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NATURAL FILLER-REINFORCED COMPOSITES: COMPARISON OF REINFORCING POTENTIAL AMONG TECHNICAL FIBERS, STEM FRAGMENTS AND INDUSTRIAL BY-PRODUCTS

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This paper is dedicated to Acad. Cristofor I. Simionescu, a great scientist, a visionary and a kind man of many talents. In 1991, he organized a meeting between P. Navard and “Petru Poni” Institute. The collaboration between our two institutions is still alive.

Fillers, originating from eleven different plants, and which can be divided into three classes: technical fibers (curauà, jute and flax), crop stem fragments (miscanthus, sorghum and maize) and industrial by-products (agave, oak chips, wet draff, wheat straws and vine shoots), were compared to glass fibers in low density polyethylene and polypropylene reinforced composites, applying similar compounding and processing conditions. On average, modulus and strength were reduced by factors of 1.5, 2 and 3, when glass fibers were replaced by technical fillers, plant stem fragments and by-product fillers respectively. There was not much difference as to the decrease in impact strength among the three classes. The fillers that exhibited a good reinforcing capacity in one matrix provided comparatively low performance in the other. The evolution of the tensile strength, elastic modulus and elongation at break of low density polyethylene composites reinforced with curauà, flax, jute and glass fibers is not correlated with that of polypropylene-based composites.

Keywords: natural filler-reinforced composites, natural fibers, mechanical properties, rheological properties

INTRODUCTION

For several decades, the substitution of glass fibers with more eco-friendly materials, such as natural fibers or fillers, has been subjected to extensive attention from the scientific community.¹⁻³ In addition to economic and environmental benefits, the lower density of ligno-cellulose-based fillers allows obtaining lighter materials, an attractive characteristic for industries, such as the automotive one.⁴⁻⁶ In spite of the many efforts devoted to this topic, the mechanical performance of natural fiber-reinforced composites is still too low for demanding applications.⁷ Nevertheless, their low cost, specific strength properties and biodegradable character have been enough to promote their use in various applications, such as decking and flooring.⁸⁻¹⁰

Much research has been devoted to the preparation, optimization and evaluation of composites reinforced with cellulose-based fibers extracted either from wood or from a large variety of annual plants.¹¹⁻¹² However, the processes for extracting the cellulosic fibers from plants require, in most cases, high consumptions of energy. Given the limited mechanical properties of such thermoplastic composites, the expensive extraction processes lead to economically non-competitive materials.^{7,13} In order to increase their potential industrial applications, it is necessary to decrease the cost of the raw material and filler processing. With this objective in mind, lignocellulosic agricultural residues (*e.g.* tree pruning, rice husk, wheat straw) were considered as potential sources of biomass-based fillers.¹⁴⁻¹⁶ However, their discontinuous supply may represent an obstacle for industrial processes. The full dedication of crops for lignocellulosic biomass production would enable reducing the cost of feedstock and ensure a reliable supply chain for the compounding industries.¹⁷ In this sense, thanks to their high photosynthesis efficiency and low nutrient requirements, miscanthus and other C4 plants have emerged as promising candidates for biomass-dedicated crop plants.¹⁸⁻²¹ Beyond their possible use as biomass for energy²²⁻²⁴ and bioethanol production,^{25,26} the high yield of miscanthus crop, for example, offers an alternative to cellulose fibers as a reliable source of lignocellulosic fillers (in the form of stem fragments) for polymer reinforcement.^{27,28} We thus have three main classes of potential fillers,

cellulose fibers, plant stem fragments and agricultural residues and industrial by-products. Many papers have been published on the preparation and processing of many different combinations of fillers and matrices. Numerous reviews have also been written, comparing the mechanical performance of such composites, prepared with many different polymeric matrices and reinforced with a multitude of different natural fillers. Similarly, many different mechanical and chemical treatments have been developed to enhance the filler-matrix adhesion and improve the mechanical performance of composites. Adding the different compositions, coupling agents, processing techniques and standards for characterization (*e.g.* ASTM, ISO, UNE), the result is a myriad of combinations that bring difficulties when willing to compare the results obtained by so many research groups.

The objective of the present work is to assess and compare the mechanical performance of different biomass-based reinforcing elements, coming from the three classes mentioned above, in order to determine their reinforcing potential. Fillers from the three classes, coming from eleven different plants, a) so-called technical fibers (curauà, jute and flax), b) ground stem fragments (miscanthus, sorghum and maize) and c) industrial by-products (agave, oak, wet draff, wheat straws, vine shoots) were used to prepare composites with the same two polymers (low-density polyethylene (LDPE) and polypropylene (PP)), and the same coupling agents. The results allow quantitatively ranking these three classes and comparing them with glass fiber-reinforced LDPE and PP composites.

EXPERIMENTAL

In this work, composites were prepared using the same processing conditions (mixing temperature, rotor speed, mixing time), employing eleven different types of biomass from different plants as fillers and the same two polymer matrices.

Materials

Polymer matrices and coupling agents

A low density polyethylene (LDPE) SABIC[®] LDPE 1965T was used as polymeric matrix (melt flow index, MFI, 65 dg/min at 190 °C and 2.16 kg, density of 919 kg/cm³). A high density polyethylene, Orevac[®] 18507 (Arkema) with a high content of maleic anhydride (MA-g-HDPE) was used as coupling agent (MFI = 5 g/10 min at 190 °C and 2.16 kg).

The second matrix was a polypropylene, Addilene[®] (PP), provided by Addiplast. A maleic anhydride-grafted polypropylene (MA-g-PP), under the code name G-3015, supplied by Eastman, was used as coupling agent, with maleic anhydride content of 2.6%, acid number 15, and molecular weight of 47000.

The two coupling agents were added in a proportion of 5% reinforcement weight basis, *i.e.* 1.5% on total weight.

Fillers

Technical fibers. Curauà is a fiber extracted from the leaves of a plant belonging to the ananas family (*Ananas lucidus*, Bromeliaceae). The plants were grown in the Pará region of Brazil and the fibers were obtained from Pematec Triangel do Brasil, Brazil. Jute and flax were both obtained from Vivabras Industria e Comercio LTDA, Brazil. They were supplied as fibers over 1 meter long. Prior to use, fibers were manually cut with scissors to approximately 1 cm. Thus, the flax, jute and curauà fibers used were much longer than the stem fragments obtained from the other plants in this study. Given their average diameter, the aspect ratio of technical fibers was also much larger than those of the fragments obtained from maize, sorghum and miscanthus, or from other plants (Table 1).

Stem fragments. Sorghum plants were harvested and dried in October 2013 by EuroSORGHO (France), which provided stem sections with lengths from 30 cm to 1 m. Miscanthus was cultivated and harvested at the Unité Expérimentale Grandes Cultures Innovation Environnement of INRA in Estrées-Mons (Picardie, France). Stems were provided in 80 cm long sections. Prior to use, all the stems were cut, ground and sieved in order to obtain samples with homogeneous size. Maize plants were cultivated, harvested and dried in October 2013 by UMR de Génétique Végétale de Moulon – INRA (Moulon, France), which provided 50-100 cm long stem sections. Maize plants were submitted to the same processing conditions as sorghum and miscanthus.

Industrial and agricultural by-products. Agave, oak chips, wheat straws, wet draff, and vine shoots were provided by Pernod-Ricard. Agave bagasse originating from Mexico was obtained as a waste product of the tequila production process, during which the stem of the plant was cooked, ground, fermented and eventually distilled. Agave bagasse had the aspect of long bundles, 10-20 cm long. Oak chips were the result of steam explosion of oak wood (*Quercus sp.*, orig. France) used for the casks where whisky aged. Before grinding, oak chips were examined by hand and the very hard pieces that could damage the grinder were eliminated. Wheat straws are the raw material for the distillation of several alcohols, such as vodka, whisky, *etc.* Vine shoots, spur

and cordon (no leaves) were collected after the harvest. Wheat straws and vine shoots were approximately 30-50 cm long. Wet draff is a barley distillery by-product. It is the wet residue of malted barley obtained after mashing and before being distilled.

