TENSILE STRENGTH CHARACTERISTICS OF POLYPROPYLENE COMPOSITES REINFORCED WITH STONE GROUNDWOOD FIBERS FROM SOFTWOOD

Joan P. López,[a,*] José A. Méndez,[a] Francesc X. Espinach,[b] Fernando Julián,[b] Pere Mutjé,[a] and Fabiola Vilaseca [a]

The behavior of stone groundwood / polypropylene injection-molded composites was evaluated with and without coupling agent. Stone groundwood (SGW) is a fibrous material commonly prepared in a high yield process and mainly used for papermaking applications. In this work, the use of SGW fibers was explored as a reinforcing element of polypropylene (PP) composites. The surface charge density of the composite components was evaluated, as well as the fiber's length and diameter inside the composite material. Two mixing extrusion processes were evaluated, and the use of a kinetic mixer, instead of an internal mixer, resulted in longer mean fiber lengths of the reinforcing fibers. On the other hand, the accessibility of surface hydroxyl groups of stone groundwood fibers was improved by treating the fibers with 5% of sodium hydroxide, resulting in a noticeable increase of the tensile strength of the composites, for a similar percentage of coupling agent. A new parameter called Fiber Tensile Strength Factor is defined and used as a baseline for the comparison of the properties of the different composite materials. Finally the competitiveness of stone groundwood / polypropylene / polypropylene-co-maleic anhydride system, which compared favorably to sized glass-fiber / polypropylene GF/PP and glass-fiber / polypropylene / polypropylene-co-maleic anhydride composite formulations, was quantified by means of the fiber tensile strength factor.

Keywords: Stone Groundwood; Polypropylene; Composites; Tensile strength

*Contact information: a: Group LEPAMAP, Department of Chemical Engineering, University of Girona, c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain; b: Design, Development and Product Innovation, Dpt. Of Organization, Business, University of Girona, c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain; * Corresponding author:joan.lopez@udg.edu*

INTRODUCTION

Stone groundwood pulp (SGW) is a fibrous material, commonly prepared from softwood, in a process that can reach 98.5 wt% yield. The most common applications of SGW are in the production of printing papers, newsprint, boards, and packaging papers. Stone groundwood pulp is frequently used in paper formulations together with mechanical pulp and recycled fibers (Sundholm 1998). Thanks to these applications, the existence of stone groundwood in the global market is guaranteed. Moreover, due to its fibrous morphology, stone groundwood can also find application as a reinforcing element of polymer matrices such as polypropylene or polyethylene (Lopez *et al.* 2011, 2012; Mendez *et al*. 2007) composite materials.

In a recent article, Lopez *et al.* (2011) investigated the micromechanics of SGW composite materials. Particular attention was paid to the interfacial shear strength

between matrix and composite, and the intrinsic tensile properties of the fibers (intrinsic tensile strength and intrinsic Young's modulus).

From a macromechanical point of view, it is significant to evaluate the tensile properties of these kinds of composite materials, mainly their tensile strength. The rigidity of those composites was evaluated and discussed in a recent article by Lopez *et al.* (2012).

A review of the available bibliography shows that the most similar materials are the composites manufactured with chemi-thermomechanical pulp (CTMP) and thermo-mechanical pulp (TMP).

Coutinho *et al.* (1997) evaluated compression-molded CTMP/PP composite materials coupled with silane and maleic polypropylene (MAPP). A 32% increase in the tensile strength, relative to the matrix, was obtained with a 30 wt% of reinforcement and with a polypropylene matrix with silane and MAPP. That increment could be seen as normal for compression-molded composites and below the possibilities of injection-molded CTMP/PP/MAPP composites. Probably the result was due to a poor dispersion of the reinforcement into the matrix. A later investigation by Costa *et al.* (2000), using a factorial plan for the analysis, obtained equivalent outcomes. The experience of the LEPAMAP research group, with SGW composites (Mendez *et al.* 2007), indicates that by injection molding and with a 30 wt% of reinforcement, a 70% increase in the tensile strength relative to the matrix, could be obtained.

Kazayawoko *et al*. (1999) used injection-molded composites with TMP fibers as reinforcement, PP homopolymer matrix, and MAPP. The final results were very similar to those of Mendez *et al*. (2007), but it is impossible to calculate the percentage of increment of the property because the matrix tensile strength was not listed. In the same research, Mendez *et al*. (2007) analyzed kraft fibers reinforced-composite materials, obtaining lower results in comparison to TMP composites for the same percentage of reinforcement.

There is an excellent research by Nygård *et al*. (2008) using two coupling agents in the preparation of PP/TMP and PP/CTMP composites. The tested method was the pelletizing of the reinforcement in a two-spindles extruding machine, followed by its injection. The composite material with coupling agent showed a 70% increase, relative to the matrix, of the tensile strength. The results are somewhat lower than those obtained by Mendez *et al.* (2007).

