC). For this, 200 mg (dry weight) of sample was placed in a 100-mL flask adding 3 mL of 72 % sulfuric acid while mixing with a glass rod. Samples were then placed in a vacuum desiccator for 1h and mixed frequently to assure total hydrolysis. Samples were then diluted by adding 84 mL of deionized water.

Standard solutions of glucose were prepared adding also 3 mL of 72 % sulfuric acid and 84 mL of deionized water to the standards. Both samples and standard solutions were placed in an autoclave for 60 minutes at 125 °C, then filtered under vacuum through a 0.22 µm of pore size nylon membrane, and finally washed twice with deionized water (as explained for acid-insoluble lignin determination). The filtered sample was used for the chromatographic determination. Cellulose was quantified by comparing the peakof the diluted and filtered sample with that of the standard solution of glucose. A differential refractometer (Waters 410) equipped with a system controller (Waters 600E), with an adsorption column ICSep ICE-ORH-801 was used. Glucose content gave directly the cellulose content. Since the adsorption columns were not able to successfully separate other sugars than glucose, hemicellulose was quantified by difference from 100 %.

Pulping

Sugarcane bagasse residues was milled and fractionated to a size lower than 5 mm, to have a homogeneous dispersion in terms of particle size before treating them in a rotatory digestor.

Two different types of treatment were carried out: organosolv and NaOH-AQ. Regarding organosolv treatment, five different pulps were produced. Temperature, time and liquid-solid ratio were kept constant at 150 °C, 25 minutes and 6:1, respectively. Ethanolamine amount was ranged from 5 to 25 %. On the other hand, bagasse residue was treated with sodium hydroxide (7 %) and antraquinone (0.1 %) at 100 °C for 60 minutes with a liquid-solid ratio of 10:1.

Disintegrating and Refining

Sometimes it is appropriate to show an equation in the Introduction, Experimental, or Results and Discussion section. Here is an example of Eq. 1, where *E* is energy (kJ), *m* is mass (kg), and *c* is the speed of light (m/s). Note that the variables are in italics; the equation is left-indented with one tab. The units are included when the variable is defined.

Paper sheets preparation

After disintegration, paper sheets were prepared in a Rapid-Köthen sheet former (ISP mod. 786 FH) according to ISO 5269-2 and conditioned at 23 °C and 50 % of relative humidity for 40 h before testing, following ISO 187.

Physical and mechanical characterization of pulps and papers

Drainage of pulps was determined with Schopper-Riegler tester (mod. 95587 PTI) following ISO standard 5267/1.

Fines content and fiber morphology were determined using a MorFi Compact analyzer (TechPap) controlled with a computer workstation. The equipment utilizes 1000 mL of 1-wt% aqueous fiber suspension by analyzing pictures taken from the suspension with a CCD video camera. About 10,000 fibers were analyzed in each test by the software MorFi v.8.2.

Tensile tests were conducted to determine tensile index and breaking length; test were performed with a Houndfield 42 Universal testing machine equipped with a 2.5 kN load cell. Testing conditions were set according to ISO standard 1924-1 and 1924-2. Internal cohesion (Scott bond) was determined with a Scott Bond testing machine (IDM mod. IBT 10A) following by TAPPI test method T569. Burst index assays were performed with a burst tester (IDM mod. EM-50), and the test conditions were set according to ISO standard 2758. Tear index was determined with Elmendorf tear instrument (mod. F53.98401 Frank PTI), and the assay conditions were set according to ISO standard 1974.

In all cases, at least seven or more tests were performed from each sample, and only those values within 95% of statistical confidence coefficient were averaged.

Results and Discussion

Chemical characterization of the raw material

The chemical composition of the bagasse residue, the raw material, was determined as described in the previous section. In addition, average compositions of softwood and hardwood were used for comparison purposes. Results are reflected in Table 1.

Table 1. Chemical characterization of the raw material, softwood and hardwood

Constituents	Sugarcane bagasse	Softwood*	Hardwood*
Cellulose (%)	36.1	40-45	38-49
Hemicellulose (%)	30.1	7-14	19-26
Lignin (%)	20.8	26-34	20-23
Extractives (%)	3.4	-	-
Ash (%)	1.6	<1	<1
*Average values reported by González et al., (2013)			

Bagasse residue showed lower cellulose content than softwood and hardwood, while hemicellulose was significantly higher. Concretely, hemicellulose accounted for 30.1 %, being higher than for some straws (rice, rye, oat, etc) and of the same magnitude than triticale (Rodríguez et al., 2008; Tarrés et al., 2017). This high hemicellulose content compared both to softwoods and hardwoods makes this source suitable to be mechanically refined, since, as reported by Boufi and Gandini (2015), the presence of amorphous polysaccharides, that hemicellulose is composed, promotes fibrillation and, thus, fiber swelling during refining. Lignin accounted for 20.8 %, being lower than for softwood and in the range of hardwood. Extractives and ash were of the same magnitude than both softwood and hardwood, as well as other straws reported in the bibliography (Mazhari Mousavi et al., 2013).

Pulp characterization

One of the main parameters in papermaking is the drainability of the pulps, since it has a strong influence on the paper machine speed. As expected, as the amount of ethanolamine was increased, Schopper – Riegler degree (°SR) was raised, as an effect of the higher specific surface of the fibers, as well as the higher presence of fines. Morphological and physical characterization can be observed in Table 2.

Table 2. Morphology, yield and drainability of organosolv pulps

Ethanolamine (%)	Yield (%)	°SR	l_w^f * (µm)	Diameter (µm)	Fines (%)
25	67.5	43	627	23.8	44.3
20	70.1	41	639	23.9	38.2
15	72.6	39	661	24.6	29.6
10	78.3	38	711	25.4	27.4
5	81.9	35	764	27.1	25.4
*Fiber length weighted in length					

As expected, yield was dramatically decreased as ethanolamine amount was increased due to the higher solubilization/removal of amorphous constituents, such as hemicellulose and lignin. In principle, lower yields should lead to stronger papers, since inter-fiber bonds are promoted (Page 1969). However, it must be taken into account that lower yields implies higher amounts of ethanolamine and, at the same time, less exploitation of the resource, which means at the same time that more residue is generated from the digestion operation. In the same extent, diameter and fiber length were decreased as the severity of the treatment was increased. Comparatively, Flandez et al., (2012) submitted corn stalks to thermomechanical treatments, obtaining fiber lengths and diameters of the same magnitude. In that work, paper sheets made of such fibers presented a breaking length of 650 m.

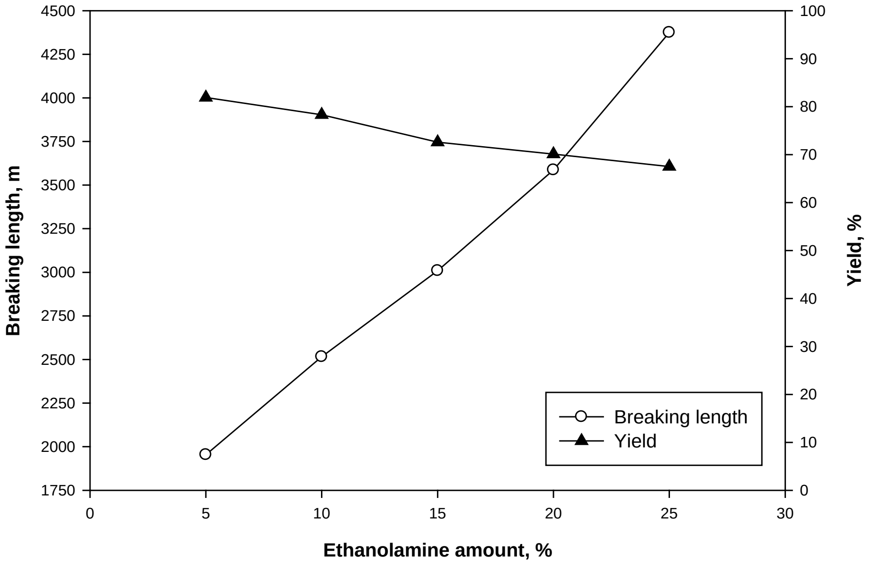

Fig. 1. Evolution of breaking length and pulp yield as ethanolamine amount was increased

As it is possible to see in the graph above (Fig. 1), paper sheets with each organosolv pulp were produced and tested at tensile. As expected, as ethanolamine amount was increased, breaking length of the obtained papers was enhanced. Comparing the obtained results with the mentioned above study, similar morphology leaded to stronger papers than in the case of corn stalks, bringing to the light the potential of bagasse to be used as source for papermaking. In fact, the achieved breaking length with the 5 % - ethanolamine pulp was of the same magnitude than papers made of bleached kraft eucalyptus pulp, while yields in such pulps are significantly lower, as reported in several works (Delgado-Aguilar et al., 2015a; González et al., 2012; Tarrés et al., 2016).

For comparison purposes, sugarcane bagasse residue was also submitted to a NaOH-AQ treatment, following the methodology described in the previous section. The obtained yield was 81.1 %, the diameter was of the same magnitude (24.5 µm) and length was slightly lower (510 µm). Both drainability and breaking length were similar to the obtained with the organosolv pulp treated with 5 % of ethanolamine (33°SR and 1839 m).

At this stage, 5 % - ethanolamine and 7 % - NaOH-AQ pulps were selected for further experimentation, since they presented a good balance in terms of yield, drainability and mechanical performance.

Mechanical refining aptitude of pulps

Both organosolv and NaOH-AQ pulps were subjected to mechanical refining process, from 0 to 2000 revolutions in the PFI mill. Depending on the pulp, the effect of applying the same energy was significantly different (Fig. 2).

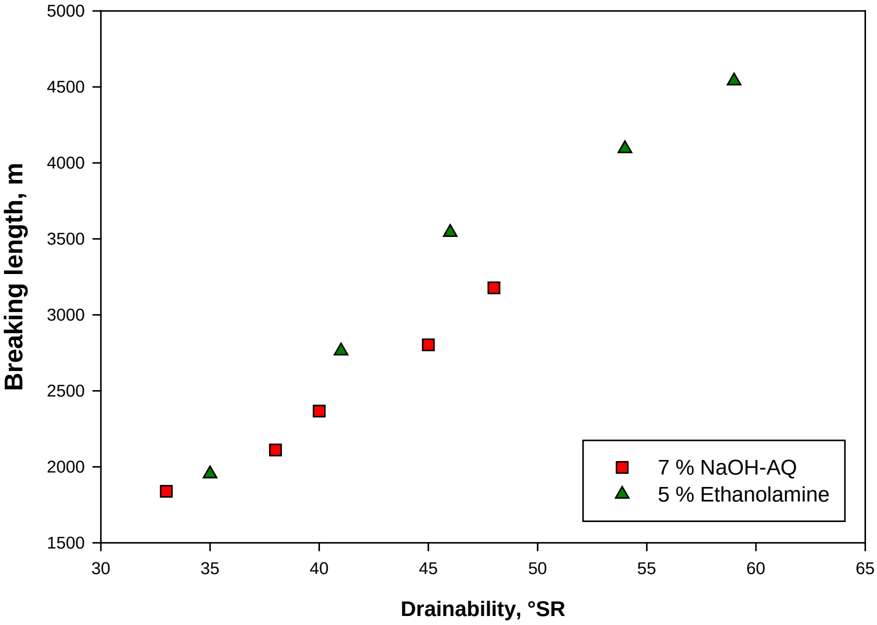

Fig. 2. Evolution of breaking length of organosolv and NaOH-AQ pulps as function of the refining degree

The graph above brings to the light the higher susceptibility of the organosolv pulp to be refined, rather than the one obtained by the addition of NaOH and anthraquinone. Exemplarily, the effect of applying 1000 PFI revolutions to the organosolv pulp increased the breaking length from 1954 to 3543 m (81 % increase) and the refining degree from 35 to 46 °SR. On the other hand, if the same energy is applied to the NaOH-AQ pulp, the breaking length just increased from 1839 to 2367 m (29 % increase). In this sense, more than the double of the applied energy is required to achieve 3543 m, but the °SR would be much higher. For instance, 2763 m and 41 °SR were achieved by submitting the organosolv pulp to 500 revolutions, while for achieving the same tensile strength with the NaOH-AQ pulp, 1500 revolutions were required, and drainability accounted for 45 °SR.

This behavior, in principle, could be explained by the fact that organosolv treatments are known for preserving much hemicellulose than NaOH-AQ processes. As explained above, the presence of such polysaccharides should promote fibrillation during refining, with the subsequent fiber swelling. In fact, this effect became apparent when organosolv pulp was refined to 2000 PFI revolutions, thus 4540 m of breaking length were achieved.

Hybrid testliner and bagasse papers

Following with the premise that there is the need of using alternative raw materials in combination with recycled fibers, the suitability of using the 5 % ethanolamine pulp was assessed. For that, first of all, a commercial testliner paper was characterized in terms of breaking length, both at machine and cross-sectional direction. Breaking length at machine direction accounted for 5534 m, while at cross-sectional direction, 2457 m. Then, this paper was teared in small pieces and disintegrated in a laboratory scale pulper to obtain recycled paper. This paper was tested at tensile, obtaining 3655 m of breaking length. This value was of the same magnitude than the one obtained by refining the organosolv pulp at 1000 PFI revolutions. Both pulps presented the same drainability (46 °SR). At this stage, one can affirm that the production of testliner from sugarcane bagasse residue is, at least, feasible. However, higher mechanical properties must be pursued, in order to palliate the strength loss during recycling due to hornification phenomena. In this sense, hybrid papers made of refined testliner (500 rev) and organosolv bagasse pulp (1000 rev) were prepared and physic-mechanically tested.

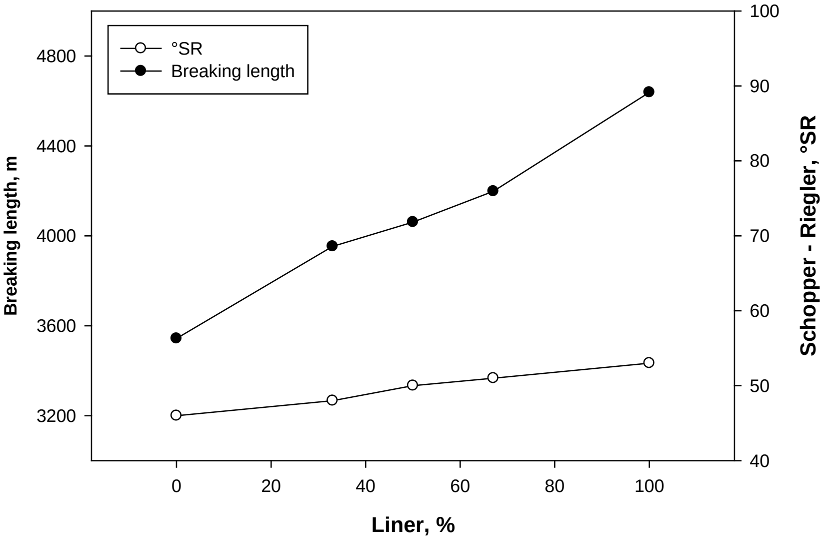

Fig. 3. Evolution of breaking length and °SR as the amount of refined liner (500 rev) was increased.

The graph above (Fig. 3) shows the evolution of breaking length and °SR as the amount of 500 rev – PFI refined liner was increased. The 0 % liner represents 100 % refined organosolv bagasse pulp. As it is possible to see, almost 4200 m could be achieved by using 33 % of organosolv pulp and, consequently, palliating the use of recycled fibers. This value, taking into account the anisotropy ratio (1.35) reported by Delgado-Aguilar et al., (2015c), could represent about 5670 m at machine direction and, in addition, considering the effect of coated starch of about 12 %, this value could be enhanced to 6350 m. In addition, basis weight of laboratory paper sheets was set at 75 g/m^2. Basis weight of testliner is usually set between 120 and 140 g/m^2, fact that, surprisingly, increases the breaking length of paper. Breaking length, in principle, takes into account basis weight. However, Fig. 4 shows how this property evolves as basis weight is increased.

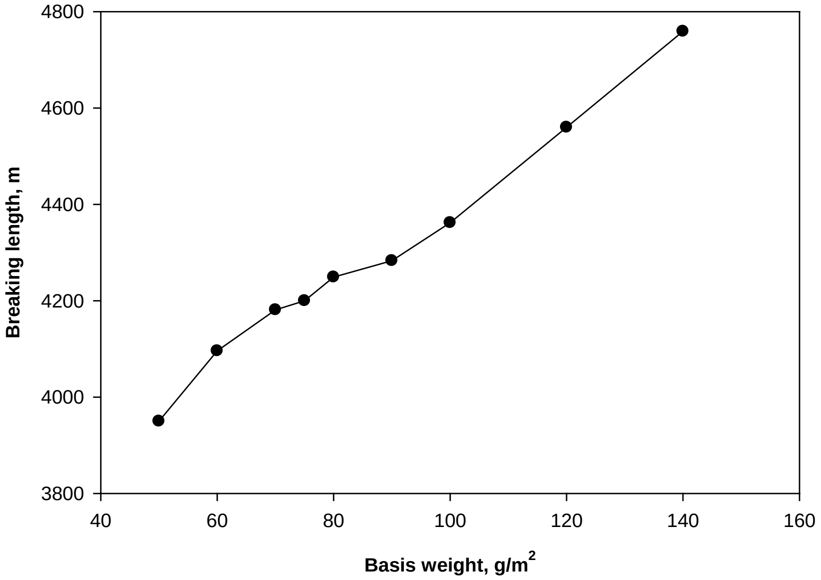

Fig. 4. Effect of basis weight on breaking length

Tensile strength of paper, as reported by Page (1969), depends on many factors, such as relative bonded area, specific bonding strength and intrinsic properties of fibers (Gülsoy et al., 2016). In this sense, as basis weight is increased, higher probability of creating bonds between fibers can lead to stronger papers. Nonetheless, the effect could be considered as statistical.

Other physic-mechanical properties of the hybrids were determined, as reflected in the table below (Table 3).

Table 3. Physic-mechanical properties of hybrid papers

%Liner	Young's Modulus (GPa)	Air permeability (s)	Internal bonding (J/m^2)	Tear Index (mN·m^2/g)	Burst Index (kPa·m^2/g)
0	3.01	46.69	195.81	2.93	1.37
33	3.18	33.92	214.41	4.41	1.56
50	3.29	29.01	227.01	5.02	1.68
67	3.45	21.91	239.91	6.01	1.74
100	3.59	9.79	256.33	7.31	1.95

In all cases, properties followed the same behavior than tensile strength, meaning that they were enhanced as the amount of refined liner was increased. Surprisingly, the behavior of air permeability was totally the contrary of expected. The table above (Table 3) brings to the light the suitability of using refined organosolv bagasse pulp in combination to recycled testliner paper to produce brown-line packaging papers, meaning that air permeability could be significantly improved (in terms of air barrier property) fitting demand and mechanical requirements.

Conclusions

In the present work, the suitability of using sugarcane bagasse residue as raw material for the production of brown-line papers was assessed, as well as the feasibility of producing high-yield pulps for their combination with recycled fibers.

1. Organosolv treatment has been found to be more suitable for producing sugarcane bagasse fibers due to its higher yield, paper properties and suitability to be refined.
2. Through the combination of refined organosolv bagasse and recycled testliner fibers it is possible to obtain papers with high potential to be used in the packaging sector. While the incorporation of such fibers slightly decreased the mechanical properties of paper, air barrier was significantly improved.
3. The use of sugarcane bagasse residue as a raw material in paper production opens a new opportunity to such residues to be used in productive processes, palliating the effect of fiber deterioration and leading to fresh and competitive papers.
4. Overall, the suitability of using alternative raw materials have been demonstrated, obtaining papers with potential use in the packaging sector.

Acknowledgments

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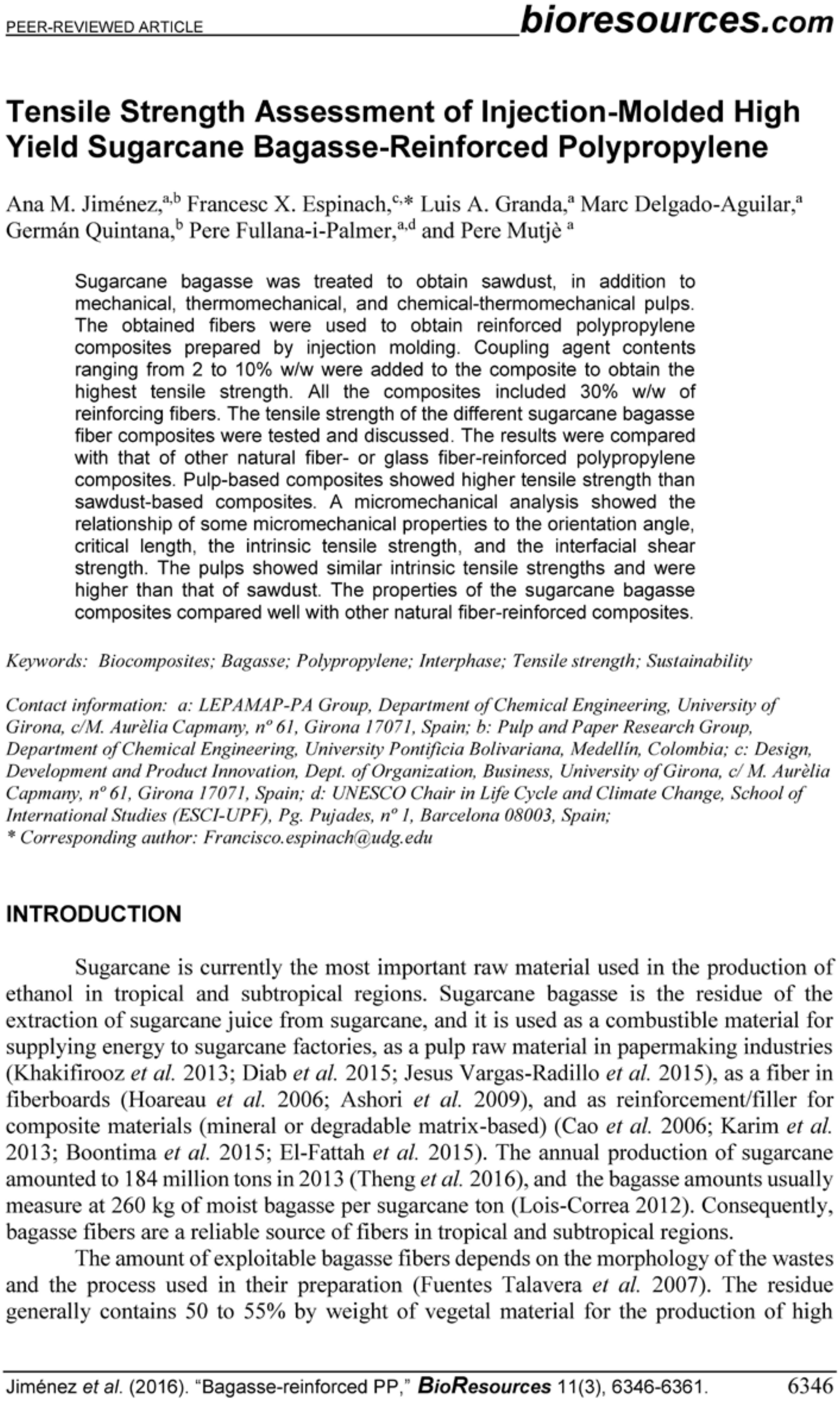
4.2. Tensile Strength Assessment of Injection-Molded High Yield Sugarcane Bagasse-Reinforced Polypropylene



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Tensile Strength Assessment of Injection-Molded High Yield Sugarcane Bagasse-Reinforced Polypropylene

Ana M. Jiménez,[a,b] Francesc X. Espinach,[c,]* Luis A. Granda,[a] Marc Delgado-Aguilar,[a] Germán Quintana,[b] Pere Fullana-i-Palmer,[a,d] and Pere Mutjè [a]

Sugarcane bagasse was treated to obtain sawdust, in addition to mechanical, thermomechanical, and chemical-thermomechanical pulps. The obtained fibers were used to obtain reinforced polypropylene composites prepared by injection molding. Coupling agent contents ranging from 2 to 10% w/w were added to the composite to obtain the highest tensile strength. All the composites included 30% w/w of reinforcing fibers. The tensile strength of the different sugarcane bagasse fiber composites were tested and discussed. The results were compared with that of other natural fiber- or glass fiber-reinforced polypropylene composites. Pulp-based composites showed higher tensile strength than sawdust-based composites. A micromechanical analysis showed the relationship of some micromechanical properties to the orientation angle, critical length, the intrinsic tensile strength, and the interfacial shear strength. The pulps showed similar intrinsic tensile strengths and were higher than that of sawdust. The properties of the sugarcane bagasse composites compared well with other natural fiber-reinforced composites.

Keywords: Biocomposites; Bagasse; Polypropylene; Interphase; Tensile strength; Sustainability

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INTRODUCTION

Sugarcane is currently the most important raw material used in the production of ethanol in tropical and subtropical regions. Sugarcane bagasse is the residue of the extraction of sugarcane juice from sugarcane, and it is used as a combustible material for supplying energy to sugarcane factories, as a pulp raw material in papermaking industries (Khakifirooz *et al.* 2013; Diab *et al.* 2015; Jesus Vargas-Radillo *et al.* 2015), as a fiber in fiberboards (Hoareau *et al.* 2006; Ashori *et al.* 2009), and as reinforcement/filler for composite materials (mineral or degradable matrix-based) (Cao *et al.* 2006; Karim *et al.* 2013; Boontima *et al.* 2015; El-Fattah *et al.* 2015). The annual production of sugarcane amounted to 184 million tons in 2013 (Theng *et al.* 2016), and the bagasse amounts usually measure at 260 kg of moist bagasse per sugarcane ton (Lois-Correa 2012). Consequently, bagasse fibers are a reliable source of fibers in tropical and subtropical regions.

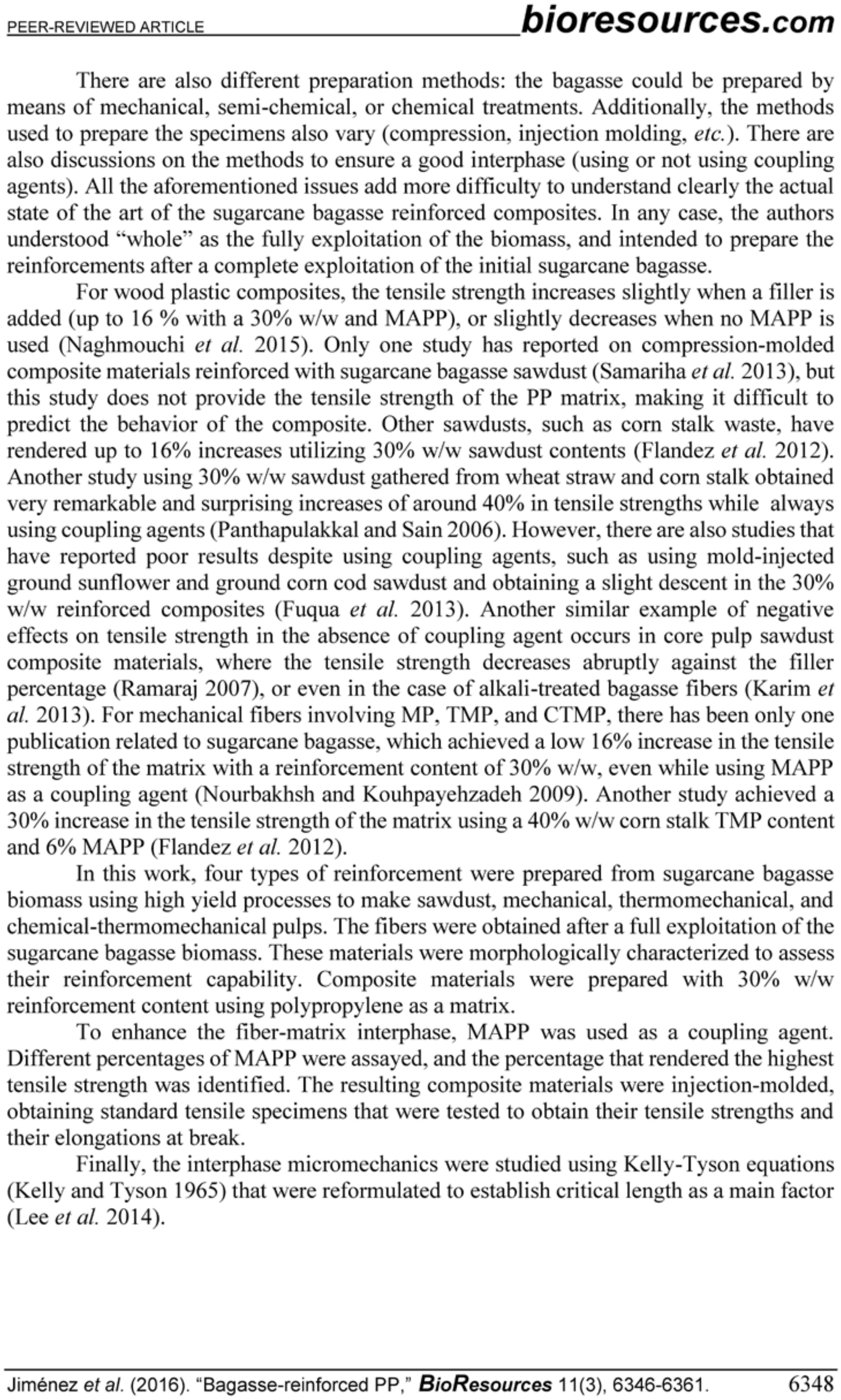
The amount of exploitable bagasse fibers depends on the morphology of the wastes and the process used in their preparation (Fuentes Talavera *et al.* 2007). The residue generally contains 50 to 55% by weight of vegetal material for the production of high

Jiménez *et al.* (2016). "Bagasse-reinforced PP," *BioResources* 11(3), 6346-6361. 6346

quality fibers and 30 to 35% by weight of pith, which results in lower quality fibers; the rest consists of other vegetable components (vessels, skin, *etc.*) and extractives (Lois-Correa 2012; Jesus Vargas-Radillo *et al.* 2015). It is possible to apply high-yield treatments to lignocellulosic materials to obtain sawdust or reinforcing fibers for composites. These treatments mainly include mechanical pulping (MP), thermo-mechanical pulping (TMP), and chemical-thermomechanical pulping (CTMP) (Nourbakhsh and Kouhpayehzadeh 2009; Reixach *et al.* 2013a; Samariha *et al.* 2013). Usually, thermal and chemical treatments involve the extraction of fiber components such as lignin, hemicelluloses, and extractives (Li *et al.* 2001). The yield of the resulting reinforcements varies from almost 100% in the case of sawdust to 85% for CTMP (Reixach *et al.* 2013a). In agreement with the principles of green chemistry, a process that makes use of a by-product and generates less by-product itself is preferable to another process that generates higher amounts of by-products (Anastas and Warner 1998). Consequently, the material with the highest properties will not always be the best because the importance of the relative property must be weighed against the process yield. Recently, the differences in yield did not justify marginal improvements in the tensile strength of CTMP-reinforced composites, such that MP-reinforced composites were favored (Reixach *et al.* 2015). In any case, when the matrix is a polypropylene, the use of MAPP is essential for obtaining a good interphase between the matrix and the reinforcement/filler; this requirement is independent of the nature of the fibers. For sugarcane bagasse, it is possible to make full use of the by-product to obtain reinforcing fibers. From a chemical point of view, both the fiber and pitch fractions have similar chemical compositions of 68 to 69% holocellulose and 21 to 22% lignin (Jesus Vargas-Radillo *et al.* 2015). Consequently, the fibers and the coupling agent should have a similar affinity.

Polypropylene (PP), which is commonly used on an industrial scale because of its relative low cost, good mechanical properties, easy processing, and availability (Bhattacharya *et al.* 2008; Harun *et al.* 2008), is also used in fiber-reinforced composites. One disadvantage of polypropylene natural fiber-reinforced composites is that the fibers are usually hydrophilic and the matrix hydrophobic, which can create difficulties in forming the composite interphase. Coupling agents such as maleic anhydride (MAPP) are employed during processing to obtain a good interphase between the fibers and the matrix (Rodriguez *et al.* 2010; Girones *et al.* 2011; Serrano *et al.* 2013). MAPP reacts with the cellulose hydroxyl groups; the resulting chemical bond and entanglement of the PP chains allows for a suitable dispersion of the reinforcing fiber in the matrix (Kazayawoko *et al.* 1999). Good compatibility at the interphase leads to better stress transfer between the two components, which then improves the mechanical and physical properties of the composites (Youssef *et al.* 2008).

Natural fibers are used as thermoplastic matrix reinforcements in a wide range of fields due to their economic benefits and renewability (Vallejos *et al.* 2006; Arrakhiz *et al.* 2013). The main advantages of natural fibers over traditional reinforcing materials are their good specific strength properties, low cost, low density, good thermal properties, enhanced energy recovery, and biodegradability when compared with mineral fibers such as carbon or glass. In contrast with other industrial crops such as jute, sisal, hemp, or bamboo (among others), bagasse fibers have been poorly studied as a source of naturally reinforcing fibers for plastic composites (Lashgari *et al.* 2011). Furthermore, analysis of the scarce bibliography (only the last 10 years) is also difficult due to the nature of the sugarcane bagasse fibers used to prepare the composites. There are some terminology issues, as there are mentions of whole or depicted sugarcane bagasse.



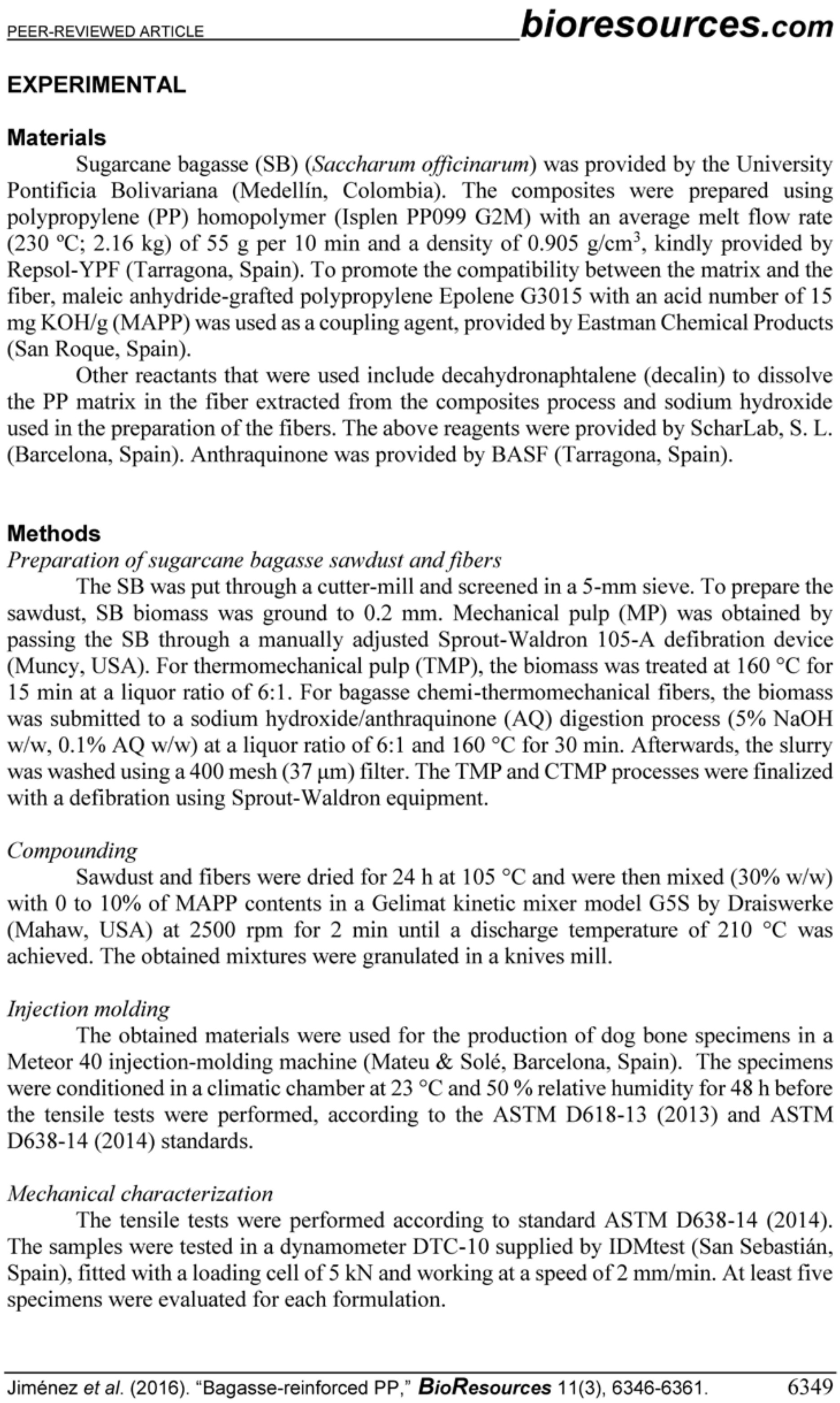
There are also different preparation methods: the bagasse could be prepared by means of mechanical, semi-chemical, or chemical treatments. Additionally, the methods used to prepare the specimens also vary (compression, injection molding, *etc.*). There are also discussions on the methods to ensure a good interphase (using or not using coupling agents). All the aforementioned issues add more difficulty to understand clearly the actual state of the art of the sugarcane bagasse reinforced composites. In any case, the authors understood "whole" as the fully exploitation of the biomass, and intended to prepare the reinforcements after a complete exploitation of the initial sugarcane bagasse.

