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

Contact information: a: LEPAMAP-PA Group, Department of Chemical Engineering, University of Girona, c/M. Aurèlia Capmany, nº 61, Girona 17071, Spain; b: Pulp and Paper Research Group, Department of Chemical Engineering, University Pontificia Bolivariana, Medellín, Colombia; c: Design, Development and Product Innovation, Dept. of Organization, Business, University of Girona, c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain; d: UNESCO Chair in Life Cycle and Climate Change, School of International Studies (ESCI-UPF), Pg. Pujades, nº 1, Barcelona 08003, Spain;
** Corresponding author: Francisco.espinach@udg.edu*

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

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).

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

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),

$$\tau = \sigma_t^m / \sqrt{3} \quad (2)$$

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),

$$L_c^F = \frac{d^F \cdot \sigma_t^F}{2 \cdot \tau} \quad (3)$$

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),

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

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.

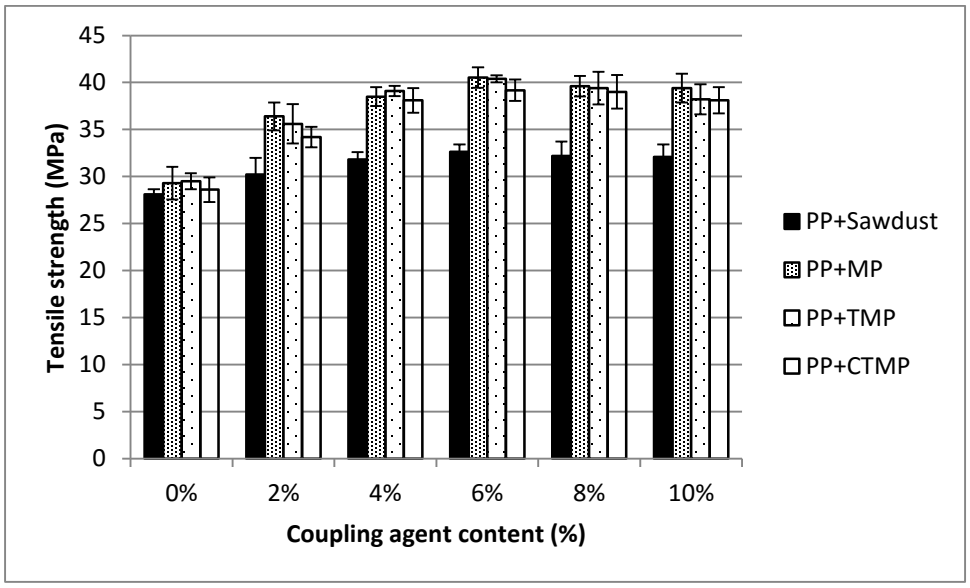

Fig. 1. Composite tensile strength *versus* MAPP content

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).

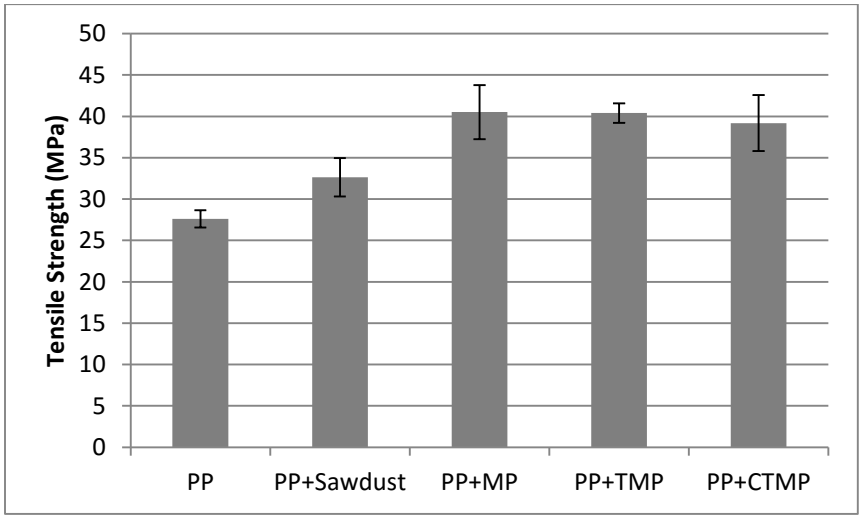

Fig. 2. Tensile strength of PP composites with sawdust, MP, TMP, and CTMP reinforcement, and 6% MAPP

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:

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

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.