Glass fibers. E-type glass fibers were supplied by Arkema (France). The chopped glass fibers had number and weighted average lengths of $L_n = 3380 \mu\text{m}$ and $L_w = 3485 \mu\text{m}$, respectively. Fiber diameter was $10 \mu\text{m}$ (aspect ratio ~ 350). Length distribution was rather monodisperse (polydispersity index = 1.03), with a minimum length around $1350 \mu\text{m}$ and a maximum around $5810 \mu\text{m}$.

All fillers were stored in a closed shelter to be protected from atmospheric agents, such as rain, direct sunlight, humidity. Before use, fillers were oven dried overnight at $70 \text{ }^\circ\text{C}$. The appearance of these fillers is shown in Figure 1.

Preparation and characterization of reinforcing elements

Stem sections of sorghum, maize, miscanthus and long fragments from industrial residues (wheat straws, vine shoots) were cut down to 2-3 cm long pieces with the help of pruning shears. After being mildly dried, all the products (oak chips, wet draff, and agave included) were ground in a Hellweg M50 granulator equipped with a 2.5 mm sieve. The result of this process was a mix of elongated fragments with high size dispersion.

Technical fibers. In order to ease their dosing during compounding, fibers (initial length of 1 m) were manually cut with scissors to approximately 1 cm. The average dimensions of the fibers are listed in Table 1. Flax fibers exhibited high weight average aspect ratio, around 74, while jute and curauà fibers showed lower values, of 54 and 37, respectively. Although presenting similar average length, the bundles of flax were thinner than the two other fibers, leading to higher mean aspect ratio values.

Stem fragments. The size of the miscanthus, maize and sorghum stem fragments was reduced to micron size by means of a coffee mill (Carrefour home). In order to ensure homogeneous fragment size, stem fragments were sieved in a Retsch AS200 Digit shaker (Retsch, Germany). Sieving was conducted on 20 g of stem plant samples with the shaker operating at 40 mm amplitude (2 mm/g) for 5 minutes. A stack of 8 sieves with open pore sizes of 1000, 600, 400, 300, 200 and $100 \mu\text{m}$ were used. The obtained stem fragments had low aspect ratios, of 6-7 for miscanthus, 3-4 for maize and 5-6 for sorghum. In the case of miscanthus, the fragments retained on the smallest sieve available ($100 \mu\text{m}$) were used in order to maximize the surface area of the fragments, hence their interaction with the polymer matrix. However, due to problems experienced during sieving (sieves being easily obstructed) for maize and sorghum, composites were prepared with the stem fragments collected in the $200 \mu\text{m}$ sieve. A more detailed characterization of fragments size is presented in Table 1.

Industrial by-products. All samples were used as received. Agave fragments showed aspect ratios of 3.6 (mean length average) and 23 (mean weight average), whilst wet draff, wheat straws and vine shoots were characterized by low aspect ratio values, ranging between 1.8 and 3.0 for number and weight averages, respectively (Table 1). Wheat straws were initially quite long (L_w around 6 mm), but at the same time their bundles were very thick (D_w around $700 \mu\text{m}$).

Table 1
Average dimensions of fillers

	Plant	Mesh size (μm)	L_n (μm)	L_w (μm)	D_n (μm)	D_w (μm)	$(L/D)_n$ (μm)	$(L/D)_w$ (μm)
Stem fragments	Miscanthus	100	261	576	87	127	2.9	4.8
	Sorghum	200	252	1073	86	172	2.3	5.0
	Maize	200	495	1359	154	269	2.6	5.7
Technical fibers	Curauà	-	592	10238	34	139	5.3	37.4
	Flax	-	746	7544	31	76	11.2	74
	Jute	-	722	12125	30	114	6.6	53.8
	E-Glass	-	3380	3458	10	10		350
Industrial by-products	Agave	-	701	11120	60	270	3.6	23
	Oak	-	202	999	48	196	3.5	9.0
	Wet draff	-	116	1328	55	378	1.7	2.6
	Wheat	-	255	5890	76	720	1.8	3.5
	Vine-shoots	-	77	1981	34	283	1.9	3.6

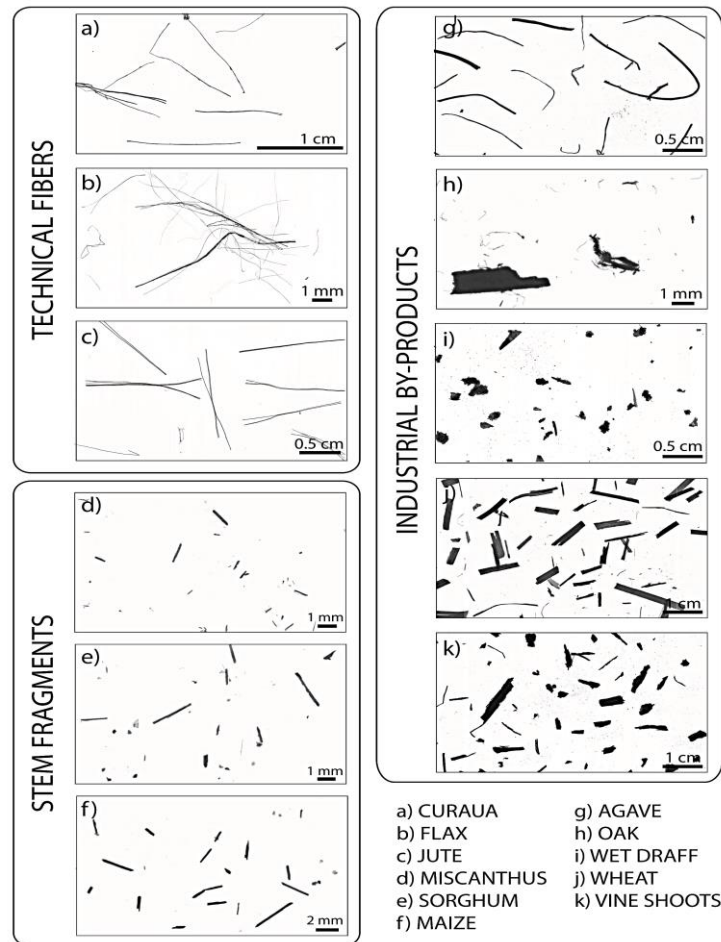


Figure 1: High-resolution images of the fillers

Table 2
Injection processing parameters

Matrix	T_{melt} (min)	T_{cyl} (°C)	T_{cyl} (°C)	P_{inj} (bar)	P_{post} (bar)
PP	4-5	200	70	400 for 15s	300 for 10s
LDPE	3	150	40	400 for 15s	300 for 10s

For all the fillers, the dimensions of fragments/fibers were measured by using a high resolution 2D scanner (Epson Perfection™ V550 Photo color Scanner), in transmission mode and with a resolution of 6400 dpi, corresponding to 4 $\mu\text{m}/\text{pixel}$. Image analysis was carried out by employing ImageJ and special plugins (Morphology > BinaryLabel8 and Geodesics > Geodesics Diameters) to label and compute the fiber size, respectively.²⁹

Composite preparation

Prior to compounding, fillers were dried overnight in an air-circulating oven operating at 60 °C. Composite blends comprising 30% (w/w) fillers were produced by means of a Haake Rheomix 600 intensive kinetic mixer, equipped with counter-rotating roller rotors operating at 60 rpm for 9 minutes with control temperature set at 180 °C for PP composites and 150 °C for LDPE composites.