For wood plastic composites, the tensile strength increases slightly when a filler is added (up to 16 % with a 30% w/w and MAPP), or slightly decreases when no MAPP is used (Naghmouchi *et al.* 2015). Only one study has reported on compression-molded composite materials reinforced with sugarcane bagasse sawdust (Samariha *et al.* 2013), but this study does not provide the tensile strength of the PP matrix, making it difficult to predict the behavior of the composite. Other sawdusts, such as corn stalk waste, have rendered up to 16% increases utilizing 30% w/w sawdust contents (Flandez *et al.* 2012). Another study using 30% w/w sawdust gathered from wheat straw and corn stalk obtained very remarkable and surprising increases of around 40% in tensile strengths while always using coupling agents (Panthapulakkal and Sain 2006). However, there are also studies that have reported poor results despite using coupling agents, such as using mold-injected ground sunflower and ground corn cod sawdust and obtaining a slight descent in the 30% w/w reinforced composites (Fuqua *et al.* 2013). Another similar example of negative effects on tensile strength in the absence of coupling agent occurs in core pulp sawdust composite materials, where the tensile strength decreases abruptly against the filler percentage (Ramaraj 2007), or even in the case of alkali-treated bagasse fibers (Karim *et al.* 2013). For mechanical fibers involving MP, TMP, and CTMP, there has been only one publication related to sugarcane bagasse, which achieved a low 16% increase in the tensile strength of the matrix with a reinforcement content of 30% w/w, even while using MAPP as a coupling agent (Nourbakhsh and Kouhpayehzadeh 2009). Another study achieved a 30% increase in the tensile strength of the matrix using a 40% w/w corn stalk TMP content and 6% MAPP (Flandez *et al.* 2012).

In this work, four types of reinforcement were prepared from sugarcane bagasse biomass using high yield processes to make sawdust, mechanical, thermomechanical, and chemical-thermomechanical pulps. The fibers were obtained after a full exploitation of the sugarcane bagasse biomass. These materials were morphologically characterized to assess their reinforcement capability. Composite materials were prepared with 30% w/w reinforcement content using polypropylene as a matrix.

To enhance the fiber-matrix interphase, MAPP was used as a coupling agent. Different percentages of MAPP were assayed, and the percentage that rendered the highest tensile strength was identified. The resulting composite materials were injection-molded, obtaining standard tensile specimens that were tested to obtain their tensile strengths and their elongations at break.

Finally, the interphase micromechanics were studied using Kelly-Tyson equations (Kelly and Tyson 1965) that were reformulated to establish critical length as a main factor (Lee *et al.* 2014).



EXPERIMENTAL

Materials

Sugarcane bagasse (SB) (*Saccharum officinarum*) was provided by the University Pontificia Bolivariana (Medellín, Colombia). The composites were prepared using polypropylene (PP) homopolymer (Isplen PP099 G2M) with an average melt flow rate (230 ºC; 2.16 kg) of 55 g per 10 min and a density of 0.905 g/cm^3, kindly provided by Repsol-YPF (Tarragona, Spain). To promote the compatibility between the matrix and the fiber, maleic anhydride-grafted polypropylene Epolene G3015 with an acid number of 15 mg KOH/g (MAPP) was used as a coupling agent, provided by Eastman Chemical Products (San Roque, Spain).

Other reactants that were used include decahydronaphtalene (decalin) to dissolve the PP matrix in the fiber extracted from the composites process and sodium hydroxide used in the preparation of the fibers. The above reagents were provided by ScharLab, S. L. (Barcelona, Spain). Anthraquinone was provided by BASF (Tarragona, Spain).

Methods

Preparation of sugarcane bagasse sawdust and fibers

The SB was put through a cutter-mill and screened in a 5-mm sieve. To prepare the sawdust, SB biomass was ground to 0.2 mm. Mechanical pulp (MP) was obtained by passing the SB through a manually adjusted Sprout-Waldron 105-A defibration device (Muncy, USA). For thermomechanical pulp (TMP), the biomass was treated at 160 °C for 15 min at a liquor ratio of 6:1. For bagasse chemi-thermomechanical fibers, the biomass was submitted to a sodium hydroxide/anthraquinone (AQ) digestion process (5% NaOH w/w, 0.1% AQ w/w) at a liquor ratio of 6:1 and 160 °C for 30 min. Afterwards, the slurry was washed using a 400 mesh (37 µm) filter. The TMP and CTMP processes were finalized with a defibration using Sprout-Waldron equipment.

Compounding

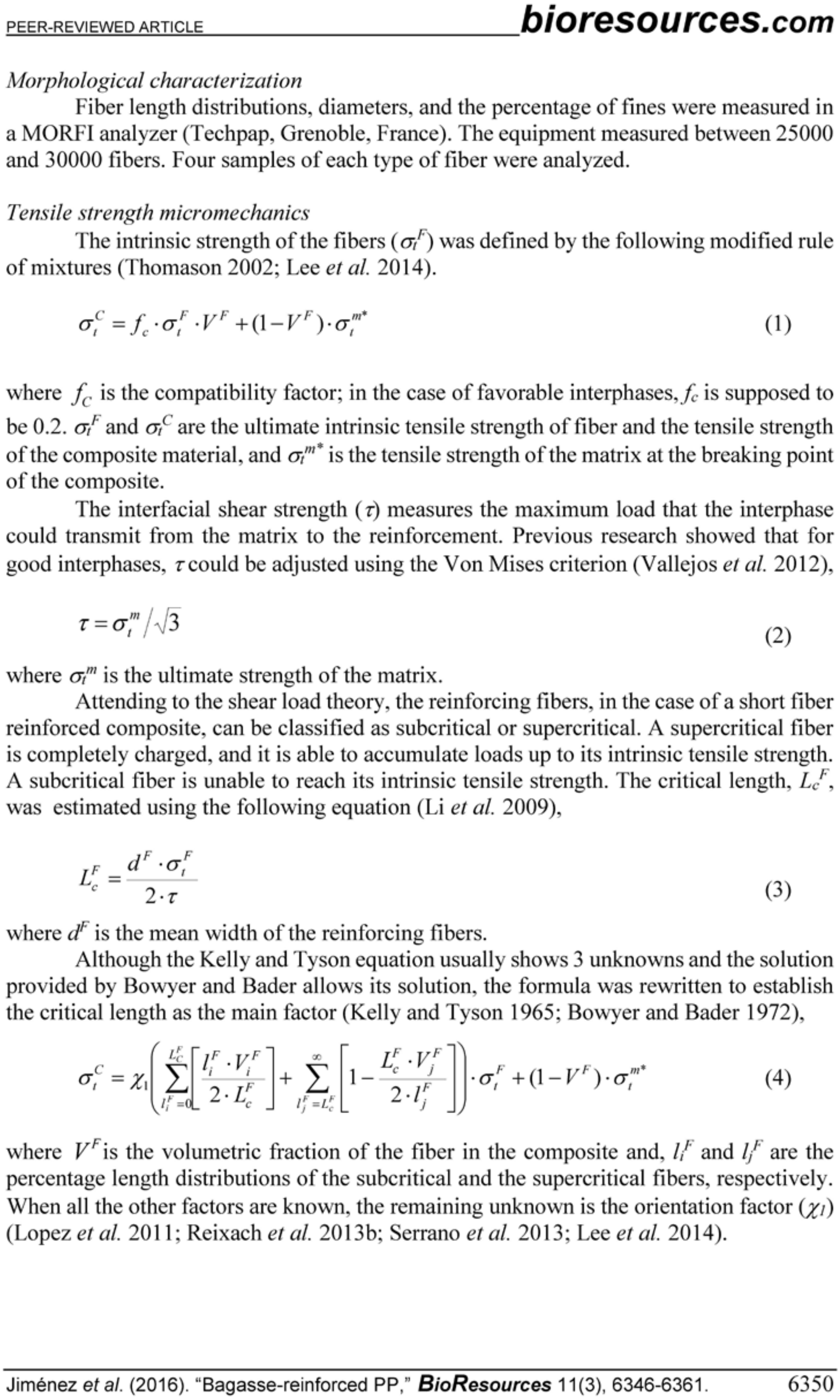
Sawdust and fibers were dried for 24 h at 105 °C and were then mixed (30% w/w) with 0 to 10% of MAPP contents in a Gelimat kinetic mixer model G5S by Draiswerke (Mahaw, USA) at 2500 rpm for 2 min until a discharge temperature of 210 °C was achieved. The obtained mixtures were granulated in a knives mill.

Injection molding

The obtained materials were used for the production of dog bone specimens in a Meteor 40 injection-molding machine (Mateu & Solé, Barcelona, Spain). The specimens were conditioned in a climatic chamber at 23 °C and 50 % relative humidity for 48 h before the tensile tests were performed, according to the ASTM D618-13 (2013) and ASTM D638-14 (2014) standards.

Mechanical characterization

The tensile tests were performed according to standard ASTM D638-14 (2014). The samples were tested in a dynamometer DTC-10 supplied by IDMtest (San Sebastián, Spain), fitted with a loading cell of 5 kN and working at a speed of 2 mm/min. At least five specimens were evaluated for each formulation.



Morphological characterization

Fiber length distributions, diameters, and the percentage of fines were measured in a MORFI analyzer (Techpap, Grenoble, France). The equipment measured between 25000 and 30000 fibers. Four samples of each type of fiber were analyzed.

Tensile strength micromechanics

The intrinsic strength of the fibers (σ_t^F) was defined by the following modified rule of mixtures (Thomason 2002; Lee *et al.* 2014).

$$\sigma_t^C = f_c \cdot \sigma_t^F \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \tag{1}$$

where f_C is the compatibility factor; in the case of favorable interphases, f_c is supposed to be 0.2. σ_t^F and σ_t^C are the ultimate intrinsic tensile strength of fiber and the tensile strength of the composite material, and σ_t^{m*} is the tensile strength of the matrix at the breaking point of the composite.

The interfacial shear strength (τ) measures the maximum load that the interphase could transmit from the matrix to the reinforcement. Previous research showed that for good interphases, τ could be adjusted using the Von Mises criterion (Vallejos *et al.* 2012),

$$\tau = \sigma_t^m / \sqrt{3} \tag{2}$$

where σ_t^m is the ultimate strength of the matrix.

Attending to the shear load theory, the reinforcing fibers, in the case of a short fiber reinforced composite, can be classified as subcritical or supercritical. A supercritical fiber is completely charged, and it is able to accumulate loads up to its intrinsic tensile strength. A subcritical fiber is unable to reach its intrinsic tensile strength. The critical length, L_c^F, was estimated using the following equation (Li *et al.* 2009),

$$L_c^F = \frac{d^F \cdot \sigma_t^F}{2 \cdot \tau} \tag{3}$$

where d^F is the mean width of the reinforcing fibers.

Although the Kelly and Tyson equation usually shows 3 unknowns and the solution provided by Bowyer and Bader allows its solution, the formula was rewritten to establish the critical length as the main factor (Kelly and Tyson 1965; Bowyer and Bader 1972),

$$\sigma_t^C = \chi_1 \left(\sum_{l_i^F=0}^{L_C^F} \left[\frac{l_i^F \cdot V_i^F}{2 \cdot L_c^F} \right] + \sum_{l_j^F = L_c^F}^{\infty} \left[1 - \frac{L_c^F \cdot V_j^F}{2 \cdot l_j^F} \right] \right) \cdot \sigma_t^F + (1 - V^F) \cdot \sigma_t^{m*} \tag{4}$$

where V^F is the volumetric fraction of the fiber in the composite and, l_i^F and l_j^F are the percentage length distributions of the subcritical and the supercritical fibers, respectively. When all the other factors are known, the remaining unknown is the orientation factor (χ_1) (Lopez *et al.* 2011; Reixach *et al.* 2013b; Serrano *et al.* 2013; Lee *et al.* 2014).

RESULTS AND DISCUSSION

Sugarcane Bagasse Morphological Characterization

Sugarcane bagasse was submitted to different treatments. Table 1 shows the yield of each process against the initial amount of biomass and the morphological characterization of each type of filler/reinforcing material.

Table 1. Morphological Characterization of the Obtained Fibers

Test	Sawdust	MP	TMP	CTMP
Yield (%)	99.2	97.11	87.63	85.07
Fiber length* (μm)	261	521	602	685
Fiber diameter (μm)	27.73	24.02	26.57	25.45
Fines content** (%)	87.94	59.01	38.32	34.25
Aspect ratio	9.4	21.7	22.6	26.9

*: weighted

**: percentage in length

Table 1 also shows that the yield against the biomass was lowered according to the aggressiveness of the treatment applied to the fiber. For sawdust the yield was 99.2%, whereas for the CTMP it was 14 points lower. Processes that add thermal or chemical treatments modify the chemical composition of the fiber surface. For SB fibers, it is probable that surface hydroxyl group density increased due to the progressive elimination of a small fraction of lignin and extractives. Reixach *et al.* (2013b, 2015) obtained yields of 99.1% for MP, 94.7% for TMP, and 90.1% for CTMP for orange tree pruning. These values are comparable to those achieved with SB. The CTMP treatment increased the average length of the fibers. This result may have been caused by the initial use of chemical treatments that separated individualized fibers without mechanical loads. The lower mean length that occurred in the MP fibers may have been due to the fact that the individualization is based only on mechanical energy, which could have damaged and broken the fibers.

The mean length of the fibers increased with the intensity of the treatments, as thermal treatment eliminates or softens some lignin and extractives, promoting individualization during the mechanical treatment (Flandez *et al.* 2012). The fiber diameter changed little between MP, TMP, and CTMP, but was slightly bigger in sawdust. The values could be considered the same at around 26 μm (95% confidence).

Table 1 also shows that fines decreased with the aggressiveness of treatment, due to the softening of the raw material that resulted in an easier separation of the fiber bundles. The aspect ratio (ratio between fiber length and diameter) also increased with the intensity of the treatments. Fibers with aspect ratios higher than 10 tend to act as reinforcements (if a good interphase is achieved), while phases with lesser aspect ratios tend to act as fillers. The obtained aspect ratios are in line with previous studies (Flandez *et al.* 2012; Vallejos *et al.* 2012).

Effect of the coupling agent on tensile strength

As mentioned previously, the matrix and fibers have hydrophobic and hydrophilic natures, respectively. Consequently, it is difficult to properly wet fibers with a matrix and create the bonds necessary to ensure a good interphase. The addition of small amounts of MAPP improves the quality of the interphase. The maleic anhydride in MAPP creates hydrogen bonds with the hydroxyl groups of the cellulose on the fiber surface. However, the polypropylene portion of the MAPP diffuses in the polymeric matrix. Figure 1 shows the behavior of the tensile strength *versus* the MAPP content. As predicted, a fast increase in the tensile strength was observed when 2 to 4% MAPP was added to the composites. For the 6% MAPP sample, the tensile strength showed a local maximum. Further additions of MAPP slightly decreased the tensile strength of the composites. Higher percentages of MAPP result in self-entanglements, which decrease the composite strength (Bledzki and Gassan 1999; Franco-Marques *et al.* 2011). Consequently, 6% MAPP achieved the best interphase, and, thus, the highest tensile strength.

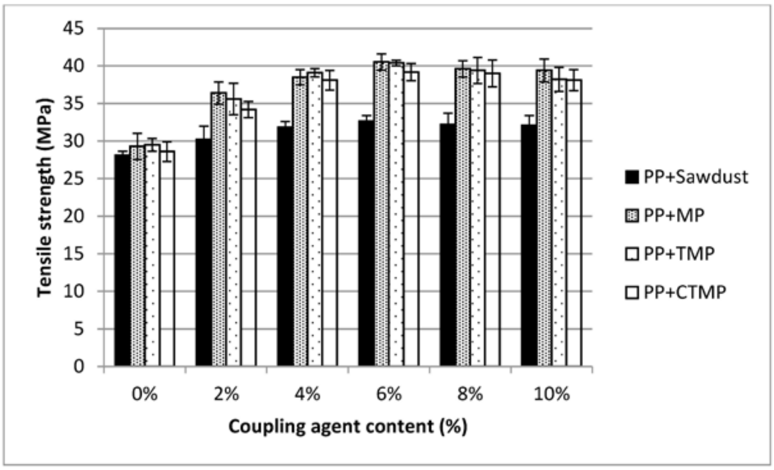
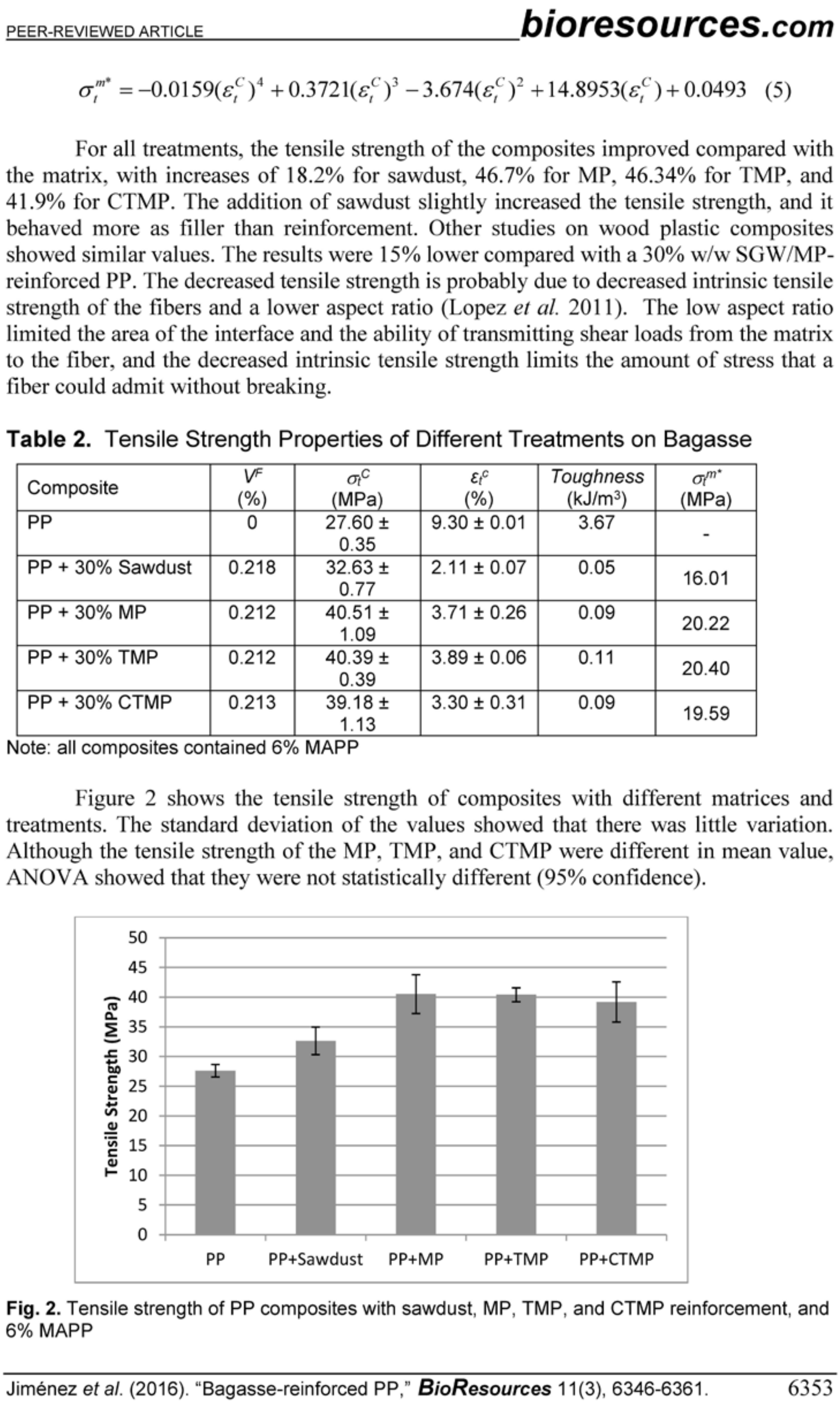


Fig. 1. Composite tensile strength *versus* MAPP content

Other studies showed that similar percentages of MAPP achieved the highest tensile strengths. In studies of stone groundwood (SGW) and orange tree pruning, 6% MAPP was the optimum dosage, with the exception of CTMP, which only required 4% MAPP (Lopez *et al.* 2012a; Reixach *et al.* 2013b). In untreated kenaf strands, the optimum dosage was 2% MAPP (Sanadi *et al.* 1995). Generally, NaOH treatment (CTMP) enhances the interaction with MAPP, allowing for better tensile strength (Lopez *et al.* 2012a). As previously mentioned, due to the treatment intensity and the expected higher presence of cellulose and hydroxyl groups on the fiber surface, CTMP was expected to produce higher tensile strengths than MP. Because the tensile strengths were almost equal for MP, TMP, and CTMP, all treatments produced fibers with similar affinity for MAPP and possibly similar surface chemical compositions.

Tensile strength properties

Table 2 shows the tensile strength (σ_t^C), maximum elongation at breaking point (ε_t^C), and toughness of the prepared composites. As a consequence of the previous section, 6% MAPP was added to all composites. Table 2 also shows the contribution of the matrix to the final strength of the composite, as represented by the mean value of the stress in the strain stress curve at the strain at break. To compute the value of σ_t^{m*}, the experimental stress strain curve of the matrix was approximated to a 4th order polynomial:



$$\sigma_t^{m*} = -0.0159(\varepsilon_t^C)^4 + 0.3721(\varepsilon_t^C)^3 - 3.674(\varepsilon_t^C)^2 + 14.8953(\varepsilon_t^C) + 0.0493 \quad (5)$$

For all treatments, the tensile strength of the composites improved compared with the matrix, with increases of 18.2% for sawdust, 46.7% for MP, 46.34% for TMP, and 41.9% for CTMP. The addition of sawdust slightly increased the tensile strength, and it behaved more as filler than reinforcement. Other studies on wood plastic composites showed similar values. The results were 15% lower compared with a 30% w/w SGW/MP-reinforced PP. The decreased tensile strength is probably due to decreased intrinsic tensile strength of the fibers and a lower aspect ratio (Lopez *et al.* 2011). The low aspect ratio limited the area of the interface and the ability of transmitting shear loads from the matrix to the fiber, and the decreased intrinsic tensile strength limits the amount of stress that a fiber could admit without breaking.

Table 2. Tensile Strength Properties of Different Treatments on Bagasse

Composite	V^F (%)	σ_t^C (MPa)	ε_t^C (%)	*Toughness* (kJ/m^3)	σ_t^{m*} (MPa)
PP	0	27.60 ± 0.35	9.30 ± 0.01	3.67	-
PP + 30% Sawdust	0.218	32.63 ± 0.77	2.11 ± 0.07	0.05	16.01
PP + 30% MP	0.212	40.51 ± 1.09	3.71 ± 0.26	0.09	20.22
PP + 30% TMP	0.212	40.39 ± 0.39	3.89 ± 0.06	0.11	20.40
PP + 30% CTMP	0.213	39.18 ± 1.13	3.30 ± 0.31	0.09	19.59

Note: all composites contained 6% MAPP

Figure 2 shows the tensile strength of composites with different matrices and treatments. The standard deviation of the values showed that there was little variation. Although the tensile strength of the MP, TMP, and CTMP were different in mean value, ANOVA showed that they were not statistically different (95% confidence).

Fig. 2. Tensile strength of PP composites with sawdust, MP, TMP, and CTMP reinforcement, and 6% MAPP

The elongation at the break decreased with the addition of the reinforcement, obtaining increasingly rigid and fragile materials. This behavior is similar to that observed in other natural fiber-reinforced composites. Compared with SGW-reinforced composites, the elongation at the break was 4.2% and was 4% for MP orange pruning fibers, where in all cases 30% reinforcement and 6% MAPP were added to the composite (Lopez *et al.* 2011; Reixach *et al.* 2015). Toughness is associated with the stress and strain at break as well as the shape of the stress-strain curve. The obtained values were very similar for MP, TMP, and CTMP, which were higher than the sawdust, showing their greater ability to absorb mechanical energy. The percentage of the matrix contribution is in line with similar studies (Reixach *et al.* 2013a; Serrano *et al.* 2013).

Fiber tensile strength factor

In previous works, some of the authors defined a fiber tensile strength factor (*FTSF*) that accounts for the net contribution of the reinforcements to the final strength of the composite. The modified rule of mixtures for the tensile strength (Eq. 1) presents two unknowns, the intrinsic tensile strength and the coupling factor. When both factors are united and renamed *FTSF*, the equation can be solved. The resulting *FTSF* accounted for the slope of the regression curve between 0 and the net contributions of the fibers to the final strength of the composite against the fiber volume fraction (Lopez *et al.* 2012a; Reixach *et al.* 2013a). The rearranged version of the rule of mixtures is:

$$\sigma_t^C - (1-V^F)\sigma_t^{m*} = f_c \cdot \sigma_t^F V^F = FTSF \cdot V^F \qquad (6)$$

The computed *FTSF* for the sawdust, MP, TMP, and CTMP was 92.24, 115.91, 114.67, and 111.55, respectively. It is clear that the MP fibers had a higher strengthening potential. Nonetheless, the TMP and CTMP showed similar results. The sawdust showed 25% less strengthening potential. This value is similar to that of SGW, with a 109.4 *FTSF* (Lopez *et al.* 2011). Nonetheless, the sugarcane bagasse fibers showed a slightly higher strengthening potential than the fibers from orange tree pruning, with *FTST* from 90.3 to 97.2 (Reixach *et al.* 2015).

Because the *FTSF* calculation does not require morphological data, it is an industry-friendly method that can differentiate the potential of various fibers without expensive or time consuming methods or machinery. For a more thorough analysis, a morphological study of the fibers inside the composite is needed.

Morphological characterization

During mixing and injection, the reinforcing fibers are submitted to attrition phenomena that reduce the mean length of the fibers. Therefore, a sample of the reinforcing fibers was obtained from inside one of the composites to determine the fiber length distribution (Fig. 3). The values of the average twice-weighted lengths within the composite were 200, 418, 480, and 514 μm for sawdust, MP, TMP, and CTMP, respectively. The sawdust displayed lesser length decreases than the rest of the fibers. TMP and CTMP showed notable decreases in their mean length, resulting in similar weighted values around 500 μm. The shape of the length distribution (Fig. 3) varied from one type to the other. Usually the length distribution inside the composite is independent of the distribution outside the composite, but in the case of SB, a slight similarity between both length distributions was found, and there was a linear correlation between the mean lengths inside and outside the composite.

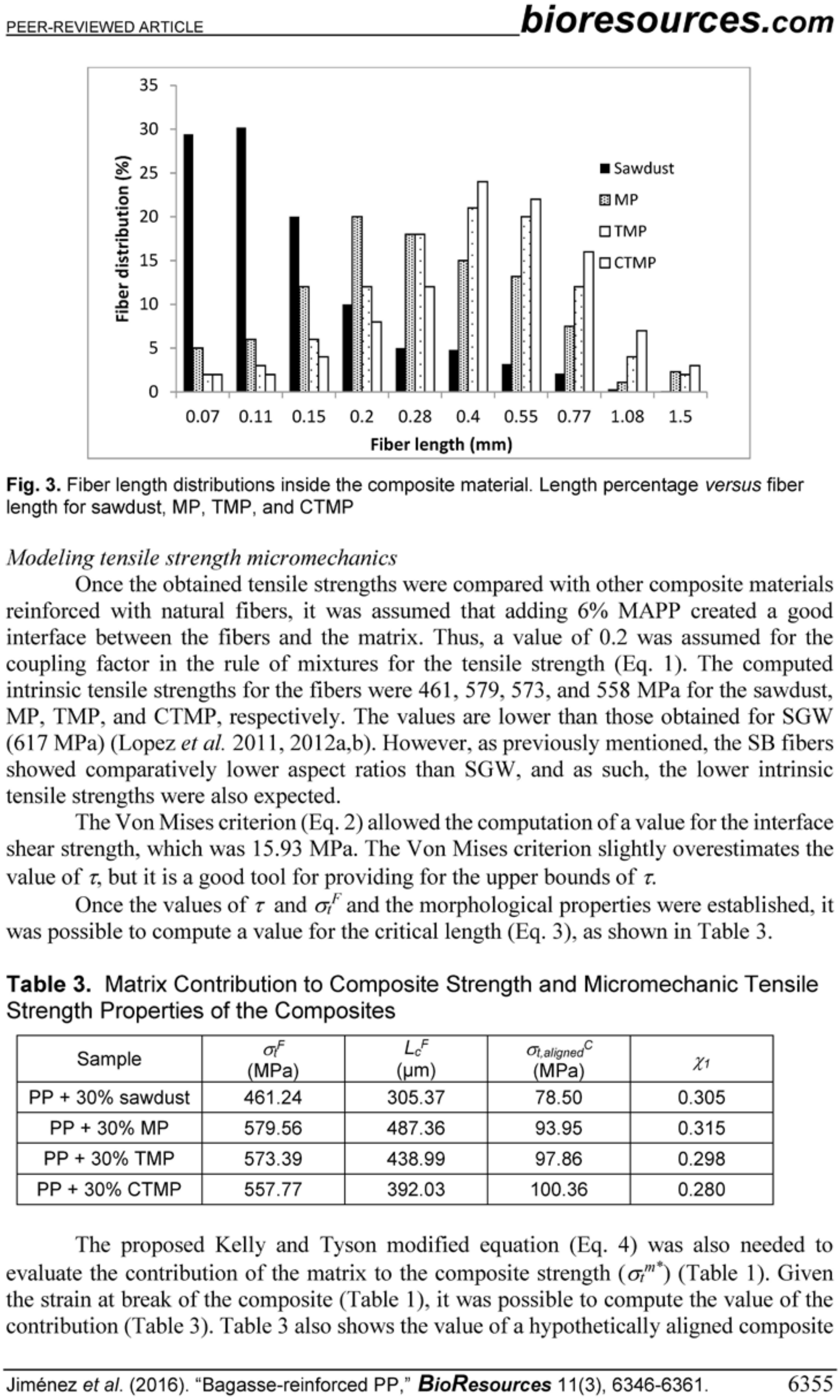


Fig. 3. Fiber length distributions inside the composite material. Length percentage *versus* fiber length for sawdust, MP, TMP, and CTMP

Modeling tensile strength micromechanics

Once the obtained tensile strengths were compared with other composite materials reinforced with natural fibers, it was assumed that adding 6% MAPP created a good interface between the fibers and the matrix. Thus, a value of 0.2 was assumed for the coupling factor in the rule of mixtures for the tensile strength (Eq. 1). The computed intrinsic tensile strengths for the fibers were 461, 579, 573, and 558 MPa for the sawdust, MP, TMP, and CTMP, respectively. The values are lower than those obtained for SGW (617 MPa) (Lopez *et al.* 2011, 2012a,b). However, as previously mentioned, the SB fibers showed comparatively lower aspect ratios than SGW, and as such, the lower intrinsic tensile strengths were also expected.

The Von Mises criterion (Eq. 2) allowed the computation of a value for the interface shear strength, which was 15.93 MPa. The Von Mises criterion slightly overestimates the value of τ, but it is a good tool for providing for the upper bounds of τ.

Once the values of τ and σ_t^F and the morphological properties were established, it was possible to compute a value for the critical length (Eq. 3), as shown in Table 3.

Table 3. Matrix Contribution to Composite Strength and Micromechanic Tensile Strength Properties of the Composites

Sample	σ_t^F (MPa)	L_c^F (µm)	$\sigma_{t,aligned}^C$ (MPa)	χ_1
PP + 30% sawdust	461.24	305.37	78.50	0.305
PP + 30% MP	579.56	487.36	93.95	0.315
PP + 30% TMP	573.39	438.99	97.86	0.298
PP + 30% CTMP	557.77	392.03	100.36	0.280

The proposed Kelly and Tyson modified equation (Eq. 4) was also needed to evaluate the contribution of the matrix to the composite strength (σ_t^{m*}) (Table 1). Given the strain at break of the composite (Table 1), it was possible to compute the value of the contribution (Table 3). Table 3 also shows the value of a hypothetically aligned composite

(χ_1=1) ($\sigma_{t,\ aligned}{}^{C}$). Given these input values and considering the restructured Kelly-Tyson model, the orientation factor (χ_1) became the only unknown. Table 3 shows the computed values.

The values of the orientation factor (χ_1) were close to 0.3 for sawdust, MP, TMP, and CTMP. The value of the orientation factor was highly related to the equipment used to prepare the specimens. In past reports, the values were between 0.25 and 0.35. Consequently, the obtained value validates assumptions to evaluate the intrinsic tensile strength and the interfacial shear strength.

Kelly and Tyson's modified equation (Eq. 4) divides the contributions to the final composite strength into three main factors: subcritical fibers (*X*), supercritical fibers (*Y*), and matrix (*Z*). Equation 4 can be rewritten as: $\sigma_t{}^C = X + Y + Z$, where

$$X = \chi_1 \left(\sum_{l_i^F = 0}^{L_C^F} \left[\frac{l_i^F \cdot V_i^F}{2 \cdot L_c^F} \right] \right) \cdot \sigma_t^F \tag{7}$$

$$Y == \chi_1 \left(\sum_{l_j^F = L_c^F}^{\infty} \left[1 - \frac{L_c^F \cdot V_j^F}{2 \cdot l_j^F} \right] \right) \cdot \sigma_t^F \tag{8}$$

$$Z = (1 - V^F) \cdot \sigma_t^{m*} \tag{9}$$

Figure 4 shows the percentage contributions for *X, Y*, and *Z*. The higher contributions were derived from the supercritical fibers and the matrix, while the subcritical fiber contributions were minor, remaining around 10% in all cases. The highest percentage contributions belonged to the supercritical fibers.

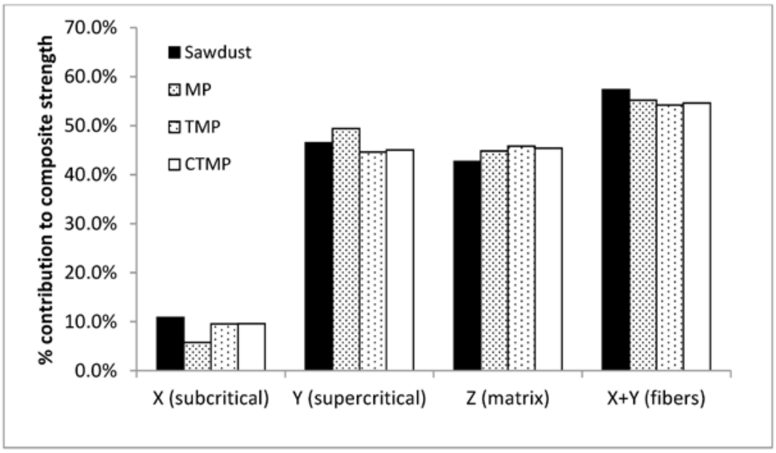


Fig. 4. X, Y, and Z percentage contributions to composite strength

If the combined contributions of the subcritical and supercritical are added together, then the fibers contributed to around 60% of the total strength. This value is similar to the 52% obtained for a 30% hemp-reinforced PP (Vallejos *et al.* 2012). For higher fiber amounts, the fiber contribution (*X*+*Y*) could grow up to around 75% (Vallejos *et al.* 2012).

