Study of the flexural modulus of lignocellulosic fibers reinforced bio-based polyamide11 green composites

H. Oliver-Ortega[a], M.F. Llop[a], F.X. Espinach[b*], Q. Tarrés[a] , M. Ardanuy[c], P. Mutjé[a]

[a] Group LEPAMAP, Department of Chemical Engineering, University of Girona, C/M. Aurèlia Capmany, nº61, Girona 17003, Spain.

[b] Design, Development and Product Innovation, Dpt. of Organization, Business Management and Product Design, University of Girona, C/M. Aurèlia Capmany, nº61, Girona 17003, Spain.

[c] Departament de Ciència dels Materials i Enginyeria Metal.lúrgica, Secció Enginyeria Tèxtil, Universitat Politècnica de Catalunya. C/ Colom, 11, 08222 Terrassa (Barcelona), Spain.

*Corresponding author

ABSTRACT

The stiffness of a material has high impact when its industrial use is considered. Moreover, this property has interest in the case of short fiber reinforced materials due to its dependence on the orientation of the fibers against the loads. Due to nowadays-environmental concerns, greener alternatives to oil-based composites are under study and development showing some promising results. In this work, a polyamide 11 reinforced with lignocellulosic fiber composite is evaluated as such sustainable alternative. Previous works showed the suitability of PA11-based composites to replace glass fiber reinforced polypropylene. Nonetheless, there is a lack of information about the flexural modulus behavior of these composites. This is of interest because, under some conditions, flexural modulus is more representative of a material behavior than

Young's modulus. The flexural moduli of these composites were analyzed under a three point bending test and the results were evaluated from macro and micromechanical points of view. The increment of the modulus with the fiber contents implied a good dispersion of the reinforcements. Nonetheless, the results were lower than those observed for the tensile modulus. This was unexpected due to the anisotropy of the bending test. The micromechanics analysis showed a lower performance of the fiber during the flexural test. These lower results were related with a non-optimal interface or with the non-adequate compression of the fibers. Additionally, the calculus of the void volume showed low void contents.

Keywords: A, Fibers; B, interface; C, Micromechanics; D, Injection molding

1 INTRODUCTION

Stiffness can be a limiting factor for the processability or the application of materials [1,2]. This property is of interest in the case of short-fiber reinforced composites where the orientation of the reinforcing fibers in the composite material and against the load plays a major role [3,4]. Young's modulus is commonly used as a reference of the stiffness of a material [5].

The higher performance and lower weight of some composites materials, mainly polymeric ones, made them increasingly industrially used material. Thus, it is common to find these composites in quotidian objects like cars, windows, furniture, etc. Their use in cars or planes reduces the weight, and as consequence fuel consumption, while the mechanical characteristics are maintained or enhanced. Among the most used composite materials there is glass fiber (GF) reinforced polypropylene [6]. The mechanical enhancement obtained by the GF combined with the chemical resistance and the toughness of polypropylene, in addition to its actual cost, made it almost a

commodity in the market. However, the poor recyclability of GF and the health problems derived from its manipulation led to take under consideration greener and more sustainable composites [7,8].

Lignocellulosic fibers have become a greener and sustainable reinforcement for composites materials [9]. There is a large quantity of literature about different fibers and treatments with polypropylene [10–12]. Moreover, these composites are nowadays available as commercial products [13,14]. However, society environmental awareness has increased in the last decades and oil derived product demand is in decrease[15]. In this sense, there is a perceived need to replace polypropylene matrices by bio-based and/or biodegradables polymers, both as virgin materials or as composite matrices.

Polyamide 11 (PA11) is a well-stablish bio-based polymer in the market since the 50's [16]. However, it has not attracted the attention of the composite researchers up to the last years. Polyamide 11 is considered an engineering plastic because is recyclable and non-biodegradable and has the typical polyamide properties [17,18]. PA11 is interesting for long-time applications such as those of the automotive industry [19]. Moreover, the low melting point regarding other polyamides allows reinforcing it with lignocellulosic fibers without any or really low degradation of such fibers [20].