The fillers were introduced in the mixer chamber in two steps, at $t = 1$ min and $t = 3$ min. MA-g-PP (or MA-g-PE depending on the matrix used) was added to the mix once the fillers were well dispersed (at $t = 5$ min) in order to minimize hydrolysis of the maleic anhydride groups and limit fiber attrition. After compounding, composites were granulated in a blade mill with a 5 mm mesh and then kept in an oven at 80 °C until used. Test specimens were injection-molded in a Haake Minijet-II (Thermo Fisher Scientific, Germany) using steel molds, complying with ISO-527-2-1BA (tensile bars) and ISO-179 (impact bars) specifications. Rheometer probe discs were injected, with a diameter of 25 mm and thickness of 1.5 mm. Injection processing parameters are reported in Table 2.

Mechanical and rheological characterization

Composite specimens were kept in a conditioned room at 23 °C and 50% humidity for at least three days before testing. Tensile tests were carried out in a Zwicki Z2.5 tensile testing machine (Zwick-Roell) operating at 0.02 mm/s (1.2 mm/min). Charpy V-notch impact tests were conducted on a pendulum Ceast 9050 (Instron Company, France) with a 1 J swing arm. Two mm indents were conducted by means of a single tooth Ceast NotchVIS manual notching machine (Instron, France). At least six specimens were tested per sample and per mechanical property.

Rheometer probe discs of 25 mm diameter and 1.5 mm thickness were injection-molded in a Haake Minijet-II (Thermo Scientific). The dynamic rheological measurements were performed on an ARES rheometer (TA Instruments), using parallel plate geometry with plates of 25 mm as diameter and 2 mm as gap. Frequency sweep tests were conducted from 100 to 0.1 rad/s on molten PP- and LDPE-based composites at 200 °C and 140 °C, respectively. Strain was fixed at 1%, ensuring that all materials were in a linear visco-elastic regime.

Thermogravimetric analysis

The thermal stability of fillers was measured by thermogravimetric analysis (TGA), using a TGA/DSC 1 STARE (Mettler Toledo). The test samples were made of 10 mg of ground matter collected between the meshes of 200 and 100 µm. The samples were heated at 10 °C min⁻¹ from 25 °C to 400 °C and at 50 °C min⁻¹ from 400 °C to 800 °C under an air gas flow of 50 mL min⁻¹. The results were analyzed using STARE software.

RESULTS AND DISCUSSION

Mechanical properties of composites

The capacity of lignocellulosic materials (technical fibers, stem fragments and industrial residues) to reinforce LDPE and PP matrices was evaluated and compared to that of glass fibers, considered as the reference. The axial ratio of the fillers and the densities and mechanical properties of LDPE- and PP-based composites are reported in Tables 3 and 4, respectively.

Tensile strength

LDPE-based composites. The addition of 30% w/w of any of the fillers (Fig. 2a, light grey bars) resulted in an improvement of the tensile strength of the neat matrix (black line), with the exception of wet draff and vine shoots fragments, which did not provide any significant improvement. The results showed that the addition of glass fibers increased the tensile strength by a factor of 2.6. As expected, technical fibers presented the best reinforcing capacity among the lignocellulosic materials tested. The incorporation of technical fibers, such as jute and flax, provided materials with similar strength to that of glass fibers. The best reinforcing properties were obtained with the curauà fibers, which increased the tensile strength of neat LDPE by a factor of 3 (from 7.2 to 21.4 MPa). Miscanthus and sorghum stems improved the tensile strength by a factor of 1.9 and 1.6, respectively. On the contrary, maize stem fragments only had a moderate effect, increasing the tensile strength by a factor of 1.3, similarly to agave and wheat straws fragments. Oak chips strengthened the neat matrix by a factor of 1.5. In part, the poor reinforcing capacity of maize and the agricultural residues tested could be ascribed to their very low aspect ratio (Table 1, Fig. 2). Nevertheless, it is interesting to note the relatively large strength provided by miscanthus fragments, in spite of their low *L/D*.

PP-based composites. The addition of the glass fibers, technical fibers and fragments from stem to PP matrix (Fig. 2a, dark grey bars) showed an improvement of the tensile strength of the neat matrix (dashed line). On the contrary, other plants did not provide any benefit in terms of reinforcement. Composites reinforced with glass fibers showed the highest tensile strength values, enhancing by a factor of 2.8 the values of the neat matrix, while the composites reinforced with technical fibers raised the tensile strength by a factor of 1.6-1.8. The best results were obtained with the addition of jute, whilst the reinforcing capacity of curauà fibers was similar to those of miscanthus fragments.

Table 3
Axial ratio of the fillers used in this work and the densities and mechanical properties of their 30% w/w LDPE-based composites

Fillers			Properties of composites					
Origin	$(L/D)_{in}$ (-)	ρ (g/cm ³)	Tensile strength (MPa)	E (GPa)	$\varepsilon_{max\ strength}$ (%)	ε_{break} (%)	Impact strength (kJ/m ²)	
Stem fragments	Neat polymer	---	0.919	7.2 (0.8)	0.13 (0.01)	n.a.	n.a.	44.8(1.1)
	Miscanthus	3-5	1.079	13.4 (0.1)	0.90 (0.02)	4.3 (0.1)	4.8 (0.1)	6.4(0.2)
	Sorghum	2-5	1.070	11.7 (0.3)	0.97 (0.03)	3.3 (0.2)	3.6 (0.2)	5.8 (0.6)
	Maize	3-6	1.053	9.3 (0.1)	0.83 (0.02)	3.0 (0.2)	3.3 (0.3)	4.5 (0.3)
Technical fibers	Curauà	5-37	1.078	21.4 (0.6)	1.40 (0.08)	3.5 (0.1)	3.7 (0.1)	10.4(0.7)
	Flax	11-74	1.088	18.0 (0.1)	1.12 (0.01)	5.8 (0.1)	6.3 (0.1)	6.7 (0.2)
	Jute	7-54	1.066	18.6 (0.2)	1.54 (0.03)	3.8 (0.1)	4.3 (0.1)	6.7 (0.3)
	E-Glass	~350	1.172	18.7 (0.5)	1.81 (0.04)	2.1 (0.1)	2.8 (0.2)	9.6 (0.4)
Industrial by-products	Agave	4-23	1.053	9.6 (0.3)	0.48 (0.01)	4.7 (0.3)	5.2 (0.4)	5.7 (0.4)
	Oak	4-9	1.049	10.8 (0.2)	0.66 (0.02)	4.8 (0.3)	5.0 (0.3)	3.8 (0.3)
	Wet draff	2-3	1.028	7.2 (0.1)	0.44 (0.02)	4.2 (0.2)	4.6 (0.4)	3.9 (0.1)
	Wheat	2-4	1.045	9.5 (0.3)	0.76 (0.01)	2.9 (0.3)	3.2 (0.4)	4.2 (0.3)
	Vine-shoots	2-4	1.022	7.0 (0.5)	0.41 (0.01)	4.0 (0.3)	4.3 (0.6)	n.a.

