High Stiffness Performance Alpha-Grass Pulp Fiber Reinforced Thermoplastic Starch-Based Fully Biodegradable Composites

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Alpha-grass was studied as the reinforcement in a starch-based polymer matrix. Mater-bi®-Y was chosen as a matrix due to its Young's modulus, in line with that of polypropylene. The test specimens were injection molded and tensile tested. The obtained results were compared to glass fiber reinforced polypropylene. The reinforcing fibers increased the Young's modulus significantly, obtaining values up to 7.2 GPa, comparable to those obtained with reinforced polypropylene. The contribution of the fibers to the final composite Young's modulus was also studied, and it was found that was in line with other natural fibers contribution to polypropylene-based composites. Finally, it was found that the value of the efficiency factor of the module remained similar to that of natural fiber reinforced polypropylene.

Keywords: Fiber-reinforced composites; Young's modulus; Thermoplastic starch; Biodegradable; Micromechanics modeling

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INTRODUCTION

The worldwide consumption of biopolymers has increased by 5 times since the 1990s, and they have found applications as packaging materials, disposable nonwovens (engineered fabrics), hygiene products, consumer goods, and agricultural tools. However, the uses of biodegradable plastics are still limited due to their poor tensile properties and difficult processability. Therefore, biopolymers are the subject of increasing amounts of research (Satyanarayana *et al.* 2009). The amount of published paper under the topic "natural fiber biodegradable composites" evolved from 33 in 2006 to 67 in 2012. Starch-based biopolymers are one of the most intensely studied biodegradable polymers. Starch is a carbohydrate polymer that can be purified from various sources by environmentally sound processes and green engineering (Cañigueral *et al.* 2009; Lopez *et al.* 2012c).

Stiffness, hygroscopic behavior, dimensional stability, strength, and fracture toughness are among the main engineering properties of composites to consider. During the conception, design, and engineering of new products, the stiffness is important, as it determines the fiber concentration needed to ensure acceptable deformations for a specific application. For structural applications, once its stability is assured, the most relevant properties are probably stiffness and dimensional stability. To effectively predict the elastic properties of a composite for a specific application, it is essential to know the elastic properties of the reinforcing fibers.

To improve the properties of the final material, a starch matrix can be strengthened and stiffened with reinforcing agents. In this sense, natural fibers can be used as reinforcing agents of starch biopolymers, without losing the environmental benefits associated with the biodegradable matrix. Natural fibers, derived from annually renewable resources, provide such environmental benefits and lead to the achievement of the desired properties (Belhassen *et al.* 2009).

Esparto (S*tipa tenacissima*), also known as alpha-grass, is an herbaceous plant native to Spain and North Africa. In these regions, alpha-fibers have been used since ancient times to prepare ropes, basketry, and espadrilles because of their toughness and resistance. Nevertheless, the most common current use of esparto-grass is in the production of fibers for high-quality lightweight paper (Belkhir *et al.* 2013; Nada *et al.* 2002). Despite the large number of works published concerning the use of fibers from plants as reinforcing agents, research devoted to alpha-fibers has remained limited (Abdelmouleh *et al.* 2007; Paiva *et al.* 2007; Valente Nabais *et al.* 2013).

This work is a part of studies on the properties of alpha grass fibers reinforced Mater-bi®-Y. The series is designed to study the tensile strength, stiffness, the flexural, impact and thermal properties, as well as the sound and thermal insulation capabilities of such materials. The already published paper (Gironès *et al.* 2013) deals with the tensile strength of the composite materials and the intrinsic tensile strength of the fibers, as well as the micromechanics of the tensile strength properties. The first article of the series established the benefits of using alpha fiber in place of glass fiber (GF) for reinforced polyolefin composites.

Starch-based thermoplastics (TPS) usually show comparatively low mechanical properties, even lower than that of low density polyethylene (LDPE). Some TPS show mechanical properties similar to some high density polyethylene (HDPE), and to our knowledge, only Mater-bi®-Y shows mechanical properties in line with polypropylene (PP). There have been numerous studies on the topic of starch-based composites, but the number decreases to 22 devoted to Mater-bi® reinforced composites, being mainly concerned with the biodegradability. The number of indexed studies dealing with the mechanical properties of Mater-bi®-Y reinforced composites is scarce, numbering five. There have been studies of the tensile properties of natural fibers reinforced Mater-bi®, but the Young's modulus has been considered only superficially and used to compute micromechanical parameters (Gironès *et al.* 2013; Lopez *et al.* 2012c). Other work has considered the impact of chemical modifications or processing conditions on the macro mechanic aspects of the tensile properties (Alvarez *et al.* 2005; Alvarez and Vazquez 2006). The tensile properties of sisal fibers reinforced Mater-bi®-Y were evaluated (Puglia *et al.* 2003), and it was found that the Young's modulus and the tensile strength of the composites failed to increase for higher than 30% fibers contents. That was possibly due to a poor dispersion of the reinforcing fibers inside the matrix.

In this work, alpha-grass fibers (AF) were used to reinforce a starch-based polymer (TPS); the Young's modulus of the materials then was evaluated and compared with that of polypropylene (PP) – glass fiber (GF) composite materials. Alpha-grass fibers were obtained with a mild cooking process. Different cooking times were evaluated, and the obtained AF was used to prepare TPS reinforced with a 20% w/w AF composites. To assess the effect of the cooking time on the Young's modulus and on the strain at break, the tensile properties of the prepared composites were evaluated.