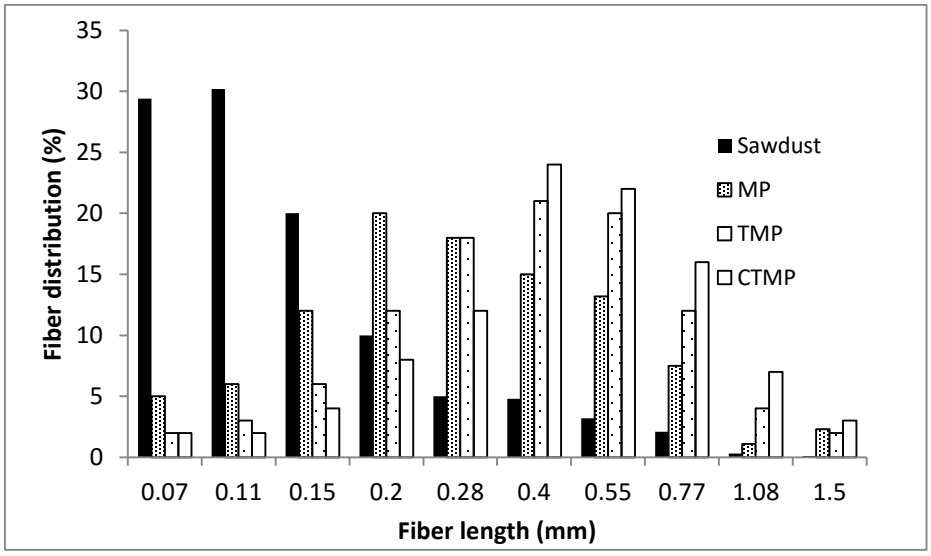

Fig. 3. Fiber length distributions inside the composite material. Length percentage *versus* fiber length for sawdust, MP, TMP, and CTMP

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.

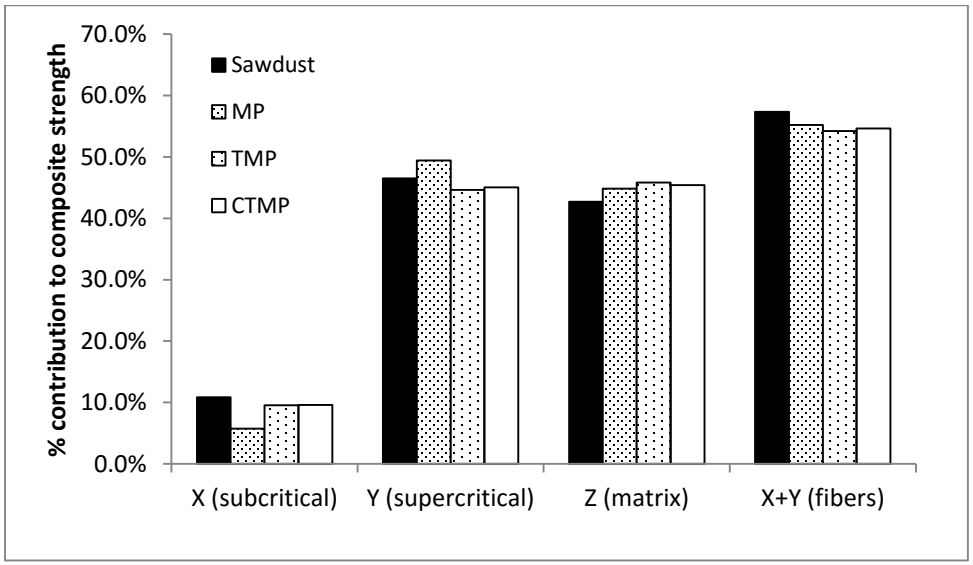

Fig. 4. X, Y, and Z percentage contributions to composite strength

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).

