

## MEAN INTRINSIC TENSILE PROPERTIES OF STONE GROUNDWOOD FIBERS FROM SOFTWOOD

Joan Pere López, José Alberto Méndez, Nour-Eddine El Mansouri, Pere Mutjé, and Fabiola Vilaseca \*

Stone groundwood (SGW) is a fibrous matter commonly prepared in a high yield process, and mainly used for papermaking applications. In this work, the use of SGW fibers is explored as reinforcing element of polypropylene (PP) composites. Due to its chemical and superficial features, the use of coupling agents is needed for a good adhesion and stress transfer across the fiber-matrix interface. The intrinsic strength of the reinforcement is a key parameter to predict the mechanical properties of the composite and to perform an interface analysis. The main objective of the present work was the determination of the intrinsic tensile strength of stone groundwood fibers. Coupled and non-coupled PP composites from stone groundwood fibers were prepared. The influence of the surface morphology and the quality at interface on the final properties of the composite was analyzed and compared to that of fiberglass PP composites. The intrinsic tensile properties of stone groundwood fibers, as well as the fiber orientation factor and the interfacial shear strength of the current composites were determined.

*Keywords:* Stone groundwood; Polypropylene; Composites; Intrinsic properties; Bowyer-Bader method; Interfacial shear strength

*Contact information:* Group LEPAMAP, Department of Chemical Engineering, University of Girona, c/ M. Aurèlia Capmany, n° 61, Girona 1707, Spain; \* Corresponding author: [fabiola.vilaseca@udg.edu](mailto:fabiola.vilaseca@udg.edu)

### INTRODUCTION

Stone groundwood pulp (SGW) is a fibrous material, commonly prepared from softwood, in a process that can reach 98.5wt% 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, and it has a very economical price (0.3-0.4 €/kg). Moreover, due to its fibrous morphology, stone groundwood can also find application as reinforcing element of composite materials, for polymer matrices such as polypropylene or polyethylene (Méndez et al. 2007).

The properties of thermoplastic composites result from a combination of the fiber and matrix properties and the ability to transfer stresses across the fiber-matrix interface. Variables such as the fiber content, uniformity of dispersion of the fibers in the matrix, fiber aspect ratio, intrinsic strength, orientation, and the interfacial strength are of prime importance to the final balance of properties exhibited by injection molded thermoplastic composites (Thomason 2002).

The determination of the intrinsic mechanical properties of natural strands (hemp, sisal, jute, etc.) as well as lignocellulosic fibers from wood and agro-forestry (mechanical pulp, thermomechanical pulp, semichemical pulp, chemical pulp or recycled fibers) is a matter of controversy. Bibliographic data for the tensile strength of most lignocellulosic fibers presents big disparities (Michel and Willis 1978; Sanadi et al. 1994; Bledzki and Gassan 1999; Beg and Pickering 2008; Oksman et al. 2009; Rodriguez 2010). Lignocellulosic fibers, being of natural origin, have a wide range of properties depending on the type, source, and age of the raw material. The pulping and the processing conditions also affect the final fiber properties. However, the determination of the intrinsic properties of the reinforcing fiber is essential to predict the mechanical properties of the composite material and to perform an interface analysis by means of the rule of mixtures (Sanadi 1994; Beckermann and Pickering 2009).

In addition, due to the wide range of fiber lengths and diameters of stone groundwood, only the estimation of the mean intrinsic tensile strength of the fiber ( $\sigma_t^F$ ), which corresponds to the fiber distribution inside the composite material, is possible. The final value of the tensile strength of the reinforcement will also be function of the degree of adhesion and compatibility between the fiber and the matrix. As a consequence, to determine the maximum mean intrinsic property of the reinforcement, composites with optimized interface are required to allow the fibers develop their maximum reinforcing capacity.

Therefore, for the preparation of composites from stone groundwood fibers and thermoplastic matrices such as polypropylene, the use of compatibilizers is required in order to ensure good stress transfer at interface. In this sense, it is widely known that one can use maleated polypropylene as a coupling agent between hydrophilic fibers and hydrophobic matrices (Mutjé et al. 2006). The ability to transfer stress across the fiber-matrix interface is often reduced to a consideration of adhesion, which a term that is used to describe a combination of complex phenomena that are difficult to measure. One of the generally accepted manifestations of adhesion is in the value of interfacial shear strength (IFSS or  $\tau$ ) (Thomason 2002).