Table 4
Densities and mechanical properties of 30% w/w PP-based composites

	Plant/fiber	ρ (g/cm ³)	Tensile strength (MPa)	E (GPa)	$\epsilon_{max\ strength}$ (%)	E_{break} (%)	Impact strength (kJ/m ²)
	---	0.905	24.0 (0.4)	1.15 (0.01)	6.4 (0.2)	---	4.0 (0.3)
Stem fragments	Miscanthus	1.027	37.4 (0.6)	3.19 (0.05)	2.3 (0.1)	2.7 (0.2)	3.2 (0.1)
	Sorghum	1.006	33.1 (0.2)	2.64 (0.02)	2.4 (0.1)	2.9 (0.2)	1.9 (0.2)
	Maize	1.011	28.9 (0.4)	2.32 (0.02)	2.2 (0.1)	2.6 (0.2)	1.6 (0.1)
Technical fibers	Curauà	1.021	38.4 (0.9)	2.97 (0.05)	2.6 (0.1)	2.7 (0.1)	4.5 (0.4)
	Flax	1.030	41.8 (0.6)	3.25 (0.03)	3.4 (0.1)	4.0 (0.1)	3.4 (0.1)
	Jute	1.033	44.2 (0.6)	3.58 (0.03)	2.6 (0.1)	3.2 (0.2)	4.9 (0.1)
	E-glass	1.121	67.1 (1.0)	4.21 (0.05)	2.6 (0.1)	2.7 (0.1)	4.8 (0.2)
Industrial by-products	Agave	1.041	21.5 (0.4)	1.62 (0.03)	2.9 (0.2)	3.2 (0.3)	1.7 (0.1)
	Oak	1.018	23.1 (0.5)	1.96 (0.03)	2.2 (0.2)	2.9 (0.4)	1.6 (0.1)
	Wet draff	1.005	19.2 (0.3)	1.50 (0.04)	2.5 (0.2)	2.7 (0.2)	1.8 (0.2)
	Wheat	1.019	22.3 (1.4)	2.14 (0.06)	1.8 (0.2)	1.9 (0.3)	2.5 (0.2)
	Vine-shoots	0.995	18.7 (0.4)	1.61 (0.07)	2.2 (0.3)	2.4 (0.4)	2.0 (0.2)

Table 5
Published properties of curauà, flax, jute * and E-Glass^{6,30,37-48}

Fiber	Diameter elementary fiber (μm)	Diameter technical fiber (μm)	Price/kg raw (US\$)	Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Curauà	7-10	65-320	0.6	1.4-1.5	500-1150	11.8-30	3.7-4.3
Flax	19	100-200	0.2-1.5	1.5	345-1500	27-39	1.2-3.2
Jute	15-30	200-600	0.35	1.4-1.5	305-800	20-55	1.2-1.8
E-Glass	10-20	-	1.3-3.2	2.5	2000-3500	70-73	2.5-3.7

*Curauà, flax, jute are composed of elementary fibers assembled in bundles (called technical fibers), it is these technical fibers that were used in this work

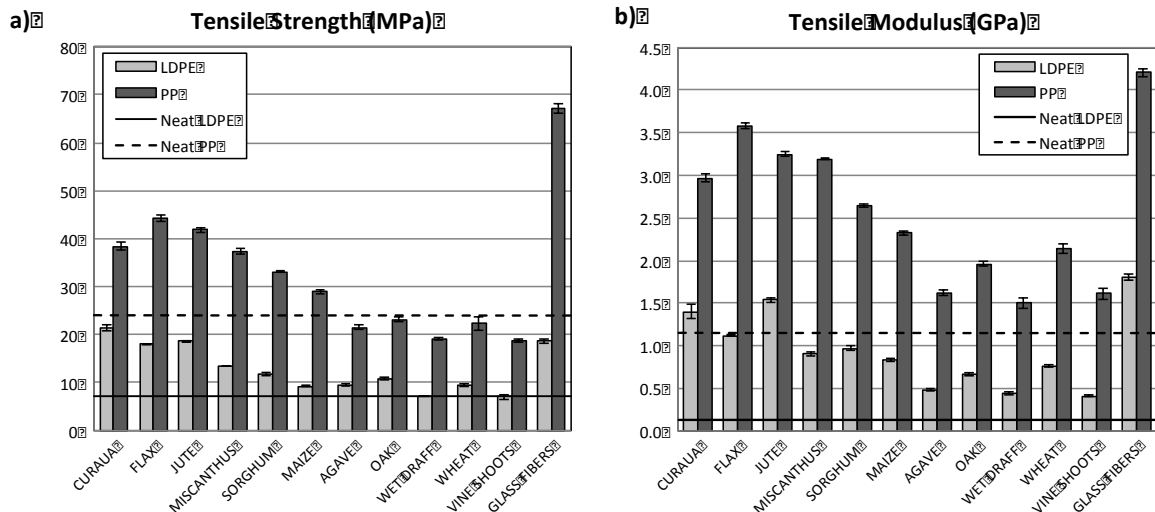


Figure 2: Values of a) tensile strength, and b) tensile modulus of various reinforcing materials in LDPE (light grey bars) and PP Addilene® (dark grey bars) matrices (lines depict the values of the neat matrices)

While the addition of glass fibers increased the tensile strength by a factor of 2.6-2.8 in both polymers, there is a difference between the behavior of plants in PP and PE. In PE, all the fillers had a reinforcing effect. This is not the case of PP, where the industrial by-products (agave, wet draff, wheat and vine shoots) produced composites with lower properties than those of the matrix. The improvements brought up by technical fibers and stems are lower in PP. This diminishment in the performance of biobased fillers in PP, compared to PE, can be assigned to two reasons. The first one consists in the fact that the coupling agents used in PP and PE composites do not have the same efficiencies, and this is a very sensitive parameter on the tensile strength. The second represents temperature. Compounds are processed at much higher temperatures in PP than in PE, which generate degradations that could lower significantly the mechanical properties of the fillers, and also can affect the interface between filler and matrix.

Tensile (Young's) modulus

LDPE-based composites. As expected, the intrinsic high rigidity of glass fibers (70-73 GPa, Table 5) significantly improved the tensile modulus of neat LDPE, rising it from 0.13 GPa to 1.81 GPa, *i.e.* by a factor of 14 (Fig. 2b, light grey bars). Composites reinforced with technical fibers (with intrinsic elastic modulus ranging between 12 and 55 GPa, Table 5) also presented considerably high Young's modulus, ranging between 1.12 and 1.40 GPa, representing increases ranging from 9 to 12. Contrary to the large differences observed in tensile strength, no significant differences were observed in Young's modulus of materials reinforced with stem fragments. Moderate improvement of Young's modulus of neat LDPE was observed if other plants were added. The modulus rose by a factor of 3.2 for vine shoots (lowest value) and by a factor of 5 for oak elements (highest value).

PP-based composites. Contrarily to tensile strength, composites exhibited Young's modulus values larger than that of the neat matrix for all types of added stem fragments (Fig. 2b, dark grey bars). The addition of glass fibers to PP produced an increase of tensile modulus by a factor of 3.7, followed by technical fibers, which caused an increase varying from a factor of 2.6 (curauà) up to 3.1 (jute). When compared to sorghum and maize, the results obtained evidenced a higher reinforcing capacity of the miscanthus fragments, which had a similar effect to that of flax fibers. Both elements conferred an increase of the modulus by a factor of 2.8. Whilst presenting a similar elastic modulus to that of the composites reinforced with miscanthus, the higher flexibility of the flax-reinforced composites was responsible for the differences observed in ultimate tensile strength. Young's modulus of the composites reinforced with other plant fragments increased by a factor of 1.3-1.9.

Again, a decreased improvement is observed for PP, compared to that of PE, for the same reasons as given for tensile strength above.

Elongation

LDPE-based composites. As it is common for fiber-reinforced composites, strain at yield (at maximum strength) and at break (Fig. 3, light grey bars) decreases as fillers are added to the neat LDPE matrix. However, considerable differences were detected among the lignocellulosic fillers tested. The highest values of elongation at break were obtained with the addition of flax elements ($\epsilon_{max} = 5.8\%$), while the lowest values were observed with glass fibers ($\epsilon_{max} = 2.1\%$). One of the reasons behind these values is the higher capacity to sustain plastic deformation of the composites containing technical fibers. Despite the fact that flax has a lower intrinsic elongation than curauà (Table 5), the elongation at break of flax-reinforced composites ($> 6\%$) is larger than that of curauà. ϵ_{break} of the composites reinforced with miscanthus, agave and oak fragments was around 5.0%, whereas industrial by-products presented values well below 5%.