Recently Zabihzadeh *et al*. (2011) carried out a classical study with CTMP/PP and MAPP composites, specifically PP with 35 wt% of TMP and 2% of MAPP. The obtained properties could be located at the low range of the material potentialities. Probably further research on the percentage of MAPP could result in higher tensile strength values.

Actually, in the case of PP, independently of the reinforcements or the fillers, the use of a coupling agent is required to achieve better mechanical performance of the final composite (Kazayawoko *et al.* 1999; Nygard *et al.* 2008; Li and Sain 2003; Sain *et al.* 2005). Once the percentages are optimized, the chemical coupling agent provides an excellent interfacial adhesion between the reinforcement/filler and the polymeric matrix.

This study evaluated the tensile strength of composite materials reinforced with SGW. It also investigated the influence of the processing techniques and the chemical treatments in the final tensile strength. Important effects were observed when comparing results for a mixer that subjects the material to high attrition *vs.* a less damaging one, with the objective to increase the yield of the composite material. To continue improving the material, the surface of the fiber was treated to improve the interfacial shear strength. A

new parameter called Fiber Tensile Strength Factor is defined and used as a baseline for the comparison of the properties of the different composite materials. Finally the results were compared with sized E-glass-fiber (GF) reinforced materials.

MATERIALS AND METHODS

Materials

The composites were prepared using the homopolymer polypropylene (PP) (Isplen PP090 G2M), which was provided by Repsol –YPF (Tarragona, Spain), as the polymer matrix. The material has an average Melt Flow Rate (MFR) (230ºC; 2.16 kg) of 30 g/10min and a density of 0.950 g/cm^3. Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) with an acid number of 15 mg KOH/g, and Mn of 24800 Da was acquired from Eastman Chemical Products (San Roque, Spain) and used as coupling agent.

Stone groundwood (SGW) derived from softwood (*Pinus radiata*) was supplied by Zubialde, S.A. (Aizarnabal, Spain) and used as lignocellulosic reinforcement. E-glass fiber (GF) was produced by Vetrotex (Chamberly Cedex, France) and provided by Maben, S. L. (Banyoles, Spain).

Other reactants used for the treatment of the fibers were sodium hydroxide (Merck, KGaA, Darmstadt. Germany) and anthraquinone (Basf AG, Germany), which were used as received. Decahydronaphthalene (decalin) (190ºC boiling point, 97% purity) supplied by Fisher Scientific was used to dissolve the PP matrix in the fiber extraction from composites process. Reagent grade acetone (95% purity) from Sigma Aldrich was used without further purification.

Methods

Compounding

Composite materials comprising 20 to 50 wt% PP/SGW and 20 to 40 wt% PP/GF with and without coupling agent were obtained. The materials were prepared in a Brabender® plastograph internal mixing machine. The working parameters were 80 rpm for SGW and 20 rpm for GF-sized, during 10 min at a temperature of 180ºC. In the case of the coupled composites, the MAH-PP was added to the plastograph with the PP pellets. The resulting blends were ground with a knives mill, dried, and stored at 80ºC for at least 24 h before processing.

Stone groundwood (SGW) fibers treatment

A gentle alkaline treatment was applied to the stone groundwood fibers to determine the influence of the surface fiber's morphology to the matrix-fiber bonding capacity. A suspension of fibers (20 g·l^{-1} consistency) was treated with sodium hydroxide (5 wt%) and anthraquinone (1 wt% regarding SGW content). The suspension was kept at 95 ºC and atmospheric pressure for 15 min. This treatment allowed the elimination of part of the extractives and increased the accessibility of the hydroxyl groups at the fiber surface. The fibers were washed with water and dried until constant weight.

Evaluation of surface charge density

The methodology used for determining the surface charge density of the studied fibers was based on the titration of a finely powdered suspension of the material with methyl-glycol-chitosan (MGCh) (Wako Chemical GMBH, Neuss, Germany) as cationic

reagent to interact with the polar groups of the surface material (Terayama 1952). The cationic reagent was added in excess, and the excess that did not interact with the surface of the substrate (material) was titrated with a solution of potassium polyvinyl sulphate, using o-toluidine (TBO) blue dye as an indicator. The values of surface charge density were shown in terms of microequivalents of MGCh per gram of material.

Composite processing

The samples for the tensile test were produced with a steel mould in an injection-molding machine (Meteor 40, Mateu & Solé). Ten test specimens from each obtained composite blend were used for the experiment. The processing temperatures were 175, 175, and 190ºC (the machine has three heating areas), the last corresponding to the injection nozzle. First and second pressures were 120 and 37.5 kgf/cm^2, respectively. Standard composite specimen samples (approximately 160 x 13.3 x 3.2mm) were obtained and used to measure the tensile properties in agreement with ASTM D638.