Quantitative estimations of tensile strength of reinforcing fibers have been performed through several mathematical models. Starting from the analysis method of Bowyer-Bader (1972), based on the Kelly-Tyson model (Equation 1), Thomason developed a methodology that allowed the determination of the tensile strength of fiberglass from the mechanical properties of its composites (Thomason 2002). Tensile strength values obtained through this mathematical approach showed good agreement with typical single fiber analysis values. This methodology allows not only the determination of the mean intrinsic fiber tensile strength ( $\sigma_t^F$ ) but also the interfacial shear strength ( $\tau$ ) and the fiber orientation factor ( $\chi_1$ ), which are essential parameters for the fiber-matrix interface evaluation.

$$\sigma_t^c = \chi_1 \left( \sum_i \left[ \frac{\tau l_i^F V_i^F}{d^F} \right] + \sum_j \left[ \sigma_t^F V_j^F \left( 1 - \frac{\sigma_t^F d^F}{4\tau l_j^F} \right) \right] \right) + (1 - V^F) \sigma_t^{m,*} \quad (1)$$

In Eq. 1,  $\sigma_t^c$  and  $\sigma_t^F$  represents the tensile strength of the composite and the reinforcing fibers;  $\sigma_t^{m*}$  corresponds to the contribution of the matrix at failure;  $d^F$  and  $l^F$  represent the fiber diameter and length, respectively, and  $V^F$  is the volume fraction of reinforcement in the composite.

The intrinsic Young's modulus of the reinforcing fiber cannot be empirically determined, and the application of the Hirsch model (Eq. 2), another approach based on the combination of parallel and series models of the rule of mixtures, is required:

$$E_t^c = \beta(E_t^F V^F + E_t^m (1 + V^F)) + (1 - \beta) \frac{E_t^F E_t^m}{E_t^m V^F + E_t^F (1 - V^F)} \quad (2)$$

In Eq. 2,  $E$  represents the Young's modulus, and  $c$ ,  $F$ , and  $m$  stand for the composite, fiber, and matrix, respectively. In this case,  $\beta$  is a parameter that determines the stress transfer between the fiber and matrix. It has been reported that theoretical and experimental values can fit when the value of  $\beta$  is 0.4 (Kalaprasad et al. 1997).

In this work, a series of well-coupled composite materials from polypropylene and stone groundwood fibers were prepared. The relevance of the surface morphology of stone groundwood fibers was analyzed and compared to that of classical reinforcing fibers such as fiberglass. The influence of the quality at interface on the final properties was also analyzed and compared with fiberglass composites. Finally, the intrinsic tensile properties of stone groundwood fibers, as well as, the fiber orientation factor and the interfacial shear strength of the current composites were determined.

## EXPERIMENTAL

### Materials

The composites were prepared using polypropylene (PP) (Isplen PP090 G2M) that was generously provided by Repsol-YPF (Tarragona, Spain) as the polymer matrix. Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) with an acid number of 15 mg KOH/g and Mn of 24800 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. (Aizarnazabal, Spain) and used as the lignocellulosic reinforcement. E fiberglass (FG) was produced by Vetrotex (Chambery Cedex, France) and provided by Maben S.L. (Banyoles, Spain).

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

## Methods

### *Composite compounding*

PP composite materials comprising 30, 40, and 50wt% of stone groundwood, or 20wt% of fiberglass were prepared. The components of the composite material (PP, SGW or FG, and MAH-PP) were compounded by means of Brabender® internal mixing. The mixing process was performed at 80 rpm rotor speed (20 rpm for fiberglass reinforced composites) and at a temperature of 180°C during 10 min. In the formulations containing MAH-PP, this was added into the plastograph together with the PP pellets. The obtained blends were ground by means of a knives mill, dried, and stored at 80°C for at least 24 h before processing.