Previous works showed the competitiveness of PA11-lignocellulosic fibers to replace PP composites [19,21–23]. However, these works have been focused on the tensile properties and the process ability of PA11-based composites and a lack of literature on flexural properties has been detected. Thus, the flexural modulus of stone groundwood fibers (SGW) reinforced PA11 and its micromechanics were studied in this work (Figure 1). The experiments returned some unexpected results, regarding the author's

experience, which led them to consider the presence of void volumes as the cause of the collapse of the fibers.

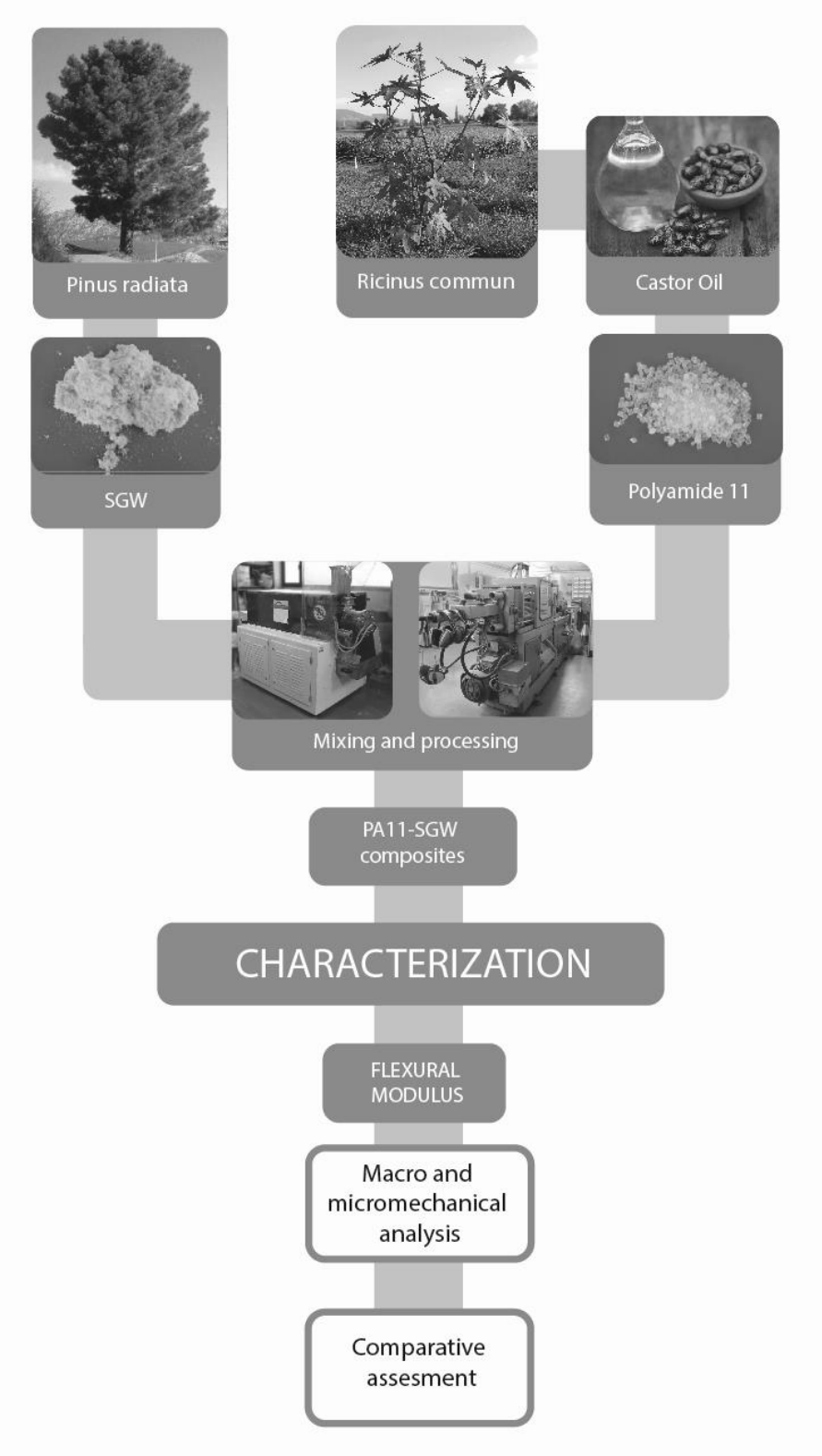

Figure 1. Scheme of the composite production and experimental workflow of the research.