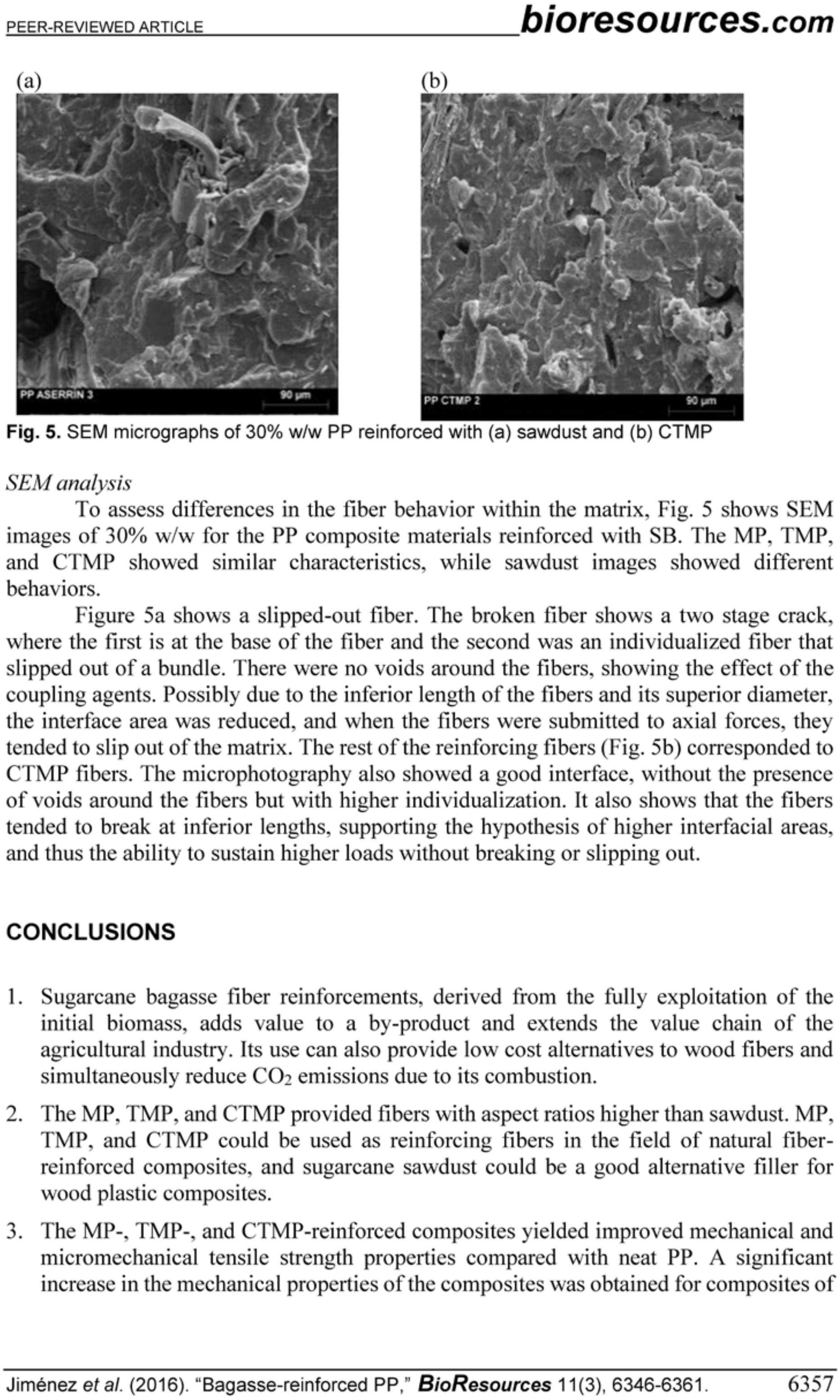


Fig. 5. SEM micrographs of 30% w/w PP reinforced with (a) sawdust and (b) CTMP

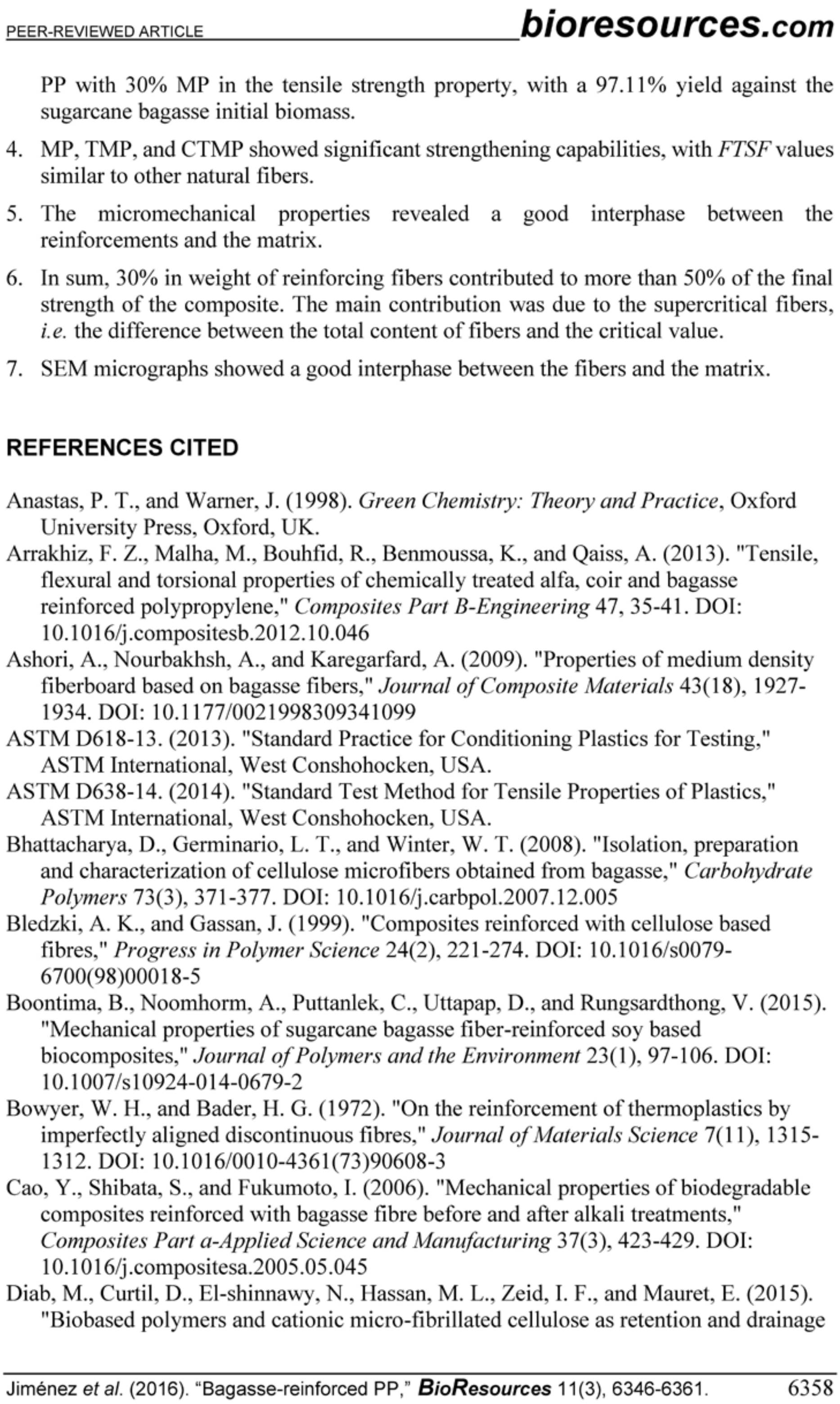
SEM analysis

To assess differences in the fiber behavior within the matrix, Fig. 5 shows SEM images of 30% w/w for the PP composite materials reinforced with SB. The MP, TMP, and CTMP showed similar characteristics, while sawdust images showed different behaviors.

Figure 5a shows a slipped-out fiber. The broken fiber shows a two stage crack, where the first is at the base of the fiber and the second was an individualized fiber that slipped out of a bundle. There were no voids around the fibers, showing the effect of the coupling agents. Possibly due to the inferior length of the fibers and its superior diameter, the interface area was reduced, and when the fibers were submitted to axial forces, they tended to slip out of the matrix. The rest of the reinforcing fibers (Fig. 5b) corresponded to CTMP fibers. The microphotography also showed a good interface, without the presence of voids around the fibers but with higher individualization. It also shows that the fibers tended to break at inferior lengths, supporting the hypothesis of higher interfacial areas, and thus the ability to sustain higher loads without breaking or slipping out.

CONCLUSIONS

1. Sugarcane bagasse fiber reinforcements, derived from the fully exploitation of the initial biomass, adds value to a by-product and extends the value chain of the agricultural industry. Its use can also provide low cost alternatives to wood fibers and simultaneously reduce CO_2 emissions due to its combustion.
2. The MP, TMP, and CTMP provided fibers with aspect ratios higher than sawdust. MP, TMP, and CTMP could be used as reinforcing fibers in the field of natural fiber-reinforced composites, and sugarcane sawdust could be a good alternative filler for wood plastic composites.
3. The MP-, TMP-, and CTMP-reinforced composites yielded improved mechanical and micromechanical tensile strength properties compared with neat PP. A significant increase in the mechanical properties of the composites was obtained for composites of



PP with 30% MP in the tensile strength property, with a 97.11% yield against the sugarcane bagasse initial biomass.

4. MP, TMP, and CTMP showed significant strengthening capabilities, with *FTSF* values similar to other natural fibers.
5. The micromechanical properties revealed a good interphase between the reinforcements and the matrix.
6. In sum, 30% in weight of reinforcing fibers contributed to more than 50% of the final strength of the composite. The main contribution was due to the supercritical fibers, *i.e.* the difference between the total content of fibers and the critical value.
7. SEM micrographs showed a good interphase between the fibers and the matrix.

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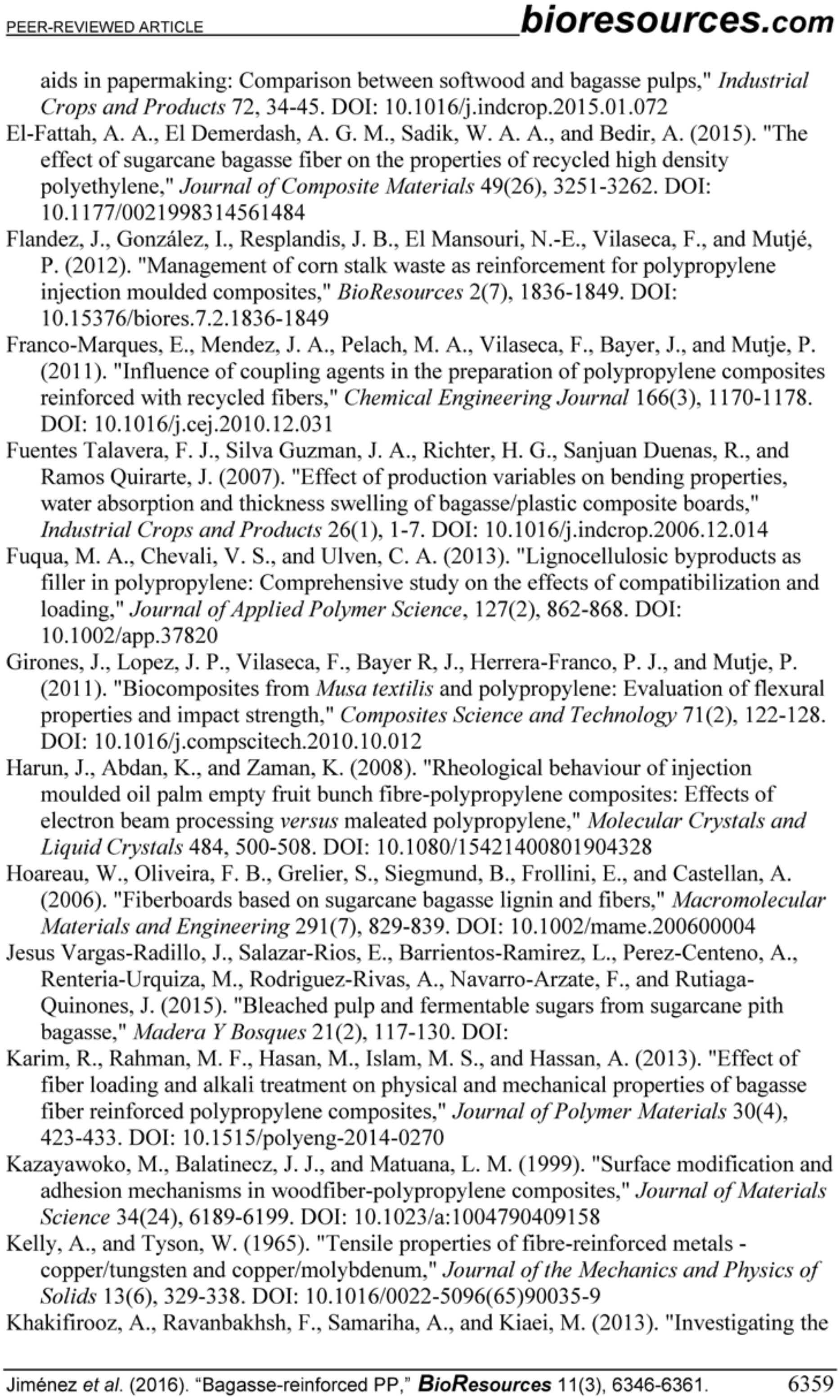

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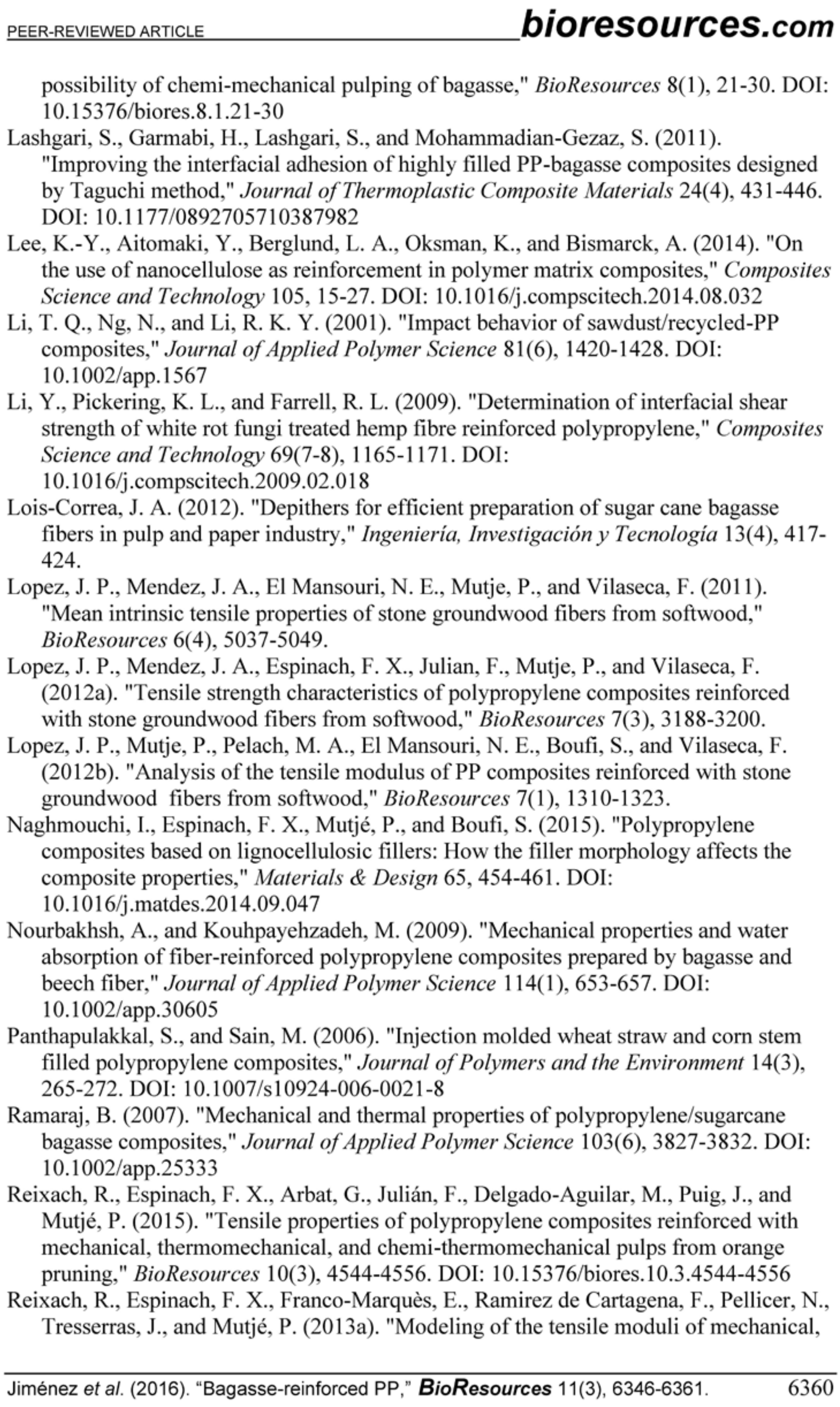

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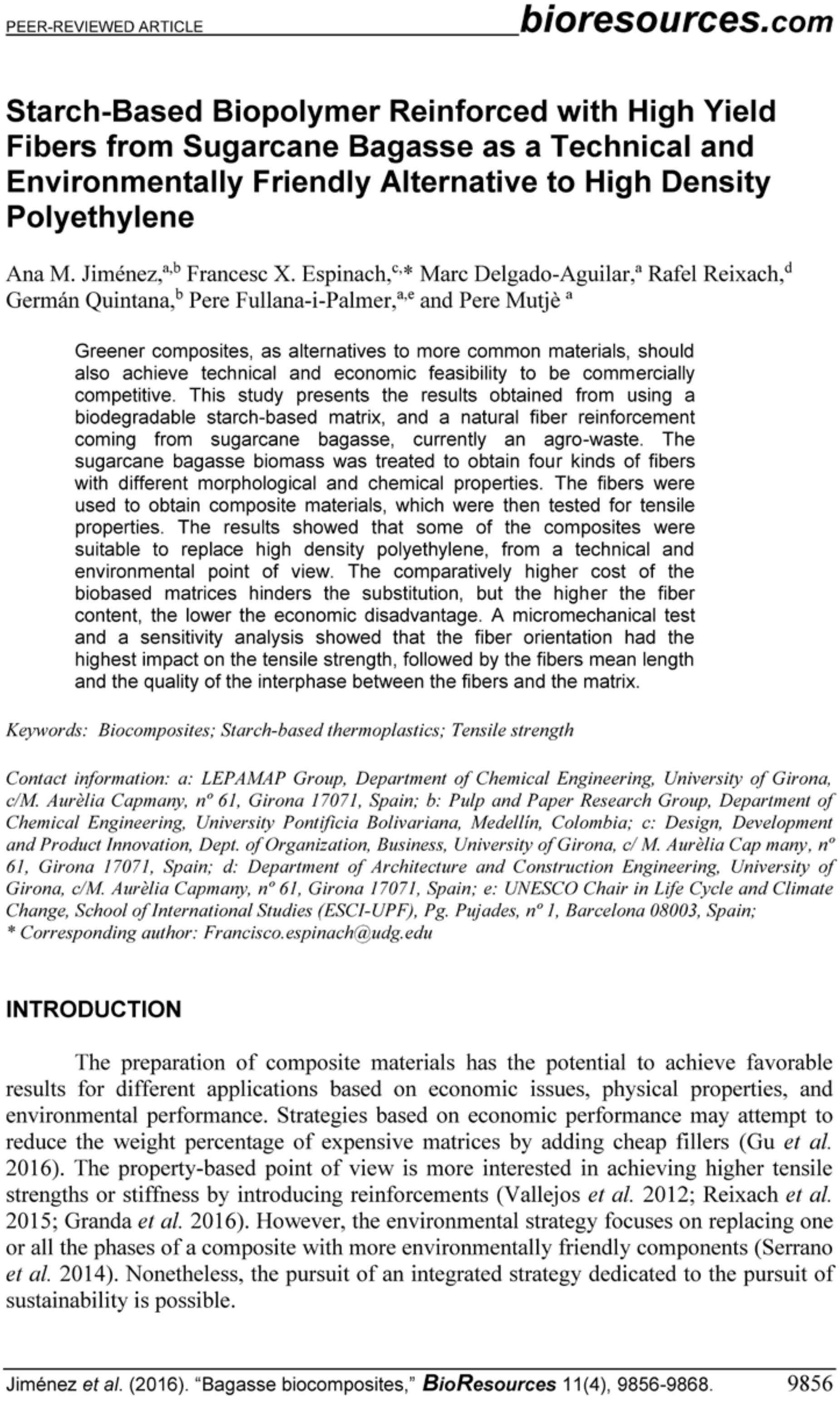
4.3. Starch-Based Biopolymer Reinforced with High Yield Fibers from Sugarcane Bagasse as a Technical and Environmentally Friendly Alternative to High Density Polyethylene



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Starch-Based Biopolymer Reinforced with High Yield Fibers from Sugarcane Bagasse as a Technical and Environmentally Friendly Alternative to High Density Polyethylene

Ana M. Jiménez,[a,b] Francesc X. Espinach,[c,*] Marc Delgado-Aguilar,[a] Rafel Reixach,[d] Germán Quintana,[b] Pere Fullana-i-Palmer,[a,e] and Pere Mutjè [a]

Greener composites, as alternatives to more common materials, should also achieve technical and economic feasibility to be commercially competitive. This study presents the results obtained from using a biodegradable starch-based matrix, and a natural fiber reinforcement coming from sugarcane bagasse, currently an agro-waste. The sugarcane bagasse biomass was treated to obtain four kinds of fibers with different morphological and chemical properties. The fibers were used to obtain composite materials, which were then tested for tensile properties. The results showed that some of the composites were suitable to replace high density polyethylene, from a technical and environmental point of view. The comparatively higher cost of the biobased matrices hinders the substitution, but the higher the fiber content, the lower the economic disadvantage. A micromechanical test and a sensitivity analysis showed that the fiber orientation had the highest impact on the tensile strength, followed by the fibers mean length and the quality of the interphase between the fibers and the matrix.

Keywords: Biocomposites; Starch-based thermoplastics; Tensile strength

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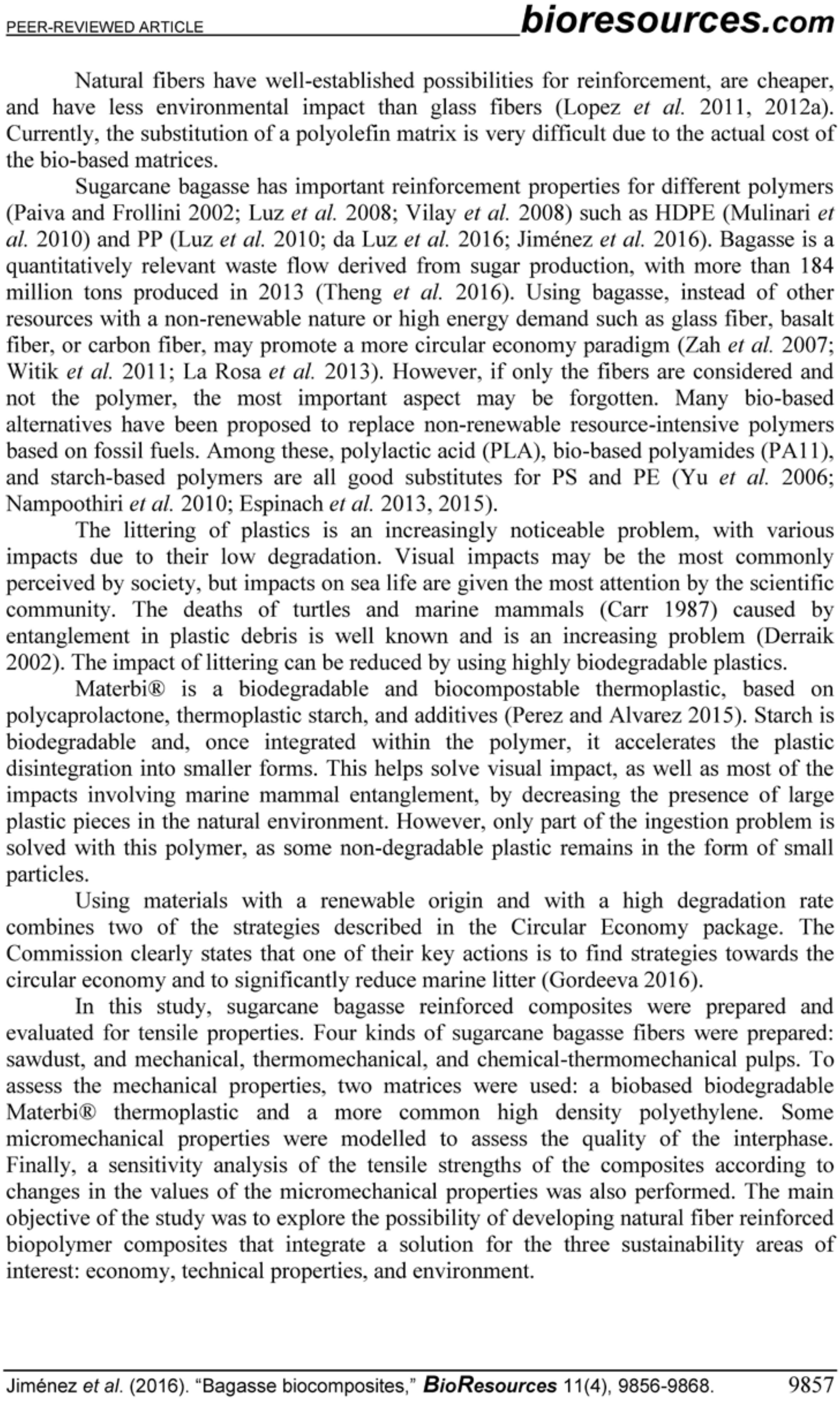
INTRODUCTION

The preparation of composite materials has the potential to achieve favorable results for different applications based on economic issues, physical properties, and environmental performance. Strategies based on economic performance may attempt to reduce the weight percentage of expensive matrices by adding cheap fillers (Gu *et al.* 2016). The property-based point of view is more interested in achieving higher tensile strengths or stiffness by introducing reinforcements (Vallejos *et al.* 2012; Reixach *et al.* 2015; Granda *et al.* 2016). However, the environmental strategy focuses on replacing one or all the phases of a composite with more environmentally friendly components (Serrano *et al.* 2014). Nonetheless, the pursuit of an integrated strategy dedicated to the pursuit of sustainability is possible.



Natural fibers have well-established possibilities for reinforcement, are cheaper, and have less environmental impact than glass fibers (Lopez *et al.* 2011, 2012a). Currently, the substitution of a polyolefin matrix is very difficult due to the actual cost of the bio-based matrices.

Sugarcane bagasse has important reinforcement properties for different polymers (Paiva and Frollini 2002; Luz *et al.* 2008; Vilay *et al.* 2008) such as HDPE (Mulinari *et al.* 2010) and PP (Luz *et al.* 2010; da Luz *et al.* 2016; Jiménez *et al.* 2016). Bagasse is a quantitatively relevant waste flow derived from sugar production, with more than 184 million tons produced in 2013 (Theng *et al.* 2016). Using bagasse, instead of other resources with a non-renewable nature or high energy demand such as glass fiber, basalt fiber, or carbon fiber, may promote a more circular economy paradigm (Zah *et al.* 2007; Witik *et al.* 2011; La Rosa *et al.* 2013). However, if only the fibers are considered and not the polymer, the most important aspect may be forgotten. Many bio-based alternatives have been proposed to replace non-renewable resource-intensive polymers based on fossil fuels. Among these, polylactic acid (PLA), bio-based polyamides (PA11), and starch-based polymers are all good substitutes for PS and PE (Yu *et al.* 2006; Nampoothiri *et al.* 2010; Espinach *et al.* 2013, 2015).

The littering of plastics is an increasingly noticeable problem, with various impacts due to their low degradation. Visual impacts may be the most commonly perceived by society, but impacts on sea life are given the most attention by the scientific community. The deaths of turtles and marine mammals (Carr 1987) caused by entanglement in plastic debris is well known and is an increasing problem (Derraik 2002). The impact of littering can be reduced by using highly biodegradable plastics.

Materbi® is a biodegradable and biocompostable thermoplastic, based on polycaprolactone, thermoplastic starch, and additives (Perez and Alvarez 2015). Starch is biodegradable and, once integrated within the polymer, it accelerates the plastic disintegration into smaller forms. This helps solve visual impact, as well as most of the impacts involving marine mammal entanglement, by decreasing the presence of large plastic pieces in the natural environment. However, only part of the ingestion problem is solved with this polymer, as some non-degradable plastic remains in the form of small particles.

Using materials with a renewable origin and with a high degradation rate combines two of the strategies described in the Circular Economy package. The Commission clearly states that one of their key actions is to find strategies towards the circular economy and to significantly reduce marine litter (Gordeeva 2016).

In this study, sugarcane bagasse reinforced composites were prepared and evaluated for tensile properties. Four kinds of sugarcane bagasse fibers were prepared: sawdust, and mechanical, thermomechanical, and chemical-thermomechanical pulps. To assess the mechanical properties, two matrices were used: a biobased biodegradable Materbi® thermoplastic and a more common high density polyethylene. Some micromechanical properties were modelled to assess the quality of the interphase. Finally, a sensitivity analysis of the tensile strengths of the composites according to changes in the values of the micromechanical properties was also performed. The main objective of the study was to explore the possibility of developing natural fiber reinforced biopolymer composites that integrate a solution for the three sustainability areas of interest: economy, technical properties, and environment.

EXPERIMENTAL

Materials

Sugarcane bagasse (SB) from *Saccharum officinarum* was provided by the University Pontificia Bolivariana (Medellín, Colombia). A starch-based polymer Mater-bi® YI014U/C, supplied by Novamont (Novara, Italy) (PTA), was used as a biodegradable thermoplastic matrix.

For comparison purposes, high density polyethylene (HDPE) Rigidex HD5226EA (INEOS Polyolefins, Barcelona, Spain), and maleic anhydride-grafted polyethylene (MAPE) Fusabond E226 (DuPont, Tamon-Carreño, Spain) composites reinforced with SB fibers were also prepared.

Other reactants used included decahydronaphtalene (decalin) to dissolve the matrix in the fiber extraction from the composites process and sodium hydroxide used to prepare the fibers. The above reagents were provided by ScharLab, S. L. (Barcelona, Spain). Anthraquinone was provided by BASF (Tarragona, Spain).

Methods

Preparation of sugarcane bagasse sawdust and fibers

The SB was run through a cutter-mill and screened in a 5-mm sieve. To prepare the sawdust (WF), SB biomass was ground to 0.2 mm. Mechanical pulp (MP) was obtained by passing the SB through manually adjusted Sprout-Waldron 105-A defibration equipment (Muncy, USA). Thermomechanical pulp (TMP) was obtained by treating the biomass at 160 °C for 15 min at a liquor ratio of 6:1. To obtain bagasse chemi-thermomechanical fibers (CTMP), the biomass was submitted to a sodium hydroxide/anthraquinone (AQ) digestion process (5% NaOH, 0.1% AQ) at a liquor ratio of 6:1 and 160 °C for 30 min. The resulting slurry was then washed. The TMP and CTMP processes were finalized with defibration using Sprout-Waldron equipment.

Compounding

Sawdust and fibers were dried for 24 h at 105 °C and then mixed (30% w/w), with the PTA matrix, without any coupling agent, in a Gelimat kinetic mixer (model G5S, Draiswerke, Mahaw, USA) at 2500 rpm for 2 min until a discharge temperature of 210 °C was achieved. The obtained mixtures were granulated in a knives mill.

Some of the MP and TMP were used to prepare 30% w/w BS/HDPE composites. The blends were produced by means of a Brabender internal mixer set for 10 min at 80 rpm rotor speed and 175 °C discharge temperature. The 6% coupling agent (MAPE) by weight of HDPE was added to the mixer with the HDPE pellets. The MAPE percentage was chosen based on the available literature and experience of the research group (Reixach *et al.* 2013).

Composites were granulated in a blade mill equipped with a 10 mm mesh and kept in an oven at 80 °C until needed in order to prevent moisture absorption.

Test specimens were molded in a Meteor-40 injection-molding machine (Mateu & Soler, Barcelona, Spain) using a steel mold according to ASTM D3641 (2015) specifications. The processing temperatures corresponding to the PTA-based composites were 120, 135 and 150ºC, being the last the injection nozzle. In the case of the HDPE-based composites, the corresponding temperatures were 175, 175, and 200 ºC. First and second pressures for the PTA-based composites were 70 and 20 kgf/cm^2, respectively. In the case of the HDPE-based composites, the corresponding pressures were 60 and 15 kgf/cm^2.

Mechanical characterization

Composite specimens were placed in a conditioning chamber (Dycometal) at 23 °C and 50% relative humidity for 48 h, according to ASTM D618-13 (2013) protocol standards. Tensile tests were carried out using an Instron 1122 universal testing machine (Northwood, MA, USA) according to ASTM D638-14 (2014) regulations.

Morphological characterization

Fiber length distributions, diameters, and the percentage of fines were measured in a MORFI analyzer (Techpap, Grenoble, France). The equipment measured between 25000 and 30000 fibers. Four samples of each type of fiber were analyzed.

Tensile strength micromechanics

The intrinsic strength of the fibers (σ_t^F) was defined by solving the modified Kelly and Tyson equation (Eq. 1) (Kelly and Tyson 1965),

$$\sigma_t^C = \chi_1\left(\sum_i\left[\frac{\tau \cdot l_i^f \cdot V_i^f}{d^f}\right] + \sum_j\left[\sigma_t^f \cdot V_j^f\left(1 - \frac{\sigma_t^f \cdot d^f}{4 \cdot \tau \cdot l_j^f}\right)\right]\right) + (1 - V^f) \cdot \sigma_t^{m*} \tag{1}$$

where σ_t^C and σ_t^f are the composite and reinforcing fiber tensile strengths, respectively. σ_t^{m*} is the contribution of the matrix at failure. The d^f and $l^f_{i,j}$ terms represent the fiber diameters and lengths, respectively. The V^f term is the volume fraction of reinforcement in the composite. The original equation was presented for aligned fibers. An orientation factor (χ_1) was later added to adapt the equation to semi-aligned fibers. The equation was solved using the solution provided by Bowyer and Bader's methodology (Bowyer and Bader 1972), which evaluated χ_1 and τ. Afterwards, it was possible to compute the value of the intrinsic tensile strength of the fibers by using the experimental values determined at composite failure.

The intrinsic Young's moduli of the fibers (E_t^f) were computed using the Hirsch model (Hirsch 1962; Rodriguez *et al.* 2010; Vilaseca *et al.* 2010; Lopez *et al.* 2011).

The modified rule of mixtures for the tensile strength (Thomason 2002; Lee *et al.* 2014) was also used (Eq. 2).

$$\sigma_t^C = f_c \cdot \sigma_t^f \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \tag{2}$$

where f_c is the coupling factor. In favorable interfaces, f_c ranges from 0.18 to 0.2.

RESULTS AND DISCUSSION

Morphological Characterization of the Fibers

The mechanical properties of composite materials are a combination of the properties of their phases. In order to fully take advantage of those properties, a correct dispersion of the reinforcement inside of the matrix and a good interphase between both components must be achieved. Additionally, there are geometric factors, such as the relative orientation of the fibers against the applied loads and the morphology of the fibers, that also affect the mechanical properties of the composites (Vallejos *et al.* 2012).

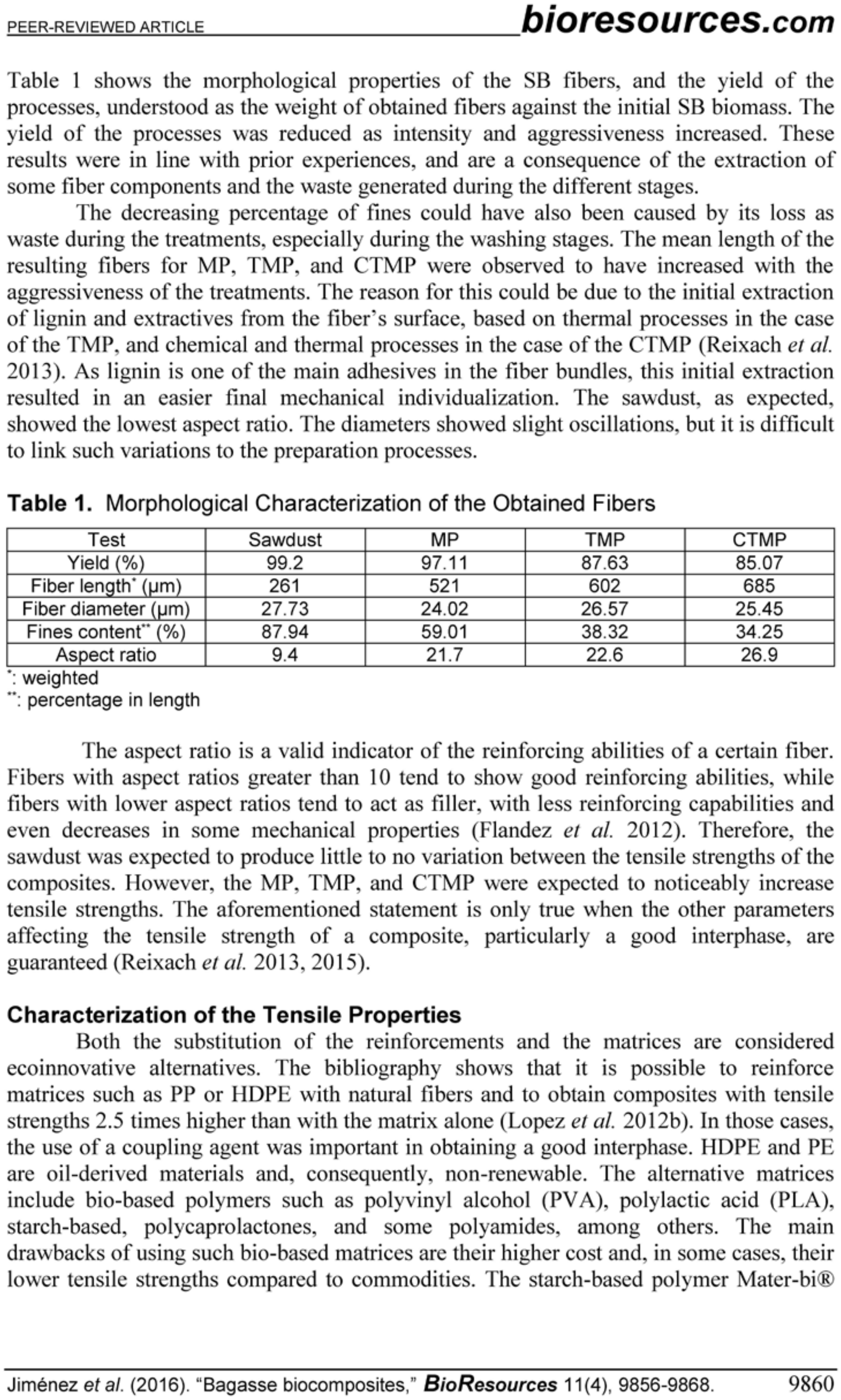


Table 1 shows the morphological properties of the SB fibers, and the yield of the processes, understood as the weight of obtained fibers against the initial SB biomass. The yield of the processes was reduced as intensity and aggressiveness increased. These results were in line with prior experiences, and are a consequence of the extraction of some fiber components and the waste generated during the different stages.