### *Stone groundwood fibers treatment*

To determine the influence of the surface fiber morphology to the matrix-fiber bonding capacity, a soft alkaline treatment was performed on stone groundwood fibers. A suspension of fibers (20 g·l<sup>-1</sup> consistency) was treated with sodium hydroxide (5 wt%) and antraquinone (1 wt% regarding fiber content). The suspension was kept at 95° C and atmospheric pressure for 15 min. This treatment allowed the elimination of part of the extractives, and to increase the accessibility of the hydroxyl groups at fiber surface. The fibers were washed with water and dried until constant weight.

### *Evaluation of polarity*

The methodology used for determining the polarity of the initial stone groundwood fibers and the treated ones 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 of the material (Terayama 1952). The cationic reagent was added in excess, and the excess not interacted with the surface of the substrate (material) was titrated with a solution of potassium polyvinyl sulphate, using *o*-toluidine (TBO) blue dye as indicator. The values of polarity are shown in terms of microequivalents of MGCh per gram of material.

### *Composite processing*

The composite blends were injection-molded in a Meteor-40 injection machine (Mateu & Solé, clamping pressure: 40 tons). The machine is equipped with three heating areas working at 175, 175, and 190° C, the highest corresponding to the nozzle. First and second pressures were 120 and 37.5 kgf·cm<sup>-2</sup>, respectively. This equipment and process allowed acquisition of specimens for mechanical characterization under tensile stresses (ASTM D638).

### *Mechanical characterization*

Processed materials were placed in a conditioning chamber (Dycometal) at 23° C and 50% relative humidity during 48 hours, in accordance with ASTM D618, prior to testing. Afterwards, composites were assayed by using a Universal testing machine (Instron™ 1122), fitted with a 5 kN load cell. Tensile properties were analyzed by means

of dog-bone specimens (of approx. 160x13.3x3.2 mm), according to the ASTM D790 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 Soxhlet 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 105 °C for 24 hours.

#### *Determination of the fiber length and fiber diameter*

Fiber length distribution and fiber diameter of the extracted stone groundwood fibers were characterized by means of a Kajanni analyzer (FS-300). A diluted aqueous suspension (1wt% 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 fiber diameter distribution were used for the present work.

## RESULTS AND DISCUSSION

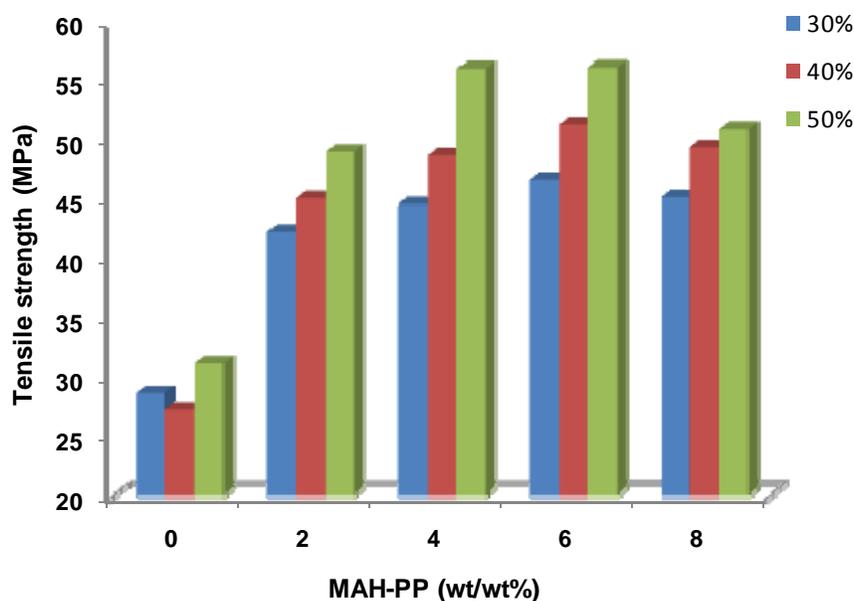
In order to evaluate the mean intrinsic tensile properties of stone groundwood fibers (SWG), PP composite materials containing different amounts of SGW fibers were prepared at different MAH-PP coupling agent content.

