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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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.

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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),

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

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 $l_{i,j}^f$ 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).

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

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®

(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

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.
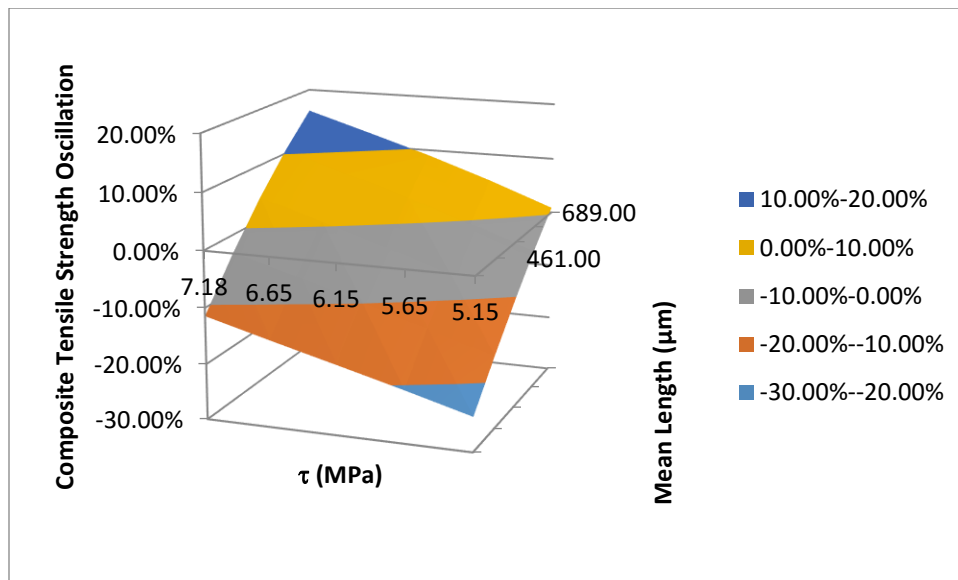

Fig. 1. Oscillation of the theoretical tensile strength of the composite versus the interfacial shear strength and the mean length of the fibers

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.
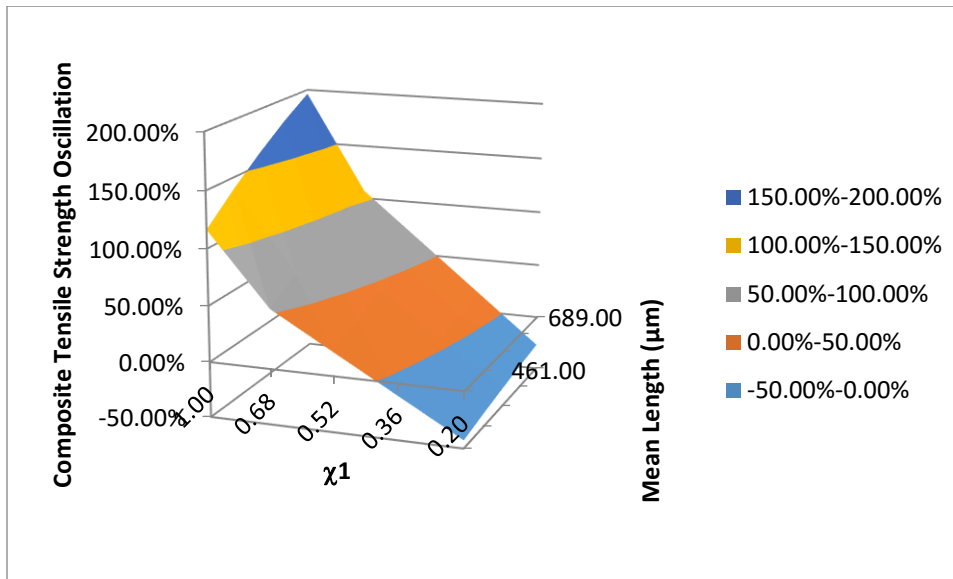

Fig. 2. Oscillation of the theoretical tensile strength of the composite versus the orientation factor and the mean length of the fibers

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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