2 MATERIALS AND METHODS

2.1 Materials

The polymeric matrix used to produce the composites was a Polyamide 11 (PA11) Rilsan® BMNO TL kindly supplied by Arkema S.A (Colombes, France). Its melting point was around 189ºC, had a density of 1.03g/cc and a Poison's ratio of 0.42. The reinforcement fiber was stoneground wood (SGW) from pine supplied by by Zubialde, S.A. (Aizarnazabal, Spain).

Dichloromethane (Extra Pure, stabilized with approx. 50ppm of amylene, Pharmpur®) and Formic acid (Extra Pure, 98-100%), both supplied by Scharlau (Sentmenat, Spain) were used to dissolve the PA11 matrix and recover the fibers.

2.2 Methods

Composite compounding and sample obtaining

Five different reinforced composites with SGW fiber contents ranging from 20 to 60% were obtained. The compounding process was performed using a Gelimat kinetic mixer as described in previous works [21,22]. The specimens for the flexural characterization (ASTM D638) were obtained by means of a Meteor-40 injection machine (Mateu&Solé, clamping pressure: 40 tons). The samples were conditioned following the ASTM D618 at 23ºC and 50%RH before the mechanical tests.

Mechanical characterization

An Universal testing machine by IDMtest fitted with a 5kN load cell was used for the mechanical characterization. The composite materials were tested under a three points bending configuration following ASTM D790. The results were obtained from an average of at least five samples.

99 The strain at break (ε_f^C) of the samples was determined following ASTM D790:

$$\varepsilon_f^C = \frac{6 \cdot D \cdot d}{L^2} \quad [1]$$

100 Where D is the experimental deflection at the center of the beam observed, d is the
101 thickness of the sample and L is the length of the support span.

102 *Composites and fiber density*

103 The experimental density of the composites (ρ^C) was obtained using a pycnometer. An
104 exact weight of an injected-molding sample of the composite was measured in the
105 pycnometer and was bring to volume with distilled water. The density was calculated
106 as:

$$\rho^C = \frac{Weight_{composite}}{V_{total} - Weight_{water} \cdot \rho_{water}} \quad [2]$$

107 Where V_{total} is the total volume of the pycnometer, and ρ_{water} is the water density
108 determined experimentally. Fiber density (ρ^F) used for the fiber volumetric fraction
109 calculus (V^F) was back calculated from ρ^C from:

$$\rho^F = \frac{Weight_{fibre} \cdot \rho^C \cdot \rho^m}{\left(\left(Weight_{matrix} + Weight_{fibre}\right) \cdot \rho^m\right) - Weight_{matrix} \cdot \rho^C} \quad [3]$$

110 Where ρ^m is the polymeric matrix density.

111 *Fiber extraction from composites and morphological analysis*

112 Knowing the mean lengths and diameters of the fibers was necessary to model the
113 mechanical behavior of the composites. As it is known, the morphology of the fibers
114 changes during the composites preparation. Thus, the morphology was obtained from
115 the processed materials. For this purpose, the extraction of the fibers was performed in

a Soxhlet apparatus with a mixture of dichloromethane and formic acid (1:1 v/v) for PA11-SGW composites. Composite samples were grinded in small pieces, placed inside a specific cellulose filter, and set into the Soxhlet equipment. The extraction was performed during 24 hours. Then, the fibers were cleaned and dried in an oven at 105ºC for 24 hours more before analysis. The analysis of the length and width were characterized by means of a MorFi analyser (Techpap SAS. Grenoble, France) following the standard ISO/FDIS 160652.