The chemical composition of stone groundwood fibers is very similar to that of wood. They show a wide fiber length distribution and a remarkably rough surface, with small valleys and hills. The chemical composition at the outer layer of lignocellulosic fibers, as stone groundwood, exhibits large content of lignin (about 75%) and only 20-25% of hemicelluloses and cellulose (15-20% hemicelluloses and 5-10% cellulose approximately) (Sundholm 1998). Consequently, the surface hydroxyl groups, aliphatic and aromatic, are less accessible, for instance, compared to fiberglass. This phenomenon is of great importance, especially if the use of compatibility agents is needed. Thus, in the case of fiberglass, one can measure the stoichiometric amount of coupling agent needed to modify the all surface hydroxyl groups of the reinforcing fiber. However, in lignocellulosic fibers such as stone groundwood, the surface hydroxyl groups are much less reactive and accessible, as some of them are aromatic.

In this work, maleated polypropylene (MAH-PP) with an acid number of 15 mg KOH/g was used as coupling agent. This represents  $2.678 \cdot 10^{-4}$  mol of maleic anhydride per gram of MAH-PP, or 6.65 mol of maleic anhydride per mol of MAH-PP. Thus, it is possible to determine the stoichiometric amount of coupling agent, if the surface hydroxyl groups of the reinforcing fibers are considered. According to Fry et al. (2003) the density of hydroxyl groups in fiberglass is between 0.8 and 1.3 -OH per nm<sup>2</sup> of

surface. Considering 1 g of fiberglass, of 10.2  $\mu\text{m}$  diameter and 2.55  $\text{g}/\text{cm}^3$  specific weight, there exists  $2.54 \cdot 10^{-6}$  mol of  $-\text{OH}$  at fiber surface. Then, the use of 1% MAH-PP coupling agent represents an equivalent amount of  $2.678 \cdot 10^{-6}$  mol of maleic anhydride (1.05 equivalent in excess) (Roberts and Constable 2003).

In the case of stone groundwood, the superficial amount of hydroxyl groups cannot be theoretically calculated. The optimum extension of the coupling agent has to be experimentally determined. For this reason, PP composites comprising 30 to 50wt% of stone groundwood were prepared by adding different amounts of MAH-PP coupling agent, in weight percentage with respect to the fiber content, which maximum tensile strength is presented in Fig. 1.



**Fig. 1.** Tensile strength of SGW-PP composites at different fiber and coupling agent content. Bar coloration indicates the fiber content in the composite: ■ 30%; ■ 40%; and ■ 50%

In all formulations, the addition of 2, 4, and 6 wt/wt% of coupling agent produced an increase in the maximum tensile strength of the composite. The decrease of tensile strength at yet higher coupling agent content is attributed to self-entanglement among the coupling agent chains, rather than with the polymer, resulting in slippage (Beg and Pickering 2008). It is observed that, for the currently tested formulations, the addition of 6wt/wt% of MAH-PP allowed the SGW fibers to develop the maximum reinforcing effect into the composite. At this formulation, the extension of the esterification reaction between maleic anhydride of the coupling agent and the hydroxyl groups of the fibers, combined with the entanglement between PP chains of the coupling agent and the matrix, developed the greatest ability of stone groundwood fibers in reinforcing PP polymer.

Although it is not feasible to exactly determine the amount of surface hydroxyl groups in stone groundwood fibers, a rough approximation can be made. In general, 1 g of pure cellulose, of 1.6  $\text{m}^2/\text{g}$  of specific surface and 0.083% of hydroxyl groups at

surface (Joly, Gauthier and Chabert 1996), has 6.02 –OH per nm<sup>2</sup> surface. Therefore, according to the numbers above, 6% of coupling agent would accomplish the stoichiometric needs. However, stone groundwood includes only 20 to 25% of hemicelluloses and celluloses at fiber surface. Thus it is difficult to predict the maximum level of hydroxyl groups at the surface in stone groundwood, although it will be much lower than that of pure cellulose. It can be stated, therefore, that a huge excess of coupling agent is needed in stone groundwood composites to accomplish the maximum reinforcing capacity of the fibers into the polymer matrix.