The decreasing percentage of fines could have also been caused by its loss as waste during the treatments, especially during the washing stages. The mean length of the resulting fibers for MP, TMP, and CTMP were observed to have increased with the aggressiveness of the treatments. The reason for this could be due to the initial extraction of lignin and extractives from the fiber's surface, based on thermal processes in the case of the TMP, and chemical and thermal processes in the case of the CTMP (Reixach *et al.* 2013). As lignin is one of the main adhesives in the fiber bundles, this initial extraction resulted in an easier final mechanical individualization. The sawdust, as expected, showed the lowest aspect ratio. The diameters showed slight oscillations, but it is difficult to link such variations to the preparation processes.

Table 1. Morphological Characterization of the Obtained Fibers

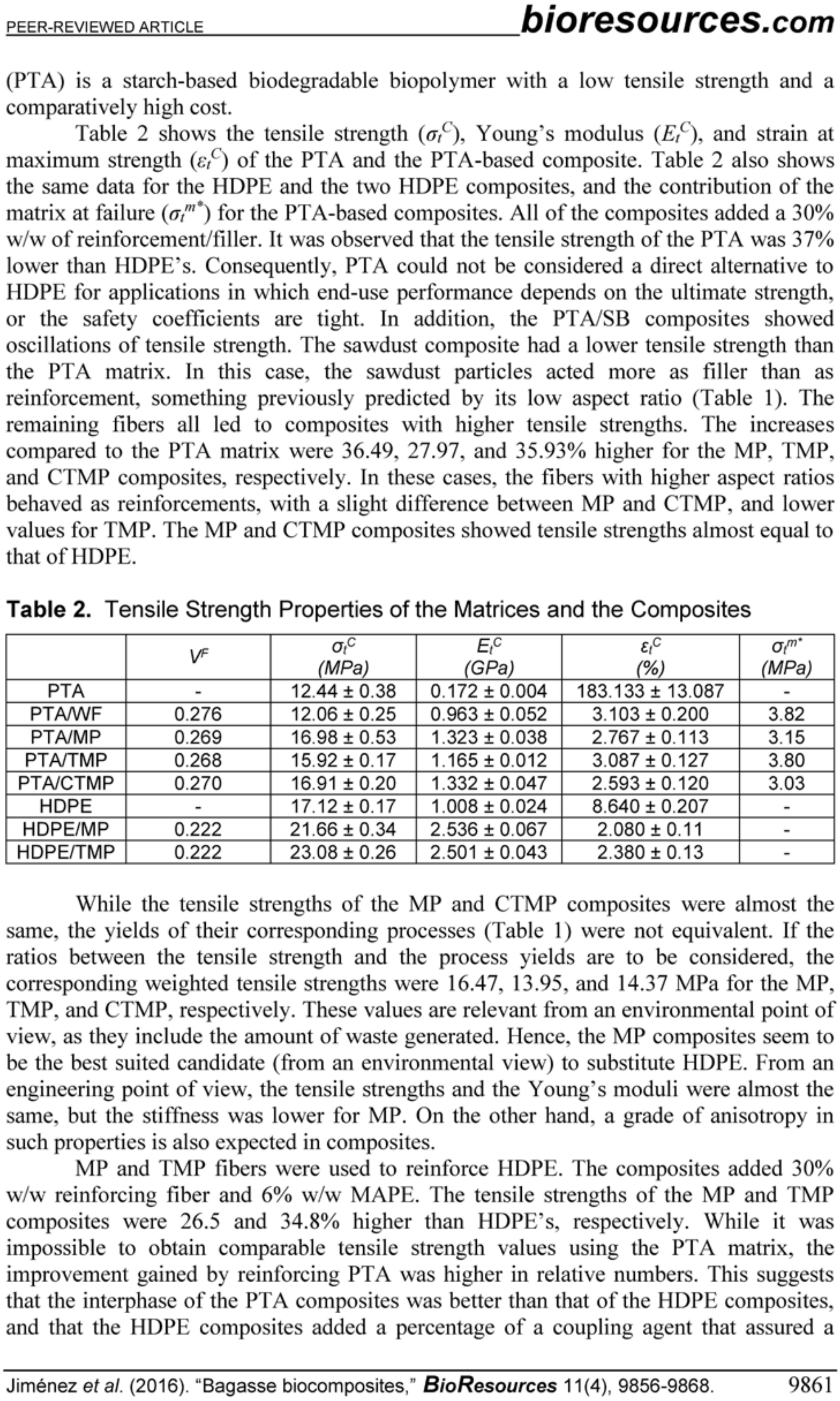
Test	Sawdust	MP	TMP	CTMP
Yield (%)	99.2	97.11	87.63	85.07
Fiber length* (µm)	261	521	602	685
Fiber diameter (µm)	27.73	24.02	26.57	25.45
Fines content** (%)	87.94	59.01	38.32	34.25
Aspect ratio	9.4	21.7	22.6	26.9

*: weighted
**: percentage in length

The aspect ratio is a valid indicator of the reinforcing abilities of a certain fiber. Fibers with aspect ratios greater than 10 tend to show good reinforcing abilities, while fibers with lower aspect ratios tend to act as filler, with less reinforcing capabilities and even decreases in some mechanical properties (Flandez *et al.* 2012). Therefore, the sawdust was expected to produce little to no variation between the tensile strengths of the composites. However, the MP, TMP, and CTMP were expected to noticeably increase tensile strengths. The aforementioned statement is only true when the other parameters affecting the tensile strength of a composite, particularly a good interphase, are guaranteed (Reixach *et al.* 2013, 2015).

Characterization of the Tensile Properties

Both the substitution of the reinforcements and the matrices are considered ecoinnovative alternatives. The bibliography shows that it is possible to reinforce matrices such as PP or HDPE with natural fibers and to obtain composites with tensile strengths 2.5 times higher than with the matrix alone (Lopez *et al.* 2012b). In those cases, the use of a coupling agent was important in obtaining a good interphase. HDPE and PE are oil-derived materials and, consequently, non-renewable. The alternative matrices include bio-based polymers such as polyvinyl alcohol (PVA), polylactic acid (PLA), starch-based, polycaprolactones, and some polyamides, among others. The main drawbacks of using such bio-based matrices are their higher cost and, in some cases, their lower tensile strengths compared to commodities. The starch-based polymer Mater-bi®



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(PTA) is a starch-based biodegradable biopolymer with a low tensile strength and a comparatively high cost.

Table 2 shows the tensile strength (σ_t^C), Young's modulus (E_t^C), and strain at maximum strength (ε_t^C) of the PTA and the PTA-based composite. Table 2 also shows the same data for the HDPE and the two HDPE composites, and the contribution of the matrix at failure (σ_t^{m*}) for the PTA-based composites. All of the composites added a 30% w/w of reinforcement/filler. It was observed that the tensile strength of the PTA was 37% lower than HDPE's. Consequently, PTA could not be considered a direct alternative to HDPE for applications in which end-use performance depends on the ultimate strength, or the safety coefficients are tight. In addition, the PTA/SB composites showed oscillations of tensile strength. The sawdust composite had a lower tensile strength than the PTA matrix. In this case, the sawdust particles acted more as filler than as reinforcement, something previously predicted by its low aspect ratio (Table 1). The remaining fibers all led to composites with higher tensile strengths. The increases compared to the PTA matrix were 36.49, 27.97, and 35.93% higher for the MP, TMP, and CTMP composites, respectively. In these cases, the fibers with higher aspect ratios behaved as reinforcements, with a slight difference between MP and CTMP, and lower values for TMP. The MP and CTMP composites showed tensile strengths almost equal to that of HDPE.

Table 2. Tensile Strength Properties of the Matrices and the Composites

	V^F	σ_t^C (MPa)	E_t^C (GPa)	ε_t^C (%)	σ_t^{m*} (MPa)
PTA	-	12.44 ± 0.38	0.172 ± 0.004	183.133 ± 13.087	-
PTA/WF	0.276	12.06 ± 0.25	0.963 ± 0.052	3.103 ± 0.200	3.82
PTA/MP	0.269	16.98 ± 0.53	1.323 ± 0.038	2.767 ± 0.113	3.15
PTA/TMP	0.268	15.92 ± 0.17	1.165 ± 0.012	3.087 ± 0.127	3.80
PTA/CTMP	0.270	16.91 ± 0.20	1.332 ± 0.047	2.593 ± 0.120	3.03
HDPE	-	17.12 ± 0.17	1.008 ± 0.024	8.640 ± 0.207	-
HDPE/MP	0.222	21.66 ± 0.34	2.536 ± 0.067	2.080 ± 0.11	-
HDPE/TMP	0.222	23.08 ± 0.26	2.501 ± 0.043	2.380 ± 0.13	-

While the tensile strengths of the MP and CTMP composites were almost the same, the yields of their corresponding processes (Table 1) were not equivalent. If the ratios between the tensile strength and the process yields are to be considered, the corresponding weighted tensile strengths were 16.47, 13.95, and 14.37 MPa for the MP, TMP, and CTMP, respectively. These values are relevant from an environmental point of view, as they include the amount of waste generated. Hence, the MP composites seem to be the best suited candidate (from an environmental view) to substitute HDPE. From an engineering point of view, the tensile strengths and the Young's moduli were almost the same, but the stiffness was lower for MP. On the other hand, a grade of anisotropy in such properties is also expected in composites.

MP and TMP fibers were used to reinforce HDPE. The composites added 30% w/w reinforcing fiber and 6% w/w MAPE. The tensile strengths of the MP and TMP composites were 26.5 and 34.8% higher than HDPE's, respectively. While it was impossible to obtain comparable tensile strength values using the PTA matrix, the improvement gained by reinforcing PTA was higher in relative numbers. This suggests that the interphase of the PTA composites was better than that of the HDPE composites, and that the HDPE composites added a percentage of a coupling agent that assured a

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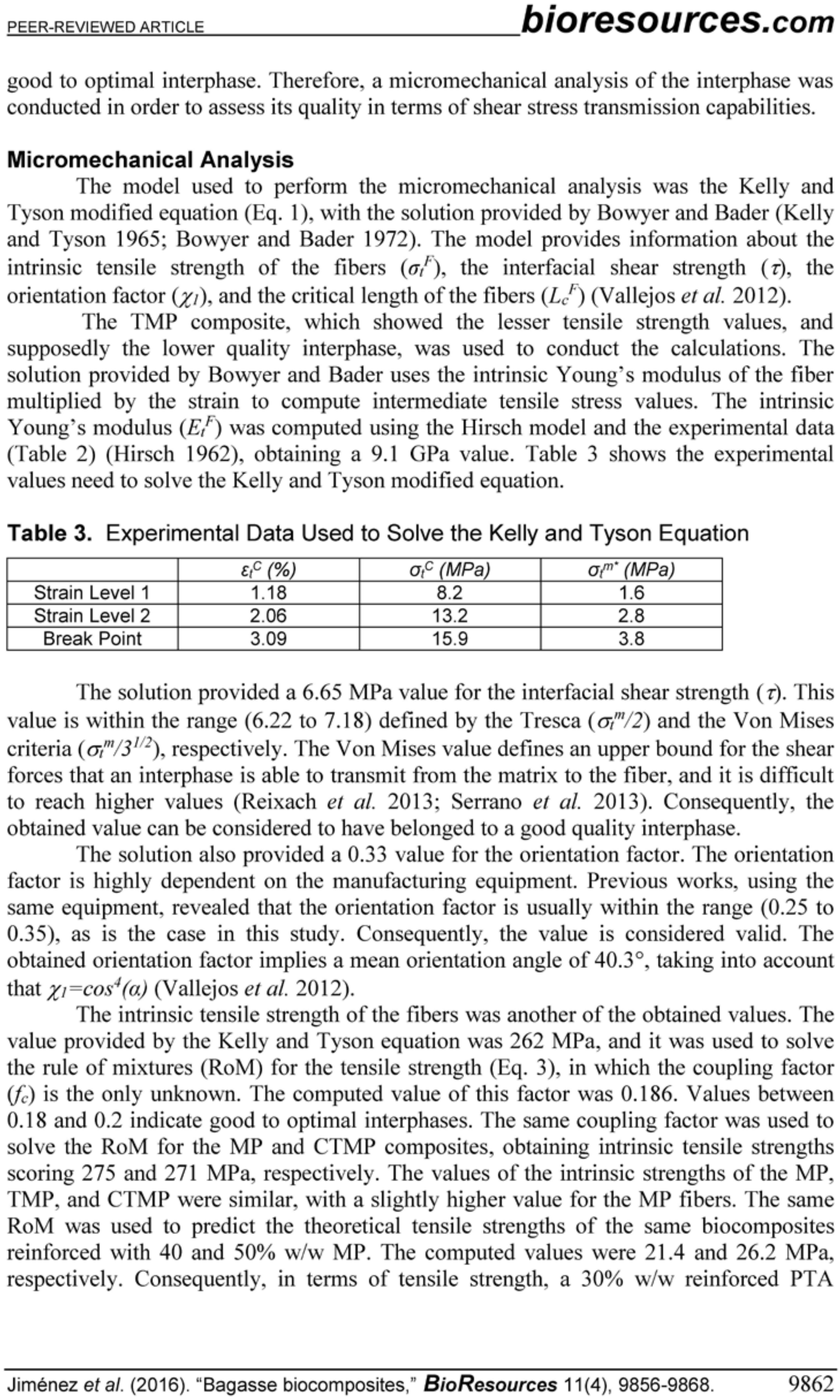


good to optimal interphase. Therefore, a micromechanical analysis of the interphase was conducted in order to assess its quality in terms of shear stress transmission capabilities.

Micromechanical Analysis

The model used to perform the micromechanical analysis was the Kelly and Tyson modified equation (Eq. 1), with the solution provided by Bowyer and Bader (Kelly and Tyson 1965; Bowyer and Bader 1972). The model provides information about the intrinsic tensile strength of the fibers (σ_t^F), the interfacial shear strength (τ), the orientation factor (χ_1), and the critical length of the fibers (L_c^F) (Vallejos *et al.* 2012).

The TMP composite, which showed the lesser tensile strength values, and supposedly the lower quality interphase, was used to conduct the calculations. The solution provided by Bowyer and Bader uses the intrinsic Young's modulus of the fiber multiplied by the strain to compute intermediate tensile stress values. The intrinsic Young's modulus (E_t^F) was computed using the Hirsch model and the experimental data (Table 2) (Hirsch 1962), obtaining a 9.1 GPa value. Table 3 shows the experimental values need to solve the Kelly and Tyson modified equation.

Table 3. Experimental Data Used to Solve the Kelly and Tyson Equation

	ε_t^C (%)	σ_t^C (MPa)	σ_t^{m*} (MPa)
Strain Level 1	1.18	8.2	1.6
Strain Level 2	2.06	13.2	2.8
Break Point	3.09	15.9	3.8

The solution provided a 6.65 MPa value for the interfacial shear strength (τ). This value is within the range (6.22 to 7.18) defined by the Tresca ($\sigma_t^m/2$) and the Von Mises criteria ($\sigma_t^m/3^{1/2}$), respectively. The Von Mises value defines an upper bound for the shear forces that an interphase is able to transmit from the matrix to the fiber, and it is difficult to reach higher values (Reixach *et al.* 2013; Serrano *et al.* 2013). Consequently, the obtained value can be considered to have belonged to a good quality interphase.

The solution also provided a 0.33 value for the orientation factor. The orientation factor is highly dependent on the manufacturing equipment. Previous works, using the same equipment, revealed that the orientation factor is usually within the range (0.25 to 0.35), as is the case in this study. Consequently, the value is considered valid. The obtained orientation factor implies a mean orientation angle of 40.3°, taking into account that $\chi_1=cos^4(\alpha)$ (Vallejos *et al.* 2012).

The intrinsic tensile strength of the fibers was another of the obtained values. The value provided by the Kelly and Tyson equation was 262 MPa, and it was used to solve the rule of mixtures (RoM) for the tensile strength (Eq. 3), in which the coupling factor (f_c) is the only unknown. The computed value of this factor was 0.186. Values between 0.18 and 0.2 indicate good to optimal interphases. The same coupling factor was used to solve the RoM for the MP and CTMP composites, obtaining intrinsic tensile strengths scoring 275 and 271 MPa, respectively. The values of the intrinsic strengths of the MP, TMP, and CTMP were similar, with a slightly higher value for the MP fibers. The same RoM was used to predict the theoretical tensile strengths of the same biocomposites reinforced with 40 and 50% w/w MP. The computed values were 21.4 and 26.2 MPa, respectively. Consequently, in terms of tensile strength, a 30% w/w reinforced PTA composite could replace an HDPE matrix, and a 40% w/w reinforced one could replace a 30% w/w MP reinforced HDPE.

The final determined value was that of the critical length, 530 µm. If the value is placed in the length distribution (Fig. 1), most of the fibers were computed as subcritical. The contributions of the subcritical and supercritical fibers of the final composite strength scored 5.23 and 7.92 MPa, respectively, with the contribution of supercritical fibers being higher.

Sensitivity Analysis

A sensitivity to variations in the micromechanical parameters model was created, in which the objective range of oscillation for each relevant variable was established. The range of variation for the orientation factor was 0.2 to 1.0, with 0.2 being the value for a random orientation of short fibers, and 1.0 being a total alignment of the fibers with the applied loads (Mehan and Schadler 2000). The interfacial shear stress was up-bounded by the Von Mises prediction of 7.18 MPa. The lower end took 5.15 MPa, defined by a 40% value oscillation. This range enclosed the Tresca value, 6.22 MPa. The last value changed was the mean length of the fibers, establishing a ± 30% oscillation and defining a [407 µm to 689 µm] range. In a previous study, some of the authors increased the mean length of natural fiber reinforcements by 21%, with some changes made in the processing of the composites (Lopez *et al.* 2012b).

Figure 1 shows the percentage oscillation of the theoretical value of the tensile strength of the composite, modelled using the Kelly and Tyson equation when the interfacial shear strength and the mean lengths varied within the defined ranges.

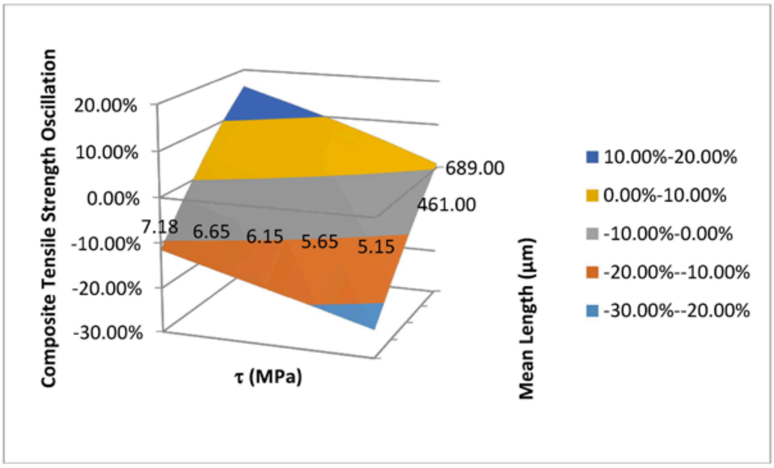


Fig. 1. Oscillation of the theoretical tensile strength of the composite versus the interfacial shear strength and the mean length of the fibers

Both parameters produced changes in the tensile strength. The mean length seemed to highly affect the tensile strength, as the slope of the surface is higher in the direction of its variation. Nonetheless, the interfacial shear strength also affects the tensile strength of the composite. If the mean length remains unchanged, the tensile strength oscillation is situated inside the range (-10.49% to 4.08%). If the interfacial shear strength remains constant the tensile strength of the composite vary inside the range (-18.2% to 9.15%). If both values changed, then the top value could increase by 16% and the lowest decrease by 23%.

Figure 2 shows the percentage oscillation of the theoretical value of the tensile strength of the composite, modelled using the Kelly and Tyson equation when the orientation factor and the mean lengths varied within the defined ranges.

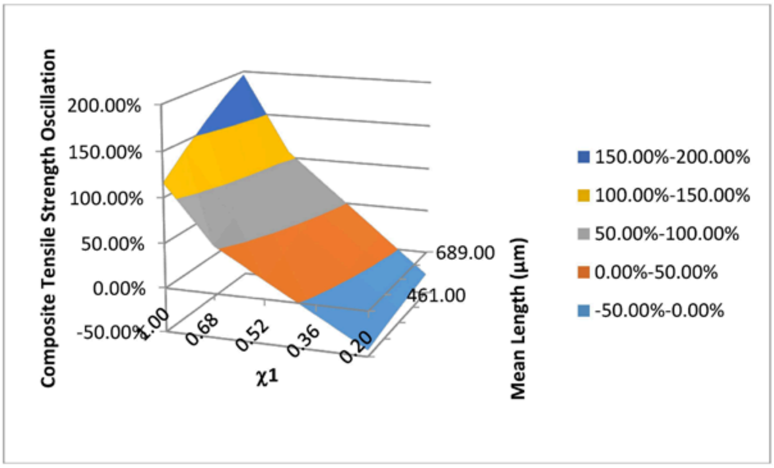


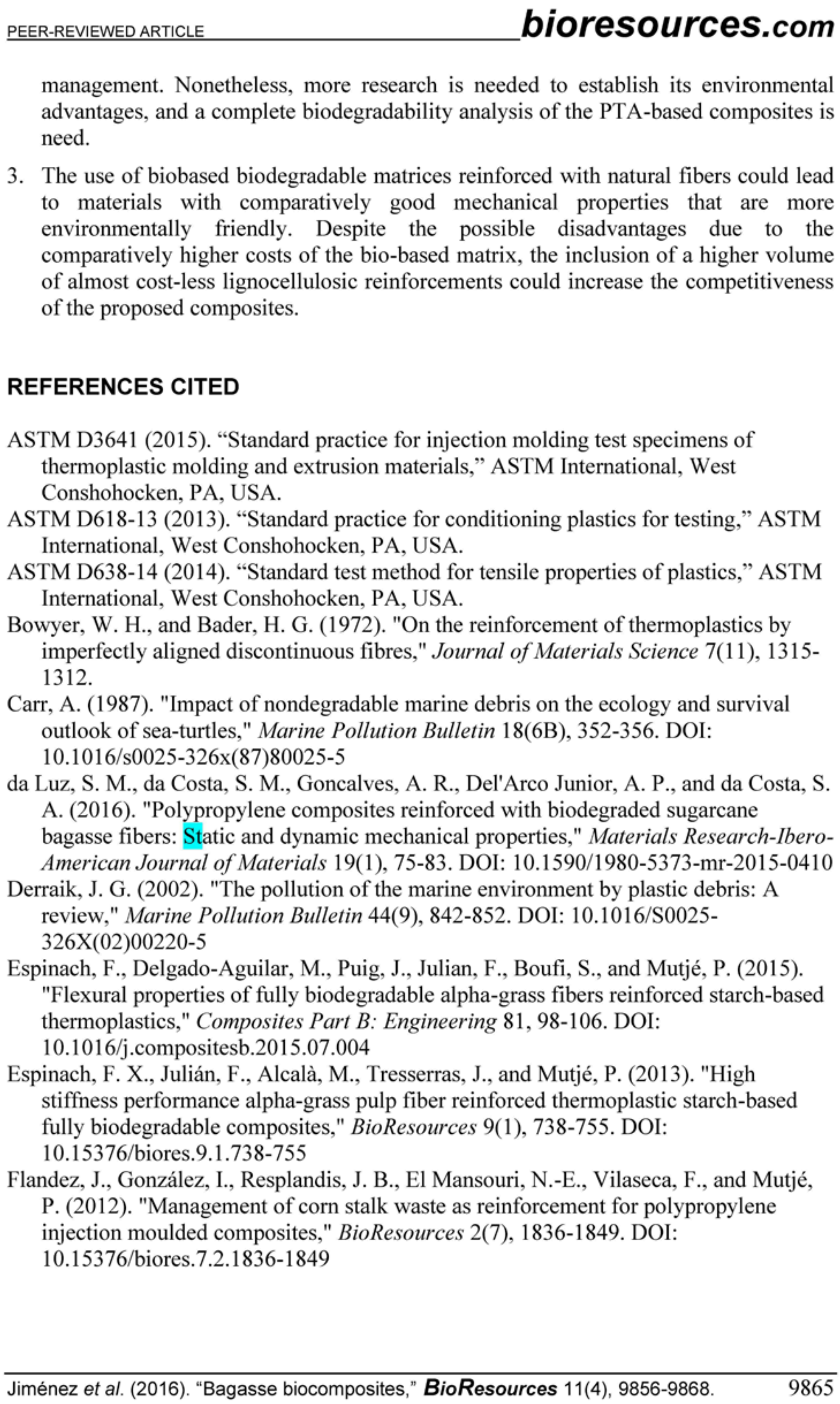
Fig. 2. Oscillation of the theoretical tensile strength of the composite versus the orientation factor and the mean length of the fibers

The orientation factor was, by far, the micromechanical property that most affected the tensile strength of the composite, which varied inside a range from -50% to 200%. Nonetheless, the more the alignment of the fibers against the applied loads increased, the more the anisotropy of the material did.

The results indicated that orientation factor had the greatest effect on the tensile strength of the composite. The other two parameters also affected the final result, but to a lesser extent.

CONCLUSIONS

1. Mater-bi® composites reinforced with sugarcane bagasse fibers were produced and tensile tested. The composites with 30% of MP reinforcing fibers showed tensile strengths similar to that of a common HDPE matrix. Modelled composites with 50% of MP reinforcing fibers showed tensile strengths similar to those of 30% SB reinforced HDPE composites.
2. From a sustainability point of view, the use of biobased and biodegradable matrices such as Mater-bi® represent an advantage over other matrices, such as polypropylene or high density polyethylene, in terms of the use of renewable materials and waste



management. Nonetheless, more research is needed to establish its environmental advantages, and a complete biodegradability analysis of the PTA-based composites is need.

3. The use of biobased biodegradable matrices reinforced with natural fibers could lead to materials with comparatively good mechanical properties that are more environmentally friendly. Despite the possible disadvantages due to the comparatively higher costs of the bio-based matrix, the inclusion of a higher volume of almost cost-less lignocellulosic reinforcements could increase the competitiveness of the proposed composites.

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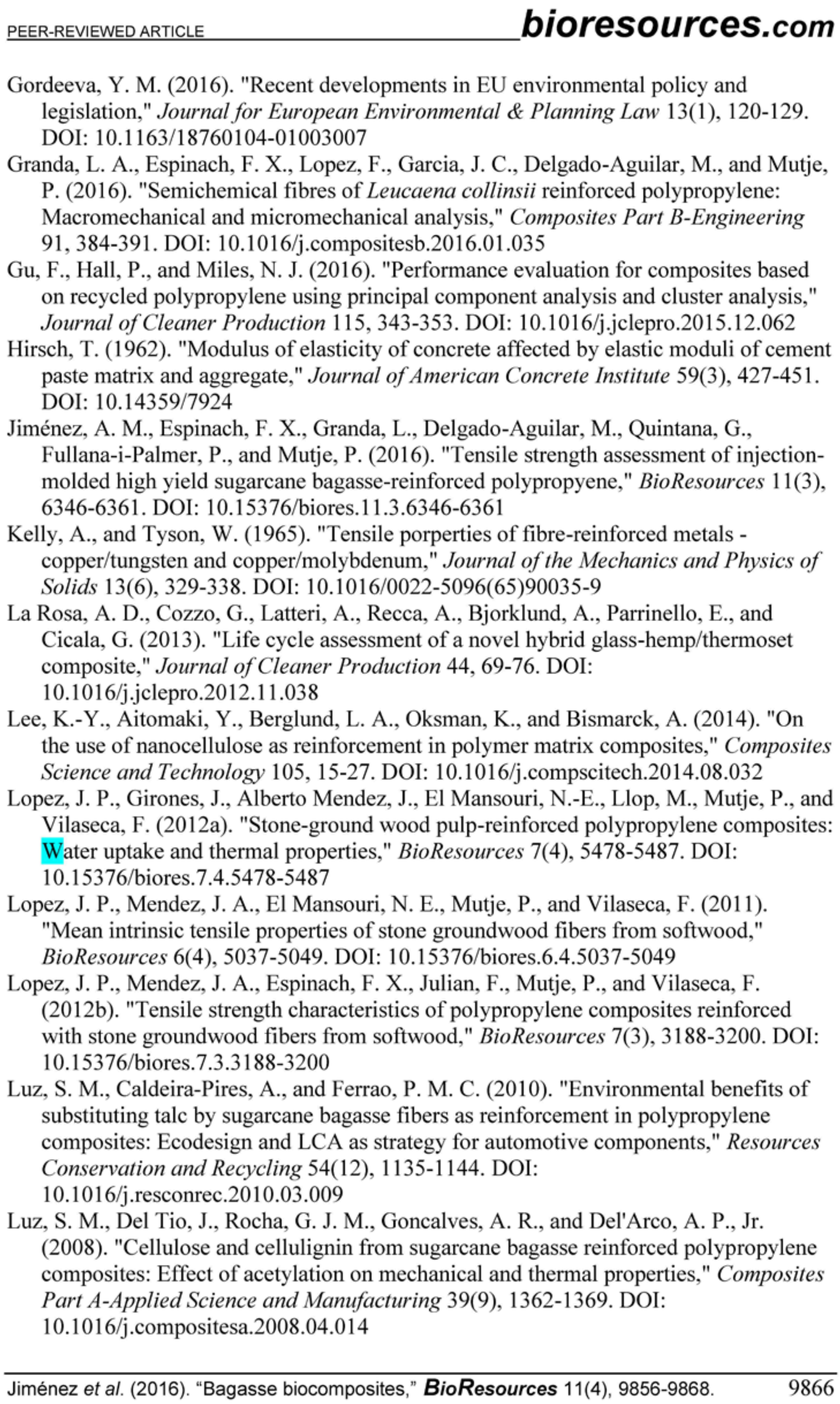

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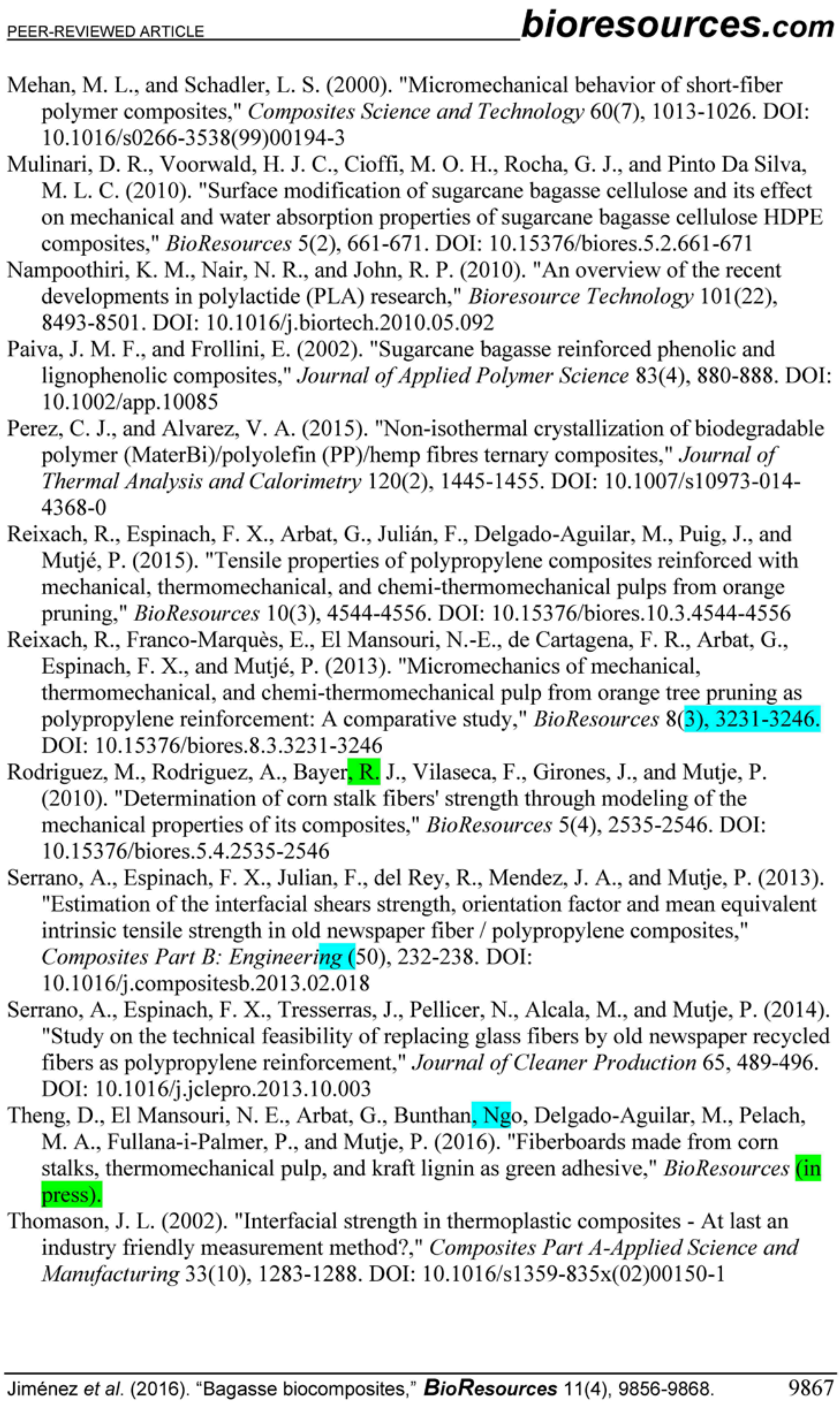

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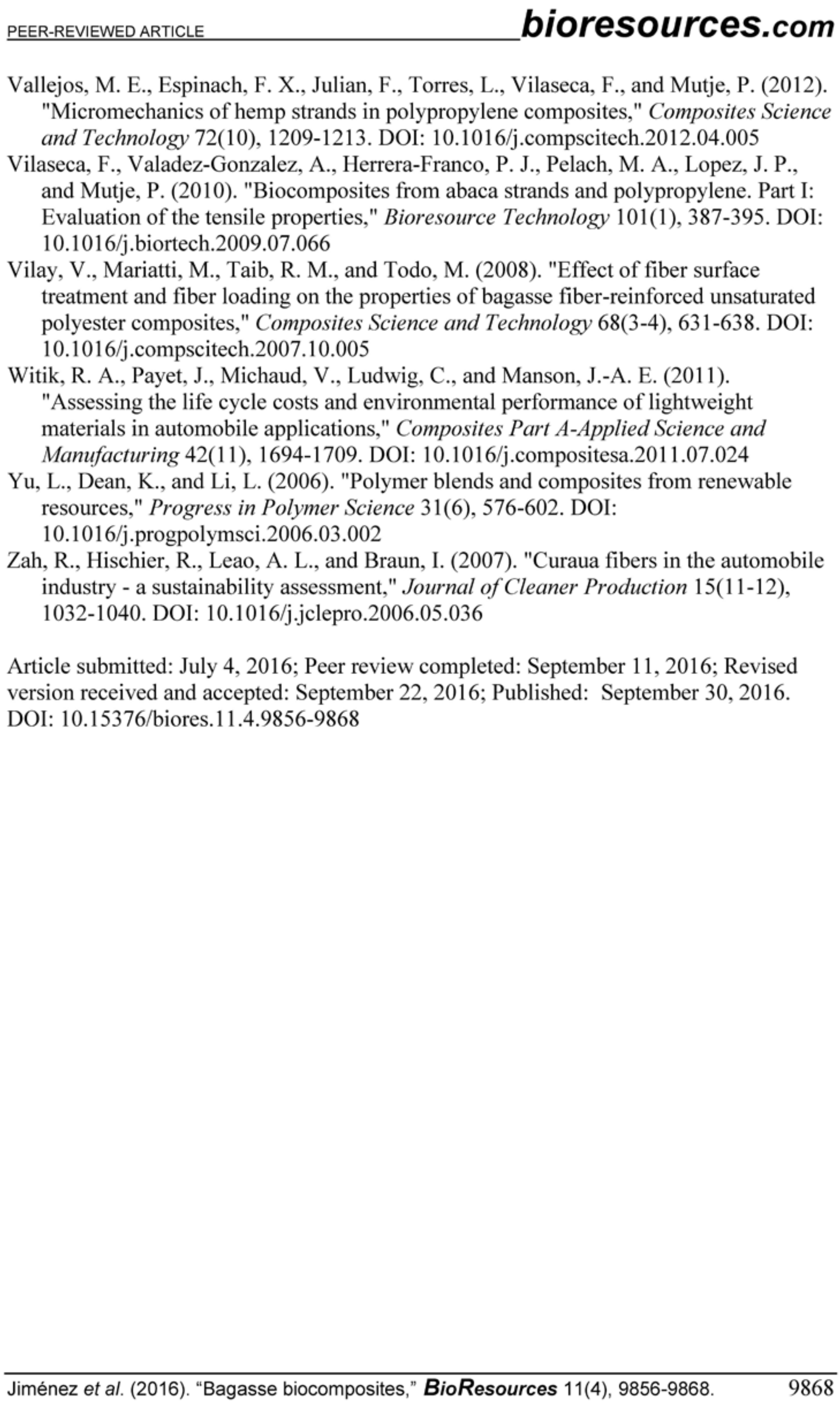

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4.4. Sugarcane Bagasse Reinforced Composites, Study On the Young's Modulus Macro and Micromechanics

PEER-REVIEWED ARTICLE **bioresources.com**

Sugarcane Bagasse Reinforced Composites: Studies on the Young's Modulus and Macro and Micro-Mechanics

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Pere Fullana-i-Palmer,[a, c] Pere Mutjè,[a] and Francesc X. Espinach [d]

The stiffness of a material greatly influences its possible use as an engineering material. Thus, despite the theoretical environmental advantages of natural fiber reinforced composites, or fully biodegradable composites, if certain mechanical properties are not achieved, a material can have fewer engineering uses. In this work, sugarcane bagasse fibers, a by-product of the sugarcane-juice extraction process, were used to obtain reinforcing fibers. Two polyolefins, a polypropylene and a high-density polyethylene, and a starch-based polymer were used as matrices. The composite materials were prepared and tested to obtain their tensile properties such as the Young's moduli. Some micromechanical models were used to obtain the intrinsic Young's moduli of the fibers and the efficiency factors. The dependence of such parameters on the matrix and fibers characteristics was studied. The fiber orientation efficiency factor was used to compute the orientation angle of the fibers inside the composite under three different distributions. Finally, the Tsai and Pagano models, and the Halpin and Tsai equations were used to compute the theoretical values of the Young's moduli of the composites.