Mechanical characterization

Prior to the mechanical testing, the specimens were stored in a Dycometal conditioning chamber at 23ºC and 50% relative humidity during 48 h, in agreement with ASTM D638. Afterwards, composites were assayed in a Universal testing machine (Instron^{TM} 1122), fitted with a 5kN load cell and operating at a rate of 2 mm/min. Tensile properties were analyzed by means of dog-bone specimens, according to ASTM D638 standard. Results were obtained from the average of at least 5 samples.

Fiber extraction from composites

Reinforcing fibers were extracted from composites by matrix solubilization, using a Soxhlet apparatus and decalin as solvent. Small pieces of composites were cut and placed inside a specific cellulose filter and set into the Soxhelt equipment. A small cotton tab was used to prevent the fibers from getting out of the filtering tube. The fiber extraction was completed after 24 hours. Once the fibers were extracted, they were rinsed with acetone and then with distilled water in order to remove the solvent residue. Finally the fibers were dried in an oven at 105ºC for 24 hours.

Determination of the fiber length and diameter

Fiber's length distribution and diameter of the extracted stone groundwood fibers were characterized by means of a Kajanni analyzer (FS-300). A diluted aqueous suspension (1 wt% consistency) of fibers was analyzed during 2 to 5 minutes, and the length of the fibers was evaluated considering an amount of individual fibers in the range of 2500 to 3000 units. A minimum of 2 samples were analyzed. The Kajanni analyzer offers complete fiber, fines, and shive morphology characterization, but only the fiber length and the fiber diameter distribution were used for the present work.

RESULTS AND DISCUSSION

The tensile strength of the composites is a combination of the properties of the matrix and the fiber, as well as the ability to transfer shear stresses in the interface between the fibers and polymeric matrix.

The most relevant characteristics are the typology of the fiber, the percentage of reinforcing fiber, the uniformity of the dispersion of the fiber inside the matrix, the aspect

ratio (ratio between fiber length and diameter), the orientation angle in connection with the direction of the tensile stress, and finally, and probably the most important, the interfacial shear strength between fiber and matrix (Thomason 2002; Vilaseca *et al*. 2010).

Table 1 shows the outcomes obtained in the tensile stress/strain test for the composite materials with 20 to 50 wt% of SGW reinforcement with and without a coupling agent. In the table, V^F is the volume fraction of the reinforcement, σ^c_t is the ultimate tensile strength of the composite, ε^c_t the composite elongation, and σ_t^{m*} is the equivalent matrix stress at the failure point of the composite,

Table 1. Stress and Strain Test Results for SGW Composites With and Without MAPP

		Uncoupled			MAPP coupled		
wt%	V^F	σ^c_t (Mpa)	ε^c_t (%)	σ_t^{m*}	σ^c_t (Mpa)	ε^c_t (%)	σ_t^{m*}
0	0	27.6(0.5)	9.3(0.2)		27.6(0.5)	9.3(0.2)	
20	0.145	28.5(0.2)	3.4(0.0)	24.1	40.6(0.4)	4.5(0.1)	26.3
30	0.225	28.6(0.4)	2.4(0.2)	21.0	46.7(0.6)	4.2(4.4)	25.8
40	0.312	27.3(0.7)	2.0(0.1)	18.8	51.4(0.6)	3.7(3.7)	24.4
50	0.404	31.2(1.3)	1.3(0.1)	13.9	56.2(1.0)	3.3(3.5)	24.1

The matrix stress at the breaking point of the composite (σ_t^{m*}) was obtained by fitting the polynomial 4th grade regression equation,

$$\sigma_t^m = -0.0159\varepsilon^4 + 0.3712\varepsilon^3 - 3.3674\varepsilon^2 + 14.895\varepsilon + 0.0493 \quad (1)$$

to the experimental stress-strain result.

SGW Composites Without Coupling Agent

Composite materials formulated with lignocellulosic reinforcement materials and polyolephinic matrixes such as PP, without coupling agent, usually show poor tensile strengths. That result is caused by the significant difference in surface charge density between the matrix and reinforcement, resulting in a bad interface. That fact is enough, by itself, to reduce the desired and expected composite material properties. It is possible to evaluate the surface charge density difference by means of the colloid titration technique (TTC) (Rouger and Mutje 1984). Table 2 shows the surface charge density test results. Data are expressed in micro-equivalents of methyl-glycol-chitosan (MGCh) per gram of reinforcement or matrix in either case. As much cationic polymer is adsorbed onto the substrate surface, higher is the surface charge density. In the present case, while in 1 g of polypropylene was of 4 microequivalents, the same amount of SGW fibers adsorbed 31.42 microequivalents of MGCh polyelectrolyte.