In order to corroborate the above statements, the authors carried out an experimental test of the influence of the degree of accessibility of the surface hydroxyl groups in lignocellulosic fibers. Stone groundwood fibers were submitted to mild alkaline treatment in soda (5wt% per dry pulp mass) and anthraquinone (0.1% per dpm) at 95°C for 15 min. This alkaline treatment represented a weight lost of 10% (yield of 90%) and an increase of the surface polarity from 24.6 to 27.7 µeq of methyl-glycol-chitosan per gram (determined by colloidal titration). The treatment was expected to cause swelling of the stone groundwood fibers and to increase of the accessibility of their superficial hydroxyl groups. After that, the ultimate tensile strength of PP composites comprising 30, 40, and 50wt% of such treated SGW, also coupled by 6wt/wt% of MAH-PP, was increased from 46.7 to 50.7 MPa, from 51.4 to 58.1 MPa and from 56.2 to 65.4 MPa, respectively. This significant increase is attributed to the rise in the accessibility of the surface hydroxyl groups of SGW, and the subsequent major extension of the esterification reaction between SGW and MAH-PP coupling agent.

The intrinsic tensile strength of reinforcing fibers inside the composite material is a function of their intrinsic properties but also of their degree of adhesion with the polymer matrix. One can say, then, that there is a maximum intrinsic tensile strength of reinforcement for each coupling level. The stress transfer in a composite material is strongly affected by the connection level between their components, and of course to the other parameters such as the fiber length and orientation factor of the reinforcement.

It is easy to find a verification of this occurrence in a regular reinforcing fiber such as fiberglass. The preparation of PP composites at 20wt% ( $V^F=0.085$ ) of sized fiberglass, with and without coupling agent, resulted in the tensile properties shown in Table 1 (Young's modulus,  $E_t^c$ , ultimate tensile strength,  $\sigma_t^c$ , and strain at break,  $\varepsilon^c$ ). It is clearly evident how the quality at fiber-matrix interface was affecting the maximum tensile strength of the final composite, due to the better transfer of load. In addition, no significant influence of the interface quality on the stiffness (Young's modulus) of the composite was observed. At this stage, and in order to develop the Bowyer-Bader methodology, other parameters must be known, such as the fiber morphology ( $l^F$  and  $d^F$ ), the intrinsic Young's modulus of the reinforcement ( $E_t^F$ ), and the matrix tensile strength at composite failure ( $\sigma^{m*}$ ). The matrix tensile strength function at any strain is obtained by fitting the equation to the experimental stress-strain results, which is  $\sigma_t^m = -0.0159\varepsilon^4 + 0.3712\varepsilon^3 - 3.3674\varepsilon^2 + 14.895\varepsilon + 0.0493$  in this case. Concerning the intrinsic Young's modulus of the reinforcement, it can be deduced from the Hirsch model (Kalaprasad et al. 1997) applied to the experimental values of the analyzed composites.

As seen in Table 1, the determined intrinsic modulus for sized-fiberglass were 69.6 and 71.6 GPa, very close to the value of 72 GPa found in the literature (Bismark et al. 2005). This good agreement between the intrinsic modulus determined experimentally and the nominal value validates the use of the Hirsch model for the intrinsic fiber Young's modulus determination.

Once the input data were known, the Bowyer-Bader methodology could be executed and the output data were obtained (also in Table 1). The most relevant results in this case were the determination of the interfacial shear strength ( $\tau$ ) and the intrinsic strength of the fiber ( $\sigma_t^F$ ). Also the mean weighted fiber length ( $l_w^F$ ), the critical fiber length ( $l_c^F$ ), and the fiber orientation factor ( $\chi_1$ ) are presented in Table 1.