Mechanical modelling

A modified Rule of Mixtures (mRoM) was used to model the flexural modulus of the composites materials:

$$E_f^C = \eta_e \cdot E_f^F \cdot V^F + (1 - V^F) \cdot E_f^m \qquad [4]$$

Where E_f^C, E_f^F and E_f^m are the flexural modulus of the composite, fiber and matrix, respectively and η_e is an efficiency factor. However, in this formula η_e and E_t^F are unknown values, which depend on the fiber stiffness and morphology, and its orientation inside the composite material. The neat fiber contribution in the composite was analyzed using a Fiber Flexural Modulus Factor *(FFMF)*, rearranging Eq. 3 as:

$$FFMF = \frac{E_f^C - (1 - V^F) \cdot E_f^m}{V^F} = \eta_e \cdot E_f^F \qquad [5]$$

FFMF led to determine the fiber neat contribution but not the intrinsic properties of the fiber. Fiber properties are usually difficult and expensive to measure. In this sense, Hirsch model [24] has been successfully applied to calculate E_f^F :

$$E_f^C = \beta \cdot (E_f^F \cdot V^F + E_f^m(1 - V^F) + (1 - \beta)\frac{E_f^F \cdot E_t^m}{E_f^F \cdot V^F + E_f^m(1 - V^F)} \quad [6]$$

Where β is a parameter related with the stress transference between both phases of the composite material and in the case of short semi aligned natural fibers reinforced composites a value of 0.4 has reported to be reliable [25].

Once the intrinsic flexural modulus is known, η_e can be obtained from the mRoM. Moreover, the η_e can be subdivided in two efficiency factors, one related with the length and another with the orientation; the length and orientation efficiency factors (η_l and η_0, respectively). The length efficiency factor was calculated with Cox and Krenchel's equation (Eq. 6 and 7). Equation 8 shows the relation between the efficiency factors.

$$\eta_l = 1 - \frac{tanh\left(\frac{\beta \cdot l^F}{2}\right)}{\frac{\beta \cdot l^F}{2}} \quad [7]$$

$$\beta = \frac{1}{r}\sqrt{\frac{E_f^m}{E_f^F \cdot (1 - v) \cdot Ln\left(\sqrt{\frac{\pi}{4 \cdot V^F}}\right)_{\beta\beta}}} \quad [8]$$

$$\eta_e = \eta_l \cdot \eta_o \quad [9]$$

Where l^F and r are the mean length and radius of the fibers, respectively, obtained from the MorFi analysis.A correction was performed in order to include the fines (fibers with lengths lower than 90µm) becausesome of the authors had shown the impact of include and discard the fines in the fiber's morphology analysis [22]. v is the Poisson's ratio of the matrix. The morphological analysis showed a reduction of the mean lengths of the fibers with the reinforcement contents. The obtained mean lengths were 377, 341, 310,

299 and 295 µm for the composites with 20 to 60% reinforcement contents, respectively. The mean diameter was 23.63 µm.

Once the η_0 was obtained, the mean orientation angle of the fibers was calculated considering a rectangular distribution of the fibers in the polymer matrix [21,26,27].

3 RESULTS AND DISCUSSION

The flexural modulus (E_f^C) of the PA11-SGW composites was analyzed due to the importance the stiffness to ensure the interest of the industry in such composites [3,28]. The experimental results for E_f^C and strain at the maximum flexural strength (ε_f^C) against the fiber volume content (V^F) are shown in Table 3. A linear tendency of the modulus was obtained with a r^2=0.986 correlation. This linearity was an indicative of a correct dispersion of the reinforcement in the PA11 matrix. Composite stiffness depends on the fiber and matrix properties, fiber content and its dispersion inside the matrix. In the case of the flexural modulus, the quality of the interface between polymer and matrix has little impact as it has been observed before for different thermoplastic reinforced composites [21,29–31].

Table 1. Flexural modulus and strain at the maximum strength of PA11 and PA11-SGW composites.