Table 2. Surface charge density of PP and Different Typologies of Fibres or Strands

MATERIAL	MGCh (μeq/g)
SGW	31.42
TMP	23.6
Bleached Kraft pulp	8.4
Cotton	17.5
PP	4

Probably the main contribution to surface charge density shown by vegetal fibers is due to the presence of extractives, in addition to lignin. In comparison to SGW, the surface charge density displayed by bleached conifer kraft pulps is very low, probably due to the relative absence of extractives and lignin. Similarly, cotton strands, with a high percentage of cellulose (90%) present a surface charge density that is almost twice that of kraft fibers. That could be due to the presence of waxy material in its surface. It is also found that TMP fibers had less surface charge density than SGW fibers. High temperatures are required to process TMP in order to partially remove some extractives.

A recent study by Lopez *et al*. (2011) noted that, for uncoupled SGW/PP, the interfacial shear strength and the intrinsic strength of the fibers are very low. In fact, the mean interfacial shear strength was 3.7 MPa. That poor interface can be confirmed by inspection of Fig. 1a, which shows the voids between fiber and matrix, in contrast with Fig. 1b, which presents the changes in the interface when a coupling agent is used.

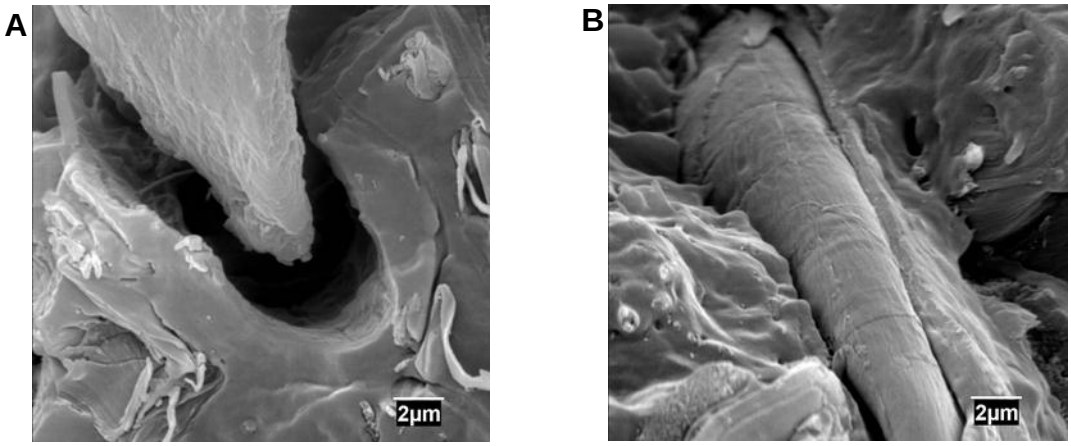

Fig. 1. Matrix fiber interface 1a) without MAPP, 1b) with MAPP

The lack of adhesion between SGW fibers during the tensile stress-strain analysis decreases its shear load transmission power and cuts down its reinforcement capabilities. The outcome was a mean intrinsic tensile strength of 280.4 MPa, which was far from the mean intrinsic tensile strength of SGW fibers with coupling agent, which was evaluated to be 617.7 MPa by Lopez *et al*. (2011). Consequently, the slight improvement of the tensile strength was mainly attributable to the mechanical anchoring and the diffusion of the polypropylene in the rough surface of the SGW fibers. It was also noticed that the strain of the composite materials decreases drastically when the percentage of reinforcement is increased, which is a typical behavior of composite materials.

SGW Composites with Coupling Agent

The behavior of SGW fibers composites, with a 6 wt% optimized percentage of coupling agent (Lopez *et al.* 2011), reflected the most competitive aspects of those materials (Table 1).

When the absolute properties of the composite materials with and without MAPP were compared, the improvement was clear. The tensile strength evolved linearly and increased noticeably with the increasing percentage of reinforcement. With regard to the materials without MAPP, there was a percentage increase in the tensile strength of 43, 63, 88, and 80%, respectively, for composites with 20 to 50 wt% of reinforcement. If the values are compared with the matrix, then the observed increase was 47, 69, 86, and 103%, respectively.