**Table 1.** Input and Output Data of the Bowyer-Bader Methodology Applied to PP Composites with 20wt% of Fiberglass

Input data							
MAH-PP	$l_w^F$ ( $\mu\text{m}$ )	$d^F$ ( $\mu\text{m}$ )	$E_t^c$ (GPa)	$\sigma_t^c$ (MPa)	$\varepsilon^c$ (%)	$E_t^F$ (GPa)	$\sigma^{m*}$ (MPa)
0%	914.9	10.2	4.1	50.7	2.97	69.6	23.1
6%	1052.0	10.2	4.1	69.1	4.7	71.6	26.5
Output data							
MAH-PP	$l_c^F$ ( $\mu\text{m}$ )	$\tau$ (MPa)		$\chi_1$		$\sigma_t^F$ (MPa)	
0%	1231.6	10.0		0.283		2415	
6%	985.0	15.3		0.303		2955	

The critical fiber length given in the results was determined following its definition, according to Eq. (3):

$$l_c^F = \frac{d^F \sigma_t^F}{2\tau} \quad (3)$$

The results from Table 1 support the above given idea that the intrinsic tensile strength of reinforcing fibers inside a composite is a function also of its degree of adhesion with the matrix. In the present case, sized-fiberglass showed intrinsic tensile strength of 2415 MPa, while the sized fiberglass developed 2955 MPa of an intrinsic tensile strength with the presence of MAH-PP coupling agent. Sized fiberglass, mainly hydrophobic and specific for PP matrices, was already sufficiently compatible with PP polymer. However, the fiber-matrix entanglement linkage was important in the presence of the coupling agent, and this allowed the reinforcement to develop a major strengthening effect. It can be stated, then, that better interfacial quality results in an intrinsic property closer to the nominal one (Bismark et al. 2005). The same explanation can be given for the increment in the interfacial shear strength ( $\tau$ ) for the composites without and with coupling agent.

Considering these previous validations, it is possible to undertake the main objective of the present work, the determination of the intrinsic tensile strength of stone groundwood fibers. Sanadi et al. already stated in 1994 that it is difficult to obtain

realistic fiber strengths for a batch of fibers and, therefore, to estimate the theoretical strength of the composites for specific fiber lengths and fiber-matrix interfacial strengths. This affirmation is still true today, unless one uses the Bowyer-Bader methodology to solve the Kelly-Tyson equation.

PP composite materials containing 30 to 50wt% of stone groundwood, non-coupled or coupled with 6wt/wt% of MAH-PP coupling agent were prepared and their tensile properties analyzed, according to the described procedure. Stress-strain curves of neat PP and its composites reinforced with SGW are shown in Fig. 2.

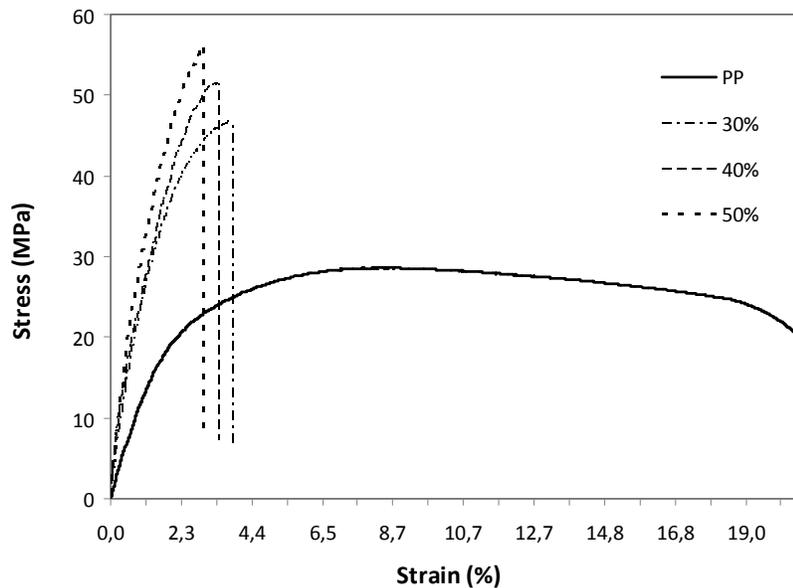


Fig. 2. Experimental curves of tensile strength of PP and stone groundwood reinforced PP