	Fibre Content (%)	V^F	E_f^C (GPa)	ε_f^C (%)
PA11-SGW	0	0.000	0.9 ± 0.1	7.4 ± 1.2
	20	0.155	1.7 ± 0.1	6.4 ± 1.0
	30	0.240	2.1 ± 0.1	5.8 ± 1.0
	40	0.329	2.6 ± 0.2	5.2 ± 1.0
	50	0.424	3.3 ± 0.3	4.2 ± 0.9
	60	0.524	4.1 ± 0.3	3.2 ± 0.9

The composites moduli were 0.9, 1.3, 1.9, 2.6 and 3.6 times higher than the PA11 matrix when the fiber content was raised from 20 to 60%. The specimen's deformations decreased, as expected, caused by the addition of the stiffer reinforcement. Nonetheless, the reduction was smothering in comparison with the obtained in the tensile properties

of the materials. In the case of 20% 30% of SGW fiber, the test specimens did not break and continued deforming after the maximum strength.

In previous works, PA11-SGW composites were proposed as greener alternative to GF reinforced PP composites. Although PP has been successfully reinforced with natural fibers, , there is a need to replace oil-based products. Figure 2 shows a comparison between PA11-SGW composites and reinforced PP available products. Flexural results from PP-GF composites were obtained from the literature and PP-SGW composites were chosen as natural reinforced PP composites due the use of the same fiber [32–34]. High contents of natural fiber were used for the comparison as it was necessary to increase the fiber contents to obtain comparatively competitive properties [21,29]. The PA11-based composites moduli were lower than the obtained for PP-SGW composites at 40 and 50% fiber contents and PP-GF composites with a 30% of reinforcement. Nonetheless, the PA11+50%SGW composite showed similar flexural modulus to PP+20%GF coupled or sized composites. The PP+30%GF values were only 0.6GPa higher than PA11+60%SGW. In addition, the strain of PA11-SGW composites was the same or higher than PP-GF and PP-SGW composites [32,34,35]. The significant differences found between SGW-based composites were not expected. This effect was not observed for the Young's Modulus were PA11-SGW achieved similar values than PP-SGW at the same fiber contents and were considered a competitive alternative to PP-based composites [41]. Nevertheless, there is a lack of literature on the flexural properties of PA11-based composites to evaluate if the values were to be considered too low. To the authors knowledge, only *Armioun et al.* [36] studied the flexural modulus of PA11 reinforced with 30% of wood flour and the obtained result was slightly lower than the obtained for the PA11+30%SGW composite. *Takeshi et al.* [37] also performed the bending test with cellulose nanofibers (CNF) reinforced PA11, and although with only

10% of CNF they achieved values similar to the 20 and 30% of PA11-SGW composites, the results can be related directly with the better properties of CNF. Moreover, a poor effect of the CNF was observed regarding the tensile results reported by *Panaitescu et al.*[38], where the tensile modulus with 5% of CNF was the same than the flexural modulus of the 10% CNF reinforced PA11.