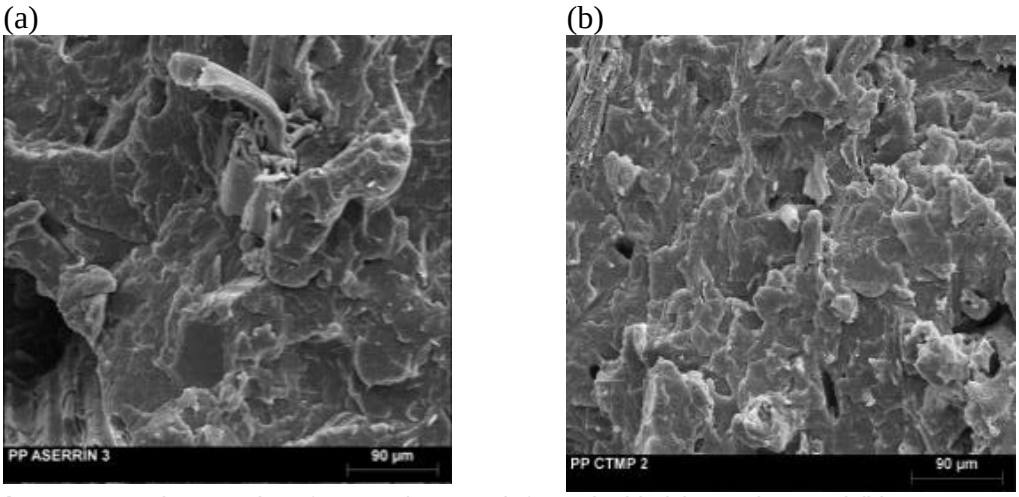

Fig. 5. SEM micrographs of 30% w/w PP reinforced with (a) sawdust and (b) CTMP

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.

REFERENCES CITED

Anastas, P. T., and Warner, J. (1998). *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, UK.

Arrakhiz, F. Z., Malha, M., Bouhfid, R., Benmoussa, K., and Qaiss, A. (2013). "Tensile, flexural and torsional properties of chemically treated alfa, coir and bagasse reinforced polypropylene," *Composites Part B-Engineering* 47, 35-41. DOI: 10.1016/j.compositesb.2012.10.046

Ashori, A., Nourbakhsh, A., and Karegarfard, A. (2009). "Properties of medium density fiberboard based on bagasse fibers," *Journal of Composite Materials* 43(18), 1927-1934. DOI: 10.1177/0021998309341099

ASTM D618-13. (2013). "Standard Practice for Conditioning Plastics for Testing," ASTM International, West Conshohocken, USA.

ASTM D638-14. (2014). "Standard Test Method for Tensile Properties of Plastics," ASTM International, West Conshohocken, USA.

Bhattacharya, D., Germinario, L. T., and Winter, W. T. (2008). "Isolation, preparation and characterization of cellulose microfibers obtained from bagasse," *Carbohydrate Polymers* 73(3), 371-377. DOI: 10.1016/j.carbpol.2007.12.005

Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibres," *Progress in Polymer Science* 24(2), 221-274. DOI: 10.1016/s0079-6700(98)00018-5

Boontima, B., Noomhorm, A., Puttanlek, C., Uttapap, D., and Rungsardthong, V. (2015). "Mechanical properties of sugarcane bagasse fiber-reinforced soy based biocomposites," *Journal of Polymers and the Environment* 23(1), 97-106. DOI: 10.1007/s10924-014-0679-2

Bowyer, W. H., and Bader, H. G. (1972). "On the reinforcement of thermoplastics by imperfectly aligned discontinuous fibres," *Journal of Materials Science* 7(11), 1315-1312. DOI: 10.1016/0010-4361(73)90608-3

Cao, Y., Shibata, S., and Fukumoto, I. (2006). "Mechanical properties of biodegradable composites reinforced with bagasse fibre before and after alkali treatments," *Composites Part a-Applied Science and Manufacturing* 37(3), 423-429. DOI: 10.1016/j.compositesa.2005.05.045