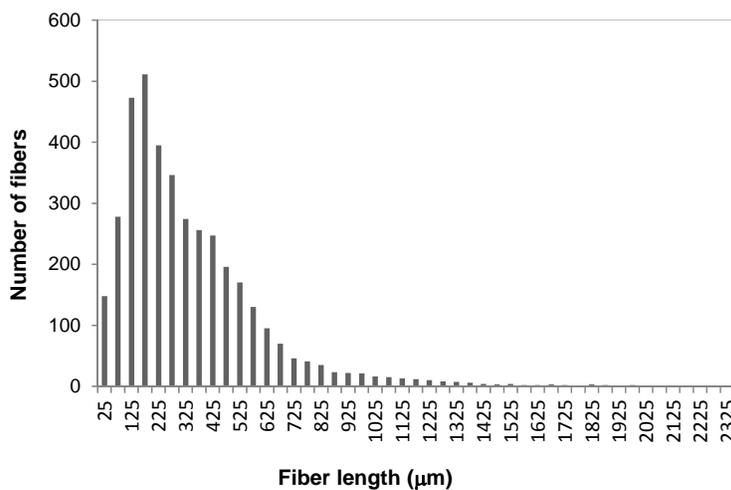


Fig. 3. Fiber length distribution of stone groundwood fibers inside a composite comprising 30wt% of reinforcement

From the experimental results, and knowing the fiber length distribution (Fig. 3), the methodology of Bowyer-Bader can be applied. The input data for the Bowyer-Bader methodology, as well as the output data, applied to PP composites containing 30 to 50wt% of stone groundwood fibers (SGW), in the cases of uncoupled and coupled composites, are presented respectively in Tables 2 and 3.

**Table 2.** Input and Output Data of the Bowyer-Bader Methodology Applied to PP Composites Reinforced with SGW Fibers Without Coupling Agent

Input data							
SGW (%)	$l_w^F$ ( $\mu\text{m}$ )	$d^F$ ( $\mu\text{m}$ )	$E_t^c$ (GPa)	$\sigma_t^c$ (MPa)	$\varepsilon^c$ (%)	$E_t^F$ (GPa)	$\sigma^{m*}$ (MPa)
30	729.7	33.5	3.5	28.6	2.4	19.5	21.0
40	723.9	32.1	4.15	27.3	2.0	17.5	18.8
50	506.2	30.9	5.05	31.2	1.2	16.7	13.9
Output data							
SGW (%)	$l_c^F$ ( $\mu\text{m}$ )	$\tau$ (MPa)	$\chi_1$	$\sigma_t^F$ (MPa)			
30	1277.3	3.85	0.372	293.6			
40	1075.3	3.7	0.393	247.9			
50	1342.1	3.45	0.369	299.7			

**Table 3.** Input and Output Data of the Bowyer-Bader Methodology Applied to PP Composites Reinforced with SGW fibers and 6wt/wt% of Coupling Agent

Input data							
SGW (%)	$l_w^F$ ( $\mu\text{m}$ )	$d^F$ ( $\mu\text{m}$ )	$E_t^c$ (GPa)	$\sigma_t^c$ (MPa)	$\varepsilon^c$ (%)	$E_t^F$ (GPa)	$\sigma^{m*}$ (MPa)
30	698.2	31.9	3.45	46.7	4.2	18.9	25.8
40	670.2	30.1	4.3	51.4	3.7	18.8	24.4
50	549.9	29.9	5.2	56.2	3.3	17.7	24.1
Output data							
SGW (%)	$l_c^F$ ( $\mu\text{m}$ )	$\tau$ (MPa)	$\chi_1$	$\sigma_t^F$ (MPa)			
30	649.9	15.71	0.292	640.1			
40	577.6	15.95	0.285	612.2			
50	566.1	15.87	0.280	601.0			

First of all, a decrease in the mean fiber length was observed with increasing fiber content of the composites, due to the attrition happening during composite fabrication. This phenomenon produces a reduction not only in the mean fiber length but also in the mean diameter. This characteristic is still more relevant for coupled composites, indicating that fibers better tied to the matrix were submitted to higher attrition phenomenon during processing.

The intrinsic Young's modulus of the stone groundwood fibers was calculated following the Hirsch model, and also considering the  $\beta$  stress transfer parameter as 0.4 (Kalaprasad et al. 1997). From the results, the mean intrinsic Young's modulus of stone groundwood fibers (SGW) was found to be  $18.2 \pm 1.1$  GPa. In 2006, Neagu et al.

determined the Young's modulus of thermomechanical pulp (TMP) to be  $21.7 \pm 4.23$  GPa. Considering the minor difference in the fiber morphology between SGW and TMP, the slight lowering in rigidity shown by the stone groundwood fibers can be easily understood.