PP-based composites. As observed for LDPE-based composites, the addition of fillers leads to poor elongation at yield and break, compared to the neat PP matrix (Fig. 3, dark grey bars). As for HDPE-based composites, flax-reinforced materials presented a significantly higher capacity to sustain deformation than the other materials (its elongation at yield was 3.4%, compared with 2.3-2.6% for the other composites tested). For the composites reinforced with jute and agave fragments, elongation at break had similar values (3.2%), as well as for the composites loaded with sorghum and oak (2.9%). The addition of glass fibers provided an elongation at break equal to 2.7%, similarly to miscanthus and wet draff fragments. Presenting similar elongation at yield to that of the other materials tested, the higher strength of the composites reinforced with jute was caused by their rigidity (high Young's modulus) of the material.

Impact strength

LDPE-based composites. The impact strength of the composites reinforced with the natural fillers tested was significantly lower than that of the composites reinforced with glass fibers. Curauà fibers were the exception, providing materials with impact strength values slightly higher than that of glass fibers (10.4 and 9.6 kJ/m², respectively). The other technical fibers provided materials with an impact strength around 7.0 kJ/m². Among the composites reinforced with stem fragments, miscanthus-based composites showed the highest value (6.4 kJ/m²), followed by sorghum. Meanwhile, agave fibers were the only industrial residue tested that provided composites with an impact strength above 5 kJ/m². The other composites evaluated exhibited very poor impact strength (Table 3).

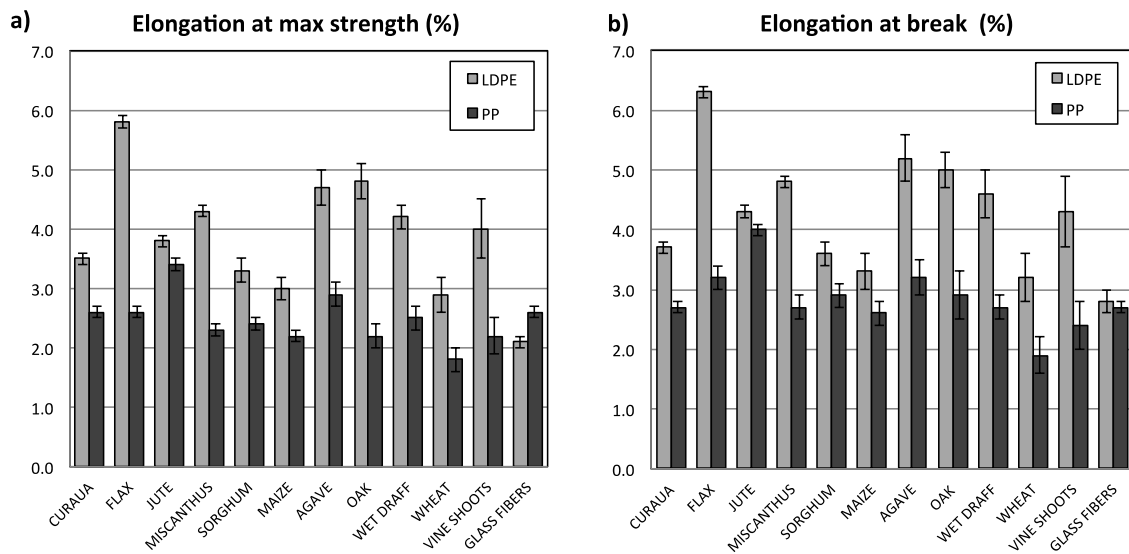


Figure 3: Values of elongation a) at maximum strength, and b) at break of various reinforcing materials in LDPE (light grey bars) and PP Addilene® (dark grey bars) matrices

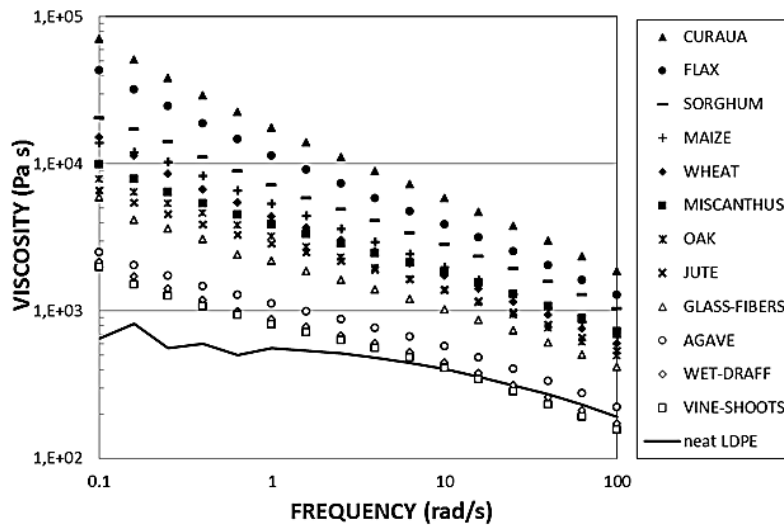


Figure 4: Frequency sweep test of LDPE-based composites with various reinforcements (tests were conducted at $\gamma = 1\%$ and $T = 140\text{ }^{\circ}\text{C}$)

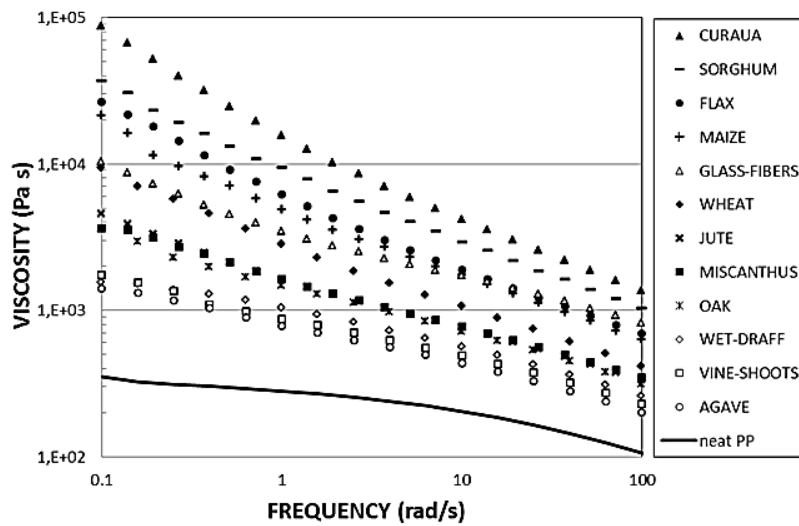


Figure 5: Dynamic viscosity of PP-based composites with various reinforcements (tests were conducted at $\gamma = 1\%$ and $T = 200\text{ }^{\circ}\text{C}$)

PP-based composites. None of the tested fillers provided composites with noticeable impact strength. When comparing the different fillers, it can be noticed that the composites containing relatively long and flexible technical fibers presented impact strength values in the same range as glass fibers (ranging between 4 and 5 kJ/m^2). The other tested fillers presented very poor impact resistances ($< 2\text{ kJ/m}^2$), with the only exception of miscanthus stem fragments, which had an impact resistance of 3.2 kJ/m^2 , not far from that of flax-reinforced composites.

One of the main limiting factors for the industrial application of natural filler-reinforced composites is their low impact resistance. Indeed, all the fillers used in this work follow the general trend observed in the literature, *i.e.* a poor ability to increase impact strength.

Rheological behavior of melt composites

Given the limited range of processing temperatures available (in order to avoid the thermal degradation of fibers), the rheological properties of the compounds are of great importance for estimating the potential industrial applications of the composites. Flow characteristics must enable an easy injection-molding process. Viscosity is the first parameter that should be considered. Figures 4 and 5 show the complex viscosity *versus* frequency for the eleven fillers in LDPE and PP. The behavior is very similar whatever the matrix polymer is. As expected, the viscosities of all the composites are higher than that of the neat polymer. Recalling that the filler concentration is the same

for all the composites (30% w/w), we see that viscosities are scattered over a large range of values, up to more than two orders of magnitude higher than that of the polymer. There is a 1.5 orders of magnitude difference between the composites with the lowest viscosities and the one with the highest. The ranking of the fillers is nearly the same in PP and LDPE. At the high end, curauà, flax, sorghum, flax and wheat provide the largest viscosities. They also have a very high shear thinning behavior at frequencies below $5\text{-}10\text{ s}^{-1}$. The shear thinning behavior is closer to the one of the matrix polymer at frequencies larger than 10 s^{-1} . Such a behavior is reminiscent of a system with a lot of interconnections between the filler particles. These interconnections are very sensitive at low frequencies where the region probed is very large. At high frequencies, the higher the frequency, the closer to inter-particle regions is the rheological probing and the viscosity is more and more similar to the one of the neat polymer. At the middle viscosity level, miscanthus, jute and oak are found, while at the lowest level, with viscosities close to the one of the neat matrix, vine shoots, agave and wet draff are located. Composites with glass fibers are positioned between the middle and the lower levels.