Diab, M., Curtil, D., El-shinnawy, N., Hassan, M. L., Zeid, I. F., and Mauret, E. (2015). "Biobased polymers and cationic micro-fibrillated cellulose as retention and drainage

aids in papermaking: Comparison between softwood and bagasse pulps," *Industrial Crops and Products* 72, 34-45. DOI: 10.1016/j.indcrop.2015.01.072

El-Fattah, A. A., El Demerdash, A. G. M., Sadik, W. A. A., and Bedir, A. (2015). "The effect of sugarcane bagasse fiber on the properties of recycled high density polyethylene," *Journal of Composite Materials* 49(26), 3251-3262. DOI: 10.1177/0021998314561484

Flandez, J., González, I., Resplandis, J. B., El Mansouri, N.-E., Vilaseca, F., and Mutjé, P. (2012). "Management of corn stalk waste as reinforcement for polypropylene injection moulded composites," *BioResources* 2(7), 1836-1849. DOI: 10.15376/biores.7.2.1836-1849

Franco-Marques, E., Mendez, J. A., Pelach, M. A., Vilaseca, F., Bayer, J., and Mutje, P. (2011). "Influence of coupling agents in the preparation of polypropylene composites reinforced with recycled fibers," *Chemical Engineering Journal* 166(3), 1170-1178. DOI: 10.1016/j.cej.2010.12.031

Fuentes Talavera, F. J., Silva Guzman, J. A., Richter, H. G., Sanjuan Duenas, R., and Ramos Quirarte, J. (2007). "Effect of production variables on bending properties, water absorption and thickness swelling of bagasse/plastic composite boards," *Industrial Crops and Products* 26(1), 1-7. DOI: 10.1016/j.indcrop.2006.12.014

Fuqua, M. A., Chevali, V. S., and Ulven, C. A. (2013). "Lignocellulosic byproducts as filler in polypropylene: Comprehensive study on the effects of compatibilization and loading," *Journal of Applied Polymer Science*, 127(2), 862-868. DOI: 10.1002/app.37820

Girones, J., Lopez, J. P., Vilaseca, F., Bayer R, J., Herrera-Franco, P. J., and Mutje, P. (2011). "Biocomposites from *Musa textilis* and polypropylene: Evaluation of flexural properties and impact strength," *Composites Science and Technology* 71(2), 122-128. DOI: 10.1016/j.compscitech.2010.10.012

Harun, J., Abdan, K., and Zaman, K. (2008). "Rheological behaviour of injection moulded oil palm empty fruit bunch fibre-polypropylene composites: Effects of electron beam processing *versus* maleated polypropylene," *Molecular Crystals and Liquid Crystals* 484, 500-508. DOI: 10.1080/15421400801904328

Hoareau, W., Oliveira, F. B., Grelier, S., Siegmund, B., Frollini, E., and Castellan, A. (2006). "Fiberboards based on sugarcane bagasse lignin and fibers," *Macromolecular Materials and Engineering* 291(7), 829-839. DOI: 10.1002/mame.200600004

Jesus Vargas-Radillo, J., Salazar-Rios, E., Barrientos-Ramirez, L., Perez-Centeno, A., Renteria-Urquiza, M., Rodriguez-Rivas, A., Navarro-Arzate, F., and Rutiaga-Quinones, J. (2015). "Bleached pulp and fermentable sugars from sugarcane pith bagasse," *Madera Y Bosques* 21(2), 117-130. DOI:

Karim, R., Rahman, M. F., Hasan, M., Islam, M. S., and Hassan, A. (2013). "Effect of fiber loading and alkali treatment on physical and mechanical properties of bagasse fiber reinforced polypropylene composites," *Journal of Polymer Materials* 30(4), 423-433. DOI: 10.1515/polyeng-2014-0270