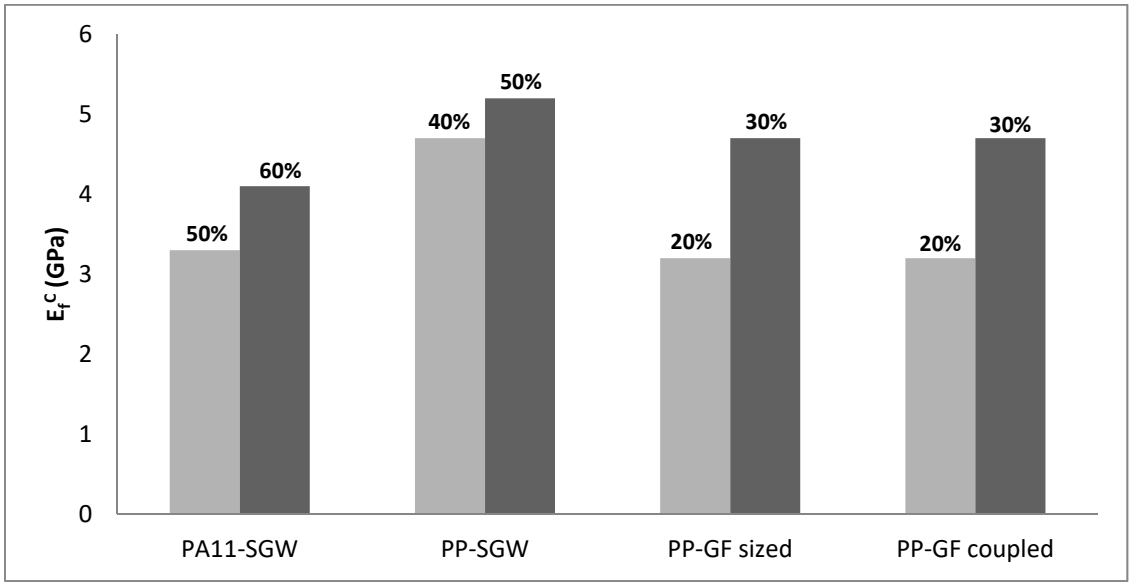

Figure 2. PA11-SGW moduli versus PP-based composites (the percentages show reinforcement contents)

A micromechanics analysis of PA11-SGW composites was proposed to explain this effect. The linear behavior of the flexural modulus allowed the use of a mRoM (Eq.3) and the *FFMF*. In Figure 3 the *FFMF* of the PA11-based composites is shown and compared with PP reinforced materials. The use of GF as reinforcement resulted in higher *FFMFs* due to the intrinsic properties of GF, higher than natural fibers' [1]. Besides, the low effect of the interface as GF coupled and sized had almost the same neat contribution to the flexural modulus was also noticeable. The *FFMF* of the SGW-based composites showed a higher stiffening effect using PP as polymer matrix than using PA11. This value was not expected as almost the same stiffening effect of SGW

was observed in the fiber tensile modulus factor (*FTMF*) despite if a PP or PA11 matrix was used[21,29].

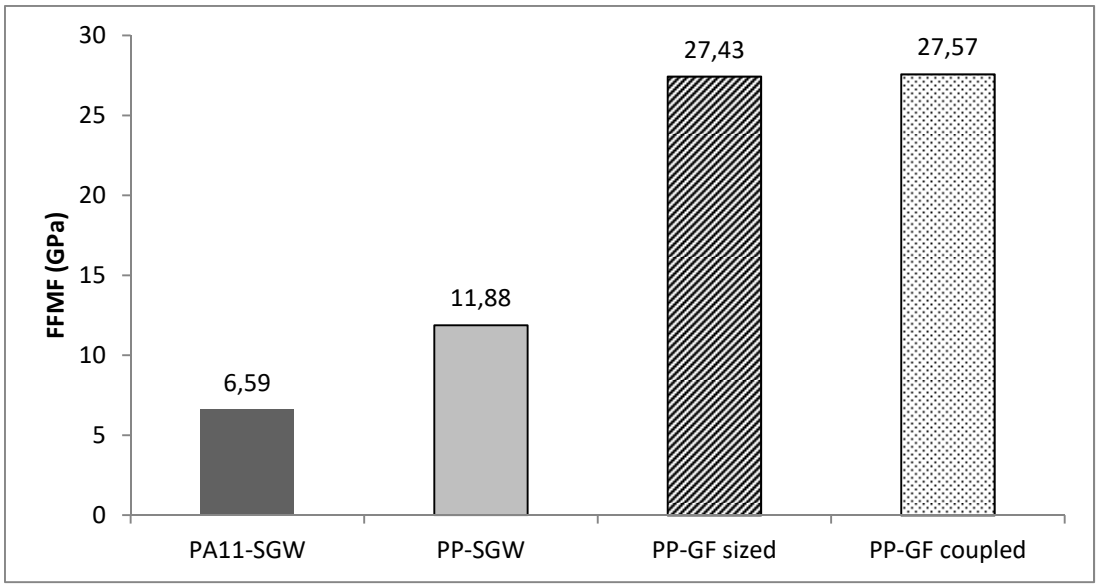

Figure 3. FFMF of PA11 and PP composites.

The observed differences between the *FTMF* and the *FFMF* indicated a lower performance of the SGW fibers in the flexural modulus of the PA11-based composites. These results were quite characteristic because due to the load configuration of the bending test, flexural values are usually higher than tensile ones. The Hirsch model and the modified rule of mixtures were used to calculate E_f^F and η_e, respectively. The results are shown in Table 2.