Once the cooking time to obtain AF with enough quality was chosen, TPS reinforced with 5 to 35% AF composite materials were prepared. Their stiffness and strain at break was also evaluated and compared with that of PP/GF composite materials. Likewise, the micromechanics of the Young's modulus of the composites were examined. The intrinsic modulus of AF was computed using the Hirsch model, and the fiber efficiency factors were also estimated to solve the rule of mixtures. The contribution of the fibers to the final Young's modulus of the composite was evaluated by introducing a fiber modulus tensile factor (FMTF). Finally, the Tsai-Pagano model was used to model the theoretical modulus of the composites and evaluate the influence of the aspect ratio on the values.

While there has been a study of the mechanical properties of AF reinforced starch-based biopolymers (Belhassen *et al.* 2009), the results showed comparatively poor Young's moduli, mainly due to the mechanical properties of the chosen matrix (BIOPar-S). In contrast, Mater-bi®-Y shows a Young's modulus comparable to that of PP, suggesting that it may be a promising matrix to obtain high performance biodegradable composite materials when reinforced with natural fibers. To the best knowledge of the authors, there have been no studies on the stiffness of AF reinforced Mater-bi®-Y composite materials. The results show high values of the Young's moduli for the prepared composite materials, and a fiber contribution to the final stiffness of the materials in line with the contribution of other natural fibers in PP-based composites (Lopez *et al.* 2011, 2012b).

MATERIALS AND METHODOLOGY

Materials

Esparto or alpha-grass (*Stipa tenacissima*), with initial strand lengths of about 30 cm, was kindly provided by Mas Clarà de Domeny, S.L. (Catalonia, Spain). Supplied by Novamont (Novara, Italy), a starch-based polymer (Mater-bi® YI014U/C, TPS from here-on), with a density of 1.3 g/cm^3, was used as a biodegradable thermoplastic matrix. TPS is biodegradable and compostable for rigid and dimensionally stable injection molded items (Bastioli 1998) with a biodegradation time of about four months in composting conditions and 30 days in anaerobic conditions (1 mm in thickness). This material contains raw materials from a natural origin, is made of thermoplastic starch in a dispersed form, and is a cellulose derivative. The principal physical properties of TPS are as follows: tensile strength 25 to 30 MPa, strain at break 2 to 6%, and tensile modulus 2100 to 2500 MPa.

For comparison, polypropylene composites reinforced with glass fiber (GF) were also prepared. The materials used were as follows: Polypropylene-composite glass fiber was Isplen PP099 K2M (Repsol-YPF, Tarragona, Spain). The E fiberglass was produced by Vetrotex (Chambery Cedex, France) and provided by Maben S.L. (Banyoles, Spain). The principal physical properties of the polypropylene were as follows: tensile strength 28 to 30 MPa, strain at break 9.1%, and tensile modulus 1500 to 1800 MPa.

Sodium hydroxide (Merck KGaA, Darmstadt, Germany) and anthraquinone (BASF AG, Ludwigshafen, Germany) were used for the treatment ("cooking") of the esparto fibers. Chloroform, acetone, and decaline, supplied by Fisher Scientific, were used to dissolve the TPS matrix.

Methods

Characterization of alpha-grass

Determination of the basic chemical composition of alpha-grass (esparto-grass) was conducted following TAPPI standard protocols. The extractives, ash, lignin, gamma, and alpha-cellulose contents were measured according to protocols T204, T211, T222, and T203, respectively.

Treatment of raw material

Alpha-grass was cut in a blade mill and classified with a 5-mm grid. The obtained raw material was homogeneous and suitable for chemical treatment. Alpha-grasses were submitted to chemical treatments to remove the extractives and a small portion of lignin. Plants were soaked in a thermostatic bath set at 98 ± 1 ºC. Then, 5% (w/w) sodium hydroxide and 0.1% (w/w) anthraquinone (based on dry fiber content) were added to the reactor and the mixture was stirred for different periods of time, *i.e.*, 150, 210, and 270 min. Although eliminating extractives is quickly accomplished, due to the relatively mild reactive conditions applied, the elimination of soluble lignin and gamma cellulose was expected to be time-dependent. The cooking process was carried out with 1:6 hydro-module.

Complete individualization was achieved with a "Sprout-Waldron" grinder. The fibers were then washed and dried.

Composite compounding

To verify and compare their performances, TPS/AF and PP/GF composite materials with a 20% (w/w) fiber reinforcement where compounded using Brabender internal mixing. The mixing process was performed for 10 min at 80 rpm rotor speed (20 rpm for the fiberglass reinforced composite) and 175 ºC.

Composite blends comprising 5 to 35% (w/w) TPS/AF were produced using a Gelimat intensive kinetic mixer for 2 min at 2500 rpm, until a discharge temperature of 175 ºC was reached. The PP/GF composite materials, comprising 5 to 35% (w/w), were produced using a Brabender internal mixer at 15 rpm and 175 ºC for 10 min to avoid the high attrition phenomena common with Gelimat mixers. All the obtained blends were ground using a blade mill, dried, and stored at 80 ºC for at least 24 h before processing.