Keywords: Biocomposites; Young's modulus; Micromechanics

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INTRODUCTION

In engineering terms, the development of materials with higher tensile and flexural strengths is very important. Such materials enable lighter designs that make it possible to fulfill all the structural requirements using less material. The composites are a clear example of such strategy. The use of a stiff matrix in conjunction with a rigid fibrous reinforcement generates a combination of materials with enhanced mechanical properties. Usually the resultant materials will show higher tensile and flexural strengths, Young's moduli, and show less ability to sustain deformations (compared to the matrix) without crack formations. As a rule, the engineering artifacts are not designed to handle the ultimate strength of the materials with which they are manufactured, it is more usual to define limit deformation states that ensure a correct deployment of a function. This is especially true for materials like steel or polymers, with high strains before the breaking point. In the case of stiffer materials, such as some fiber-reinforced polymers, their low strains at break point emphasize the importance of the ways such materials will deform and respond under loads. Usually, the Young's modulus is seen as an indicator of the stiffness of a material (Serrano *et al.* 2014).

The most common thermoplastic fiber-reinforced materials are the glass fiber-reinforced polyolefins. The use of glass fibers (GF) ensures a material with highly enhanced tensile strengths and Young's modulus. In fact, composite materials with low amounts of GF could double or triple the tensile strength or the Young's moduli of their matrices (Lopez *et al.* 2011, 2012b). Nonetheless, the GF has some drawbacks, mainly related to the amount of energy required to manufacture them. Further, such composites difficult to recycle, and their abrasiveness results in early wearing out of manufacturing machinery, as well as an unhealthy working environment for its operators (Wang *et al.* 1993; Granda *et al.* 2016). A lot of effort has been devoted to searching for more environmentally friendly and healthier alternatives to GF as composite reinforcement, and many authors have pointed to natural fibers as a possible replacement (Martinez-Urreaga *et al.* 2015; Scarponi and Messano 2015; da Luz *et al.* 2016; Granda *et al.* 2016). In contrast to GF, the natural fibers are cheap, easily available, and a renewable source of reinforcement material. In addition, these materials are less abrasive or non-abrasive in nature, and are healthier to handle (Dicker *et al.* 2014; Fazita *et al.* 2016). However, the natural fibers also possess some disadvantages, mainly related to the high standard deviations of their intrinsic properties, and their lower relative strengthening and stiffening abilities. Nevertheless, there are some studies that have shown that it is possible to obtain comparable tensile strengths or Young's modulus by using natural fibers in place of GF (HDPE) (Hill and Hughes 2010; Lopez *et al.* 2012a; Majeed *et al.* 2013; Reixach *et al.* 2013b).

There is a growing environmental concern towards the substitution of oil-based materials. Thereby, the use of polyolefin is also a matter of concern. Some researchers have pointed out that bio-based polymers can be used as possible substitutes, being the most discussed: polylactic acids, caprolactones, some polyamides, and starch-based polymers. While some of the abovementioned polymers show higher mechanical properties than the polyolefins, others, such as the starch-based polymers have very low tensile strengths and Young's moduli. There are studies showing the mechanical capabilities of natural fiber-reinforced bio-based polymers (Oksman *et al.* 2003; Hu and Lim 2007). Such works show a promising road towards more environmentally friendly composite materials that could be a real alternative to GF- reinforced polyolefin.

In this work two polyolefins, polypropylene and high-density polyethylene, as well as a starch based polymer, were used as matrices. The used reinforcing fibers were sugarcane bagasse (SB). SB is a fibrous byproduct of the sugarcane crushing process after its juice extraction. SB is commonly used as biofuel, as pulp for papermaking, or as a component for building materials. These materials contain fibers originated from the sugarcane and it constitutes core (40 to 50%), pith (30 to 35%), vessels, and skin. Such fibers show different morphologies and intrinsic properties, and some researchers have used only the core or the core and pith fibers to obtain higher mechanical properties. In this work, the SB was used as received, without any separation. The SB was then submitted to different treatments to obtain SB sawdust, and mechanical, thermomechanical, and chemo-thermomechanical pulps. Different composite materials were obtained by mixing a 30 wt% of the SB fibers with the proposed matrices. Those materials were tensile tested to obtain their Young's moduli and their strain at break. Hirsch equation and the modified rule of mixtures were used to obtain the intrinsic

Young's moduli of the different SB reinforcements, as well as other micromechanical properties such the efficiency, length, and orientation factors. The limit and mean orientation angles of the fibers were also computed, attending to different possible fiber configurations. The mean angles were compared with the mean orientation angle predicted by the tensile strength micromechanics to choose the most probable fiber distribution (Jiménez *et al.* 2016a,b). Finally, the Tsai and Pagano model, and the Halpin and Tsai equations were used. The intrinsic Young's moduli obtained with the Hirsch equation was then employed to calculate the theoretical Young's moduli of the composites and compared it with the experimental results.

EXPERIMENTAL

Materials

Sugarcane bagasse (SB) from *Saccharum officinarum* was provided by the University of Pontificia Bolivariana (Medellín, Colombia).

Three different matrices were used to prepare the composites, two polyolefins and a starch-based polymer. The two polyolefins used were: a polypropylene (PP) homopolymer (Isplen PP099 K2M), kindly provided by Repsol-YPF (Tarragona, Spain), and a high-density polyethylene (HDPE) Rigidex HD5226EA (INEOS Polyolefins, Barcelona, Spain). The starch-based polymer (PTA), was a Mater-bi® YI014U/C, supplied by Novamont (Novara, Italy).

Other reactants used for the fiber treatments were sodium hydroxide (Merck KGaA, Germany) and anthraquinone (BASF AG, Germany). These were used without any further purification.

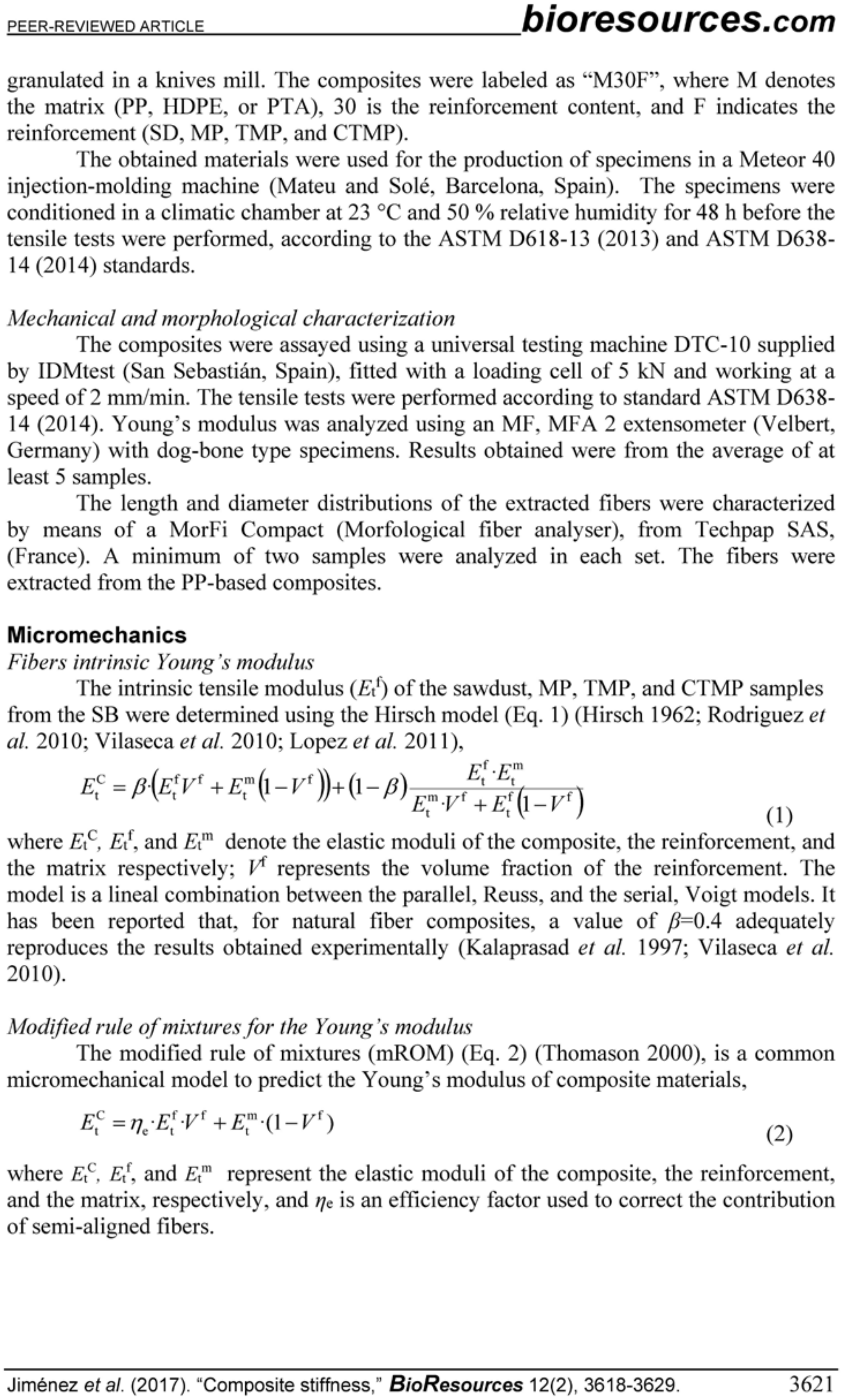
Methods

Preparation of sugarcane bagasse derivatives

The SB biomass was ground and screened through a cutter-mill, using a 5 mm sieve. The sawdust (SD) was then prepared by further grinding to 0.2 mm through a mill. To obtain mechanical pulp (MP), some SB samples were defibered in a Sprout-Waldron refiner (Muncy, USA), under cold aqueous conditions. This process showed almost 100% yield with respect to the starting material. Another SB sample was submitted to a thermo-mechanical process (vaporization followed by defibering). For this purpose, the SB was heated to 160 ºC for 15 min using a fiber to liquor ratio of 6:1. The resulting pulp was water rinsed and passed through the Sprout-Waldron equipment to obtain the thermo-mechanical pulp (TMP) with around 95% yield. For SB CTMP fibers, the SB was submitted to a sodium hydroxide/antraquinone (AQ) cooking process (5% NaOH w/w, 0.1% AQ w/w) in a liquid to fiber ratio of 6:1, working at 160 ºC for 30 min. Afterwards, the slurry was washed and passed through the Sprout-Waldron equipment, giving around 90% yield.

Compounding and injection molding

The SD, MP, TMP, and CTMP fibers were dried for 24 h at 105 °C. Then the fibers were mixed (30% w/w) with the PP, HDPE, and PTA matrices in a Gelimat kinetic mixer model G5S by Draiswerke (Mahaw, USA). The process parameters used were 2500 rpm for 2 min until discharge temperatures of 210, 180, and 140 °C were attained, for the PP, HDPE, and PTA polymers, respectively. The obtained mixtures were



granulated in a knives mill. The composites were labeled as "M30F", where M denotes the matrix (PP, HDPE, or PTA), 30 is the reinforcement content, and F indicates the reinforcement (SD, MP, TMP, and CTMP).

The obtained materials were used for the production of specimens in a Meteor 40 injection-molding machine (Mateu and Solé, Barcelona, Spain). The specimens were conditioned in a climatic chamber at 23 °C and 50 % relative humidity for 48 h before the tensile tests were performed, according to the ASTM D618-13 (2013) and ASTM D638-14 (2014) standards.

Mechanical and morphological characterization

The composites were assayed using a universal testing machine DTC-10 supplied by IDMtest (San Sebastián, Spain), fitted with a loading cell of 5 kN and working at a speed of 2 mm/min. The tensile tests were performed according to standard ASTM D638-14 (2014). Young's modulus was analyzed using an MF, MFA 2 extensometer (Velbert, Germany) with dog-bone type specimens. Results obtained were from the average of at least 5 samples.

The length and diameter distributions of the extracted fibers were characterized by means of a MorFi Compact (Morfological fiber analyser), from Techpap SAS, (France). A minimum of two samples were analyzed in each set. The fibers were extracted from the PP-based composites.

Micromechanics

Fibers intrinsic Young's modulus

The intrinsic tensile modulus (E_t^f) of the sawdust, MP, TMP, and CTMP samples from the SB were determined using the Hirsch model (Eq. 1) (Hirsch 1962; Rodriguez *et al.* 2010; Vilaseca *et al.* 2010; Lopez *et al.* 2011),

$$E_t^C = \beta \cdot \left(E_t^f V^f + E_t^m\left(1 - V^f\right)\right) + \left(1 - \beta\right)\frac{E_t^f \cdot E_t^m}{E_t^m \cdot V^f + E_t^f\left(1 - V^f\right)} \qquad (1)$$

where E_t^C, E_t^f, and E_t^m denote the elastic moduli of the composite, the reinforcement, and the matrix respectively; V^f represents the volume fraction of the reinforcement. The model is a lineal combination between the parallel, Reuss, and the serial, Voigt models. It has been reported that, for natural fiber composites, a value of β=0.4 adequately reproduces the results obtained experimentally (Kalaprasad *et al.* 1997; Vilaseca *et al.* 2010).

Modified rule of mixtures for the Young's modulus

The modified rule of mixtures (mROM) (Eq. 2) (Thomason 2000), is a common micromechanical model to predict the Young's modulus of composite materials,

$$E_t^C = \eta_e \cdot E_t^f \cdot V^f + E_t^m \cdot (1 - V^f) \qquad (2)$$

where E_t^C, E_t^f, and E_t^m represent the elastic moduli of the composite, the reinforcement, and the matrix, respectively, and η_e is an efficiency factor used to correct the contribution of semi-aligned fibers.

Efficiency, length, and orientation factors

The efficiency factor can be expressed as the product of the orientation factor and the length efficiency factor ($\eta_e = \eta_o \cdot \eta_l$). Usually the η_o is a consequence of the process and the machinery parameters, and η_l is linked to the morphology of the reinforcements (Vallejos *et al.* 2012).

The length factor was computed according to Cox-Krenchel's model (Krenchel 1964),

$$\eta_l = 1 - \frac{\tanh\left(\beta \cdot l^f / 2\right)}{\left(\beta \cdot l^f / 2\right)} \qquad (3)$$

with

$$\beta = \frac{1}{r}\sqrt{\frac{E_t^m}{E_t^f \cdot (1-\nu) \cdot Ln\sqrt{\pi / 4 \cdot V^f}}} \qquad (4)$$

where β denotes the coefficient of the stress concentration rate at the ends of the fibers, r indicates the fiber mean radius, l^f represents the fiber's weighted length, and ν is the Poisson's ratio of the matrix. The values for the PP, HDPE, and PTA were 0.36, 0.30 and 0.44, respectively (Pena *et al.* 2012; Espinach *et al.* 2013a; Reixach *et al.* 2013a). The efficiency factor η_e can be expressed as $\eta_e = \eta_o \cdot \eta_l$ and the identity was used to calculate η_l.

Tsai and Pagano model and Halpin and Tsai equations

The Tsai and Pagano model (Eq. 9) and the Halpin and Tsai equations (Eq. 10, 11) (Halpin and Pagano 1969; Halpin and Tsai 1969) can be also used to predict the intrinsic Young's modulus of the reinforcements. In this case, the equations were used to back-calculate the Young's modulus of the composite, using the intrinsic Young's modulus of the fibers computed by the Hirsh model. The stiffness in the fiber direction is given by:

$$E_t^C = \frac{3}{8}E^{11} + \frac{5}{8}E^{22} \qquad (5)$$

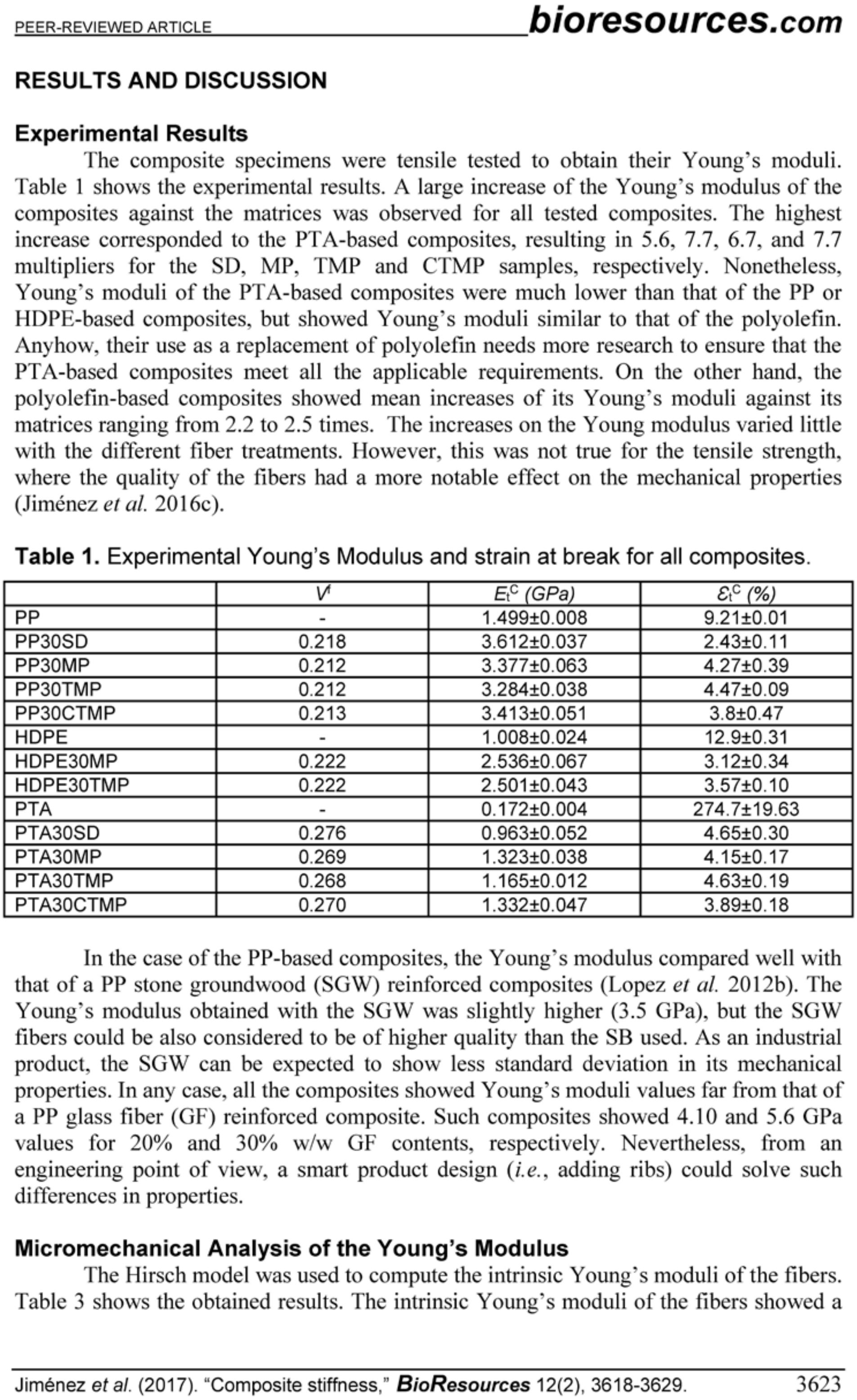
Here, E^{11} and E^{22} are the longitudinal and transversal elastic modulus, calculated by the Halpin –Tsai equations (Espinach *et al.* 2013b):

$$\eta_l = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2\left(l^f / d^f\right)} \quad (6a), \qquad E^{22} = \frac{1 + 2\eta_t \cdot V^f}{1 - \eta_t V^f} E_t^m \quad (6b)$$

Parameters η_l and η_t are given by,

$$\eta_l = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2\left(l^f / d^f\right)} \quad (7a), \qquad \eta_t = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2} \quad (7b)$$

where l^f and d^f represent the length and diameter of the SB, respectively.



RESULTS AND DISCUSSION

Experimental Results

The composite specimens were tensile tested to obtain their Young's moduli. Table 1 shows the experimental results. A large increase of the Young's modulus of the composites against the matrices was observed for all tested composites. The highest increase corresponded to the PTA-based composites, resulting in 5.6, 7.7, 6.7, and 7.7 multipliers for the SD, MP, TMP and CTMP samples, respectively. Nonetheless, Young's moduli of the PTA-based composites were much lower than that of the PP or HDPE-based composites, but showed Young's moduli similar to that of the polyolefin. Anyhow, their use as a replacement of polyolefin needs more research to ensure that the PTA-based composites meet all the applicable requirements. On the other hand, the polyolefin-based composites showed mean increases of its Young's moduli against its matrices ranging from 2.2 to 2.5 times. The increases on the Young modulus varied little with the different fiber treatments. However, this was not true for the tensile strength, where the quality of the fibers had a more notable effect on the mechanical properties (Jiménez *et al.* 2016c).

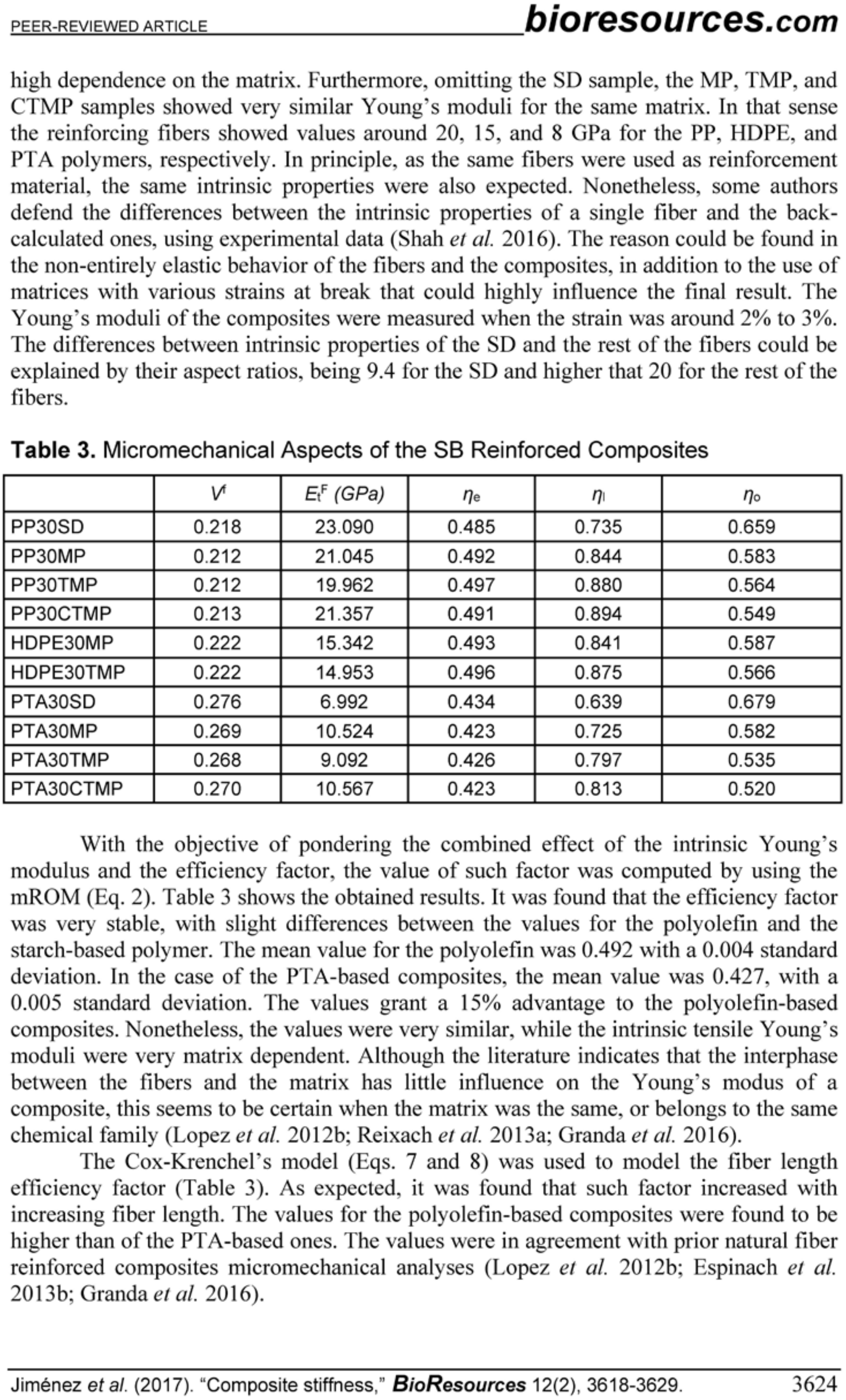
Table 1. Experimental Young's Modulus and strain at break for all composites.

	V^f	E_t^C (GPa)	ε_t^C (%)
PP	-	1.499±0.008	9.21±0.01
PP30SD	0.218	3.612±0.037	2.43±0.11
PP30MP	0.212	3.377±0.063	4.27±0.39
PP30TMP	0.212	3.284±0.038	4.47±0.09
PP30CTMP	0.213	3.413±0.051	3.8±0.47
HDPE	-	1.008±0.024	12.9±0.31
HDPE30MP	0.222	2.536±0.067	3.12±0.34
HDPE30TMP	0.222	2.501±0.043	3.57±0.10
PTA	-	0.172±0.004	274.7±19.63
PTA30SD	0.276	0.963±0.052	4.65±0.30
PTA30MP	0.269	1.323±0.038	4.15±0.17
PTA30TMP	0.268	1.165±0.012	4.63±0.19
PTA30CTMP	0.270	1.332±0.047	3.89±0.18

In the case of the PP-based composites, the Young's modulus compared well with that of a PP stone groundwood (SGW) reinforced composites (Lopez *et al.* 2012b). The Young's modulus obtained with the SGW was slightly higher (3.5 GPa), but the SGW fibers could be also considered to be of higher quality than the SB used. As an industrial product, the SGW can be expected to show less standard deviation in its mechanical properties. In any case, all the composites showed Young's moduli values far from that of a PP glass fiber (GF) reinforced composite. Such composites showed 4.10 and 5.6 GPa values for 20% and 30% w/w GF contents, respectively. Nevertheless, from an engineering point of view, a smart product design (*i.e.*, adding ribs) could solve such differences in properties.

Micromechanical Analysis of the Young's Modulus

The Hirsch model was used to compute the intrinsic Young's moduli of the fibers. Table 3 shows the obtained results. The intrinsic Young's moduli of the fibers showed a



high dependence on the matrix. Furthermore, omitting the SD sample, the MP, TMP, and CTMP samples showed very similar Young's moduli for the same matrix. In that sense the reinforcing fibers showed values around 20, 15, and 8 GPa for the PP, HDPE, and PTA polymers, respectively. In principle, as the same fibers were used as reinforcement material, the same intrinsic properties were also expected. Nonetheless, some authors defend the differences between the intrinsic properties of a single fiber and the back-calculated ones, using experimental data (Shah *et al.* 2016). The reason could be found in the non-entirely elastic behavior of the fibers and the composites, in addition to the use of matrices with various strains at break that could highly influence the final result. The Young's moduli of the composites were measured when the strain was around 2% to 3%. The differences between intrinsic properties of the SD and the rest of the fibers could be explained by their aspect ratios, being 9.4 for the SD and higher that 20 for the rest of the fibers.

Table 3. Micromechanical Aspects of the SB Reinforced Composites

	V^f	E_t^F (GPa)	η_e	η_l	η_o
PP30SD	0.218	23.090	0.485	0.735	0.659
PP30MP	0.212	21.045	0.492	0.844	0.583
PP30TMP	0.212	19.962	0.497	0.880	0.564
PP30CTMP	0.213	21.357	0.491	0.894	0.549
HDPE30MP	0.222	15.342	0.493	0.841	0.587
HDPE30TMP	0.222	14.953	0.496	0.875	0.566
PTA30SD	0.276	6.992	0.434	0.639	0.679
PTA30MP	0.269	10.524	0.423	0.725	0.582
PTA30TMP	0.268	9.092	0.426	0.797	0.535
PTA30CTMP	0.270	10.567	0.423	0.813	0.520

With the objective of pondering the combined effect of the intrinsic Young's modulus and the efficiency factor, the value of such factor was computed by using the mROM (Eq. 2). Table 3 shows the obtained results. It was found that the efficiency factor was very stable, with slight differences between the values for the polyolefin and the starch-based polymer. The mean value for the polyolefin was 0.492 with a 0.004 standard deviation. In the case of the PTA-based composites, the mean value was 0.427, with a 0.005 standard deviation. The values grant a 15% advantage to the polyolefin-based composites. Nonetheless, the values were very similar, while the intrinsic tensile Young's moduli were very matrix dependent. Although the literature indicates that the interphase between the fibers and the matrix has little influence on the Young's modus of a composite, this seems to be certain when the matrix was the same, or belongs to the same chemical family (Lopez *et al.* 2012b; Reixach *et al.* 2013a; Granda *et al.* 2016).

The Cox-Krenchel's model (Eqs. 7 and 8) was used to model the fiber length efficiency factor (Table 3). As expected, it was found that such factor increased with increasing fiber length. The values for the polyolefin-based composites were found to be higher than of the PTA-based ones. The values were in agreement with prior natural fiber reinforced composites micromechanical analyses (Lopez *et al.* 2012b; Espinach *et al.* 2013b; Granda *et al.* 2016).

Once the fiber length efficiency factor was known, it was possible to compute the value of the fiber orientation efficiency factor, by the ratio between η_e and η_l. Table 3 shows the results. It was found that such factor was less matrix-dependent and more fiber typology-dependent. The values of the orientation efficiency factor decreased against the intensity of the treatments and the length of the fibers. Anyhow, when the SD-based composites were discarded, the value was very steady. The values of length and orientation efficiency factor, when η_e is stable, could be read as the factor having the greatest influence on the Young's modulus of the composite.

A very interesting study by Fukuda and Kawata (1974) established a connection between the fiber orientation angle and a defined limit angle (α_o). The cited authors propose different fiber distributions inside the matrix and then compute the fiber orientation factor from such limit angle:

Rectangular distribution:

$$\eta_O = \frac{\sin(\alpha_O)}{\alpha_O}\cdot\left(\frac{3-\nu}{4}\cdot\frac{\sin(\alpha_O)}{\alpha_O}+\frac{1-\nu}{4}\cdot\frac{\sin(3\alpha_O)}{3\alpha_O}\right) \tag{8}$$

Triangular distribution:

$$\eta_O = 4\cdot\frac{1-\cos(\alpha_O)}{\alpha_O^2}\cdot\left(\frac{3-\nu}{4}\cdot\frac{1-\cos(\alpha_O)}{\alpha_O^2}+\frac{1+\nu}{4}\cdot\frac{1-\cos(3\alpha_O)}{9\alpha_O^2}\right) \tag{9}$$

These equations were used to compute the limit angle. Then, an orientation parameter (f_p) suggested by Sanomura and Kawamura (2003) (Eq. 10) was used to compute the mean orientation angle of the fibers inside the composite (α) (Table 4).

$$f_p = \frac{\sin(2\alpha_O)}{2\alpha_O} = 2\cdot\cos^2(\alpha)-1 \tag{10}$$

Table 4. Limit Angle and Mean Orientation Angle of the Fibers for the Rectangular and Triangular Distributions

	Rectangular		Triangular	
	α_o	α	α_o	α
PP30SD	42.4	23.9	62.0	33.7
PP30MP	48.6	27.1	71.8	38.1
PP30TMP	50.1	27.9	74.4	39.2
PP30CTMP	51.4	28.5	76.4	40.1
HDPE30MP	49.0	27.3	72.9	38.4
HDPE30TMP	50.7	28.2	75.2	39.6
PTA30SD	40.1	22.6	58.3	32.0
PTA30MP	47.7	26.6	70.5	37.6
PTA30TMP	51.1	28.6	76.8	40.2
PTA30CTMP	52.8	29.2	78.9	41.1

It was found that, independently of the fiber distribution, the SD-based composites showed the lowest orientation angles. The reason could be due to its lower aspect ratio. On the other hand, the MP, TMP, and CTMP fibers showed similar orientation angles, regardless of the fiber distribution. The mean orientation angles were 28.05º ± 0.871 and 39.4º ± 1.191, for the rectangular and triangular distribution, respectively. If the value is compared with orientation angle obtained from the micromechanical analysis of the tensile strength (41.9º), the most similar orientation belongs to the triangular distribution hypothesis (Jimenez *et al.* 2004; Jiménez *et al.* 2016a).

Finally, the Tsai and Pagano model, and the Halpin and Tsai equations were used to compute a theoretical Young's modulus of the composites. The intrinsic Young's moduli of the fibers computed by the Hirsh equation were used (Tables 3 and 5). The Halpin and Tsai equations, contrary to the Hirsch equation, account for some morphological properties of the fibers. Table 5 shows the obtained results.