Table 2. Flexural modulus of PA11 composites, modulus efficiency factors, and mean orientation angle

Fibre Content (%)	V^F	E_f^F (GPa)	η_e	η_l	η_0	α (º)
0	0.000	-	-	-	-	-
20	0.155	12.0	0.491	0.841	0.584	47.7
30	0.240	11.7	0.498	0.851	0.585	47.6
40	0.329	12.1	0.502	0.858	0.585	47.6
50	0.424	13.1	0.502	0.871	0.577	48.3

60	0.524	13.9	0.508	0.891	0.570	48.9
Mean	-	**12.6**	**0.500**	**0.862**	**0.580**	**48.0**
S.D.	-	**0.9**	**0.006**	**0.019**	**0.007**	**0.6**

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222 The E_f^F of the SGW fibers rendered a mean value of 12.6MPa. The literature shows
223 higher values for the same reinforcement used with PP [34]. Furthermore, the E_f^F of
224 SGW fiber in PA11 was lower than the fibers intrinsic Young's modulus (E_t^F). This
225 phenomena is opposite to the obtained in PP-SGW composites, where E_f^F was 1.35
226 times higher than the $E_t{}^F$ calculated using Hirsch model [34,39]. Although the different
227 E_f^F, the obtained η_e rendered a mean value of 0.5. The results were similar to the η_e
228 obtained in the tensile properties of PA11-SGW composites and other short-fiber
229 composites using natural and man-made fibers, where the values ranged between 0.4-
230 0.5 [21,34,40,41]. This result agreed with the *FFMF*, where a lower reinforcement
231 effect of the fiber was observed for PA11. The η_l and η_0 were almost the same than the
232 obtained in the study of the micromechanics of the tensile modulus for PA11-SGW
233 composites [21]. Observing the higher values of the length efficiency factor in front of
234 the orientation efficiency factor, a higher impact of the length of the reinforcement
235 fibers in the η_e than its orientation was concluded. In addition, a mean orientation angle
236 calculated as described in a previous work [21], was similar to the obtained during the
237 study of the tensile properties of PA11-SGW. There was a little difference from the
238 39.5º mean orientation angle obtained from the micromechanics of the flexural strength.
239 The difference of 9º was related with the cosinus shape of the equation where little
240 difference in the η_0 rendered high differences of the obtained angle.

241 Considering the obtained performance for tensile properties of PA11-SGW, a possible
242 explanation for the low E_f^F obtained can be a lower impact of the reinforcement due to

the fibers working poorly at compression. Bending test subjects the section of the specimens to tensile and compression loads. During the tensile strength analysis work, some scanning electronic microscope (SEM) micrographs showed the presence of voids in the material structure, mainly related with the slip-out of fibers when were submitted to tensile stress [22]. Moreover a similar lower contribution of the fiber to the flexural strength was observed in PA11-SGW composites [42]. The adequate but not strong interface of PA11-SGW can cause the apparition of some gaps during the bending test which can make the loaded fibers collapse, reducing the impact of the fiber in the flexural properties [43]. On the other hand, *Shibata S. et al.* [44] described the effect of the fiber compression on the Young's and flexural modulus in different natural fiber reinforce PP. It was found that a correct compression of the fibers rendered in better performance of the fibers inside the composite material. The poor work of SGW fibers inside the PA11-SGW composites can be also related with a no correct compression of the fibers, which led to void volume in the composite material.