Figure 6 shows temperature sweeps conducted at $5\text{ }^{\circ}\text{C}$ for the composites reinforced with five fillers, including glass fibers. The results indicate that the slope of viscosity *versus* temperature is similar to the one of PP, suggesting that thermal degradation between $180\text{ }^{\circ}\text{C}$ and $230\text{ }^{\circ}\text{C}$ does not affect much the viscosity. The ranking of viscosities among the different fillers can have different origins. The main one is the way space is filled with the filler particles. This depends on the axial ratio of the filler and its length. Curauà provides the highest viscosities. When looking at Figure 7, images of curauà composites reveal the presence of numerous tiny sub-micron size fibrils. These fibrils make a very tight interconnected network and this can explain why the viscosity at low frequencies is the highest. Although not shown in Figure 7, flax fibers made the same type of entangled networks at these concentrations.³¹ The occurrence of a higher number of fiber-fiber interactions and physical crosslinking thus produces a considerable increase in viscosity.³¹ Sorghum (Fig. 7), maize and wheat are composed of thick blocks of various tissues present in the stem, but mainly coming from the outside sclerenchyma. They are broken into thinner pieces when compounded and injected. The presence of these elongated thin pieces leads to a quite high viscosity. The other materials, as can be noted on Figure 7 for oak, give no clear structure, with more rounded particles, not leading to strong interconnections. The case of glass fibers is different. Although the fibers are long and slender, they have no roughness and their high rigidity and low adhesion with the matrix means that they can be easily oriented (Fig. 7). This orientation decreases the ability to build a connected network and this leads to decreasing viscosity, compared to the fillers that are able to interconnect.

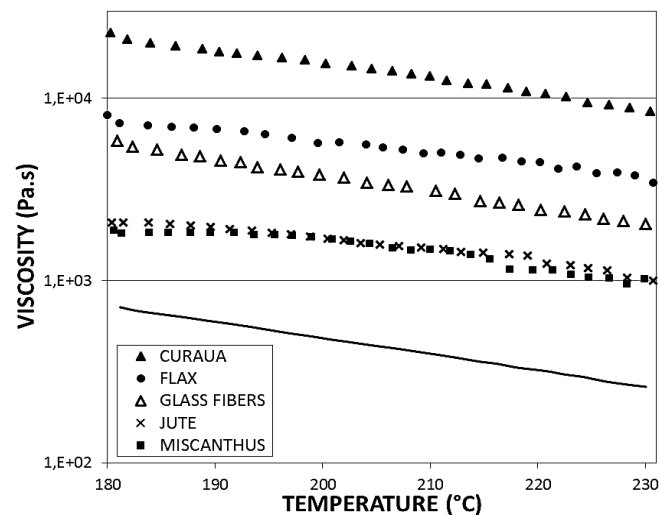


Figure 6: Temperature sweep test performed on PP-based composites with various reinforcements (symbols mark the fragments added within the composites, the black line stands for neat PP; tests were conducted at $\gamma = 1\%$ and $\omega = 1\text{ rad/s}$)

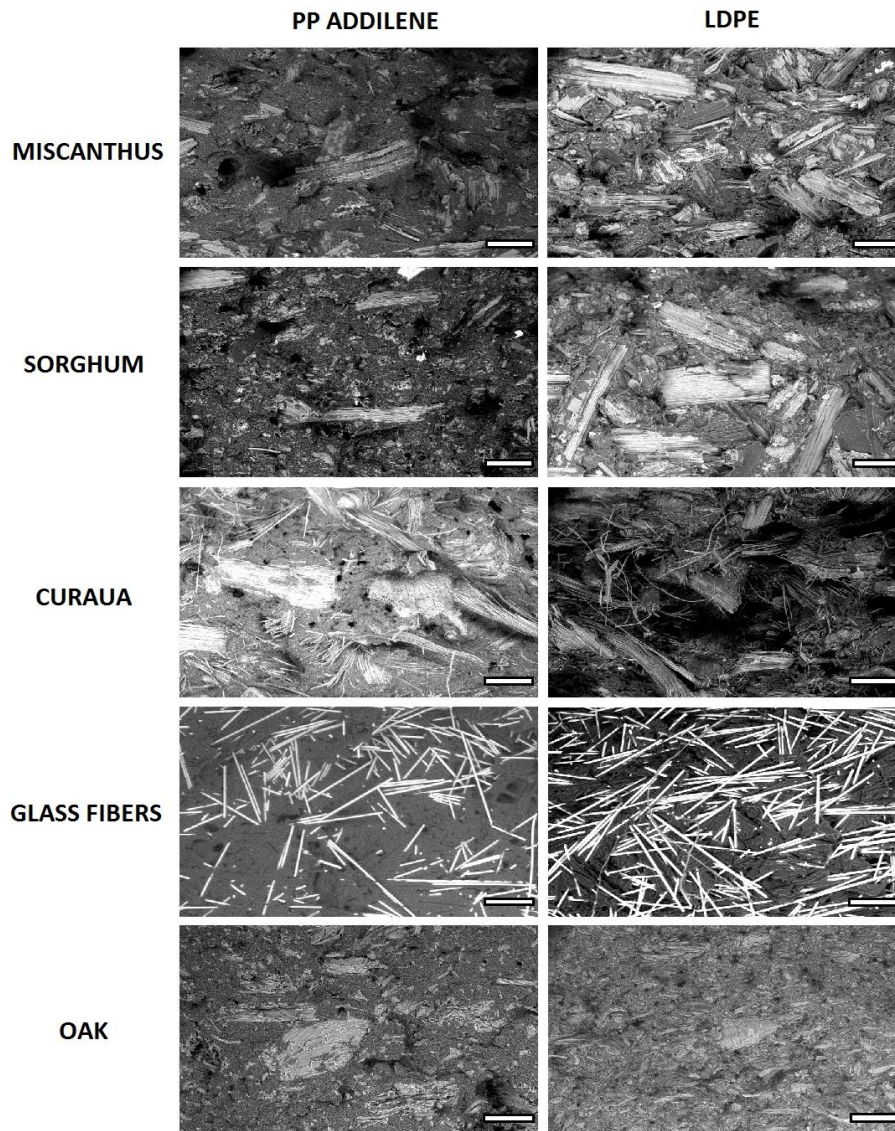


Figure 7: SEM images of composites prepared with stem fragments (miscanthus and sorghum), technical fibers (curauà), glass fibers and industrial by-products (oak). The length of the scale bar is 200 μm

Thermal properties

Due to their high content of low molar mass soluble sugars, the generation of odors was remarkably high during the processing of the composites reinforced with sorghum and maize fragments, in particular when using PP. Thermogravimetric analysis was conducted on the stem pieces of miscanthus and sorghum and on two technical fibers, jute and curauà. TGA and DTGA curves (Fig. 8) show that at temperatures as low as 180 °C, sorghum fragments suffered considerable thermal degradation, because of the weak heat resistance of soluble sugars. Miscanthus fragments and curauà fibers resisted temperatures of 210-230 °C with only minor weight losses (< 5%). As it could be expected from their TGA/DTGA curves, the compounding tests conducted with sorghum and maize fragments generated unpleasant odors, further evidencing the thermal degradation suffered by these plants at the temperatures required for the processing of polypropylene (180-200 °C). In spite of the obvious thermal degradation suffered during processing (odors and darkening), sorghum and maize fragments were still able to provide some reinforcement to the polymeric matrix. However, the odors generated during processing could render these composites unsuitable for some applications. Miscanthus fragments (as well as technical fibers) provided composites with better mechanical properties (higher tensile strength and Young's modulus) without the odor inconveniences provided by maize and sorghum.