Kazayawoko, M., Balatinecz, J. J., and Matuana, L. M. (1999). "Surface modification and adhesion mechanisms in woodfiber-polypropylene composites," *Journal of Materials Science* 34(24), 6189-6199. DOI: 10.1023/a:1004790409158

Kelly, A., and Tyson, W. (1965). "Tensile properties of fibre-reinforced metals - copper/tungsten and copper/molybdenum," *Journal of the Mechanics and Physics of Solids* 13(6), 329-338. DOI: 10.1016/0022-5096(65)90035-9

Khakifirooz, A., Ravanbakhsh, F., Samariha, A., and Kiaei, M. (2013). "Investigating the

possibility of chemi-mechanical pulping of bagasse," *BioResources* 8(1), 21-30. DOI: 10.15376/biores.8.1.21-30

Lashgari, S., Garmabi, H., Lashgari, S., and Mohammadian-Gezaz, S. (2011). "Improving the interfacial adhesion of highly filled PP-bagasse composites designed by Taguchi method," *Journal of Thermoplastic Composite Materials* 24(4), 431-446. DOI: 10.1177/0892705710387982

Lee, K.-Y., Aitomaki, Y., Berglund, L. A., Oksman, K., and Bismarck, A. (2014). "On the use of nanocellulose as reinforcement in polymer matrix composites," *Composites Science and Technology* 105, 15-27. DOI: 10.1016/j.compscitech.2014.08.032

Li, T. Q., Ng, N., and Li, R. K. Y. (2001). "Impact behavior of sawdust/recycled-PP composites," *Journal of Applied Polymer Science* 81(6), 1420-1428. DOI: 10.1002/app.1567

Li, Y., Pickering, K. L., and Farrell, R. L. (2009). "Determination of interfacial shear strength of white rot fungi treated hemp fibre reinforced polypropylene," *Composites Science and Technology* 69(7-8), 1165-1171. DOI: 10.1016/j.compscitech.2009.02.018

Lois-Correa, J. A. (2012). "Depithers for efficient preparation of sugar cane bagasse fibers in pulp and paper industry," *Ingeniería, Investigación y Tecnología* 13(4), 417-424.

Lopez, J. P., Mendez, J. A., El Mansouri, N. E., Mutje, P., and Vilaseca, F. (2011). "Mean intrinsic tensile properties of stone groundwood fibers from softwood," *BioResources* 6(4), 5037-5049.

Lopez, J. P., Mendez, J. A., Espinach, F. X., Julian, F., Mutje, P., and Vilaseca, F. (2012a). "Tensile strength characteristics of polypropylene composites reinforced with stone groundwood fibers from softwood," *BioResources* 7(3), 3188-3200.

Lopez, J. P., Mutje, P., Pelach, M. A., El Mansouri, N. E., Boufi, S., and Vilaseca, F. (2012b). "Analysis of the tensile modulus of PP composites reinforced with stone groundwood fibers from softwood," *BioResources* 7(1), 1310-1323.

Naghmouchi, I., Espinach, F. X., Mutjé, P., and Boufi, S. (2015). "Polypropylene composites based on lignocellulosic fillers: How the filler morphology affects the composite properties," *Materials & Design* 65, 454-461. DOI: 10.1016/j.matdes.2014.09.047

Nourbakhsh, A., and Kouhpayehzadeh, M. (2009). "Mechanical properties and water absorption of fiber-reinforced polypropylene composites prepared by bagasse and beech fiber," *Journal of Applied Polymer Science* 114(1), 653-657. DOI: 10.1002/app.30605

Panthapulakkal, S., and Sain, M. (2006). "Injection molded wheat straw and corn stem filled polypropylene composites," *Journal of Polymers and the Environment* 14(3), 265-272. DOI: 10.1007/s10924-006-0021-8

Ramaraj, B. (2007). "Mechanical and thermal properties of polypropylene/sugarcane bagasse composites," *Journal of Applied Polymer Science* 103(6), 3827-3832. DOI: 10.1002/app.25333