The void volume fraction was computed to establish its possible impact on the stiffness of the composites. V^m and V^F used in the Hirsch model were obtained from the densities of the phases. The density of the fiber (ρ^F) was not measured directly; it was back calculated from the composite density (ρ^C) as:

$$\rho^C = \frac{W^m + W^F}{V^m + V^C} \quad [10]$$

Where W^m and W^F were the polymer and fiber weights, respectively. The relation between the weight and the density of each phase can easily replace volumes. It was observed that the density of SGW fibers was 1.401g/cc in PA11-SGW composites and 1.335g/cc in PP-SGW composites [39]. Considering that PP-SGW composites have a better interface due to the use of a coupling agent, which stablishes covalent bonds with

the fibers, there was an error in the calculation of the density of the PA11-SGW fibers. The ρ^F of PP-SGW was used to compute V^F and the intrinsic flexural modulus of SGW were recomputed by using the Hirsch model. Nonetheless, the obtained values were not noticeably different from the original ones (E_f^F was 11.8 and η_e was 0.506). It was difficult to input the effect of the void volume in the ρ^C, as the air weight in the gaps was depreciable but not its volume. The void volume was considered as the difference in the V^F obtained using both densities (Table 3).

Table 3. Volume fractions of fibre and polymer matrix depending of the fibre density used and the volume of air estimated.

ρ^F= 1.401 g/cc		ρ^F= 1.335 g/cc		*Difference in volume*	*Percentage of void volume in the composite* (%)	*Percentage of void volume in the composite by Armioun et al. method* [36] (%)
V^F	V^m	V^F	V^m	V^{air}		
0.155	0.845	0.162	0.838	0.006	0.64	0.98
0.240	0.760	0.248	0.752	0.009	0.89	1.30
0.329	0.671	0.340	0.660	0.011	1.07	1.44
0.424	0.576	0.436	0.564	0.012	1.18	1.46
0.524	0.476	0.536	0.464	0.012	1.20	2.22

The percentage of void volume estimated increased when the fiber content increases up to a maximum of 1.20% of the total volume. Arminoun et al. [36] estimated the void volume in the PA11 composites as a relation between the theoretical and the experimental density of the composites. Applying their estimation and using 1.335g/cc as ρ^F, the obtained results increased. However, both results were lower than the reported in the literature, probably due to the different methods of composite compounding and

injection conditions. This assumption was reinforced by the differences in the tensile strength results between the literature and the author's results [19,21,22].

Other authors obtained composites with different fiber compression rates, due to the morphology of the fiber, that achieved differences in the modulus [28]. A different compression performance in PP and PA11 matrices can be another explanation for the obtained difference in the density. Further researcher will be necessary to understand the lower flexural stiffening impact of the reinforcement.

4 CONCLUSIONS

In this work, the flexural modulus of PA11-SGW composites was analyzed and a micromechanics study was performed. The flexural modulus of the PA11-SGW composites improved the PA11 matrix modulus. SGW fibers used as reinforcement were correctly dispersed in the composite obtaining an enhancement of the modulus. A composite with a 60% of SGW fiber content showed a 3.6 times higher flexural modulus than PA11. Moreover, the minimum strain of the composites was 3.23% for a 60% fiber content.

The results were compared with PP-GF and PP-SGW composites. The PP-based composites showed higher flexural moduli at the same fiber contents. It was necessary to increase the fiber content up to 50% to obtain comparatively competitive results. PA11-SGW composites with high content of fiber can replace PP-GF sized and coupled. Nonetheless, the PA11-SGW composites modulus results are lower than the observed at the same fiber contents for PP-SGW composites. A lower neat contribution of the SGW fiber in the PA11-based composites was observed in the *FFMF*. This result differs from the *FTMF* where no considerable differences were observed between PA11 and PP composites reinforced with SGW. Hirsch model was used to calculate the fiber's

intrinsic flexural modulus and the obtained value (12.6GPa) was lower than values reported in the literature for SGW fibers. The η_e, η_l and η_0 remained similar to those found for the micromechanics of the tensile modulus. It was observed a higher influence of the length of the fibers in the flexural modulus of the composite material than the orientation of such fibers. The flexural behavior of PA11-SGW composites was related with the presence of voids in the structure of the composites. This can prevent a correct behavior of the reinforcement under compression loads, leading to its collapse. An approximation of the void volume was performed by the difference of the SGW fiber's density back calculated from PA11 and PP-based composites. The maximum void volume was determined to be 1.2% of the total volume. Another methodology proposed in the literature rendered to a maximum of 2.22% the void volume in the composites materials.

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