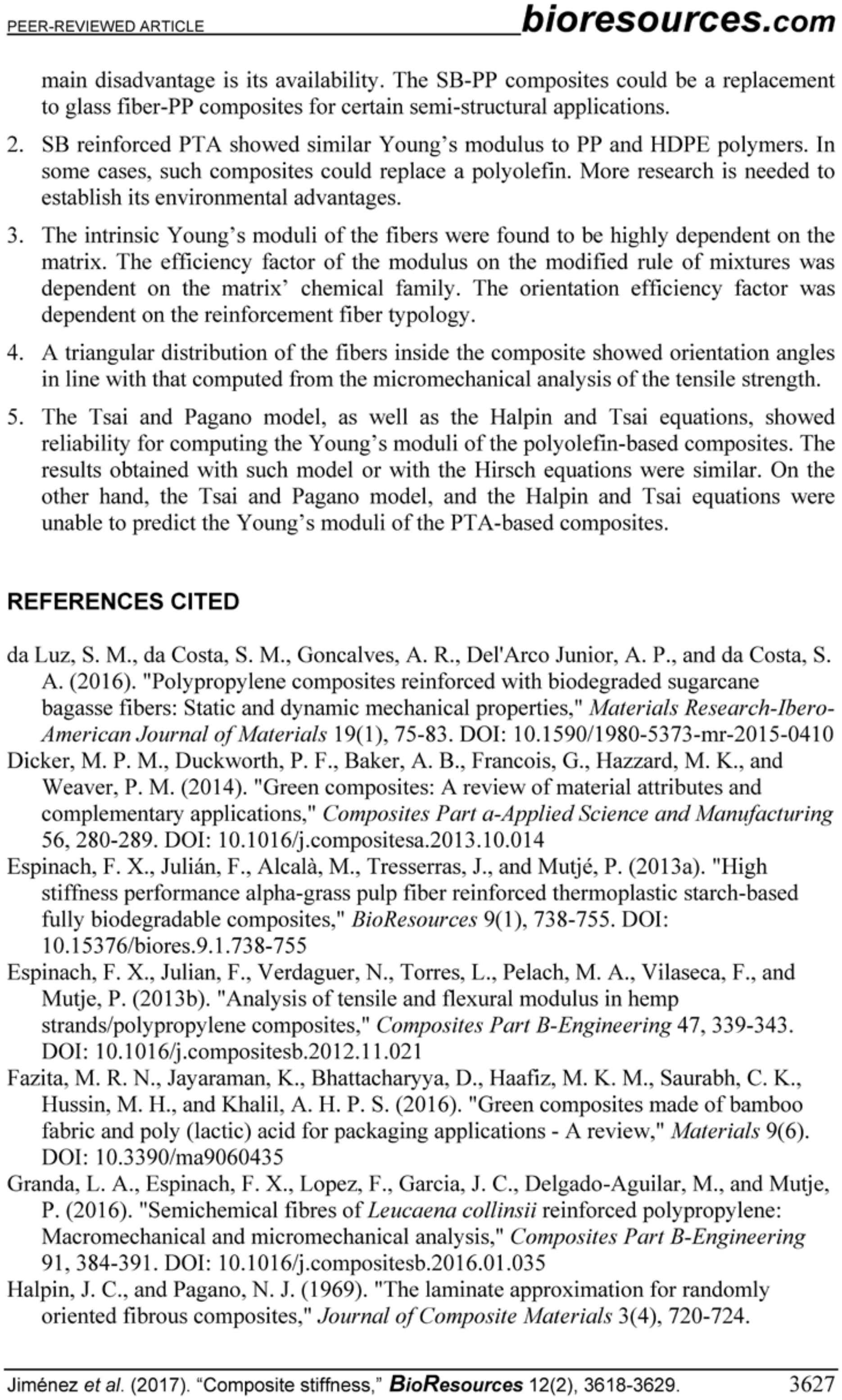
Table 5. Theoretical Young's Moduli of the Composites Computed by Using the Tsai and Pagano Model, and the Halpin and Tsai Equations

	E_t^F *(GPa)*	E_t^C *(GPa)*	E_t^{C*} *(GPa)*	*Error*	*Error (%)*
PP30SD	23.090	3.61	3.25	0.36	11.08%
PP30MP	21.045	3.38	3.32	0.06	1.81%
PP30TMP	19.962	3.28	3.29	-0.01	0.30%
PP30CTMP	21.357	3.41	3.40	0.01	0.29%
HDPE30MP	15.342	2.54	2.50	0.04	1.60%
HDPE30TMP	14.953	2.50	2.50	0.00	0.00%
PTA30SD	6.992	0.96	0.57	0.39	68.42%
PTA30MP	10.524	1.32	0.78	0.54	69.23%
PTA30TMP	9.092	1.16	0.77	0.39	50.65%
PTA30CTMP	10.567	1.33	0.84	0.49	58.33%

It was found that the Tsai and Pagano model, and the Halpin and Tsai equations predicted very well the Young's moduli of the polyolefin-based composites. In fact, the percentage errors, excluding the SD, were very low, and inside the standard deviations of the experimental Young's moduli. On the other hand, the predicted Young's moduli of the PTA-based composites showed high error percentages. A later analysis of the Halpin and Tsai equations showed that when the Young's modulus of the matrix was lower than 1, the model showed difficulties in converging with the experimental results.

CONCLUSIONS

1. Sugarcane bagasse reinforced polyolefin composites showed Young's moduli similar to that of high quality natural fiber reinforced polyolefin. The main advantages of SB are its low cost, and little need of treatments, for preparing SD and MP samples. The



main disadvantage is its availability. The SB-PP composites could be a replacement to glass fiber-PP composites for certain semi-structural applications.

2. SB reinforced PTA showed similar Young's modulus to PP and HDPE polymers. In some cases, such composites could replace a polyolefin. More research is needed to establish its environmental advantages.
3. The intrinsic Young's moduli of the fibers were found to be highly dependent on the matrix. The efficiency factor of the modulus on the modified rule of mixtures was dependent on the matrix' chemical family. The orientation efficiency factor was dependent on the reinforcement fiber typology.
4. A triangular distribution of the fibers inside the composite showed orientation angles in line with that computed from the micromechanical analysis of the tensile strength.
5. The Tsai and Pagano model, as well as the Halpin and Tsai equations, showed reliability for computing the Young's moduli of the polyolefin-based composites. The results obtained with such model or with the Hirsch equations were similar. On the other hand, the Tsai and Pagano model, and the Halpin and Tsai equations were unable to predict the Young's moduli of the PTA-based composites.

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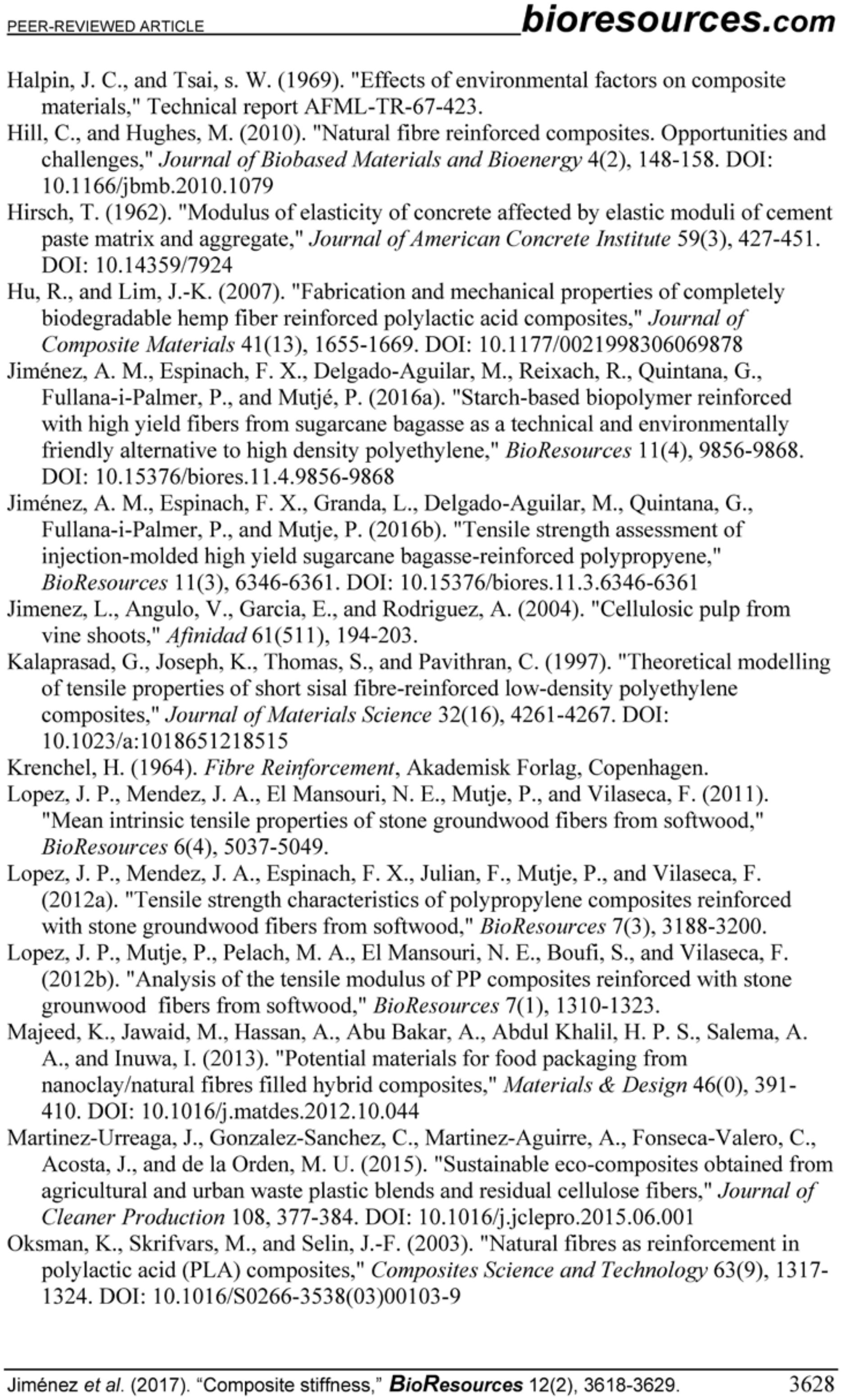

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4.5. Cellulose Nanofibers Modified with Alkyl Ketene Dimer for Oil Absorbent Aerogels

CELLULOSE CHEMISTRY AND TECHNOLOGY

CELLULOSE NANOFIBERS MODIFIED WITH ALKYL KETENE DIMER FOR OIL ABSORBENT AEROGELS

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Nanofibrillated cellulose consists of interconnected cellulose nanofibers, isolated from wood or agricultural byproducts, which leads to a three dimensional, porous and flexible structure. In this sense, the present work aims to develop hydrophobic aerogels for oil absorbing. Different percentages of alkyl ketene dimer (AKD) were added to the cellulose nanofiber (CNF) gel in order to partially hydrophobize the surface thereof. After mechanical stirring in an Ultraturrax and two cycles of sonication at 80 watts for 2 minutes, the CNF gel was poured into aluminum dishes and frozen at -80ºC for two hours. Then, the samples were freeze-dried for 48 hours. Water and oil absorption capacity was determined both under static and dynamic conditions in an oil-water mixture.

Keywords: aerogel, cellulose nanofibers, sugarcane bagasse, oil absorption

INTRODUCTION

Cleaning oil spills in a marine environment is a challenging task. Nowadays, several methods are used, such as the collection of the oil on the water surface (taking advantage of their different densities), dispersing oil in water easing its natural degradation or *in situ* burning.[1]None of the above-mentioned methods seems to be efficient nor environment-friendly. In this sense, many efforts have been made to solve this issue, such as depositing sawdust on the water-oil mix surface with the purpose of removing the hydrophobic component. However, sawdust also absorbs water, which makes its reusequite difficult.[2] More recently, silica aerogels,[3,4] carbon nanotubes and even carbon nanotube aerogels,[5,6] manganese oxide fiber membranes,[7] among other materials, have been used for oil removal. However, the above-mentioned materials still present the drawback of their non-renewable nature and their presence is incipient.

Cellulose nanofibers (CNFs) have become one of the main topics of research among cellulose and polymer scientists and techniciansin recent years. Nanocellulose offers a wide range of applications, such as in paper reinforcement,[8-11] films,[12,13] biomedicine,[14-16] among others. Moreover, nanocellulose is also attractive because it is based on renewable and abundant resources and can be processed on large scale using well-established pulp, paper and wood industry methods. Among all the explored applications, aerogels made of CNF are a product of interest due to their lightweight, great specific surface and their high porosity. Moreover, CNF aerogels present great mechanical properties, which gives them remarkable dimensional stability. CNF, in its native form, has a highly hydrophilic character (even greater than that of sawdust), whichalso makesits use for oil removaldifficult. In this sense, methods for CNF modification areunder study and are mainly focused on the hydrophobization of its surface. There is some literature available reporting on themodification of CNF through silanation[17] and acetylationtechniques.[18] The main drawback of these methods is the use of organic solvents, which at first sight, makes difficult their implementation on a large scale mainly because of the strict safety regulations that these products are forced to comply with.

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Alkyl ketene dimer (AKD) is a product broadly used in the papermaking industry with the purpose of hydrophobizing papers that are supposed to be used under wet conditions or for applications where it is imperative that the dimensional stability should remain constant in the presence of water, such as outdoor banners. The main mechanism of AKD is based on blocking the OH groups present on the cellulose surface and, thus, avoiding any hydrogen bond with water.

On the other hand, environmental concernsurge research to take advantage of the by-productsobtained from other activities, such is the case of sugarcane bagasse. Sugarcane bagasse is produced in large quantities by the sugar and alcohol industries in Brazil, China, Indonesia, Mexico, Colombia and other South-American countries.[19]After extracting the juice from sugarcane for biofuel production, what remains is called bagasse. The resulting stalks are commonly used for the production of pulp, paper, board and feed as a substitute for wood.

With these considerations, the present work aims to develop hydrophobic aerogels (made of TEMPO oxidized CNF and mechanical LCNF from bagasse) modified with alkyl ketene dimer (AKD) for use as oil remover. In addition, the present work suggests a possible application of these products for environmental purposes, such as oil discharges in the high seas.

EXPERIMENTAL

The experimental procedure followed in this work is reflected in Figure 1.

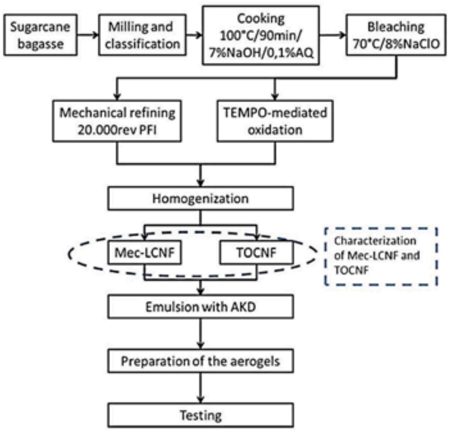


Figure 1: Experimental procedure of the present work

Preparation of chemical-thermomechanical pulp

Bagasse biomass, provided by the Pontifical Bolivarian University (Medellín, Colombia), was ground and classified in a knife mill with a 5mm pore size sieve at the bottom. The biomass was treated in an atmospheric reactor at 100 ºC for 90 minutes, with a NaOH charge of 7 wt% over dry weight of fiber and 0.1% of antraquinone. The liquor ratio was 10:1 with regard to the amount of fiber (dry weight).

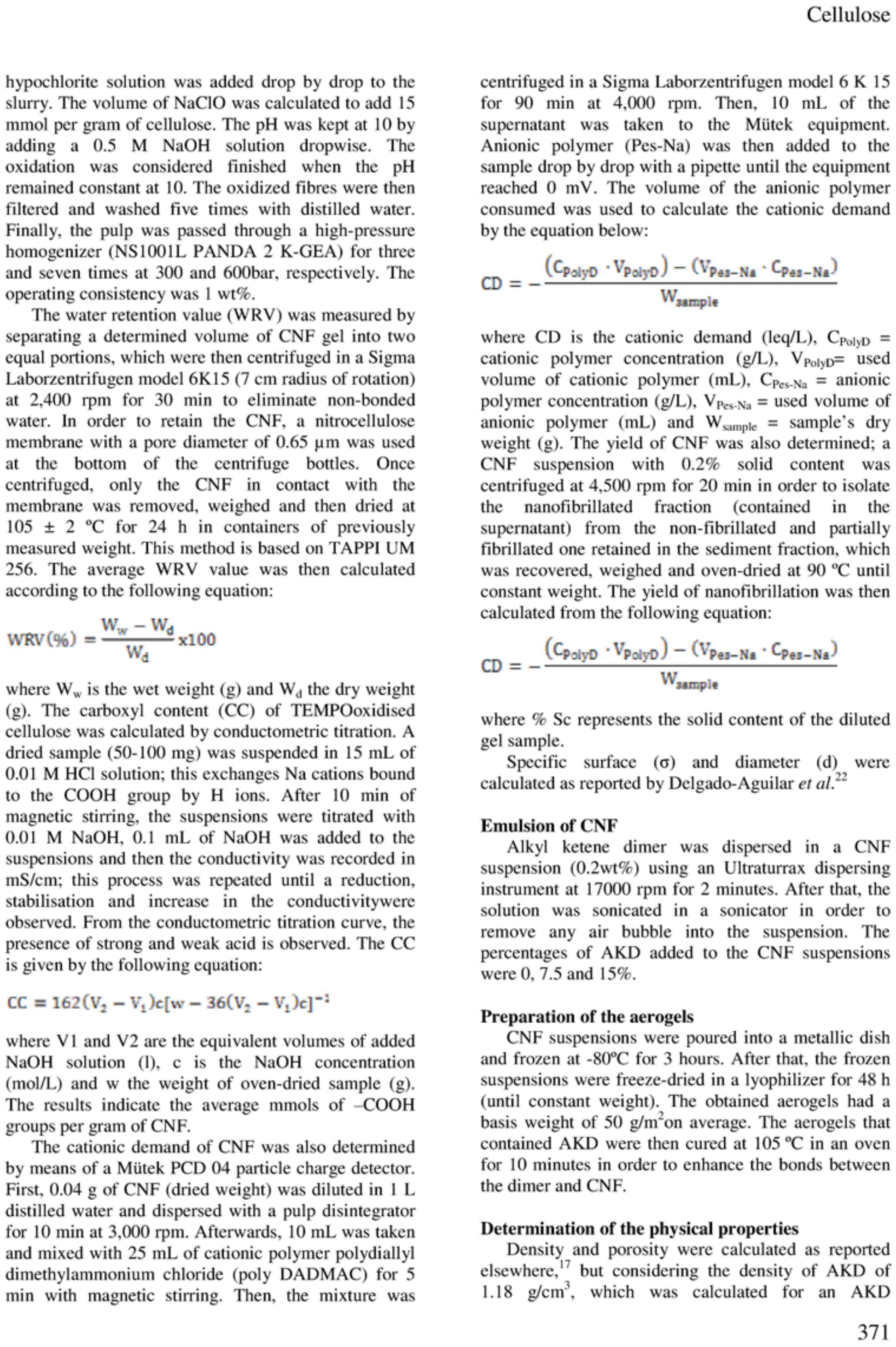
Pulp bleaching

The pulp was subjected to a bleaching process with a sodium hypochlorite charge of 8 wt% over dry weight of fiber at 10 wt% consistency and 70 ºC for six hours; a kappa number of 4was obtained.

Preparation of CNF

Mechanical LCNF (Mec-LCNF): the unbleached pulp was refined in a PFI refiner (IDM) at 20.000 revolutions and then passed through a high-pressure homogenizer (NS1001L PANDA 2 K-GEA) for three and seven times at 300 and 600 bar, respectively. The operating consistency was 1 wt%.

TEMPO oxidized CNF (TOCNF): the bleached pulp was oxidized following a method reported elsewhere,[20] varying the oxidation degree. In a typical experiment, 15 g of cellulose fibres was dispersed in distilled water containing TEMPO (0.016 g per g of fibre) and NaBr (0.1 g per g of fibre). The mixture was stirred for 15 min in order to assure good dispersion of all the substances. After this, a 15% sodium



hypochlorite solution was added drop by drop to the slurry. The volume of NaClO was calculated to add 15 mmol per gram of cellulose. The pH was kept at 10 by adding a 0.5 M NaOH solution dropwise. The oxidation was considered finished when the pH remained constant at 10. The oxidized fibres were then filtered and washed five times with distilled water. Finally, the pulp was passed through a high-pressure homogenizer (NS1001L PANDA 2 K-GEA) for three and seven times at 300 and 600bar, respectively. The operating consistency was 1 wt%.

The water retention value (WRV) was measured by separating a determined volume of CNF gel into two equal portions, which were then centrifuged in a Sigma Laborzentrifugen model 6K15 (7 cm radius of rotation) at 2,400 rpm for 30 min to eliminate non-bonded water. In order to retain the CNF, a nitrocellulose membrane with a pore diameter of 0.65 µm was used at the bottom of the centrifuge bottles. Once centrifuged, only the CNF in contact with the membrane was removed, weighed and then dried at 105 ± 2 ºC for 24 h in containers of previously measured weight. This method is based on TAPPI UM 256. The average WRV value was then calculated according to the following equation:

$$\mathrm{WRV}(\%) = \frac{W_w - W_d}{W_d} x100$$

where W_w is the wet weight (g) and W_d the dry weight (g). The carboxyl content (CC) of TEMPOoxidised cellulose was calculated by conductometric titration. A dried sample (50-100 mg) was suspended in 15 mL of 0.01 M HCl solution; this exchanges Na cations bound to the COOH group by H ions. After 10 min of magnetic stirring, the suspensions were titrated with 0.01 M NaOH, 0.1 mL of NaOH was added to the suspensions and then the conductivity was recorded in mS/cm; this process was repeated until a reduction, stabilisation and increase in the conductivitywere observed. From the conductometric titration curve, the presence of strong and weak acid is observed. The CC is given by the following equation:

$$\mathrm{CC} = 162(V_2 - V_1)c[w - 36(V_2 - V_1)c]^{-1}$$

where V1 and V2 are the equivalent volumes of added NaOH solution (l), c is the NaOH concentration (mol/L) and w the weight of oven-dried sample (g). The results indicate the average mmols of –COOH groups per gram of CNF.

The cationic demand of CNF was also determined by means of a Mütek PCD 04 particle charge detector. First, 0.04 g of CNF (dried weight) was diluted in 1 L distilled water and dispersed with a pulp disintegrator for 10 min at 3,000 rpm. Afterwards, 10 mL was taken and mixed with 25 mL of cationic polymer polydiallyl dimethylammonium chloride (poly DADMAC) for 5 min with magnetic stirring. Then, the mixture was centrifuged in a Sigma Laborzentrifugen model 6 K 15 for 90 min at 4,000 rpm. Then, 10 mL of the supernatant was taken to the Mütek equipment. Anionic polymer (Pes-Na) was then added to the sample drop by drop with a pipette until the equipment reached 0 mV. The volume of the anionic polymer consumed was used to calculate the cationic demand by the equation below:

$$\mathrm{CD} = -\frac{\left(C_{\mathrm{PolyD}} \cdot V_{\mathrm{PolyD}}\right) - \left(V_{\mathrm{Pes-Na}} \cdot C_{\mathrm{Pes-Na}}\right)}{W_{\mathrm{sample}}}$$

where CD is the cationic demand (leq/L), C_{PolyD} = cationic polymer concentration (g/L), V_{PolyD}= used volume of cationic polymer (mL), $C_{\mathrm{Pes\text{-}Na}}$ = anionic polymer concentration (g/L), $V_{\mathrm{Pes\text{-}Na}}$ = used volume of anionic polymer (mL) and W_{sample} = sample's dry weight (g). The yield of CNF was also determined; a CNF suspension with 0.2% solid content was centrifuged at 4,500 rpm for 20 min in order to isolate the nanofibrillated fraction (contained in the supernatant) from the non-fibrillated and partially fibrillated one retained in the sediment fraction, which was recovered, weighed and oven-dried at 90 ºC until constant weight. The yield of nanofibrillation was then calculated from the following equation:

$$\mathrm{CD} = -\frac{\left(C_{\mathrm{PolyD}} \cdot V_{\mathrm{PolyD}}\right) - \left(V_{\mathrm{Pes-Na}} \cdot C_{\mathrm{Pes-Na}}\right)}{W_{\mathrm{sample}}}$$

where % Sc represents the solid content of the diluted gel sample.

Specific surface (σ) and diameter (d) were calculated as reported by Delgado-Aguilar *et al.*[22]

Emulsion of CNF

Alkyl ketene dimer was dispersed in a CNF suspension (0.2wt%) using an Ultraturrax dispersing instrument at 17000 rpm for 2 minutes. After that, the solution was sonicated in a sonicator in order to remove any air bubble into the suspension. The percentages of AKD added to the CNF suspensions were 0, 7.5 and 15%.

Preparation of the aerogels

CNF suspensions were poured into a metallic dish and frozen at -80ºC for 3 hours. After that, the frozen suspensions were freeze-dried in a lyophilizer for 48 h (until constant weight). The obtained aerogels had a basis weight of 50 g/m^{2}on average. The aerogels that contained AKD were then cured at 105 ºC in an oven for 10 minutes in order to enhance the bonds between the dimer and CNF.

Determination of the physical properties

Density and porosity were calculated as reported elsewhere,[17] but considering the density of AKD of 1.18 g/cm^3, which was calculated for an AKD suspension in water at 17.85wt% consistency. Basis weight was also calculated taking into account the surface of the aerogel and its weight.

Preliminary tests

In order to have a preliminary idea of the character of the aerogels, a drop of colored water (with disulfine blue) and a drop of motor oil wereput on the aerogel surface. Moreover, a mixture of oil and colored water was prepared on a Petri dish and a modified and unmodified aerogel was placed on the liquid surface.

Determination of the oil absorption potential

Two different experiments were carried out in order to bear out the oil absorption capacity of the produced aerogels: (i) under static conditions and (ii) under dynamic conditions.

Static conditions: 100mL of oil was added to 900mL of water, having a total volume of 1L. Aerogels were suspended in the liquid mixture for 10 minutes.

Dynamic conditions: 100mL of oil was added to 900mL of water, having a total volume of 1L. The mixture was stirred at 500rpm during the entire test. Aerogels were suspended in the liquid mixture for 10 minutes.

Aerogels were weighed and then dried at 105ºC in order to evaporate the water. Finally, the aerogels were weighed again in order to assess the amount of water evaporated.

RESULTS AND DISCUSSION

Table 1 shows the results of the characterization of Mec-LCNF and TOCNF.

TOCNF presented a lower degree of polymerization than Mec-LCNF. This is mainly due to the introduction of carboxylic groups into the cellulose chains during TEMPO-mediated oxidation. However, Mec-LCNF also presenteda low degree of polymerization in comparison with cellulose, that is about 2000 on average.[23] This indicates that the mechanical treatment (homogenization) also causes depolymerization and thus reduction of (nano)fiber length.

Water retention value results (WRV) indicatedthat TOCNF can chemically retain more water than Mec-LCNF, and this property influences the results of the static and dynamic tests on oil and water absorption of the aerogels. The percentage is expressed as the amount of water that the aerogels can retain per gram of (L)CNF, which means that TOCNF can retain 17 gH_2O/g, whereas Mec-LCNF can retain about 8.5 gH_2O/g. The cationic demand and carboxyl content are parameters related to the specific surface area of (L)CNF (σ). TOCNF presented higher carboxyl content due to the TEMPO-mediated oxidation process, which introducesthis negatively-charged group in the primary alcohol of carbon 6 atom of the cellulose chain. TEMPO-mediated oxidation of cellulose fibres allows obtaining nanofibre suspensions with yields of nanofibrillation higher than 90% after passing the suspension through high pressure homogenization/microfluidization; this means that most of the fibres have diametres within thenanometric scale. On the other hand, Mec-LCNF presented a lower yieldof nanofibrillation (about 30%). Overall results show thatTOCNF has better water affinity, bonding capacity and homogeneity than its mechanicallyproduced counterparts.

Table 1
Characterization of the obtained (L)CNF

CNF type	DP	WRV (%)	CC (μeq-g/g)	CD (μeq-g/g)	Yield (%)	σ (m^2/g)	d (nm)
TOCNF	488	1706	881.3	1235	95.1	172.61	14.47
Mec-LCNF	803.6	847	76.6	216.38	31.0	68.18	36.67

Table 2
Density and porosity of the aerogels produced in this study

CNF type	AKD (%)	Nomenclature	Density (g/cm^3)	Porosity (%)
TOCNF	0	TOCNF-0	0.0031	99.79
	7.5	TOCNF-7,5	0.0043	99.73
	15	TOCNF-15	0.0050	99.67
Mec-LCNF	0	Mec-LCNF-0	0.0089	99.40
	7.5	Mec-LCNF-7,5	0.0097	99.35
	15	Mec-LCNF-15	0.0107	99.29

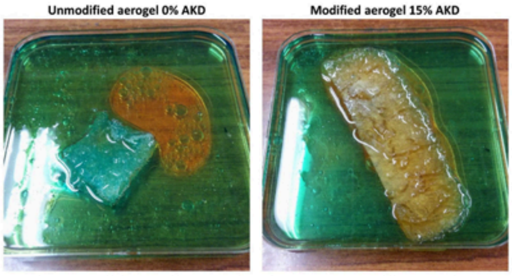


Figure 2: Different affinity of aerogels when suspended in an oil-water mixture

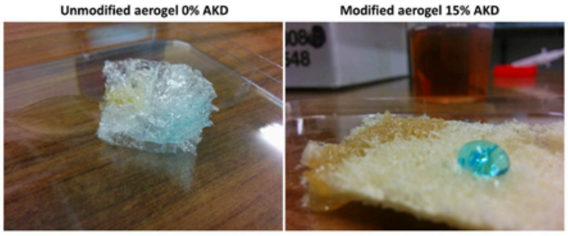


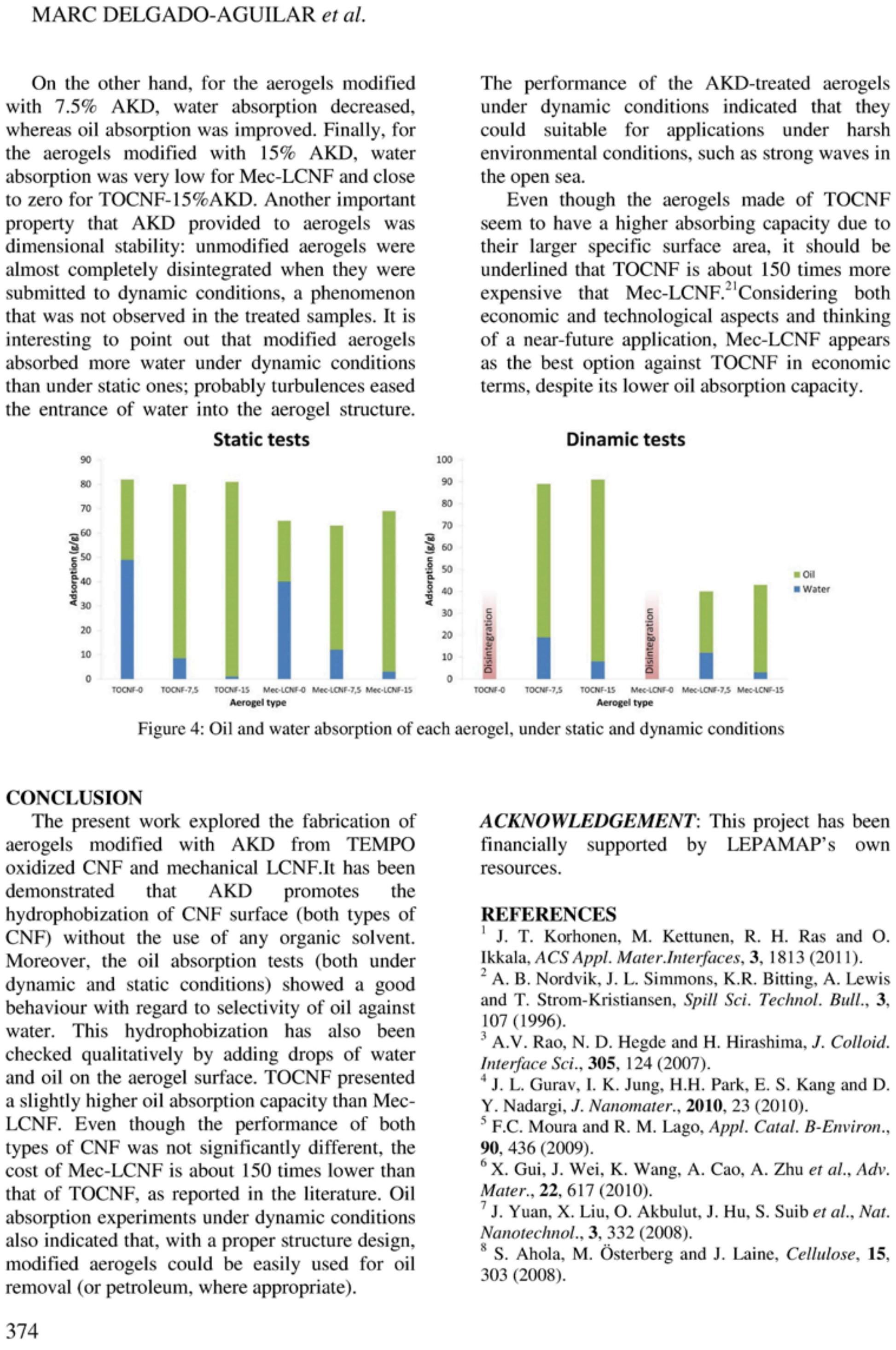
Figure 3: Drop shape for unmodified and AKD modified aerogels

Table 2 shows both parameters for the aerogels produced in the present study. Cellulose aerogels are characterized by their high porosity and low density, which make them an interesting absorbing material. The samples made of Mec-LCNF were denser than those produced from TOCNF. The main reason for this is that TOCNF has higher yield of nanofibrillation and specific surface area than Mec-LCNF; consequently, it has a better ability to create more expanded, highly porous three-dimensional networks that absorb liquids better. However, porosity was close to 100% in all aerogel samples produced, regardless of the CNF grade.

Aerogel density increased after AKD treatment and this increase was in relation to the amount of AKD added. Since the amount of CNF remained always constant for all types of aerogels, an increase in the AKD content produced denser samples. On the other hand, porosity remained without significant variations throughout the whole set of samples. The result seems to indicate that the presence of AKD did not affect the aerogel formation. However, by blocking the OH groups on the CNF surface, AKD reduces nanofibres water affinity, which enables aerogels to absorb mainly oil. Figure 2 shows how the unmodified aerogel prefers water against oil, while the one modified with 15% AKD has a greater affinity for oil.

The degree of hydrophobicity can be qualitatively assessed by the deposition of one drop of water (coloured) and one drop of oil on the aerogel surface (Figure 3).The left picture shows that both water and oil are absorbed into the structure of an untreated aerogel, probably by capillarity and, in the case of water, also by chemical affinity. However, the AKD-treated samples clearly show that hydrophobicity was successfully attained by reducing the chemical affinity between CNF and water.

Figure 4 shows that, both under static and dynamic conditions, aerogels made of TOCNF absorbed more water than those made of Mec-LCNF, mainly due to the higher water affinity that TOCNF develops after TEMPO oxidation. Overall unmodified aerogels absorbedmuch more water than oil under static conditions. This is mainly due to the water's lower viscosity, which allows water to penetrate the aerogel's porous structure; besides, during the experiment the samples stayed mainly floating on the top of the mixture and, due to the differences in density between oil and water, oil remained also on top, whichdid not allow better contactbetween the aerogel and the water.



On the other hand, for the aerogels modified with 7.5% AKD, water absorption decreased, whereas oil absorption was improved. Finally, for the aerogels modified with 15% AKD, water absorption was very low for Mec-LCNF and close to zero for TOCNF-15%AKD. Another important property that AKD provided to aerogels was dimensional stability: unmodified aerogels were almost completely disintegrated when they were submitted to dynamic conditions, a phenomenon that was not observed in the treated samples. It is interesting to point out that modified aerogels absorbed more water under dynamic conditions than under static ones; probably turbulences eased the entrance of water into the aerogel structure.

The performance of the AKD-treated aerogels under dynamic conditions indicated that they could suitable for applications under harsh environmental conditions, such as strong waves in the open sea.

Even though the aerogels made of TOCNF seem to have a higher absorbing capacity due to their larger specific surface area, it should be underlined that TOCNF is about 150 times more expensive that Mec-LCNF.[21]Considering both economic and technological aspects and thinking of a near-future application, Mec-LCNF appears as the best option against TOCNF in economic terms, despite its lower oil absorption capacity.

Figure 4: Oil and water absorption of each aerogel, under static and dynamic conditions

CONCLUSION

The present work explored the fabrication of aerogels modified with AKD from TEMPO oxidized CNF and mechanical LCNF.It has been demonstrated that AKD promotes the hydrophobization of CNF surface (both types of CNF) without the use of any organic solvent. Moreover, the oil absorption tests (both under dynamic and static conditions) showed a good behaviour with regard to selectivity of oil against water. This hydrophobization has also been checked qualitatively by adding drops of water and oil on the aerogel surface. TOCNF presented a slightly higher oil absorption capacity than Mec-LCNF. Even though the performance of both types of CNF was not significantly different, the cost of Mec-LCNF is about 150 times lower than that of TOCNF, as reported in the literature. Oil absorption experiments under dynamic conditions also indicated that, with a proper structure design, modified aerogels could be easily used for oil removal (or petroleum, where appropriate).