As it will be discussed later, in agreement with Sanadi *et al.* 1994, an easy way to evaluate the behavior of composite materials is by working out the coupling factor $f_c = \chi_1 \cdot \chi_2$, where χ_1 is the orientation factor and χ_2 is the length and interface factor. The coupling factor is defined by the modified rule of mixtures:

$$\sigma_t^c = f_c \cdot \sigma_t^F V^F + (1 - V^F)\sigma_t^{m*} \quad (2)$$

Table 3. Evolution of the Coupling Factor (f_c), Length and Interface Factor (χ_2), Fiber Weighted Lengths (l_w^F), and the Aspect Ratio (l_w^F/d^F), against the Percentage of Reinforcement for Composites with 6 wt% MAPP

wt%	V^F	f_c	χ_2	l_w^F	l_w^F/d^F
20	0.145	0.2	0.7	778	23.2
30	0.225	0.19	0.67	698.2	21.9
40	0.312	0.18	0.63	670.2	22.25
50	0.404	0.17	0.6	549.9	18.4

As it could be found in Table 3 (considering a σ_t^F = 617.7 MPa), in the best case the value of f_c equals 0.2, and it is considered an optimum value (Lopez *et al*. 2011; Sanadi *et al.* 1994). When V^F increases, f_c decreases, with a mean value of 0.185. Apparently the decrease has little significance, but it has a great importance over the absolute value of the tensile strength and so susceptible of being improved. Table 2 also shows the evolution of the length and interface factor (χ_2), computed from f_c and χ_1. The orientation factor (χ_1) was calculated by means of Bowyer-Bader's methodology (Lopez *et al*. 2011; Bowyer and Bader 1972). The mean value for χ_1 was 0.285. It was also found that the value of χ_2 decreased with the percentage of reinforcement. From the data it is observed that the χ_2 factor showed a good evolution with the mean weighted lengths of the SGW fibers. The evolution of the weighted lengths (Thomason 2000) and the aspect ratio shown in Table 2, display a small influence on the tensile strength. The observed tendency of the fiber's length was similar to that found by Thomason (2002) for glass fiber composites, thus the fiber length decreases with the fiber content in the composite.

Taking in account that the interface for the composites was optimized with a 6 wt% of MAPP (Lopez 2011), a logical way to increase the coupling factor and the

tensile strength of the composite was the increase of χ_2. The coupling factor (f_c) could be improved by avoiding the decrease of the fiber lengths during the composite preparation.

The coupling factor f_c is a function of the orientation factor (χ_1), the interface shear strength (τ), and the aspect ratio (l_w^F / d^F). Thus $f_c = \chi_1 . \chi_2$ and $\chi_2 = \tau \frac{l_w^F}{\sigma_t^F d^F}$ for $l_w{}^F < l_c^F$ and $\chi_2 = 1 - \frac{\sigma_t^F d^F}{4 l_w^F \tau}$ for $l_w{}^F \geq l_c^F$, being l_c^F the critical length. In any of the cases, the increasing of the weighted length of the fibers causes an increase on the value of χ_2.

Increasing the Aspect Ratio of the fibers

With the objective to diminish the shear loads during the composite preparation, different composites where formulated with 30, 40, and 50 wt% of SGW fibers and a 6% of MAPP. The materials were prepared by means of a high-intensity kinetic mixer (Gelimat). Figure 2 displays increases of σ_t^c of 2.3, 10.3, and 7.4% for the 30 to 50 wt% composites in comparison to those prepared by means of the Brabender mixer.