Composite processing

Composites were granulated in a blade mill provided with a 10-mm mesh. Then, to prevent moisture absorption, they were kept in an oven at 80 ºC until required. Test specimens were injection-molded in a Meteor-40 injection-molding machine (Mateu & Soler, Barcelona, Spain) using a steel mould complying with ASTM D3641-12 specifications. The processing temperatures were 175, 175, and 190 ºC (the machine has three heating areas), the last corresponding to the injection nozzle. The first and second pressures were 120 and 37.5 kgf/cm^2, respectively. Before testing, the processed materials were conditioned following ASTM D618-13, at 23 ºC and 50% relative humidity for 48 h.

Mechanical characterization

Tensile tests were carried out with an Instron 1122 universal testing machine, fitted with a 5 kN load cell and operating at a rate of 2 mm/min. Young's modulus was analyzed using extensometer in dog-bone specimens following ASTM D638-10 standards. The Young's modulus was measured using an extensometer. All of the results are presented as averages of at least five samples.

Fiber extraction from composites and morphological analysis

Injection-molded composites were successively refluxed in chloroform, acetone, and decahydronaphthalene (decalin) to eliminate the components of the polymeric matrix. After each treatment, fibers were filtered and washed several times in the hot solvent.

Fiber aliquots were collected and analyzed using an automatic fiber morphology analyzer (MorFi Compact Analyser - Techpap SAS, Grenoble).

Density of composites and fiber / volume fraction

The density of the fibers (ρ^f) was determined according to Eq. 1,

$$\rho^f = \frac{w^f \cdot \rho^m}{\rho^m / \rho^c \cdot \left(w^m + w^f\right) - w^m} \tag{1}$$

$$V^f = \frac{w^f \cdot \rho^m}{w^f / \rho^f + w^m / \rho^m} \tag{2}$$

where ρ^c and ρ^m denote the specific weight of the composite and the matrix, respectively, as determined with a pycnometer. The transformation of the fiber load in weight (w^f) into volume fraction (V^f) is given by Eq. 2.

Analysis of composites

The rule of mixtures, RoM (Eq. 3) (Thomason 2000), is a common micro-mechanical model used to predict the Young's modulus of composite materials (Vilaseca *et al.* 2010),

$$E_t^C = \eta_e \cdot E_t^f \cdot V^f + E_t^m \cdot (1 - V^f) \tag{3}$$

where E_t^C, E_t^f, and E_t^m are the Young's moduli of the composite, the reinforcement, and the matrix, respectively, and V^f is the volume fraction of the reinforcement. η_e is the efficiency factor used to correct the contribution of semi-aligned fibers. The efficiency factor η_e can be expressed as $\eta_e = \eta_o \cdot \eta_l$.

The Hirsch model (Eq. 4) has been successfully used by other authors to obtain the intrinsic tensile modulus (E_t^f) of natural fiber composites (Kalaprasad *et al.* 1997; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Vilaseca *et al.* 2010). This model was used in this research to compute the intrinsic Young's modulus of the alpha-grass fibers,

$$E_t^C = \beta \cdot \left(E_t^f V^f + E_t^m \left(1 - V^f\right)\right) + \left(1 - \beta\right) \frac{E_t^f \cdot E_t^m}{E_t^m \cdot V^f + E_t^f \left(1 - V^f\right)} \tag{4}$$

where E_t^C, E_t^f, and E_t^m are the elastic moduli of the composite, the reinforcement, and the matrix, respectively, and V^f is the volume fraction of the reinforcement. In the model, β is the parameter that determines the fiber-matrix stress transfer. It has been reported that the value of β is primarily influenced by the orientation of the fibers and by the stress concentration effects at the fiber ends (Li *et al.* 2000). A value of β=0.4 has been reported to adequately reproduce results obtained experimentally for natural fiber composites (Kalaprasad *et al.* 1997; Rodriguez *et al.* 2010; Vilaseca *et al.* 2010).

Once E_t^f is known, it is possible to introduce the value in the RoM to calculate the efficiency factor.

According to the Cox-Krenschel model, the fiber length efficiency factor is defined by Equation 5 (Krenchel, 1964),

$$\eta_l = 1 - \frac{\tanh\left(\beta \cdot l^f / 2\right)}{\left(\beta \cdot l^f / 2\right)} \tag{5}$$

with:

$$\beta = \frac{1}{r}\sqrt{\frac{E_t^m}{E_t^f \cdot (1-\nu) \cdot Ln\sqrt{\pi / 4 \cdot V^f}}} \tag{6}$$

where β is the coefficient of the stress concentration rate at the fiber ends, r is the fiber's mean radius, l^f is the fiber's weighted length, and ν is the Poisson's ratio of the matrix, which was assumed to be 0.44 (Lawrence *et al*. 2004).

Once the efficiency and the fiber length efficiency factors were known, it was possible to use the identity $\eta_e = \eta_o \cdot \eta_l$ to compute the fiber orientation factor (Espinach *et al.* 2013; Lopez *et al.* 2012b; Reixach *et al.* 2013).

Halpin-Tsai-Pagano model

In general, the elastic moduli of unidirectional short fiber composites were estimated using the Halpin-Tsai equations (Halpin and Tsai 1969) with a modification proposed by Halpin (1969) that accounts for the fiber aspect ratio l/d. Equation 7 shows the Tsai-Pagano model (Halpin and Pagano 1969; Halpin and Tsai 1969), which uses a combination of the expected longitudinal to the transversal term in ratios of 3/8 and 5/8, respectively.

The Tsai-Pagano model (Eq. 7) and the Halpin-Tsai equations (Eqs. 8 and 9) were also used to predict the intrinsic tensile modulus of the fibers. The calculation was made following Lopez *et al*. (2012b).