Comparison of the different fillers used as reinforcement

Low density, cost and environmental impact are among the advantages often assigned to natural fibers, when compared to glass fibers. However, this is not always true and, depending on their quality and intrinsic properties, some natural fibers can reach market prices higher than fiberglass (Table 5). Technical fibers are the end product of several processing techniques (*e.g.* retting, scutching, hackling) and, although they do not require expensive/polluting chemical treatments, these (mostly mechanical) methods are time-consuming and generate large amounts of by-products. In the case of flax, the amount of fibers in the stem has been estimated to be of 33%,³³ although fiber yield is usually around 20-30% of original straw weight.^{33,34} Fiber content in curauà leaves represents only about 5 to 8% weight.^{35,36} Depending on the plants and methods selected (hence the quality of the technical fibers produced), the yield of these processes might be as low as 1-2% of the plant initial weight.

Fragments from stems, although being harvested directly from the field at the dimensions of a few cm, must be subjected to grinding to decrease their size, which could be a costly process depending on the required final size. Moreover, to improve their performance, only specific size fractions must be selected by sieving, generating a by-product fraction. Nevertheless, in the case of miscanthus, approximately 80% of the stem weight was recovered in the form of useful reinforcing fragments. In the case of oak, agave, vine shoots, wheat straws and wet draff, the raw materials consist in pruning waste and production by-products, therefore they have no significant cost and do not generate additional waste. The cost of the final materials is thus ranking from the technical fibers, then the stem fractions to the by-products, in decreasing order. This is also the ranking of mechanical properties.

Among the biomass tested, curauà shows very good properties, with a tensile strength higher than those of LDPE reinforced with glass fibers (Fig. 9). Also, curauà-reinforced composites have better elongation at break (Fig. 9) and impact strength (Table 3) than fiberglass. This indicates the very good potential of this fiber. However, this comes at a cost, and curauà-reinforced composites presented a much higher viscosity than the rest of the materials tested. In terms of elasticity, flax technical fibers were the material whose composites allowed higher deformation, followed by the miscanthus fragments and the more rigid curauà fibers. As also observed for LDPE composites, PP composites reinforced with sorghum or maize, had sensibly lower densities (Tables 3 and 5), which could be ascribed to the thermal degradation and volatilization of some of their components. Maize and sorghum stem fragments gave lower reinforcing capacities, compared to miscanthus. More surprisingly, the composites reinforced with curauà also presented a slightly lower density than those with miscanthus/flax/jute. Given the high thermal stability of curauà, this result could have been caused by a deficient compaction during injection molding, because of the high viscosity of the material. Indeed, when harsher injection conditions were used (higher temperature and injection pressure), test bars with higher density (up to 1.039 g/cm³) could be obtained. However, this did not significantly change the mechanical performance of the composites (tensile strength increased from 38.4 to 38.7 MPa).

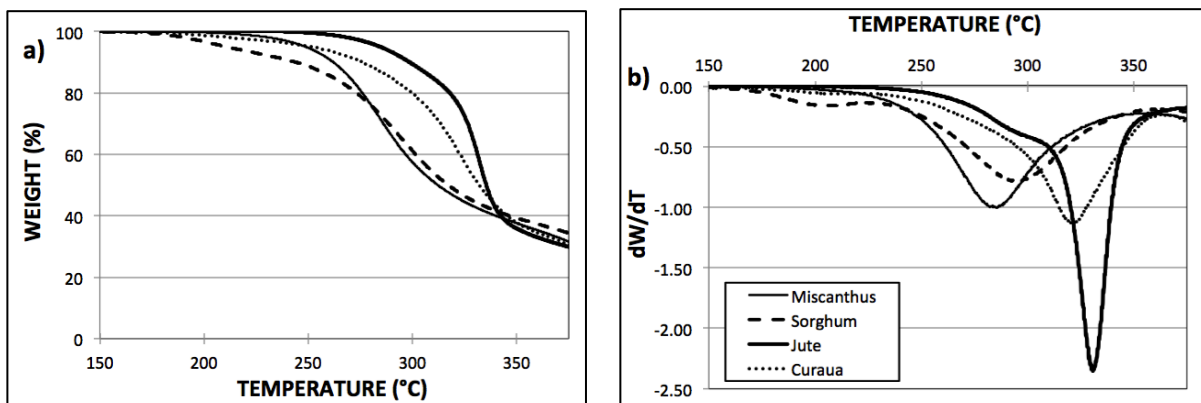


Figure 8: a) TGA, and b) dTGA curves of various reinforcing materials. Curves were normalized at 130 °C to suppress the effects of humidity content. Line style describes the tested fragments

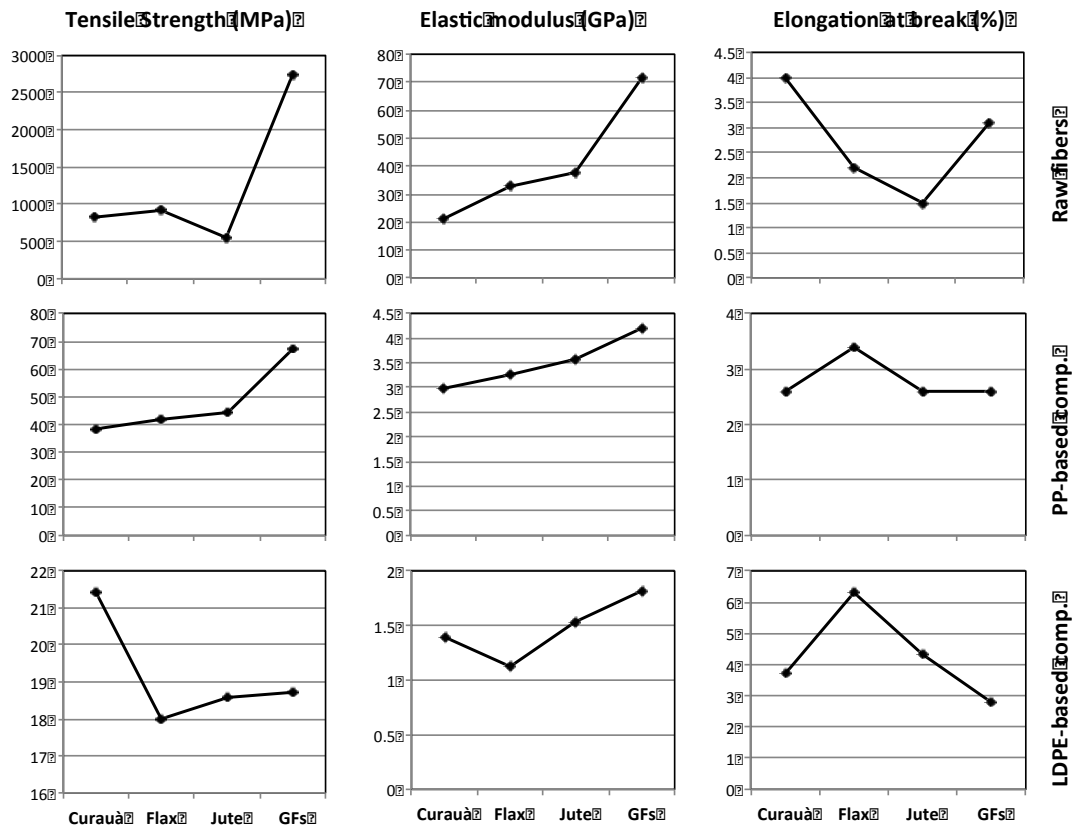


Figure 9: Comparison of mechanical properties (tensile strength, elastic modulus and elongation at break) of raw fibers (first row), PP-based composites (second row) and LDPE-based composites (third row) reinforced with stem fragments and glass fibers

Figure 9 shows that the evolution of the tensile strength, elastic modulus and elongation at break of the initial curauà, flax, jute and glass fibers (first row) is not correlated with that for PP and LDPE-composites. Even more, the evolution of the tensile strength of PE and PP indicates their totally different behavior. This shows that the mechanical performance of the initial biomass-based fibers does not totally reflect the properties of the final product, maybe for reasons linked to thermal degradation. However, this can be challenged considering the first column of Figure 9: it is in the polymer needing the lowest temperatures of compounding and processing with LDPE that the differences between the initial fibers and the composites are the most evident. The tendency/ease of fibers towards fibrillation and their subsequent dispersion/orientation might also account for these disparities.