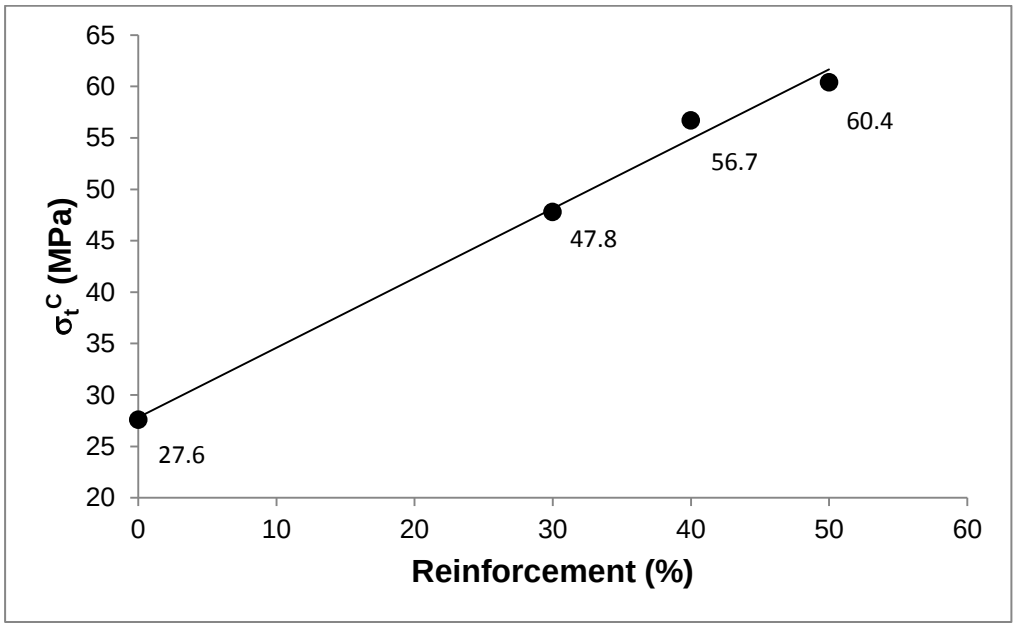

Fig. 2. Tensile strength of the composites prepared in a multikinetic mixer

As a consequence, the new coupling factors are 0.2, 0.205, and 0.185. That corresponds to a percentage f_c improvement of 5.5, 13.9, and 8.8%, respectively. The values of the length and interface factor were also increased, being 0.7, 0.72, and 0.65, somewhat better than the old ones.

To corroborate the results, the fibers were extracted from the 50 wt% composite material. The output showed a length distribution with a weighted length of 665.3 μm. While the shape of the distributions was similar, the mean weighted length was increased by 21%.

It could be observed that the achieved improvement was substantial. This could be a consequence of two factors: the decreasing of the shear loads and the intrinsic flexibility of SGW fibers.

The Brabender mixer has two screw mixers that turn in opposite directions, creating an intense shear load on the fibers. In the case of the multikinetic mixer, the effect is different and an increment of the mechanical strength of the fibers is observed, a fact that we ascribe to the lesser stress on the fibers. The mixer is equipped with a set of blades, rotating in the same direction, which minimize the shear loads on the fibers. That hypothesis could be verified by the evaluation of the fiber's lengths.

To be able to compare PP/SGW fibers composites prepared with the Brabender and the multikinetik mixer, and later with PP/GF fibers composites, a Fiber Tensile Strength Factor (FTSF) was defined as $FTSF = f_c \cdot \sigma_t^F$, being respectively f_c the coupling factor, and σ_t^F the intrinsic tensile fibers strength. The FTSF clearly defines the reinforcement capacity of the fibers. The calculation of FTSF could be achieved by rearranging the modified rule of mixtures,

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

where $f_c \cdot \sigma_t^F = FTSF$ is the slope of the line: $\sigma_t^c - (1-V^F)\sigma_t^{m*} = f\left(V^F\right)$.

The FTSF for the composites prepared in the Brabender mixer and the multikinetic mixer are 109.4 and 117.1, respectively, in line with the increasing of the σ_t^c for the 50 wt% composite. FTSF is useful to compare composite materials with different reinforcement and with the same or different matrix.

Increase on the Reinforcement Capabilities of SGW

A new set of SGW/PP/MAPP composite materials comprising 20 to 50 wt% of SGW fibers treated with NaOH and antraquinone and 6 wt% of MAPP was prepared with the multikinetic mixer. Table 4 shows the properties of those materials.

Table 4. Tensile Properties and Elongations for SGW/PP/MAPP Composite Materials with NaOH-Treated Fibers

		6 % MAPP		
wt%	V^F	σ^c_t (MPa)	ε^c_t (%)	σ_t^{m*} (MPa)
0	0	27.6 (0.5)	9.3 (0.2)	27.6
20	0.145	44.9 (0.4)	5.03 (0.1)	26.8
30	0.225	50.7 (0.7)	4.48 (0.2)	26.2
40	0.312	58.1 (0.5)	4.39 (0.2)	26.0
50	0.404	68.1 (0.5)	3.97 (0.2)	25.4

It was verified that there was a remarkable increase in the tensile strength of the composite in comparison to materials prepared with untreated SGW fibers (Table 1,

Fig. 2). Thus for 20, 30, 40, and 50 wt% composites, the increments were respectively higher than 10, 8, 13, and 21%. There were no significant changes in the values of the fiber's mean lengths and diameters, relative to the untreated fibers. The value of FTSF for the composite with treated fibers, computed from the data on Table 4, was 132. That reflects a 21% increase relative to the original 109.35. The same 21% was observed for the σ_t^c, evolving from 56.2 to 68.1 MPa. The improvement is likely due to the fibers chemical treatments, resulting in a fiber surface with a more accessible hydroxyl groups, and thus higher esterification ability. Additionally, it could also be due to the elimination of extractives and the consequent improvement of the interfacial contact.

Böras and Gatenholm (1999) worked out the chemical composition of the surface of that kind of fibers. Table 5 compares the composition of the fibers surface with the composition of coniferous wood.

A clear coincidence in all the components was observed, except in the case of the extractives. From the work of Böras and Gatenholm (1999), it is observed that almost all the extractives were removed.