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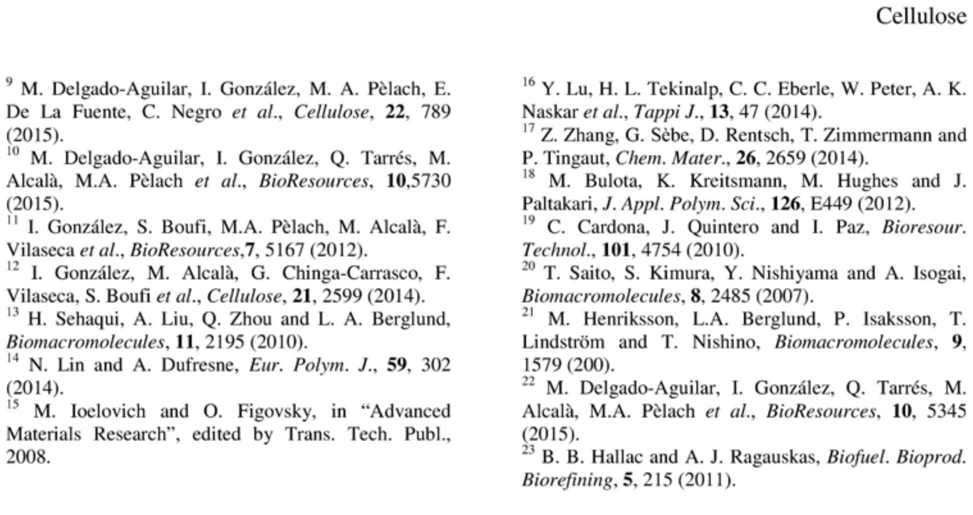

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5. DISCUSSION

Sugarcane bagasse is the residue of the extraction of sugarcane juice, and it is mainly used as a combustible material for supplying energy to sugarcane factories, as a pulp raw material in papermaking industries (Khakifirooz et al., 2013; Diab et al., 2015; Vargas-Radillo et al., 2015) , as a fiber in fiberboards (Ashori et al., 2009; Hoareau et al., 2006), and as reinforcement/filler for composite materials (mineral or degradable matrix-based) (Boontima et al., 2015; Cao et al., 2006; El-Fattah et al., 2015; Karim et al., 2013). The annual production of sugarcane reaches 184 million tons (Theng et al., 2016), and the amount of bagasse is usually 260 kg of moist bagasse per sugarcane ton (Lois-Correa, 2012). Consequently, bagasse fibers are a reliable source of fibers in tropical and subtropical regions.

Agricultural wastes, as well as wood, are mainly composed of cellulose, hemicellulose and lignin, and small amounts of other chemical components such as resin, fatty acids, triglycerides, sterols and steryl esters, usually classified as extractives (Johannsson, et al., 2002). Table 1 represents a comparison of the main components of bagasse with hardwood and softwood.

Table 4: Chemical composition of sugar cane raw material, softwood, and hardwood

Constituents	Sugarcane bagasse	Softwood*	Hardwood*
Cellulose (%)	36.1	40-45	38-49
Hemicellulose (%)	30.1	7-14	19-26
Lignin (%)	20.8	26-34	20-23
Extractives (%)	3.4	-	-
Ash (%)	1.6	<1	<1

*Literature (Gonzalez, et al., 2013)

As can be seen from Table 1 above, cellulose content in sugarcane bagasse is lower than in softwood and hardwood, while hemicellulose is higher, with values above of some straws like rice, rye, and oats (Rodríguez et al., 2008; Tarrés et al., 2017). Lignin, extractives, and ash content values were similar than other straws (Mousavi et al., 2013). It is possible to apply high yield treatments to this lignocellulosic material to obtain sawdust or reinforcing fibers for composites. These treatments mainly include mechanical pulping (MP), thermo-mechanical pulping (TMP), and chemical-thermomechanical pulping (CTMP) (Reixach et al., 2013a). Usually, thermal and chemical treatments involve the extraction of fiber components such as lignin and extractives (Li et al., 2001).

Therefore, in this work, the fibers providing from bagasse were used to papermaking, prepare composite materials and nano-fibrillated cellulose. The use of natural fibers as reinforcement of polyolefin is one of the main strengths of LEPAMAP research group, having an over 70 research papers in the scientific journal, book chapters, and patents in this issue.

5.1. Sugarcane bagasse for papermaking

Organosolv pulping

One of the most important parameters in papermaking is the drainability of the pulps because of its influence on the speed of the paper machine: the degree of drainability or Schopper Riegler degree is proportional to the amount of ethanolamine. Table 2 shows the yields, morphological properties, Schopper Riegler degrees and breaking lengths obtained for the bagasse pulps with different ethanolamine content.

Table 5: Yields, morphological properties and Schopper-Riegler degrees of organosolv pulps

Ethanolamine (%)	Yield (%)	°SR	l_w^f * (µm)	Diameter (µm)	Fines (%)
25	67.5	43	627	23.8	44.3
20	70.1	41	639	23.9	38.2
15	72.6	39	661	24.6	29.6
10	78.3	38	711	25.4	27.4
5	81.9	35	764	27.1	25.4
*Fiber length weighted in length					

Moreover, as presented in Table 2, solubilization of components such as hemicellulose and lignin caused a reduction in yield due to the amount of ethanolamine applied. The low yield should obtain stronger papers as it favors the bonds between the fibers. This attribute is reduced because more ethanolamine is required and more waste is generated. Also, the fiber diameter and length are reduced as treatment increases, acquiring magnitudes similar to those found by Flandez et al., (2012)

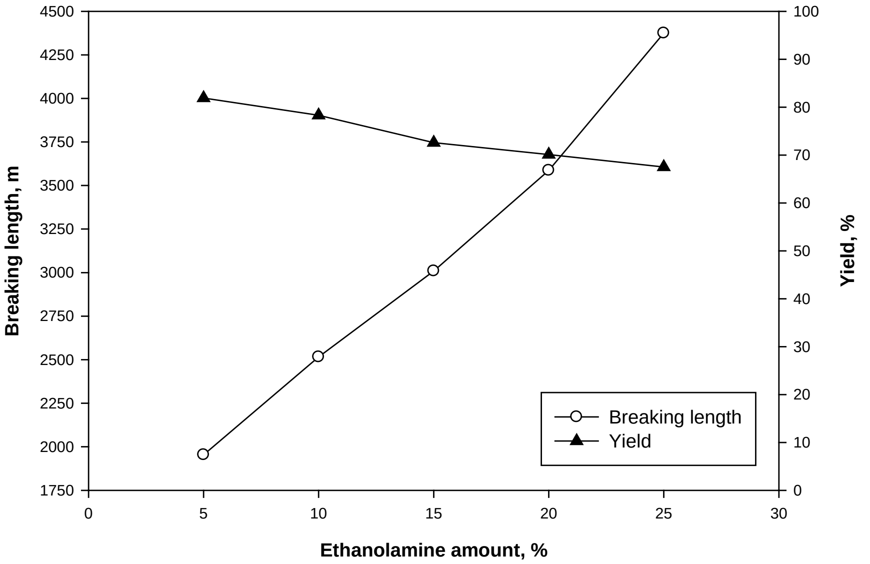

Figure 5: Evolution of breaking length and yield with the ethanolamine increase

The breaking length from Figure 1 decreases with the increase of ethanolamine amount. The breaking length obtained for the pulp with 5% ethanolamine has the same magnitude as the papers made from pulp bleached eucalyptus, with yields of pulps significantly lower (Delgado-Aguilar et al., 2015a González et al., 2012, Tarrés et al., 2016).

As a contrast, the bagasse was subjected to a different treatment, i.e., with NAOH-AQ. In this case, the obtained yield was 81.1%, the diameter was of the same magnitude (24.5 µm) and the length was lower (510 µm). Drainability and breaking length were similar to those obtained with organosolv pulp treated with 5% ethanolamine (33 ° SR and 1839 m).

Mechanical refining process

A mechanical refining process of 0 to 2000 revolutions of PFI was carried out for both pulps, organosolv, and NaOH-AQ. See Figure 2.

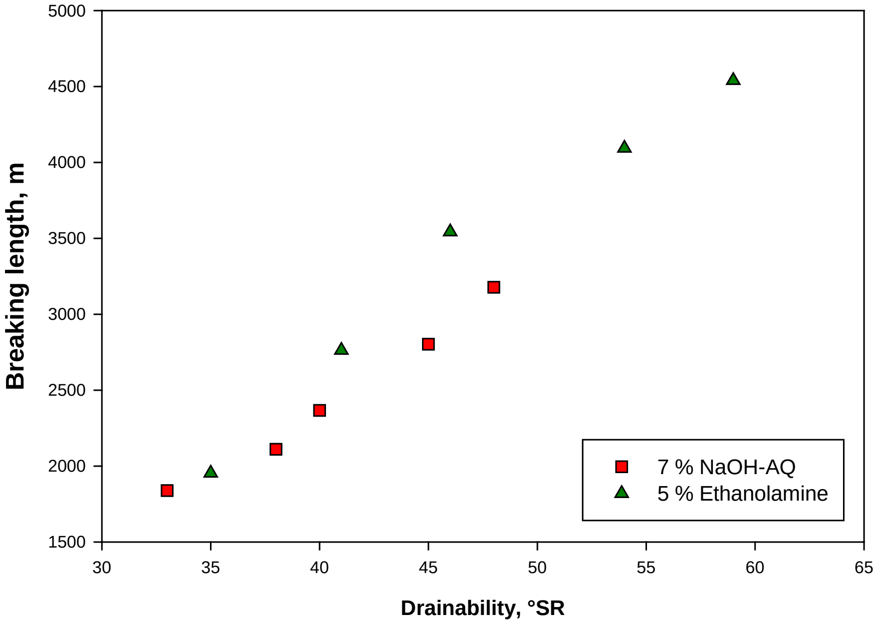

Figure 6: Evolution of breaking length of organosolv and NaOH-AQ pulps as function of the refining degree

Applying 1000 PFI revolutions to organosolv samples caused an increase of the length of rupture from 1954 to 3543 m (81% increase) and in the Schopper-Riegler degree from 35 to 46. With the same energy, the NaOH-AQ pulp increased from 1839 to 2367 m (29% increase), which reflects that an energy twice as higher should be applied to reach 3543m, but with a Schopper grade considerably increased; this is because the organosolv processes retain hemicellulases causing fibrillation during refining and swelling of the fibers, so that a value of 4540 m is achieved with the 2000 PFI revolutions.

Hybrid testliner and bagasse papers

As an option to the use of alternative raw materials, the preparation of hybrid paper, consisting of a mixture of 5% ethanolamine pulp and commercial testliner, was previously disintegrated and evaluated. This commercial testliner has a breaking length of 3655 m, which represents a similar value to that obtained from organosolv pulp at 1000 PFI revolutions. Due to the above, it can be said that the production of bagasse testliner is feasible, seeking to find greater mechanical properties.

Hybrid papers of organosolv pulps (1000 rev) and testliner (500 rev) are evaluated and shown in Figure 3.

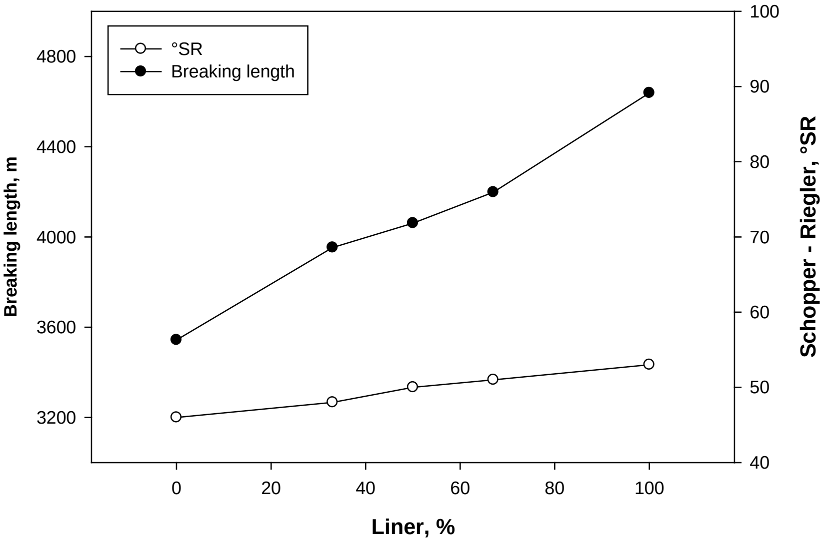

Figure 7: Evolution of breaking length and °SR as the amount of refined liner (500 rev) was increased.

The evolution of breaking length and Schopper degree shows that increase is visible by using 33% of organosolv pulp and other testliner, with a breaking length 4200 m. This sufficient behavior asserts the use of the hybrid paper to produce packaging papers.

5.2. Composite materials

The first published paper intended to research on the interphase between the bagasse fibers and a polypropylene matrix. It is known that the tensile strength of a composite depends greatly on: the nature of the fibers and the matrices, the dispersion of the fibers, the morphology of the reinforcement, the orientation of such reinforcement, and the quality of the interphase between the fibers and the matrix (Méndez et al., 2007; Lopez et al., 2012; Vallejos et al., 2012; Reixach et al., 2013).

Four types of sugarcane bagasse were prepared; sawdust (WF), and mechanical, thermomechanical and chemo-thermomechanical pulps (MP, TMP, CTMP). Preparing such reinforcement implies changes on the morphology and the chemical composition of the surface of the reinforcement, as well as different yields against the initial biomass. Table 3 shows the obtained yields and the morphological properties.

Table 6: Morphological Characterization of the Obtained Fibers

Test	Sawdust	MP	TMP	CTMP
Yield (%)	99.2	97.11	87.63	85.07
Fiber length* (µm)	261	521	602	685
Fiber diameter (µm)	27.73	24.02	26.57	25.45
Fines content** (%)	87.94	59.01	38.32	34.25
Aspect ratio	9.4	21.7	22.6	26.9

(Jiménez et al., 2016)

It was found that the length of the fibers increased inversely proportional to the process yield. This is in agreement with the published bibliography (Lopez et al., 2012; Reixach et al., 2013). The aspect ratio of the fibers, due to the slight changes in the diameters, evolved in the same direction as the length of the fibers. Hence, it was expected that the tensile strengthening capabilities of the reinforcement evolved positively with the severity of its treatments. In addition to the length increases, it was also known that the treatment modifies the chemical composition of the fiber's surfaces, decreasing the lignin contents and increasing the presence of OH groups on such surfaces (Reixach et al., 2013; Reixach et al., 2015). These four types of sugarcane bagasse- based reinforcement were used all along the composite materials research stage.

The first prepared composites were based on a polypropylene matrix. Such matrix is hydrophobic, while the reinforcements are hydrophilic, the cause of a chemical incompatibility between the phases. In order to obtain good interphases, and attending to the published literature, a maleic anhydride-grafted polypropylene (MAPP) was used as coupling agent (Lopez et al., 2012; Serrano et al., 2013; Serrano et al., 2014). Thus, composite materials with a 30% wt. of the reinforcements and MAPP contents in the range from 0 to 10% were prepared and tensile tested. Figure 4 shows the behavior of the tensile strength of the different composites against the MAPP contents.

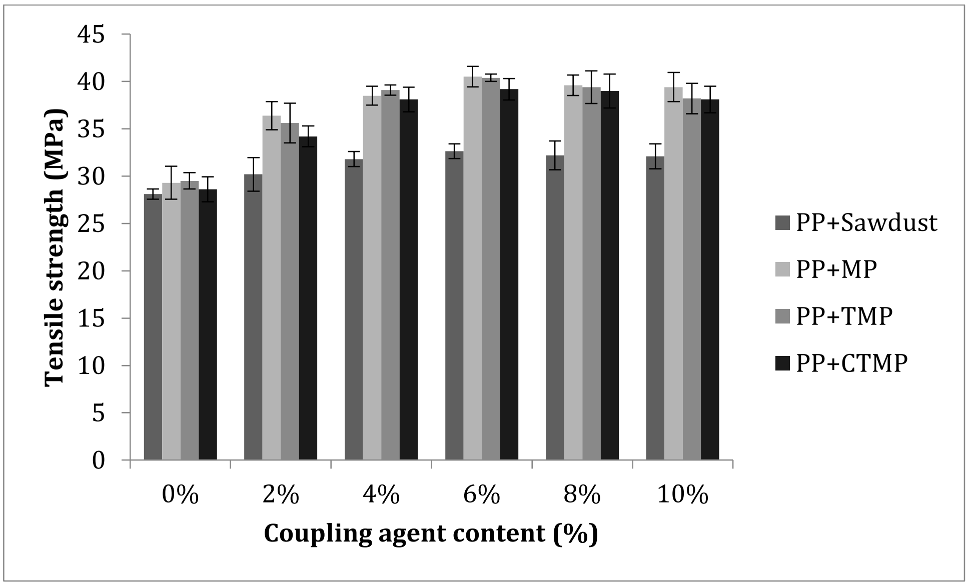

Figure 8*:* Composite tensile strength versus MAPP content*.

*(Jiménez et al., 2016)

It was found that the tensile strength of the composites increased quickly with small percentages of MAPP. Then, evolved positively, reaching its maximum values for a 6% wt. of MAPP content. Then, the tensile strength tended to decrease. The literature suggests that higher MAPP contents derive in the self-entanglement of the MAPP, decreasing the composite strength (Bledzki et al., 1999; Franco-Marques et al., 2011). This content of coupling agent was used to prepare the rest of the polyolefin-based composites.

Once the interphase was enhanced, it started the research on the quality of such interphase. To do so, different micro mechanics' models were used. The first model was a Fiber Tensile Strength Factor (*FTSF*). Such factor is based on a modified rule of mixtures (mRoM) for the tensile strength:

$$\sigma_t^C = f_c \cdot \sigma_t^F \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \quad [1]$$

Where f_C is the compatibility factor; in the case of favorable interfaces, f_c is supposed to be 0.2. σ_t^F and σ_t^C are the ultimate intrinsic tensile strength of fiber and the tensile strength of the composite material, and σ_t^{m*} is the tensile strength of the matrix at the breaking point of the composite.

The *FTSF* intends to measure the isolated contribution of the fibers to the tensile strength of the composite against its volume fraction, and could be formulated as (Lopez et al., 2012; Reixach et al., 2013):

$$\sigma_t^C - (1 - V^F)\sigma_t^{m*} = f_c \cdot \sigma_t^F V^F = FTSF \cdot V^F \quad [2]$$

Table 4 shows all the values need to use the model.

Table 7: Tensile strength of the sugarcane bagasse- based composites adding a 30% of reinforcement and a 6% of the coupling agent.

Composite	V^F	σ_τ^X	ε_t^c	$\sigma_\tau^{\mu*}$
		(MPa)	(%)	(MPa)
PP	0	27.60 ± 0.35	9.30 ± 0.01	-
PP + 30% Sawdust	0.218	32.63 ± 0.77	2.11 ± 0.07	16.01
PP + 30% MP	0.212	40.51 ± 1.09	3.71 ± 0.26	20.22
PP + 30% TMP	0.212	40.39 ± 0.39	3.89 ± 0.06	20.4
PP + 30% CTMP	0.213	39.18 ± 1.13	3.30 ± 0.31	19.59

The contribution of the matrix to the tensile strength of the composite at the failure point of the composite was computed by using a polynomial regression of the stress strain curve of the matrix:

$$\sigma_t^{m*} = -0.0159(\varepsilon_t^C)^4 + 0.3721(\varepsilon_t^C)^3 - 3.674(\varepsilon_t^C)^2 + 14.8953(\varepsilon_t^C) + 0.0493 \qquad [3]$$

Figure 5 shows the values of the FTSF for every kind of reinforcement. The FTSF matches the slope of the regression curve passing through the (0,0) point.

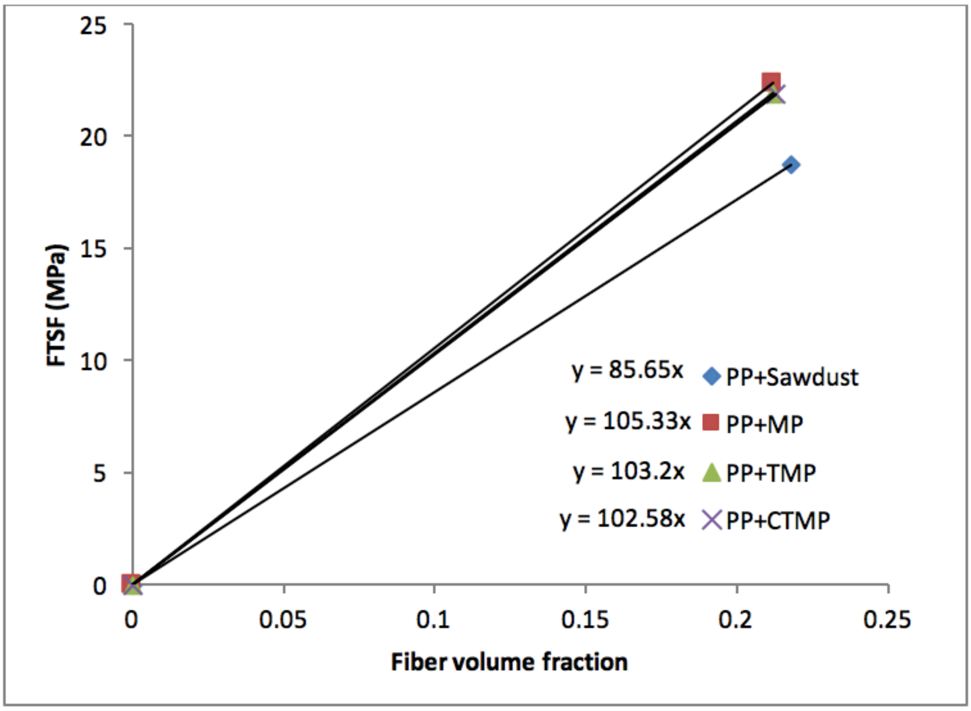

Figure 9: Fiber Tensile Strength Factor for the sugarcane bagasse fibers

Unlike the mRoM, the *FTSF* could be solved without knowing the intrinsic tensile strength of the fibers or the coupling factor. It was found that the MP showed the highest strengthening capabilities, although was slightly different to that of the TMP and the CTMP. On the other hand, the WF showed noticeably lower strengthening power (25% less).

Then, a value of 0.2 for the coupling factor was proposed in order to obtain the intrinsic tensile strength of the fibers by using the mRoM (Equation 1), being 461, 579, 573 and 558 MPa, for the WF, MP, TMP, and CTMP, respectively.

As it was assumed a good interphase, the Von Mises criteria were used to compute the interfacial shear strength of the composites, being 15.93 MPa.

These values were used with the modified Kelly and Tyson model in order to obtain, the critical length and the orientation factor (Kelly et al., 1965; Bowyer et al., 1972; Li et al., 2009; Vallejos et al., 2012). First, the equation was solved assuming an orientation factor with unitary value (aligned composite), and then the ratio between the theoretical aligned composite strength and the experimental strength of the composite was assumed to be the value of the orientation factor.

Figure 6 shows the fiber length distribution for every kind of sugarcane bagasse-based reinforcement.

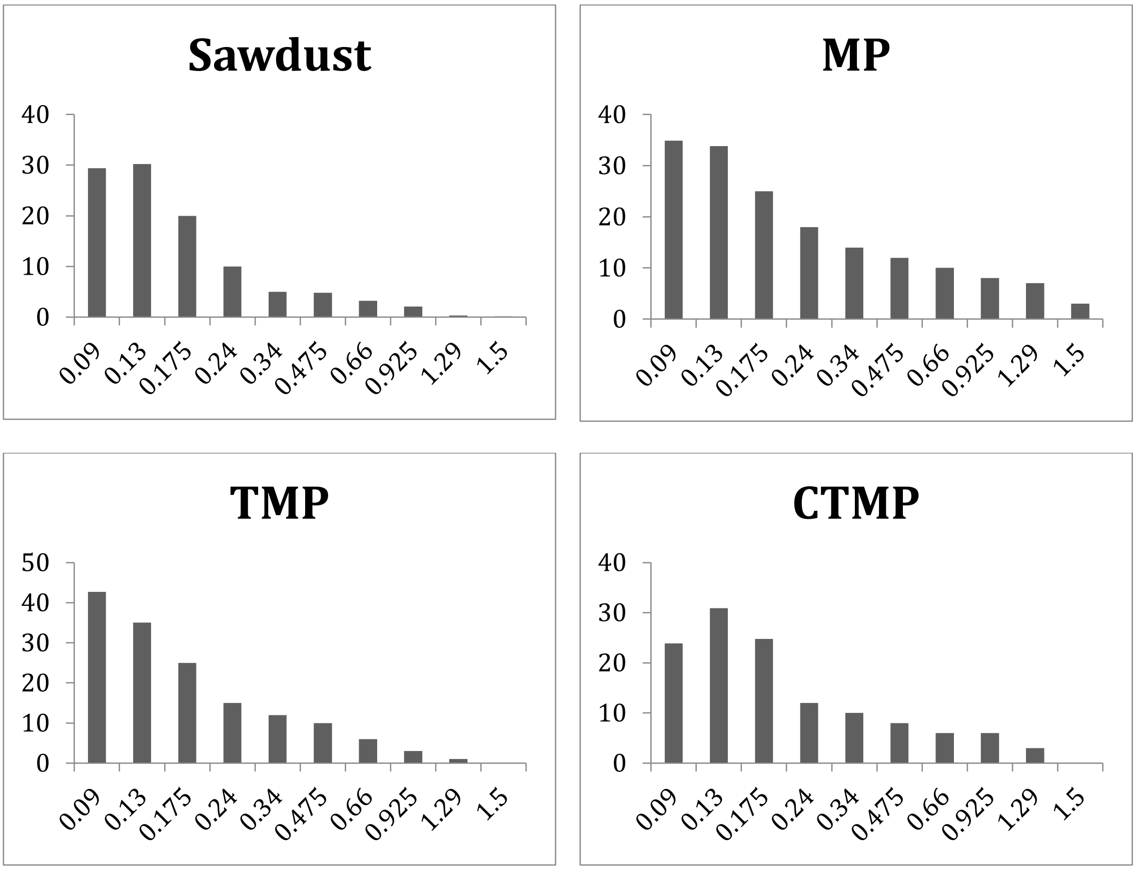

Figure 10: Fiber length distributions inside the composite material*.

*Length percentage versus fiber length for sawdust, MP, TMP, and CTMP. (In all the figures the horizontal axis represents the length of the fibers and the vertical axis the percentage of fibers)

The mean lengths for the WF, MP, TMP, and CTMP were 200, 418, 480 and 514 µm, respectively. This length is referred to the fibers extracted from the composite and compared with the lengths of the original fibers (Table 1), it was found that were slightly lower. This phenomenon is assumed to be due to the attrition during the composite preparation process (Kalaprasad et al., 1997; Granda et al., 2015).

Table 5 shows the values of the micromechanical properties of the composites.

Table 5: Matrix Contribution to Composite Strength and Micromechanics Tensile Strength Properties of the Composites

Sample	σ_τ^Φ	L_c^F	χ_1
	(MPa)	(µm)	
PP + 30% sawdust	461.24	305.37	0.305
PP + 30% MP	579.56	487.36	0.315
PP + 30% TMP	573.39	438.99	0.298
PP + 30% CTMP	557.77	392.03	0.28

(Jiménez et al., 2016)

The obtained orientation factor, in the range from 0.28 to 0.32 coincided with previously computed ones, and assuming that this value is highly determined by the equipment used to prepare the test specimens, were considered satisfactory (Vallejos et al., 2012; Reixach et al., 2013; Granda et al., 2016)

The Kelly and Tyson model divides the fibers between subcritical and supercritical ones, depending on their ability of fully absorb its intrinsic tensile strength. The formulae used to compute such values are:

$$X = \chi_1 \left(\sum_{l_i^F = 0}^{L_C^F} \left[\frac{l_i^F \cdot V_i^F}{2 \cdot L_c^F} \right] \right) \cdot \sigma_t^F \qquad [4]$$

$$Y == \chi_1 \left(\sum_{l_j^F = L_c^F}^{\infty} \left[1 - \frac{L_c^F \cdot V_j^F}{2 \cdot l_j^F} \right] \right) \cdot \sigma_t^F \qquad [5]$$

$$Z = (1 - V^F) \cdot \sigma_t^{m*} \qquad [6]$$

Being X, Y and Z the contributions of the subcritical and supercritical fibers and the matrix respectively. Table 6 shows the percentage contribution.

Table 8: X, Y, and Z percentage contributions to composite strength

	X	Y	Z	X+Y
Sawdust	10.80%	46.50%	42.70%	57.30%
MP	5.80%	49.40%	44.80%	55.20%
TMP	9.60%	44.60%	45.80%	54.20%
CTMP	9.60%	45.00%	45.40%	54.60%

(Jiménez et al., 2016)

It was found that for the composites containing a 30% wt. of reinforcement the contribution of the fibers was higher than the 50%, being the supercritical fibers the highest contributors to the tensile strength of the composite.

Once the tensile strength of the sugarcane bagasse reinforced PP-based composites was researched, it was found interesting to compare the behavior of the reinforcing fibers when the matrix was changed. This was the purpose of the second published paper of the composite series.

A new batch of composites was prepared. Two matrices were used, a high-density polyethylene (HDPE), and a starch-based polymer (PTA). Figure 7 shows the strain-stress curves for such matrices.

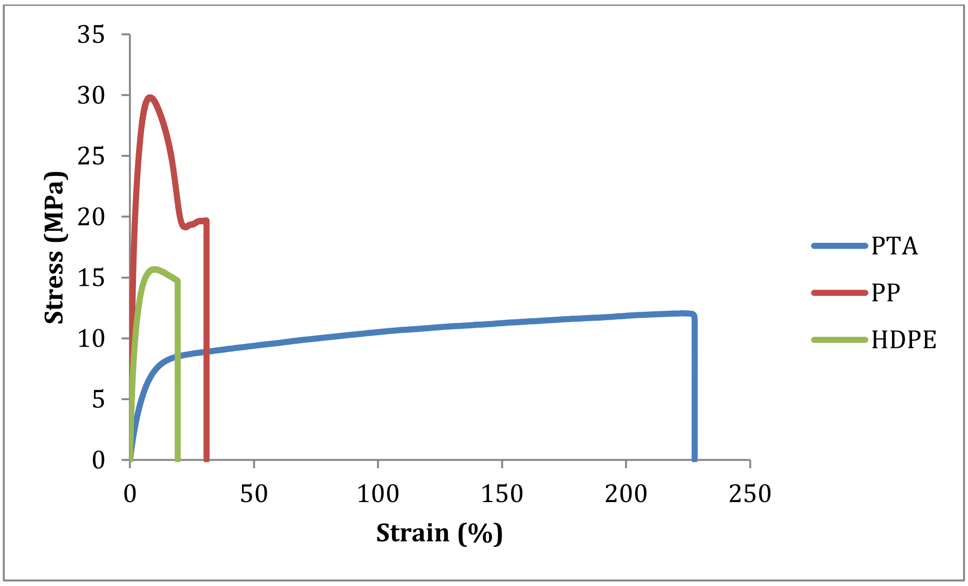

Figure 11*:* Stress strain curves for the matrices used in the research.

The HDPE is a polyolefin, and thus hydrophobic, showed similar to PP incompatibilities with the hydrophilic reinforcement. Hence, a 6% wt. of maleic anhydride-grafted polyethylene (MAPE) was added to the HDPE-based composites. Then, composites reinforced with 30 % wt. of SW, MP, TMP, and CTMP were prepared and tested. Table 7 shows the obtained results.

Table 9: Tensile Strength Properties of the Matrices and the Composites

	V^F	σ_t^C	E_t^C	ε_t^C
		(MPa)	*(GPa)*	*(%)*
PTA	-	12.44 ± 0.38	0.172 ± 0.004	183.133 ± 13.087
PTA/WF	0.276	12.06 ± 0.25	0.963 ± 0.052	3.103 ± 0.200
PTA/MP	0.269	16.98 ± 0.53	1.323 ± 0.038	2.767 ± 0.113
PTA/TMP	0.268	15.92 ± 0.17	1.165 ± 0.012	3.087 ± 0.127
PTA/CTMP	0.27	16.91 ± 0.20	1.332 ± 0.047	2.593 ± 0.120
HDPE	-	17.12 ± 0.17	1.008 ± 0.024	8.640 ± 0.207
HDPE/MP	0.222	21.66 ± 0.34	2.536 ± 0.067	2.080 ± 0.11
HDPE/TMP	0.222	23.08 ± 0.26	2.501 ± 0.043	2.380 ± 0.13

(Jiménez et al., 2016)

The tensile strength of the used matrices was lower than that of the PP used in the first article. In the case of the PTA, its value is almost half that of the PP. Consequently, it was expected that the tensile strength of the composites was also lower. This was corroborated by comparing the values of table 2 and table 5. In both cases, the tensile strength increased with the addition of the reinforcements. The obtained values for the pulps were similar, while the WF showed less strengthening capabilities, as it was the case when reinforcing a PP (Figure 8). Hence, a good interphase was supposed in the case of the HDPE and the PTA. In the case of the WF, it was found that the tensile strength tends to decrease. In this case, the sugarcane bagasse fibers act more as a filler than as a reinforcement.

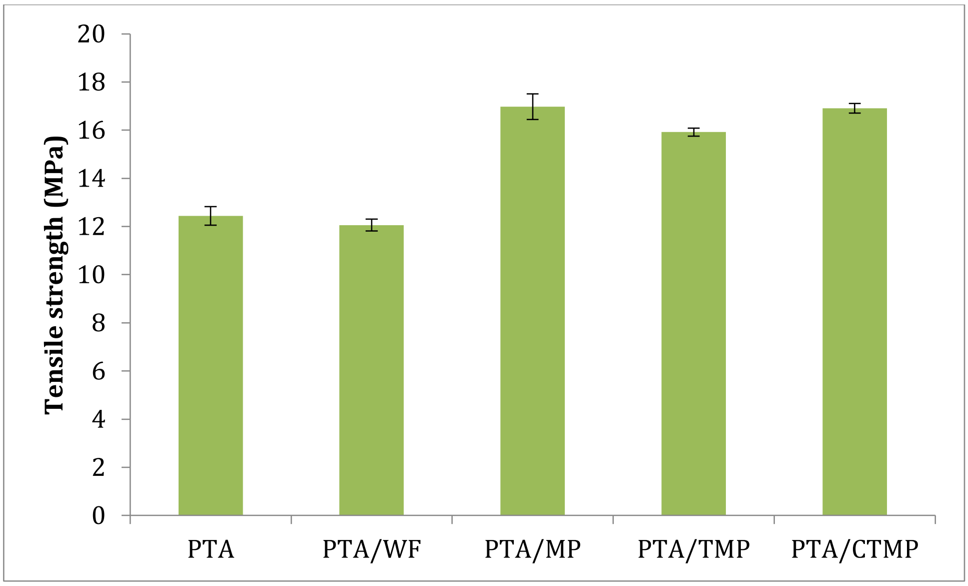

Figure 12*:* Tensile strength of the PTA-based composites against the reinforcement nature.

The Young's moduli represent another important factor when choosing a material, in his cases, the PTA-based composites were highly penalized by the initial low value of Young's modulus its matrix. Nonetheless, the addition of a 30%wt. of reinforcing fibers increased noticeably the stiffness of the materials (Figure 9). In that sense, the PTA-based composites showed Young's moduli comparable to that of a HDPE.

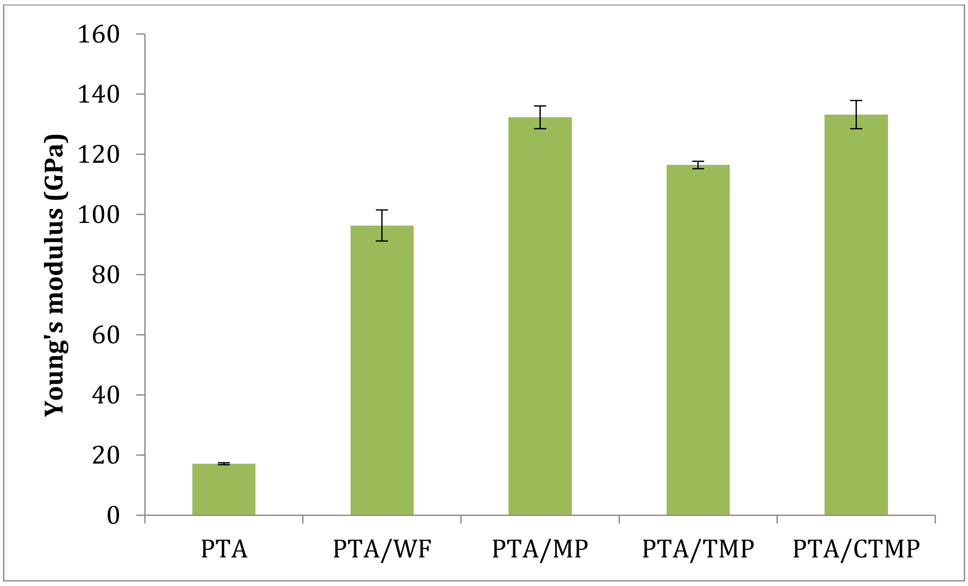

Figure 13*:* Young’s modulus the PTA-based composites against the reinforcement nature.