The stiffness is given by:

$$E_t^C = \frac{3}{8}E^{11} + \frac{5}{8}E^{22} \tag{7}$$

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

$$E^{11} = \frac{1 + 2\left(l^f / d^f\right)\eta_l V^f}{1 - \eta_l V^f} E_t^m \quad \text{(8a)}, \qquad E^{22} = \frac{1 + 2 \cdot \eta_t V^f}{1 - \eta_t V^f} E_t^m \quad \text{(8b)}$$

with the parameters η_l and η_t given by,

$$\eta_l = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2\left(l^f / d^f\right)} \quad (9a), \qquad \eta_t = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2} \quad (9b)$$

where l^f and d^f are the length and diameter of the fibers, respectively.

RESULTS AND DISCUSSION

Chemical Characterization of the Alpha-Grass Stalks

The knowledge of the chemical composition of the raw material allows a proper selection of the chemical treatments. The main goal of cooking the alpha-grass was to remove the extractives and ash, thus obtaining neat fibers with high cellulose content and a surface capable of chemical interaction. A good fiber-matrix interphase is very important for obtaining composite materials with good mechanical properties (tensile, flexural, and impact strength) (Girones *et al.* 2013). Moreover, it is important to retain the lignin content, as it influences the intrinsic modulus of the fibers, and at the same time has little influence in the fiber-matrix interaction (Neagu *et al.* 2006).

Alpha-grass stalks had 45% alpha-cellulose, 24.1% gamma-cellulose, 23.4% lignin, 7.6% extractives, and 3.2% ash contents (w/w). This composition agreed with other published studies (Belkhir *et al.* 2013; Ben Brahim and Ben Cheikh 2007; Marrakchi *et al.* 2011; Nadji *et al.* 2006; Paiva *et al.* 2007). However, other researchers found lower lignin contents (Bouiri and Amrani 2010). The obtained chemical composition allowed the use of a mild treatment to remove most of the extractives and ash and retain the alpha-cellulose and the lignin.

Effect of Alpha-Grass Cooking Time on the Composite's Young's Modulus and Strain at Break

Table 1 shows the Young's modulus and strain at break of TPS reinforced with 20% w/w alpha-fibers. The fibers were obtained by submitting alpha-grass to an alkali solution cooking for different periods of time. The specimens were prepared by injection molding. For comparison purposes, the mechanical properties of the neat TPS matrix and PP/GF have also been included in Table 1.

Table 1. Tensile Properties of TPS and 20% w/w Reinforced TPS and PP Composites

Reaction time (minutes)	Young's' Modulus (GPa)	Tensile strain at break (%)
150	5.1 (0.2)	1.8 (0.1)
210	4.5 (0.2)	2.0 (0.1)
270	4.9 (0.2)	1.8 (0.2)
Neat TPS	2.5 (0.1)	3.4 (0.1)
PP / GF	4.05 (0.1)	3.6 (0.2)

The Young's modulus or stiffness of the composite reinforced with 20% AF was increased by 104%, 80%, and 96% with respect to the matrix as the cooking time was increased. These increases were noticeable in comparison with composites made with

20% w/w mechanical pulp from stone groundwood reinforced polypropylene (PP/SGW), which gained only a 76% increase with respect to the matrix (Lopez *et al.* 2011, 2012a). The observed differences, as a function of treatment time, can be considered insignificant. In this sense, it was noted that the deformations also remained almost unchanged, confirming that the rigidity suffered no major changes due to the duration of treatment. The 150-min treatment was chosen as satisfactory for obtaining AF with enough stiffening capabilities. Moreover, in a recent article (Gironès *et al.* 2013) the authors found that the same cooking time was enough to obtain fibers with the required quality to create good fiber-matrix interphases. If the data are introduced in the rule of mixtures (Eq. 3), with an efficiency factor of 0.5 ± 0.05 (Espinach *et al.* 2013; Lopez *et al.* 2012b; Reixach *et al.* 2013), then the intrinsic modulus E_t^f reaches a value of 32.4 GPa. Taking this into account, TPS and AF densities of 1.3 and 1.375 g/cm^3, respectively, were used to evaluate the volume fractions of the fibers. Other authors (Paiva *et al.* 2007) obtained an intrinsic Young's modulus of 19 GPa for AF with a single strand tensile test, but they used single non-mould injected strands, and they did not specify its chemical composition. In Fig. 1 (Paiva *et al.* 2007), the strand has a visible lumen that tends to disappear or be filled by the polymer once the strand is mould-injected, mostly due to the high pressures of the process. This may explain the differences found in the value of the intrinsic modulus (Shibata *et al.* 2008). In the case of the PP/GF composites, with an intrinsic modulus of 72 GPa for the GF and densities of 2.45 g/cm^3 and 0.9 g/cm^3 for the GF and the PP, respectively, the efficiency factor of the rule of mixtures was 0.445.

General Aspects of the Modulus of AF / TPS Composites

Assuming a proper dispersion of the reinforcement within the polymer matrix, the main factors that affect the Young's modulus of injection-molded specimens are the following: the fiber content, stiffness, and orientation, and the matrix stiffness (Thomason 2000). The role of the aspect ratio of the reinforcement will be discussed later.