Table 5. Chemical Composition of Fibers Surface and Conifer Wood

Component	Surface composition (%)	Conifer Wood composition (%)
Cellulose	40.8	41-46
Hemicellulose	27.6	25-32
Lignin	27.6	26-31
Extractives	0.69	10-15

Chemi-thermomechanical pulp (CTMP) fiber surface model

The analysis performed by Boras and Gatenholm (1999) showed that the CTMP fiber surface is rough and chemically heterogeneous. It consists mostly of carbohydrates (cellulose and hemicellulose), lignin, and extractives. On the basis of the O/C ratio, the proportions obtained are approximately 40% carbohydrates, 28% lignin, and 32% extractives. There is also an assumption that extractives cover an equal area of both carbohydrates and lignin. The carbohydrate phase can consist of an ordered cellulose phase in the form of fibrils, which might be coated with a hemicellulose phase. ESCA, AFM, and DCA analyses indicate that lignin exists as irregular patches at the CTMP fiber's surface. Extractives are proposed to be located as globular particles spread over both carbohydrates and lignin. The surface charge density of the CTMP is shown to be between the TMB 23.4 and the bleached kraft pulp 8.4 microequivalents of MGCh (Table 2).

SGW/PP Compared with GF sized/PP

Table 6 shows the tensile stress-strain test outputs for GF sized/PP and GF/PP/MAPP composites.

Table 6. Tensile Stress-Strain Properties for GF sized/PP Composite Materials with and without Coupling Agents. The standard deviation is within parenthesis.

		GF sized			GF with 6% MAPP		
wt%	V^F	σ^c_t (MPa)	ε^c_t(%)	σ_t^{m*} (MPa)	σ^c_t (MPa)	ε^c_t(%)	σ_t^{m*}(MPa)
0	0	27.6 (0.5)	9.3 (0.2)		27.6 (0.5)	9.3 (0.2)	
20	0.084	50.9 (0.5)	3.1 (0.1)	23.3	67.85 (0.9)	4.7 (0.2)	26.5
30	0.136	58.5 (4.3)	3.0 (0.2)	23.1	79.85 (1.2)	4.4 (0.2)	26.1
40	0.197	67.1 (1.7)	2.4 (0.1)	21.0	101.2 (0.7)	3.7 (0.1)	24.4

It is verifiable that the MAPP had a plain impact on the tensile properties of the on the GF/PP composites, when it was duly coupled. The Fiber Tensile Strength Factor (FTSF) was used to compare GF sized/PP composites with SGW/PP composites. Table 7 shows the values of the FTSF of the analyzed materials. FTSF for GF-sized composites were computed from the data on Table 6.

Table 7. Fiber Tensile Strength Factor for the analyzed Composite Materials and relationship between the Fiber Tensile Strength Factor and the Intrinsic Tensile Strengths for GF and SGW for the prepared Composites. (1) (Thomason 2002)

Composite material	FTSF	Ratio**	Tensile strength σ_t^F (MPa)	σ_t^F (MPa)/σ_t^{SGW}
SGW/PP/MAPP	109.35	1	617.7(1)	1
SGW/PP/MAPP	132.35	1.21	750(2)	1.2
GF sized PP	273.85	2.5	2415(1)	3.9
GF/PP/MAPP[(1)]	427.75	3.9	2955(1)	4.8

* (1) (Mendez, Vilaseca, Pelach, Lopez, Barbera, Turon, Girones and Mutje, 2007), (2) (Sanadi, Young, Clemons and Rowell, 1994)** Ratio column refers to the ratio between the FTFS of the material ant the FTSF of the SGW (109.35).

Tensile strength equivalencies can be shown in terms of ratios. Thus, the equivalences for sized GF, relative to untreated SGW or treated SGW, were 2.5 and 2. This means that to achieve the same tensile strength as a 15 wt% sized glass fiber composite, a 37.5 wt% SGW composite or a 30 wt% treated SGW composite has to be formulated. If the intrinsic tensile strengths or its ratio are compared, it is observed that the yield of the GF sized and the GF/MAPP is lower that the obtained with SGW fibers.

In systems prepared with low shear loads and for glass fibers, the FTSF could reach values of around 471.2 (Thomason 2002). As it could be observed, there are major differences between reinforcements, especially between SGW and sized GF. In order to standardize the comparison, we assumed that the value of σ_t^F for treated SGW fibers was

750 MPa (Sanadi *et al.* 1994), which was higher than 617 MPa, the value corresponding to the untreated SGW fibers.

CONCLUSIONS

SGW fibers exhibited good performance as reinforcement for composite materials with a PP matrix and MAPP as a coupling agent. Their dispersion ability was rather good due to the presence of lignin and some extractives. In all the studied cases, the tensile strength of the composite increased linearly as the percentage of reinforcement increased.