From a macro-mechanic point of view, the PTA-based composites showed mechanical properties comparable to the polyolefin. Consequently, a smart product design could allow its use as a replacement of HDPE or even PP.

The study continued deepening on the quality of the interphase between the fibers and the matrices. In this case, the modified Kelly and Tyson equation, and the solution proposed by Bowyer and Bader were used to find the values of the intrinsic tensile strength of the fibers, the interfacial shear strength, the orientation factor and the critical length. The analysis was made with the data of the TMP-based composites as PTA reinforcement, as they showed the lower tensile strengths, and thus the feeblest interphase. Figure 10 shows the weighted length distribution of the TMP fibers extracted from the PTA-matrix

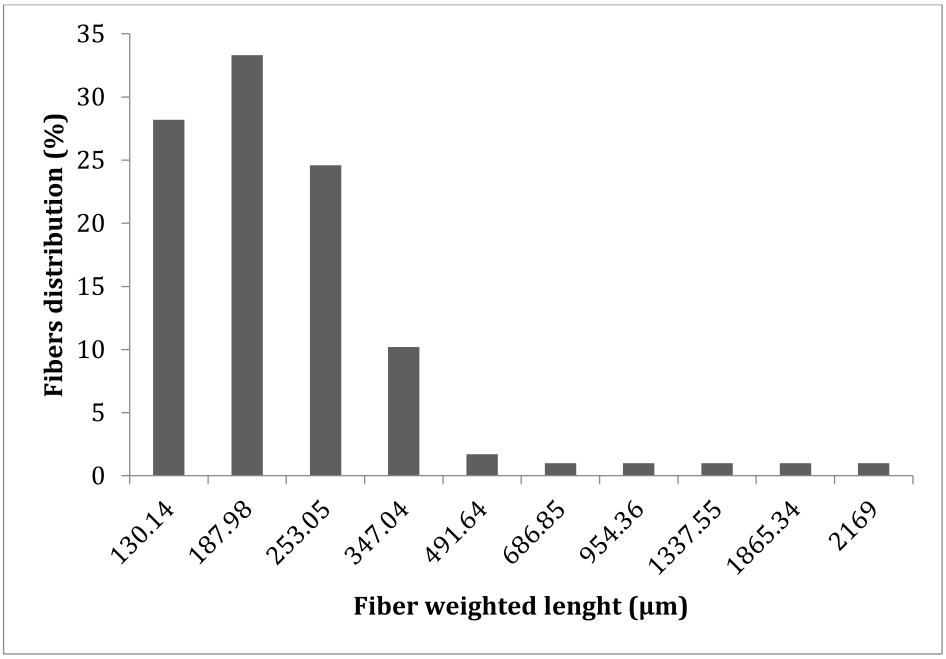

Figure 14*:* Weighted fiber length distributions of the TMP inside the PTA-based composite material.

In order to apply the Bowyer and Bader solution, it needs to know two intermediate values of the stress-strain curves for the composite and the matrix. Figure 11 shows such points.

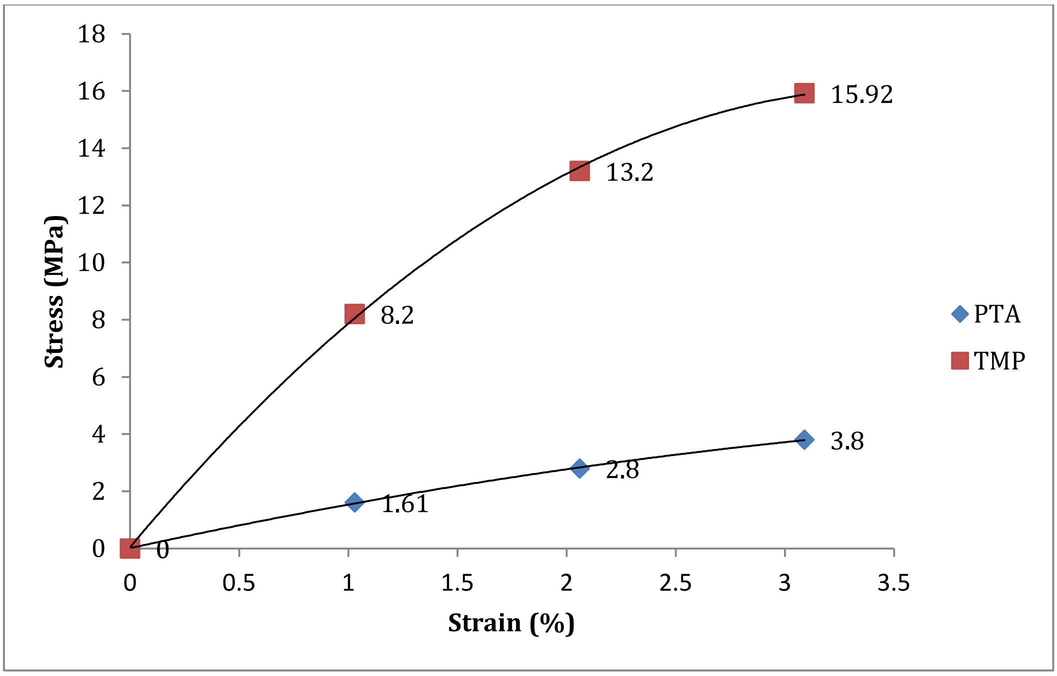

Figure 15*:* Stress-strain curves of the PTA matrix and the TMP reinforced composite.

Once the equation was solved it was found that the interfacial shear strength had a value of 6.65 MPa. The value is slightly inferior to 7.18, defined by the Von Mises criteria, but it was close enough, and consequently, the interphase was defined as a good quality one. The orientation factor was found to be 0.33, also inside the expected values. The obtained orientation factor implies a mean orientation angle of 40.3°, taking into account that $\chi_1 = \cos^4(\alpha)$ (Vallejos et al., 2012).

The intrinsic tensile strength of the fibers was also obtained, accounting 262 MPa. This value is noticeably inferior to that of the same fibers as PP reinforcement (Table 3). The intrinsic tensile strength of the fibers is more a composite-based value than a fiber-based value (Shah et al., 2016). Using this value, it was possible to solve the mRoM (Equation 1), obtaining the value of the coupling factor for the composite. Such value was found to be 0.186, indicating a good interphase.

Finally, a sensitivity analysis of the tensile strength of the composite against variations of the micromechanics variables was carried on. It was found that the orientation factor was the property with the highest impact on the final tensile strength of the composites.

Figure 12 shows the evolution of the tensile strength of the composites against the orientation factor. The lines present different mean fiber lengths.

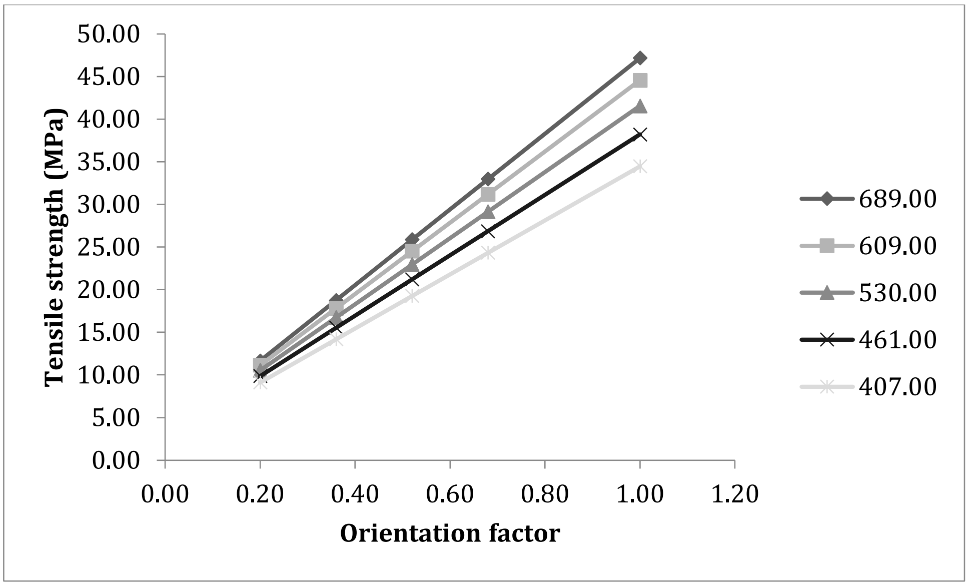

Figure 16: Impact of the orientation factor and the mean length of the fibers on the tensile strength of the composites.

The last of the published papers researched Young's moduli of the composites. While the tensile strength of a material is an important property to establish the limit loads that a material could safely sustain Young's modulus shows how a material deforms under load. Usually, the products or artifacts are designed to ensure a proper deformation under the previewed loads and rarely to its point of failure. Hence, the stiffness of a material and its micro mechanics are of a scientific and practical value.

The study was carried out for the PP, HDPE and PTA-based composites, reinforced with a 30% wt. of the different kinds of reinforcements. Table 8 shows the experimental values.

Table 10: Experimental Young’s Modulus and strain at break for all composites

	V^f	E_t^C (GPa)	ε_t^C (%)
PP	-	1.499±0.008	9.21±0.01
PP30SD	0.218	3.612±0.037	2.43±0.11
PP30MP	0.212	3.377±0.063	4.27±0.39
PP30TMP	0.212	3.284±0.038	4.47±0.09
PP30CTMP	0.213	3.413±0.051	3.8±0.47
HDPE	-	1.008±0.024	12.9±0.31
HDPE30MP	0.222	2.536±0.067	3.12±0.34
HDPE30TMP	0.222	2.501±0.043	3.57±0.10
PTA	-	0.172±0.004	274.7±19.63
PTA30SD	0.276	0.963±0.052	4.65±0.30
PTA30MP	0.269	1.323±0.038	4.15±0.17
PTA30TMP	0.268	1.165±0.012	4.63±0.19
PTA30CTMP	0.27	1.332±0.047	3.89±0.18

(Jiménez et al., 2017).

The PP-based composites showed Young’s modulus that compared well with that of a PP stone ground wood (SGW) reinforced composites (Lopez et al., 2012). All the composites showed Young’s moduli values far from that of a PP glass fiber (GF) reinforced composite (Lopez et al., 2012; Granda et al., 2016).

The PTA-based composites showed a highly noticeable increase of its Young’s moduli compared to the matrix. The initial Young’s modulus of the PTA matrix is comparatively to PP or HDPE very low, but the addition of a 30% wt. of reinforcing fibers allowed Young’s moduli comparable to HDPE or PP.

To fully understand the contribution of every phase to the final Young's moduli of the composites a micro mechanics analysis was carried on. The first micro mechanics model used was the Hirsch equation (Equation 7), that allowed computing the intrinsic Young's moduli of the fibers (Hirsch, 1962; Rodriguez et al., 2010; Vilaseca et al., 2010; Lopez et al., 2011),

$$E_t^C = \beta\cdot\left(E_t^f V^f + E_t^m\left(1-V^f\right)\right) + \left(1-\beta\right)\frac{E_t^f \cdot E_t^m}{E_t^m\cdot V^f + E_t^f\left(1-V^f\right)} \qquad (7)$$

where E_t^C, E_t^f, and E_t^m E_t^C, E_t^F, E_t^m denote the elastic moduli of the composite, the reinforcement, and the matrix respectively; V^f represents the volume fraction of the reinforcement. The model is a linear combination of the parallel, Reuss, and the serial, Voigt models. It has been reported that, for natural fiber composites, a value of β=0.4 adequately reproduces the results obtained experimentally (Kalaprasad et al., 1997; Vilaseca et al., 2010).

Once the intrinsic Young's modulus of the reinforcements was known, it was possible to use the modified rule of mixtures for Young's modulus (mROM) (Equation 8) (Thomason, 2000),

$$E_t^C = \eta_e\cdot E_t^f\cdot V^f + E_t^m\cdot(1-V^f) \qquad (8)$$

where E_t^C, E_t^f, and E_t^m E_t^C, E_t^F, E_t^m represent the elastic moduli of the composite, the reinforcement, and the matrix, respectively, and η_e $\eta_e$is an efficiency factor used to correct the contribution of semi-aligned fibers. The mRoM was used to compute the value of the efficiency factor. Table 9 shows the computed values.

Table 11: Micromechanical Aspects of the SB Reinforced Composites

	V^f	E_t^F *(GPa)*	η_e	η_l	η_o
PP30SD	0.218	23.09	0.485	0.735	0.659
PP30MP	0.212	21.045	0.492	0.844	0.583
PP30TMP	0.212	19.962	0.497	0.88	0.564
PP30CTMP	0.213	21.357	0.491	0.894	0.549
HDPE30MP	0.222	15.342	0.493	0.841	0.587
HDPE30TMP	0.222	14.953	0.496	0.875	0.566
PTA30SD	0.276	6.992	0.434	0.639	0.679
PTA30MP	0.269	10.524	0.423	0.725	0.582
PTA30TMP	0.268	9.092	0.426	0.797	0.535
PTA30CTMP	0.27	10.567	0.423	0.813	0.52

(Jiménez et al., 2017)

It was found that the efficiency factor was very stable, with slight differences between the values for the polyolefin and the starch-based polymer. On the other hand, the intrinsic tensile Young's moduli were very matrix dependent (Lope et al., 2012; Reixach et al., 2013; Granda et al., 2016).

The Cox-Krenchel's model (Cox, 1952; Krenchel, 1964) was used to model the fiber length efficiency factor (Table 7), and it was found that such factor increased with increasing fiber length. The values agreed with prior studies (Lopez et al., 2012; Espinach et al., 2013; Granda et al., 2016). Then, it was possible to compute the value of the fiber orientation efficiency factor, by the ratio between η_e and η_l. Table 7 shows the results. It was found that such factor was less matrix-dependent and more fiber typology-dependent. The values of the orientation efficiency factor decreased against the intensity of the treatments and the length of the fibers. Assuming a triangular distribution of the fibers inside the composite it was possible to compute a mean orientation angle of 39.4º from the fiber orientation efficiency factor (Fukuda and Kawata, 1974; Sanomura and Kawamura, 2003).

The same micro mechanics' factors were computed by using The Tsai and Pagano model (Eq. 9) and the Halpin and Tsai equations (Eq. 10, 11) (Halpin and Pagano, 1969; Halpin and Tsai, 1969). Unlike the Hirsch model, the Halpin and Tsai equations and morphological data. In the past, it has been proven that such models rendered very similar outputs (Lopez et al., 2012; Espinach et al., 2013; Serrano et al., 2014; Granda et al., 2016). Nonetheless, in the case of the PTA-based composites, the initial value of Young's modulus of the matrix, below 1 GPa, prevents obtaining satisfactory outputs. Table 10 shows the computed values and the comparative error.

Table 12: Theoretical Young's Moduli of the Composites Computed by Using the Tsai and Pagano Model, and the Halpin and Tsai Equations

	E_t^F (GPa)	E_t^C (GPa)	E_t^{C*} (GPa)	*Error*	*Error (%)*
PP30SD	23.09	3.61	3.25	0.36	11.08%
PP30MP	21.045	3.38	3.32	0.06	1.81%
PP30TMP	19.962	3.28	3.29	-0.01	0.30%
PP30CTMP	21.357	3.41	3.4	0.01	0.29%
HDPE30MP	15.342	2.54	2.5	0.04	1.60%
HDPE30TMP	14.953	2.5	2.5	0	0.00%
PTA30SD	6.992	0.96	0.57	0.39	68.42%
PTA30MP	10.524	1.32	0.78	0.54	69.23%
PTA30TMP	9.092	1.16	0.77	0.39	50.65%
PTA30CTMP	10.567	1.33	0.84	0.49	58.33%

(Jiménez et al., 2017)

5.3. Cellulose nanofibers

Cellulose nanofibers (CNFs) are attractive because are based on renewable and abundant resources and can be processed at large scale using well-established pulp, paper, and wood industry methods (Ahola et al., 2008; Gonzáles et al. 2012). Among all the explored applications, aerogels made of CNF are a product of interest due to their lightweight, great specific surface and, thus, their huge porosity (Moon et al., 2011). Moreover, aerogels made of CNFs present great mechanical properties, a fact that confers them a good dimensional stability (Belbekhouche et al., 2011). CNFs, in their native form, have a huge hydrophilic character (even greater than the above-mentioned sawdust), what would make also difficult their use for oil removal. In this sense, chemical modification of CNF is also in a growing stage, mainly focused on the hydrophobization of their surface (Zhang et al., 2014; Bulota et al., 2012).

The paper shows a lower degree of polymerization is observed in Tempo oxidized CNF (TOCNF) than in Mechanical Ligno-CNF (MecLCNF), because oxidation in the application of TEMPO introduces carboxylic groups in the cellulose chains (Hallac et al., 2011; Hassan et al., 2015). The mechanical treatment (homogenization) also causes depolymerization, so the degree of polymerization of MecLCNF is also low. Table 11 shows the results of the characterization of MecLCNF and TOCNF.

Table 13: Characterization of the Obtained (L)CNF

CNF type	DP	WRV (%)	CC (μeq-g/g)	CD (μeq-g/g)	Yield (%)	σ (m^2/g)	d (nm)
TOCNF	488	1706	881.3	1235	95.1	172.61	14.47
Mec-LCNF	803.6	847	76.6	216.38	31	68.18	36.67

Water retention (WRV) is higher in chemical CNFs, in TOCNF it is 17 gH2O / g and in MEcLCNF of 8.5 gH2O / g. The TOCNF present higher values for the cationic demand and the carboxyl content, due to the TEMPO oxidation introducing carboxyl groups in the cellulose chain and also allowing yields higher than 90% after the homogenization processes; Which shows that TOCNF has a better affinity to water and a binding capacity greater than that presented by MecLCNF.

Table 14: Density and porosity of the Aerogels produced in this study

CNF type	AKD (%)	Nomenclature	Density (g/cm^3)	Porosity (%)
TOCNF	0	TOCNF-0	0.0031	99.79
	7.5	TOCNF-7.5	0.0043	99.73
	15	TOCNF-15	0.005	99.67
Mec-LCNF	0	Mec-LCNF-0	0.0089	99.40
	7.5	Mec-LCNF-7.5	0.0097	99.35
	15	Mec-LCNF-15	0.0107	99.29

Table 12 shows both parameters in aerogels produced for the present study. Cellulose aerogels are characterized by their high porosity and low density that make them an interesting absorbent material. The density is higher in MecLCNF than in TOCNF, this is because the TOCNF have a higher yield and specific surface area than MecLCNF; This behavior generates the possibility of creating expanded and porous three-dimensional networks to improve the absorption of liquids. Adding ketene dimer alkyl (AKD) caused denser samples without affecting the formation of aerogel, the addition of 15% AKD resulted in a higher affinity for oils aerogels.

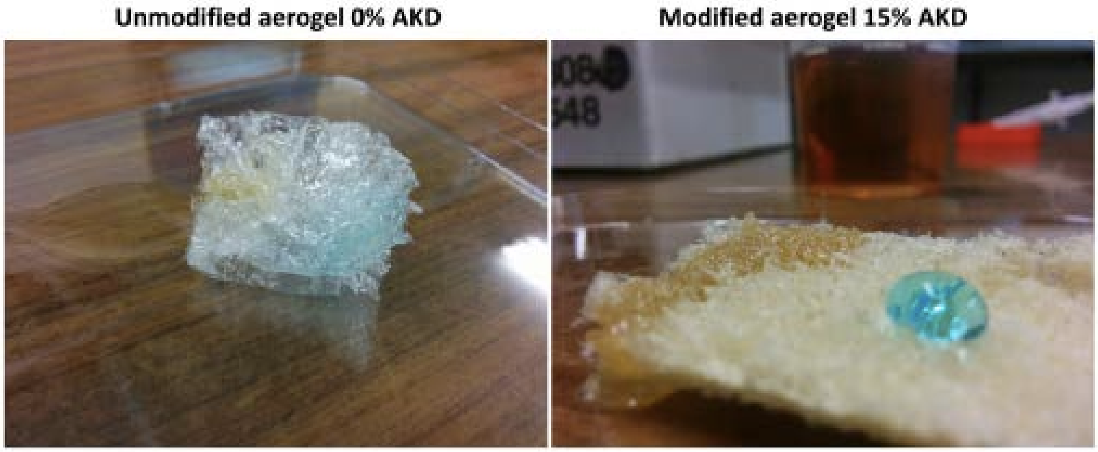

Figure 17: Drop shape for unmodified and modified aerogels with AKD

The degree of hydrophobicity measured was one drop of colored water and one drop of oil (Figure 13). The untreated aerogel absorbs water and oil droplets (left) while aerogel treated with AKD (right) shows hydrophobicity as it keeps the water droplet on the surface. MecLCNF appears as the best option against TOCNF, which is 150 times more expensive than the MeCNF in economic terms, despite its lower oil absorption capacity.

Looking deeper into this topic cellulose aerogels was needed to better understand their properties and behavior internally, this in order to expand research in the article; So we conducted a research visit at the University of Salerno, Italy, where continued experimentation is presented below.

Two types of nano-fibrillated cellulose (NFC) gels, NFC from Eucalyptus (CNF-Euca) and Lignocellulosic NFC from Bagasse (LNFC-Bagasse), have been evaluated in the preparation of aerogels by two different extraction techniques: freeze drying and supercritical CO_2 extraction. Figure 14 shows the gels from NFC.

Figure 18: Gels from NFC-Euca (left) and LNFC-Bagasse (right)

The DSC test performed involved three steps, heating the sample up to 85°C, cooling up to -20°C and a later heating ramp up to T= 85°C. The instrument used was a DSC Q20 from TA Instruments. The sample holder was hermetically sealed, which means that water remains within the pan in liquid or gaseous form. The pan weight before and after DSC analysis was compared to verify that there were no weight losses.

In Figure 15, the results from the DSC of NFC-Euca and LNFC-Bagasse gels are reported. The thermograms report the heat flow as a function of the temperature.

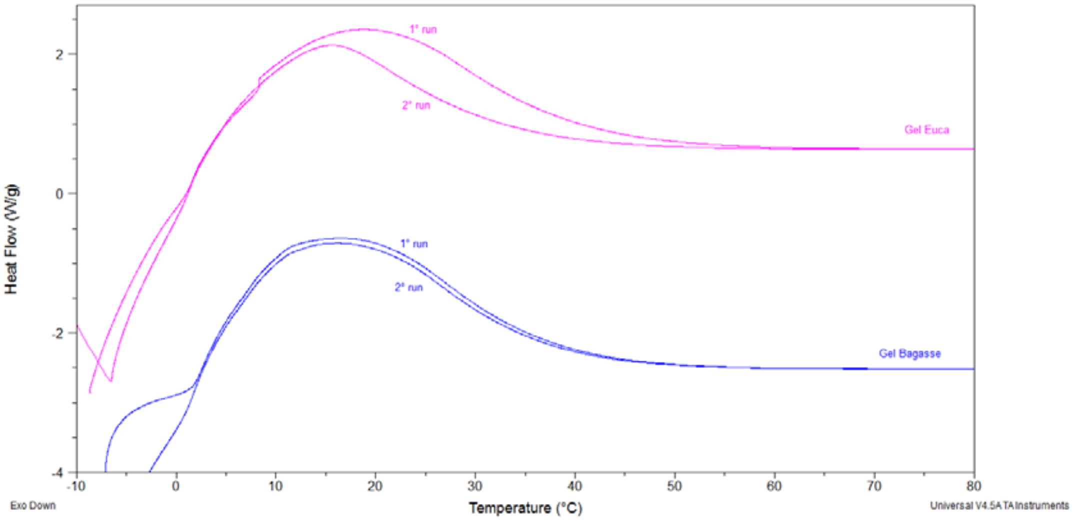

Figure 19: DSC for gels of NFC-Euca and LNFC-Bagasse

Both gel samples show an endothermic phenomenon which is present in the first and second heating run at about the similar temperatures. The maximum peak for Euca is located between 19.22°C and 16ºC, and enthalpies in the range of 195.6 J/g and 158 J/G, for the first and the second run, respectively. The maximum peak for Bagasse is located between 16°C and 15ºC, and enthalpies in the range of 333 J/g and 350 J/G, for the first and the second run, respectively.

The observed phenomenon is probably due to the extraction of water present in the gels. This phenomenon is reversible, as it is observed both in the first and second heating runs. Moreover, the enthalpies are compatible with the energy needed to break the electrostatic interactions and hydrogen bonds.

The aerogels were confectioned used two techniques:

Freeze-drying

The aerogels were made by carrying the gel to a cylindrical container, immersed them in liquid nitrogen, and subjecting them to lyophilization for 4 days at -20ºC.

Extraction with super critical CO_2

A solvent (water-acetone) exchange was performed to the cylindrical containers with the gel inside the solvent, for 3 hours at room temperature. Then, supercritical carbon dioxide (CO_2) extraction was performed in an SFX 200 supercritical Carbon dioxide extractor (ISCO Inc.) at 40°C and 2900 PSI. The obtained aerogels are shown in Figure 16.

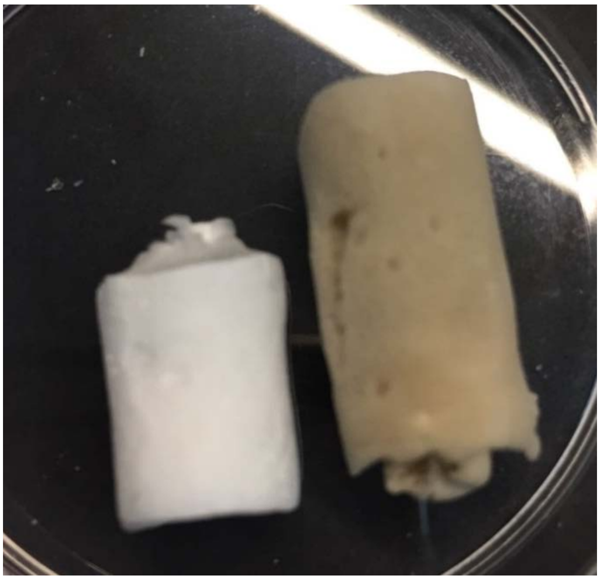

Figure 20: Aerogels from NFC-Euca (left) and LNFC-Bagasse (right) with freeze drying technique.

Characterization of aerogels

The thermograms obtained from DSC analysis of the of NFC-Euca and LNFC-Bagasse aerogels are reported in Figure 17. The DSC test performed involved three steps, heating the sample up to 200°C, cooling up to -40°C and a new heating ramp up to T= 200°C.

Both aerogel samples show an endothermic phenomenon in the first DSC heating run.

This endothermic peak could be tentatively associated with condensation reactions. The high enthalpy value of the observed process (403 J/g for NFC-Euca and 216J/g for LNFC-Bagasse) suggests that a polycondensation process takes place with the formation of a cross-linked structure. In addition, since it is not a reversible process, the second runs are not reported. The phenomenon is the same for the two techniques of aerogel confection.

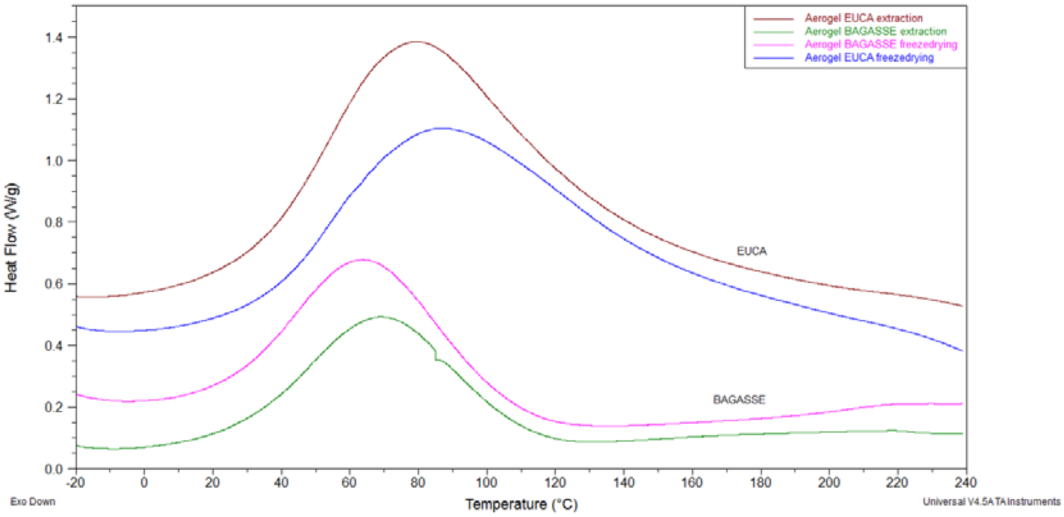

Figure 21: First heating run of DSC test for aerogels of NFC-Euca and LNFC-Bagasse with freeze drying and super critical extraction

Figure 18 shows the TGA analysis for aerogels from Euca and Bagasse with freeze drying and super critical extraction.

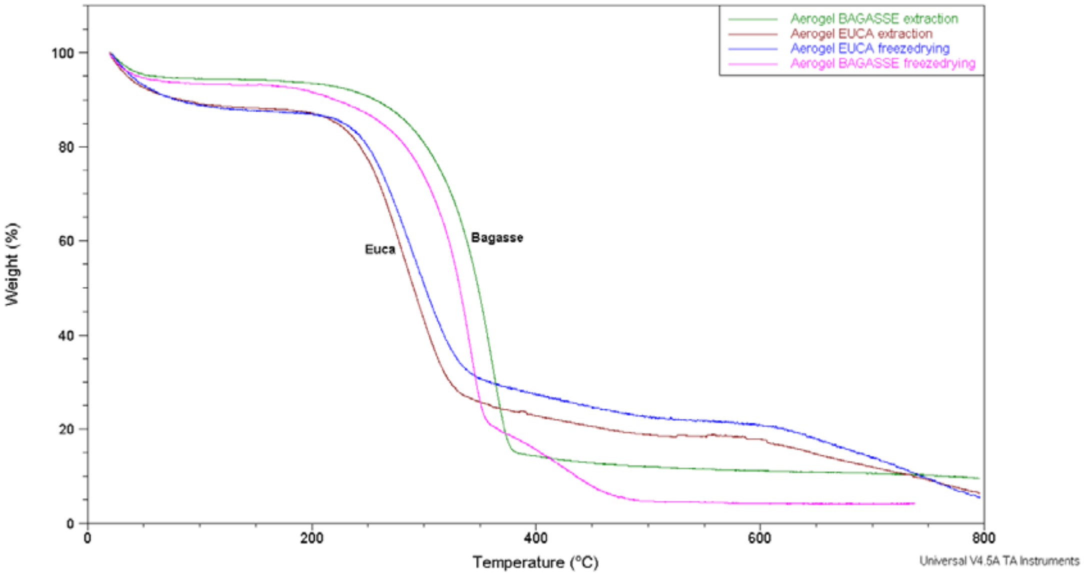

Figure 22: TGA for aerogels of NFC-Euca and LNFC-Bagasse with freeze drying and super critical extraction

The TGA of the tested materials was conducted in nitrogen, by using a TQ500 machine of TA Instruments. The followed measurement parameters were applied: balance purge flow of 40ml/min and sample purge flow of 60ml/min.

It is observed in the TGA analysis (Fig. 9) that Euca had a greater enthalpy, which is represented by the losing of water in the test, and the polycondensation is lower for Bagasse. These results confirmed the obtained with the DSC test. There is no significant difference in the energy of each technique (freeze drying and supercritical extraction).

Figure 19 shows the X-Ray analysis for aerogels with freeze drying and super critical extraction. The X ray diffraction patterns with nickel filtered Cu Kα radiation were obtained with automatic Bruker D8 Advance diffractometers.

The X Ray tests show the refraction centered about 15 θ degree and something remains in the freeze drying process. Future mechanical tests are needed to improve understanding of this phenomena.

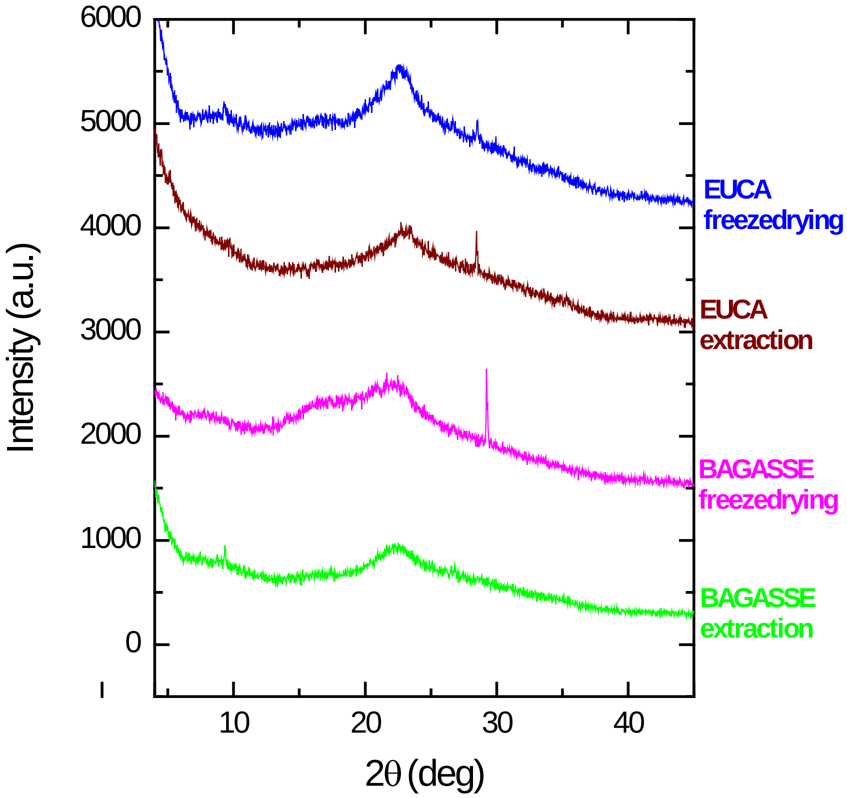

Figure 23: X-Ray for aerogels of NFC-Euca and LNFC-Bagasse with freeze drying and super critical extraction

The samples from freeze drying and extraction were immersed in different solvents for twenty-four hours, to observe if they were soluble in the medium (Acetone, ethanol and ethyl acetate). It was found that aerogels do not solubilize in the medium or in water.

6. CONCLUSIONS

The suitability of using sugarcane bagasse residue as raw material for the production of brown-line papers was assessed, as well as the feasibility of producing high-yield pulps for their combination with recycled fibers.

Organosolv treatment has been found to be more suitable for producing sugarcane bagasse fibers due to its higher yield, paper properties and suitability to be refined.

Through the combination of refined organosolv bagasse and recycled testliner fibers, it is possible to obtain papers with high potential to be used in the packaging sector. While the incorporation of such fibers slightly decreased the mechanical properties of paper, air barrier was significantly improved.

The results obtained for sugarcane bagasse pulps allow to conclude, the rupture length increases when the amount of ethanolamine added and this is because the contact with the reagents causes the lignin and the extractives to be removed and the fibers.

The sugarcane bagasse reinforcement adds value to a by-product and extends the value chain of the agricultural industry. Its use can also provide low-cost alternatives to wood fibers and simultaneously reduce CO_2 emissions due to its combustion.

The MP-, TMP-, and CTMP-reinforced composites yielded improved mechanical and micromechanical tensile strength properties compared with neat PP. A significant increase in the mechanical properties of the composites was obtained for composites of PP with 30% MP in the tensile strength property, with a 97.11% yield against the sugarcane bagasse initial biomass.

In sum, 30% by weight of reinforcing fibers contributed to more than 50% of the final strength of the composite. The main contribution was due to the supercritical fibers.

From a sustainability point of view, the use of biobased and biodegradable matrices such as Mater-bi® represent an advantage over other matrices, such as polypropylene or high-density polyethylene, in terms of the use of renewable materials and waste management.

Sugarcane bagasse reinforced polyolefin composites showed Young's moduli similar to that of high-quality natural fiber reinforced polyolefin. The main advantages of SB are its low cost, and little need of treatments, in the case of SD and MP. The main disadvantage is its availability, only profitable near sugarcane refineries. SB-PP composites could be a replacement to glass fiber-PP composites for certain semi-structural applications.

SB reinforced PTA showed similar Young’s moduli to PP and HDPE. In some cases, such composites could replace a polyolefin.

It has been demonstrated that AKD promotes the hydrophobization of CNF surface (both types of CNF) without the use of any organic solvent. Moreover, the oil absorption tests (both in dynamic and static conditions) showed a good behavior with regard to a selectivity of oil against water.

TOCNF present a higher oil absorption capacity than Mec-LCNF. Even though the difference between both is not significant and the cost of Mec-LCNF is about 150 times lower than TOCNF, as reported in the bibliography.

The main advantage of having performed the oil absorption capacity in dynamic conditions is that it brings to light that with a proper structure design, modified aerogels could be easily used for oil removal (or petroleum, where appropriate).

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