Table 2 and Figure 1 show the linear increase of the Young's modulus of TPS composite materials as the AP fiber content increased. This behavior was expected, as it was previously observed for fiberglass (GF) (Thomason 2000) and natural-based reinforcements (Mendez *et al.* 2007; Vilaseca *et al.* 2010) by other authors. The behavior also supports, always presuming a proper dispersion of the fibers in the matrix, the linear nature of the modified rule of mixtures (Eq. 3). Table 2 also shows the decrease of the strain at break as the stiffness of the composite materials increased.

Table 2. Young's Modulus and Strain at Break of AF/TPS and GF/PP

	TPS / AF			PP / GF		
Fiber content (% w/w)	V^f (v/v)	E_t^c (GPa)	ε_t^c (%)	V^f (v/v)	E_t^c (GPa)	ε_t^c (%)
0	0	2.5 (0.1)	3.4 (0.1)	0	1.5 (0.1)	9.3 (0.1)
5	0.047	3.1 (0.1)	2.8 (0.2)	0.019	2.05 (0.1)	7.1 (0.1)
15	0143	4.8 (0.2)	2.1 (0.1)	0.064	3.6 (0.2)	4.4 (0.2)
25	0.240	6.2 (0.2)	1.6 (0.1)	0.114	5.05 (0.2)	2.8 (0.2)
35	0.337	7.2 (0.3)	1.4 (0.1)	0.173	6.6 (0.3)	2.3 (0.2)

The Young's modulus is not significantly affected by the quality of the bonding at the fiber-matrix interphase (Karmaker and Youngquist 1996). This fact corroborates the theory according to which improving the quality of the interfacial adhesion between the parts of a composite does not substantially affect the stiffness of the final material (Coutinho *et al.* 1997; Doan *et al.* 2006; Karmaker and Youngquist 1996; Mendez *et al.* 2007). The compatibility between the AF and the matrix was discussed in a previous article (Gironès *et al.* 2013), highlighting the high chemical resemblance between the alpha-fibers (with alpha-cellulose as the main component) and the thermoplastic matrix used (starch-based. This compatibility is in agreement with other reported studies (Averous *et al.* 2001; Belhassen *et al.* 2009; Puglia *et al.* 2003; Thomason 2002). Thus, PP/GF composites were prepared without any coupling agent. In the present case, the Young's modulus of the 35% TPS/AF composite is 9% higher than that of the 35% PP/GF composite, supporting the high performance of the AF in stiffening the TPS. On the other hand, the Young's modulus of TPS is 1.67 times higher than that of PP; consequently, adding 35% by weight AF to TPS and, GF to PP, increased the Young's modulus of the plain TPS and PP matrix by 2.88 and 4.4 times, respectively.

As shown in Table 2, at the same fiber weight content, the Young's modulus of the TPS-AF composites was higher than that of PP-GF composites. Figure 1 shows the linear evolution of the Young's modulus of the TPS-AF and PP-GF composites. The linear regression shows two almost parallel lines with a slight tendency to converge at high fiber contents (the slope of the TPS-AF line is slightly smaller than that of PP-GF). Considering that commercial GF-PP compounds usually add GF weight fractions from 5 to 25%, the stiffening ability of AF on TPS largely surpasses that of GF on PP. For instance, 15% w/w AF and 25% w/w GF had the same stiffening effect on their respective matrixes. Usually when natural fiber reinforced composites are compared with GF-reinforced composites, the polymeric matrix is the same (Lopez *et al.* 2012b; Vallejos *et al.* 2012; Vilaseca *et al.* 2010). In those cases, the density of the matrix is the same, while the density of the GF is higher than that of the natural fibers, and consequently the volume fraction of the natural fibers is higher than that of the GF.

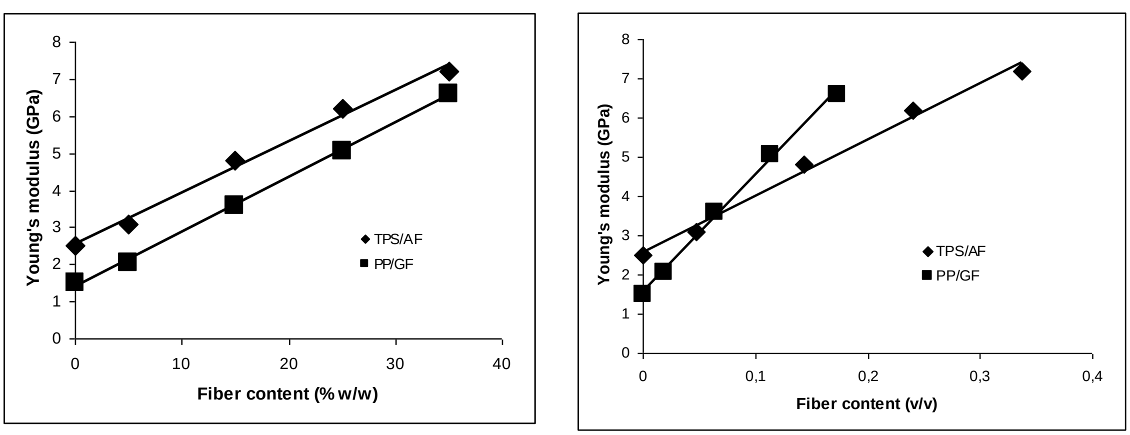

Fig. 1. Young's Modulus of AF/TPS and GF/PP with respect to fiber weight and volume

Figure 1 also shows the Young's modulus of the tested composite materials against their fiber volume fractions. Due to the likeness between the densities of TPS and AF, the values of the weight fractions and volume fractions remained almost equivalent, while the volume fraction of the GF was noticeably smaller than its weight fraction. A regression line shows the effect with a higher slope for GF. This result implies that when the fiber content is higher than 5% w/w, the volume content of AF will increase faster than that of GF. The main implication is the presence of more AF fibers in the TPS-AF composites and a possible effect on the tensile strength due to the higher chance of defects on the fiber surface.