There were different scenarios derived from the studied instances:

- The FTSF of non-treated SGW fibers was practically four times lower than the FTSF of GF with MAPP. In the best case scenario, a 50% of SGW can substitute for 13% of GF/MAPP or 25% of sized GF.
- In the case of treated SGW fibers, the FTSF was three times lower than that of GF/MAPP and twice lower than sized GF. That means that a 50% content of treated SGW could replace 16% of GF/MAPP or 25% of sized GF.
- Probably the use of SGW fibers as an alternative to GF must be restricted to semi-structural applications, where the mechanical requirements are lower, and keep GF/PP composites for structural purposes.
- In all the cases, the savings of PP/SGW with regards to GF/PP were noticeable.

REFERENCES CITED

Boras, L., and Gatenholm, P. (1999). "Surface composition and morphology of CTMP fibers," *Holzforschung* 53(2), 188-194.

Bowyer, W. H., and Bader, H. G. (1972). "On the reinforcement of thermoplastics by imperfectly aligned discontinuous fibres," *J. Mater. Sci.* 7(11), 1315-1312.

Costa, T. H. S., Carvalho, D. L., Souza, D. C. S., Coutinho, F. M. B., Pinto, J. C., and Kokta, B. V. (2000). "Statistical experimental design and modeling of polypropylene-wood fiber composites," *Polymer Testing* 19(4), 419-428.

Coutinho, F. M. B., Costa, T. H. S., and Carvalho, D. L. (1997). "Polypropylene-wood fiber composites: Effect of treatment and mixing conditions on mechanical properties," *J. Appl. Polym. Sci.* 65(6), 1227-1235.

Kazayawoko, M., Balatinecz, J. J., and Matuana, L. M. (1999). "Surface modification and adhesion mechanisms in woodfiber-polypropylene composites," *J. Mater. Sci.* 34(24), 6189-6199.

Li, H. J., and Sain, M. M. (2003). "High stiffness natural fiber-reinforced hybrid polypropylene composites," *Polymer-Plastics Technology and Engineering* 42(5), 853-862.

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

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

Mendez, J. A., Vilaseca, F., Pelach, M. A., Lopez, J. P., Barbera, L., Turon, X., Girones, J., and Mutje, P. (2007). "Evaluation of the reinforcing effect of ground wood pulp in the preparation of polypropylene-based composites coupled with maleic anhydride grafted polypropylene," *J. Appl. Polym. Sci.* 105(6), 3588-3596.

Nygard, P., Tanem, B. S., Karlsen, T., Brachet, P., and Leinsvang, B. (2008). "Extrusion-based wood fibre-PP composites: Wood powder and pelletized wood fibres - A comparative study," *Composites Science and Technology* 68(15-16), 3418-3424.

Rouger, J., and Mutje, P. (1984). "Correlation between the cellulose fibers beating and the fixation of a soluble cationic polymer," *British Polymer Journal* 16(2), 83-86.

Sain, M., Suhara, P., Law, S., and Bouilloux, A. (2005). "Interface modification and mechanical properties of natural fiber-polyolefin composite products," *Journal of Reinforced Plastics and Composites* 24(2), 121-130.

Sanadi, A. R., Young, R. A., Clemons, C., and Rowell, R. M. (1994). "Recycled newspaper fibers as reinforcing fillers in thermoplastic: 1. Analysis of tensile and impact properties in polypropylene," *Journal of Reinforced Plastics and Composites* 13(1), 54-67.

Sundholm, J. (1998). *Mechanical Pulping*, Finnish Paper Engineers Ass. and TAPPI.

Terayama, H. (1952). "Method of colloid titration (a new titration between polymer ions)," *Journal of Polymer Science* 8(2), 243-253.

Thomason, J. L. (2000). "The influence of fibre properties on the properties of glass-fibre-reinforced polyamide 6,6," *Journal of Composite Materials* 34(2), 158-172.

Thomason, J. L. (2002). "The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: 5. Injection moulded long and short fibre PP," *Composites Part A - Applied Science and Manufacturing* 33(12), 1641-1652.

Vilaseca, F., Valadez-Gonzalez, A., Herrera-Franco, P. J., Pelach, M. A., Lopez, J. P., and Mutje, P. (2010). "Biocomposites from abaca strands and polypropylene. Part I: Evaluation of the tensile properties," *Bioresource Technology* 101(1), 387-395.

Zabihzadeh, S. M., Ebrahimi, G., and Enayati, A. A. (2011). "Effect of compatibilizer on mechanical, morphological, and thermal properties of chemimechanical pulp-reinforced PP composites," *Journal of Thermoplastic Composite Materials* 24(2), 221-231.

Article submitted: March 1, 2012; Peer review completed: April 22, 2012; Revised version received and accepted: May 15, 2012; Published: June 5, 2012.