Compounding temperature, rotor speed, mixing time and injection conditions, which were kept constant for each matrix for the sake of comparison between the different fillers, were not optimized for each blend, which can explain such a result. Figure 10 shows the specific mechanical energy (*SME*), which characterizes the thermomechanical treatment applied to the fibers during the processing and the temperature variation between the applied mixing temperature and the maximum temperature assessed during the compounding within the mixing chamber. *SME* is given by the integration of the torque times, the rotor speed for the duration of the mixing and divided by the mass introduced in the mixer. The variation of the *SME* values for each kind of fiber does not exhibit the same trend if the matrix used is LDPE or PP. In general, the mechanical energy needed for preparing LDPE-based composites (light grey bars) is higher than that needed for PP-based composites (dark grey composites), with the exception of miscanthus fragments and jute fibers. This is not in agreement with the viscosity ranking, where most of the composites were found to have higher dynamic viscosities in PP than in LDPE. Even more incongruous is the case of miscanthus composites, which have a much higher viscosity in PE, while their *SME* is lower in PP. These divergences can have two main causes, first the fact that the final viscosity does not reflect the whole dispersion and distribution processes, or that the dynamic viscosities, measured at very small deformations, do not describe the

flow at high deformations. However, the largest differences between *SME* values of LDPE- and PP-based composites are observed for curauà and flax-based composites, in agreement with their highest viscosities (Figs. 4 and 5).

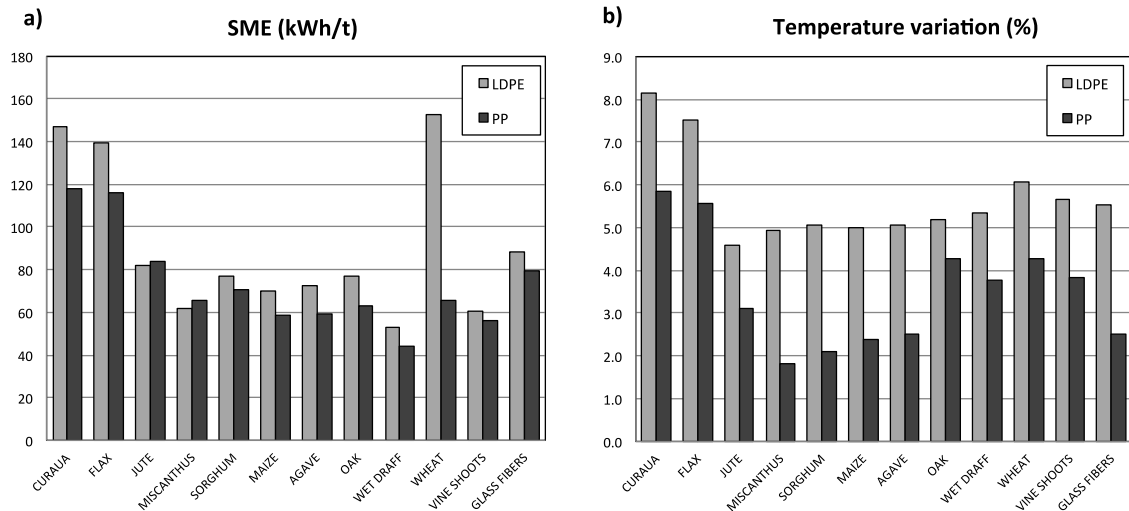


Figure 10: Specific mechanical energy values (a) and temperature variation (b) for LDPE- (light grey bars) and PP-based (dark grey bars) composites with various reinforcements

Table 6
Average mechanical performance of the three filler classes compared to glass fibers (GF)

Class	Tensile modulus	Tensile strength	Impact
Technical fibers	GF/1.3 (PP)	GF/1.5 (PP)	GF/1.2 (PP)
	GF/1.3 (PE)	GF/1 (PE)	GF/1-1.2 (PE)
Stem fragments	GF/2.2 (PP)	GF/1.2 (PP)	GF/2 (PP)
	GF/2.1 (PE)	GF/1.6 (PE)	GF/1.1 (PE)
By-products	GF/2.5 (PP)	GF/3 (PP)	GF/3 (PP)
	GF/3.6 (PE)	GF/2 (PE)	GF/1.4 (PE)

Temperature variation during compounding in LDPE- and PP-based composites is shown in Figure 10b. The variation is very similar for the fillers in the two polymer matrices, which is coherent with the fact that the ranking of viscosities is similar in the two matrices.

CONCLUSION

Fibers originating from eleven different plants and divided into three classes, *i.e.* technical fibers (curauà, jute and flax), plant stem fragments (miscanthus, sorghum and maize) and industrial by-products (agave, oak chips, wet draff, wheat straws and vine shoots), were used as fillers in LDPE- and PP-based composites. Table 6 reveals the main results of this work. Comparing these eleven types of biomass-based fillers under very similar conditions, we show that the three classes we selected present clear mean values of mechanical properties, compared to glass fibers. Without surprise, the long technical fibers having large proportions of cellulose, a very strong molecule, provide the best results. They are closely followed by stem fragments, in particular miscanthus, which also offers quite good results. Industrial by-products, with no specific shape, produce the worst composites. Table 6 gives quantitative estimates of the properties of these three classes. In PP, the strength of the composites is reduced by a factor of 1.5, when glass fibers were substituted by technical fibers, halved when the reinforcing element was plant stem fragments and reduced to a third when the reinforcement was made by industrial by-products. These proportions are similar to those observed when analyzing the evolution of Young's modulus of PE-based composites (the modulus was reduced by factors of 1.5, 2 and 3, when glass fibers were replaced by technical, plant stem fragments and by-product fillers, respectively). The modulus follows a very similar trend in PE and PP. However, impact strength does not follow the same pattern. There is not much difference in the decrease of impact strength among the three classes. This is because the physical mechanisms controlling impact, in particular, the way

energy is dissipated around the fillers, are different from the mechanisms involved in the stretching of the composites. In an investigation on only one plant filler, it has been also recently shown that the biological tissues involved in impact for a composite made with sorghum stem fragments are different from the ones involved in a tension experiment.⁴⁹

The compounding was performed in the same manner for all biomass fillers. The results point out that, even if the intrinsic mechanical properties of the reinforcement have an important role in the ultimate properties of the composites, the processing conditions have a high impact on the mechanical performance of materials. With the processing conditions (compounding temperature, rotor speed, coupling agent characteristics and content) not being optimized for the characteristics of each fiber, the relative reinforcing potential of each plant was affected by the polymeric matrix used and the injection-molding conditions. As a result, the fillers that exhibited a very prominent reinforcing capacity in one matrix provided comparatively low performance in the other (see flax, for example).

Finally, we demonstrated that, under the conditions applied, the evolution of the tensile strength, elastic modulus and elongation at break of the initial curauà, flax, jute and glass fibers (first row) is not correlated with the ones of PP- and LDPE-based composites.

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