Due to the similarity in densities between TPS (1300 kg/m^3) and AF (1375 kg/m^3), the composite density changed slightly with the AF content. On the other hand, the higher density of GF (2450 kg/m^3) in comparison with PP (905 kg/m^3) increased the density of the composite materials when the GF content increased (Table 3).

Table 3. Specific Young's Moduli for TPS/AF and PP/GF

TPS / AF			PP / GF		
V^F (v/v)	ρ^c (kg/m^3)	E_t^c/ρ^c (GPa/g.cm^{-3})	V^F (v/v)	ρ^c (kg/m^3)	E_t^c/ρ^c (GPa/g.cm^{-3})
0	1300	1.9	0	905	1.65
0.047	1300	2.4	0.019	930	2.2
0143	1310	3.65	0.064	1000	3.6
0.240	1320	4.7	0.114	107.5	4.7
0.337	13250	5.45	0.173	11600	5.7

Consequently, when the specific Young's moduli were estimated, the effect was that both moduli almost coincided. The regression line of the TPS-AF composites (Fig. 2) shows a displacement of its origin and a very slight increase in its slope. The regression line of the GF-PP composites shows a slight decrease in its slope, centered on the 15% composite material. The result was that the specific Young's moduli of both composite materials were almost the same and their regression lines almost coincided. The effects on the values of the specific Young's modulus and their regression lines are similar to that shown in Fig. 1. The regression line of the TPS-AF composites changed its origin and reduced its slope, while the regression line of the PP-GF composites had a lesser slope with a pivot point at 15% fiber content.

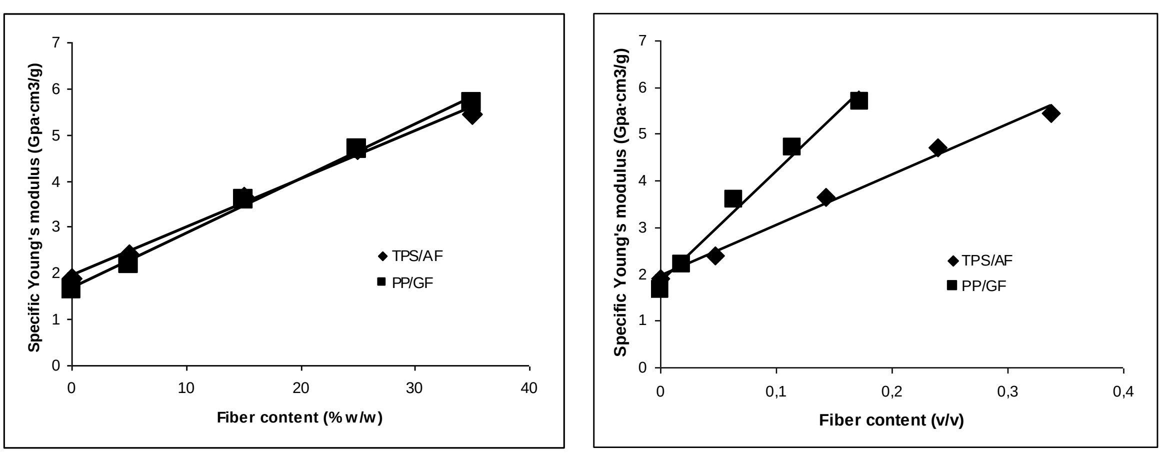

Fig. 2. Specific Young's Modulus of AF/TPS and GF/PP with respect to fiber weight and volume

Micromechanics of the Young's Modulus of AF / TPS Composites

The rule of mixtures (Eq. 3) is a common model used to predict the Young's modulus of short fiber composites. In the present work, the moduli of the composite materials and the matrix were experimentally obtained (Table 2), while the efficiency factor and the intrinsic modulus remained unknown. The contribution of the fibers to the Young's modulus of the composite material is represented by the term $\eta_e \cdot E_t^f \cdot V^f$ (Lopez *et al.* 2012b; Serrano *et al.* 2013), and its value could be easily calculated from the RoM.

To determine the global contribution of the reinforcements to the Young's moduli of the composite materials as a function of the fiber content, a fiber tensile modulus factor (*FTMF*) (Lopez *et al.* 2012b) was defined, isolating the contribution of the fibers to the Young's modulus of the composite in the modified rule of mixtures (Eq. 3). The *FTMF* was defined as:

$$FTMF = \frac{E_t^C - (1 - V^f) \cdot E_t^m}{V^f} = \eta_e E_t^f \quad (10)$$

The value of $\eta_e \cdot E_t^f$ shows the influence of the reinforcement on the Young's modulus of the composite, which is determined by the slope of the line in Fig. 2. The proposed *FTMF* can be directly evaluated from the data obtained in the stress-strain test without further manipulation of the composite.