Reixach, R., Espinach, F. X., Arbat, G., Julián, F., Delgado-Aguilar, M., Puig, J., and Mutjé, P. (2015). "Tensile properties of polypropylene composites reinforced with mechanical, thermomechanical, and chemi-thermomechanical pulps from orange pruning," *BioResources* 10(3), 4544-4556. DOI: 10.15376/biores.10.3.4544-4556

Reixach, R., Espinach, F. X., Franco-Marquès, E., Ramirez de Cartagena, F., Pellicer, N., Tresserras, J., and Mutjé, P. (2013a). "Modeling of the tensile moduli of mechanical,

thermomechanical, and chemi-thermomechanical pulps from orange tree pruning," *Polymer Composite* 34(11), 1840-1846. DOI: 10.1002/pc.22589

Reixach, R., Franco-Marquès, E., El Mansouri, N.-E., de Cartagena, F. R., Arbat, G., Espinach, F. X., and Mutjé, P. (2013b). "Micromechanics of mechanical, thermomechanical, and chemi-thermomechanical pulp from orange tree pruning as polypropylene reinforcement: A comparative study," *BioResources* 8(3). DOI: 10.15376/biores.8.3.3231-3246

Rodriguez, M., Rodriguez, A., Bayer R, J., Vilaseca, F., Girones, J., and Mutje, P. (2010). "Determination of corn stalk fibers' strength through modeling of the mechanical properties of its composites," *Bioresources* 5(4), 2535-2546.

Samariha, A., Bastani, A., Nemati, M., Kiaei, M., Nosrati, H., and Farsi, M. (2013). "Investigation of the mechanical properties of bagasse flour/polypropylene composites," *Mechanics of Composite Materials* 49(4), 447-454. DOI: 10.1007/s11029-013-9361-3

Sanadi, A. R., Caulfield, D. F., Jacobson, R. E., and Rowell, R. M. (1995). "Renewable agricultural fibers as reinforcing fillers in plastics - mechanical- properties of kenaf fiber-polyprolene composites," *Industrial & Engineering Chemistry Research* 34(5), 1889-1896. DOI: 10.1021/ie00044a041

Serrano, A., Espinach, F. X., Julian, F., del Rey, R., Mendez, J. A., and Mutje, P. (2013). "Estimation of the interfacial shears strength, orientation factor and mean equivalent intrinsic tensile strength in old newspaper fiber / polypropylene composites," *Composites Part B: Engineering* (50), 232-238. DOI: 10.1016/j.compositesb.2013.02.018

Theng, D., El Mansouri, N. E., Arbat, G., Bunthan, Ngo, Delgado-Aguilar, M., Pelach, M. A., Fullana-i-Palmer, P., and Mutje, P. (2016). "Fiberboards made from corn stalks, thermomechanical pulp, and kraft lignin as green adhesive," *BioResources* (in press).

Thomason, J. L. (2002). "Interfacial strength in thermoplastic composites - at last an industry friendly measurement method?," *Composites Part a-Applied Science and Manufacturing* 33(10), 1283-1288. DOI: 10.1016/s1359-835x(02)00150-1

Vallejos, M. E., Canigueral, N., Mendez, J. A., Vilaseca, F., Corrales, F., Lopez, A., and Mutje, P. (2006). "Benefit from hemp straw as filler/reinforcement for composite materials," *Afinidad* 63(525), 354-361.

Vallejos, M. E., Espinach, F. X., Julian, F., Torres, L., Vilaseca, F., and Mutje, P. (2012). "Micromechanics of hemp strands in polypropylene composites," *Composites Science and Technology* 72(10), 1209-1213. DOI: 10.1016/j.compscitech.2012.04.005

Youssef, H. A., Ismail, M. R., Ali, M. A. M., and Zahran, A. H. (2008). "Effect of the various coupling agents on the mechanical and physical properties of thermoplastic-bagasse fiber composites," *Polymer Composites* 29(9), 1057-1065. DOI: 10.1002/pc.20473

Article submitted: Feb. 26, 2016; Peer review completed: May 9, 2016; Revised version received: May 18, 2016; Accepted: May 26, 2016; Published: June 13, 2016.
DOI: 10.15376/biores.11.3.6346-6361