In this case, the *FTMF*s of the TPS/AF and PP/GF composites were 17.1 and 31.7, respectively. The *FTMF* of PP/GF composites was 1.8 times higher than that of TPS/AF, meaning that with equal increases in the volume fraction of the fibers, GF is expected to have a stiffening effect 1.8 times higher than AF. On the other hand, AF were comparable to mechanical pulp from stone groundwood, which scored a 10.31 (Lopez *et al.* 2012b), or 60% less.

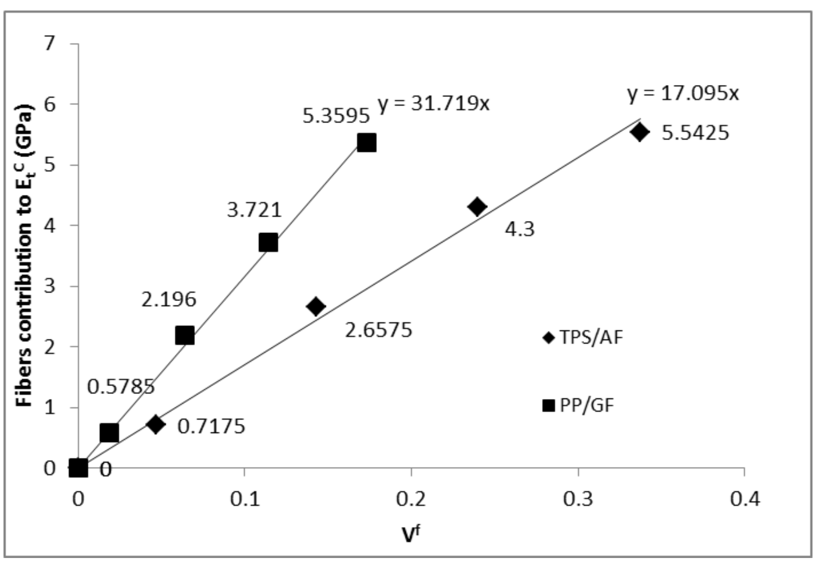

Fig. 3. Fiber tensile modulus factor for the TPS/AF and PP/GF composite materials

Determination of Young's moduli of the fibers

Other authors used the Hirsch model (Eq. 4) to obtain the value of the intrinsic modulus of natural fibers with enough accuracy. Table 4 shows, among other values, the calculated intrinsic Young's modulus.

Table 4. Micromechanical Parameters of TPS-AF Composites at Different Fiber Contents

Fiber content (w/w)	E_t^f (GPa)	η_e	l^f (µm)	d^f (µm)	η_l	η_o
5	30.5	0.44	955	17.3	0.94	0.47
15	38.7	0.54	898	17.3	0.95	0.57
25	36.6	0.52	844	17.3	0.955	0.545
35	32.3	0.48	768	17.3	0.95	0.505

The obtained mean intrinsic Young's modulus for the AF was 34.5 ± 3.8 GPa, a value 2.1 times smaller than that of fiberglass (71.6 GPa). The obtained relation between the *FTMF* of the composite materials was 1.8; the difference is probably due to slight changes in the values of the efficiency factors of the composite materials.

The value of the intrinsic property was used to estimate the efficiency factor with the RoM (Eq. 3). The mean value of the efficiency factor was 0.5. From the data in Table 4, it can be observed that the value of the efficiency factor for the Young's modulus (η_e) and the compatibility factor described by the rule of mixtures for the tensile strength (f_c) (Sanadi and Caulfield 2000; Vilaseca *et al.* 2010) are different. While the compatibility factor (f_c) was about 0.2, the efficiency factor averaged 0.495 and was found to be within the range of 0.5 ± 0.05, similar to that of another natural fiber reinforced composites (Lopez *et al.* 2012b).

Generally, a distribution of fiber lengths and fiber orientations exists in short fiber reinforced polymers. Therefore, to elucidate their implication in the rule of mixtures, the orientation factor (η_o) as well as the length factor (η_l) must be determined. The length factor can be measured from the Cox-Krenchel model described in the experimental section using the mean fiber length and diameter of the reinforcement inside the composite material (see also Table 4). The Poisson's ratio for homopolymer polypropylene (v_m) was 0.44, according to the literature (Lawrence *et al.* 2004). To apply the Cox-Krenchel model, it was necessary to know the length and diameter of the fibers inside the composite, and consequently it was necessary to extract the fibers from the matrix by dissolution of the TPS. It was found that the main length of the reinforcement fibers decreased with the fiber content, a direct effect of the increase of the attrition during the composite preparation when the percentage of fiber increased (Bourmaud and Baley 2007; Karmaker and Youngquist, 1996; Vallejos *et al.* 2012). On the other hand, the mean diameter of the fibers remained almost constant and was not affected by the material preparation and manufacturing; the results are in line with that obtained by Belkhir *et al.* (2013), although a different chemical cooking process was used. The length factor showed little variation with respect to the aspect ratio of the reinforcement.

Knowing the efficiency factors as well as the length efficiency factors, it was possible to calculate the value of the orientation efficiency factors shown in Table 4. Similar to what happens with the efficiency factor, the orientation factor for the modulus is completely different from the fiber orientation factor described for tensile strength (Girones *et al.* 2013).

Fukuda and Kawada studied the variation of the elasticity modulus of short fiber reinforced thermoplastics with orientation distribution, and they obtained the same result given by Eq. 11 (Fukuda and Kawata 1974; Sanomura and Kawamura 2003). Therefore, assuming a rectangular distribution (square packing), the orientation efficiency factor can be solved by

$$\eta_o = \frac{\sin(\alpha)}{\alpha}\left(\frac{3-\nu}{4}\frac{\sin(\alpha\ )}{\alpha} + \frac{1+\nu}{4}\frac{\sin(3\alpha\ )}{3\alpha}\right) \tag{11}$$

where α denotes the fiber orientation limit angle.

The mean fiber orientation efficiency factor (η_O) of the studied composites was 0.522, which resulted in a mean fiber orientation angle of α = 52.6 º, using the square packing equation approximation. The value of the orientation angle of the reinforcement in the composite obtained by another route (tensile strength) was similar. Therefore, the mean fiber orientation factor deduced from the tensile strength was found to be χ_1=0.285 (Girones *et al.* 2013), which would provide a mean orientation angle of the fibers inside the composite of α =43º, considering the relation "$\chi_1=\cos^4\alpha$" (Mittal *et al.* 1987).

Therefore, although the value of the orientation efficiency factor described in the rule of mixtures applied to the Young's modulus (η_O) is distinct from the orientation factor from the rule of mixtures applied to tensile strength (χ_1), the values of the resulting orientation angle of the reinforcement in the composite obtained in every case were very similar.

Influence of the Aspect Ratio on the Prediction of the Composite Modulus

The Halpin-Tsai equations (Halpin and Pagano 1969; Halpin and Tsai 1969; Lopez *et al.* 2012b; Puglia *et al.* 2008) with a modification proposed by Halpin (1969) that accounts for the fiber aspect ratio (l^f/d^f) frame a well-known model to evaluate the modulus of a short fiber composite. The inclusion of the aspect ratio, and thus the explicit evaluation of its impact, distinguishes that model from Hirsch's. Table 5 shows the value of the longitudinal, transversal, and Young's moduli.

Table 5. Moduli Evaluated using the Halpin-Tsai Model

Fiber content (w/w)	E^{11} (GPa)	E^{22} (GPa)	E_t^C (GPa)	E_t^{C*} (GPa)
5	3.855	2.796	3.1	3.193
15	6.613	3.474	4.8	4.651
25	9.490	4.310	6.2	6.252
35	12.352	5.316	7.2	7.955

The Tsai-Pagano model is suitable for adjusting the Young's modulus of SGW PP composites when they are measured using an extensometer. This is opposite to what happens when the Young's modulus is determined without an extensometer, as found in the literature (Puglia *et al.* 2008), where experimental results did not fit with the Tsai-Pagano model.

The longitudinal modulus is higher than the transversal modulus, indicating the anisotropy of the property and the semi-aligned nature of the composite. The theoretical Young's moduli, derived from the application of the Tsai-Pagano equations, are represented in Fig. 4 and compared with the experimental values.

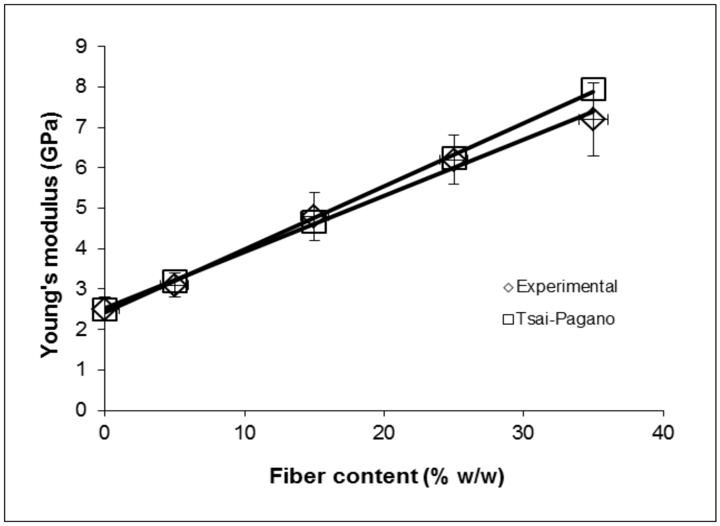

Fig. 4. Experimental and Tsai-Pagano Young's moduli with respect to AF content (w/w)

Figure 4 shows a good adjustment of the Tsai-Pagano model with the experimental results. The figure also shows a slight tendency to overestimate the value of the Young's modulus, but the value remains inside the 99% confidence interval of the experimental results. The slight discrepancies between the experimental and calculated values seemingly highlight the small influence of the aspect ratio of the AF fibers in the value of the Young's modulus.

CONCLUSIONS

1. The starch-based polymer Mater-bi® reinforced with alpha-grass fibers (TPS/AF) showed a high stiffness performance. When compared with polypropylene reinforced with fiberglass (PP/GF), it obtained a higher Young's modulus with the same fiber weight contents and similar specific properties. In terms of stiffness, TPS/AF composite materials can replace PP/GF composites.
2. A mild cooking treatment of the fibers was sufficient to obtain fibers a good 34.5 GPa intrinsic modulus, with enough stiffening capabilities.
3. The specific Young's modulus and the Fiber Modulus Tensile Factor (*FMTF*) showed that GF had higher stiffening power per volume content with respect to Alpha fibers.
4. The modulus efficiency factor was not affected by the nature of the matrix, being similar to that of other natural fiber reinforced polyolefin matrix composites, and around 0.5

5. The aspect ratio has a slight influence in the estimation of the theoretical Young's modulus of the TPS/AF composites with the Halpin-Tsai model.

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