Concerning the strength results, it is relevant to mention the different intrinsic tensile strength property for SGW that was shown in uncoupled or coupled composites. As mentioned before, the fiber reinforcement can only develop its higher strengthening capacity in a well-linked situation. Therefore, in the present case, the intrinsic property found for a non-coupled composite structure is not representative of the real reinforcing capacity of the stone groundwood fibers. As a consequence, the mean intrinsic strength of the stone groundwood reinforcing fibers can only be assumed as the average of the fiber strength determined for couple-composites, which was  $617.7 \pm 20.1$  MPa. This was not the case of the mean Young's modulus of the stone groundwood, which can be evaluated taking both coupled and uncoupled composites.

In relation to the obtained fiber orientation factor ( $\chi_1$ ), it is observed that the average of the orientation factor for coupled composites was lower than that of non-coupled composites. The degree of adhesion of the composites is mathematically represented by the interfacial shear strength ( $\tau$ ) of the composites. In the present case, the interfacial shear strength of the well-bonded composites was about 15.84 MPa. This value is in agreement with the value predicted by the Von Misses criterion (Pegoretti et al. 1996; Vilaseca et al. 2010), which corresponds to the matrix strength divided by the square root of 3 ( $\tau = \sigma_t^m / \sqrt{3}$ ). The poor adhesion and compatibility at fiber-matrix interface in non-coupled composites is numerically expressed by the lower interfacial shear strength determined for this type of composites (Table 2).

## CONCLUSIONS

1. The effect of the quality at the fiber-matrix interface on the final properties of composites has been demonstrated, either for fiberglass and for stone groundwood composites.
2. The Bowyer-Bader methodology as an analytical method to solve Kelly-Tyson equation applied on the mechanical properties of fiber-reinforced polypropylene composites allows for the determination of the mean intrinsic tensile strength of the reinforcing fibers at failure.
3. The use of Bowyer-Bader methodology, applied to well-bonded composites, allowed the estimation of the mean intrinsic tensile strength of stone groundwood to be  $617.7 \pm 20.1$  MPa.
4. The intrinsic Young's modulus of stone groundwood fibers was determined to be  $18.2 \pm 1.1$  GPa, deduced from the application of the Hirsch model to both non-coupled and coupled composites.

## ACKNOWLEDGMENTS

The authors are thankful to the Catalan Government and the University of Girona for funding the research by the specific Research Program.

## REFERENCES CITED

- Beckermann, G. W., and Pickering, K. L. (2009). "Engineering and evaluation of hemp fibre reinforced polypropylene composites: Micro-mechanics and strength prediction modeling," *Composites Part A* 40(2), 210-217.
- Beg, M. D. H., and Pickering, K. L. (2008). "Mechanical performance of kraft fiber reinforced polypropylene composites: Influence of fiber length, fiber beating and hygrothermal ageing," *Composites Part A* 39, 1748-1755.
- Bismark, A., Mishra, S., and Lampke, T. (2005). *Plant Fibers as Reinforcement for Green Composites in Natural fibers, Biopolymers and Biocomposites*, Mohanty A.K., Misra, M., and Drzal, L. T. (eds.), Taylor & Francis ISBN: 978-0-8493-1741-5
- Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibres," *Prog. Polym. Sci.* 24, 221-274.
- Bowyer, W. H., and Bader, M. G. (1972). "On the reinforcement of thermoplastics by imperfectly aligned discontinuous fibres," *J. Mater. Sci.* 7, 1315-1321.
- Fry, R. A., Tsomaia, N., Pantano, C. G., and Mueller, K. T. (2003). "<sup>19</sup>F MAS NMR quantification of accesible hydroxyl sites on fiberglass surfaces," *J. Am. Chem. Soc.* 125, 2378-2379.
- Joly, C., Gauthier, R., and Chabert, B. (1996) "Physical chemistry of the interface in polypropylene/cellulosic-fibre composites," *Compos. Sci. Technol.* 56(7), 761-765.
- Kalaprasad, G., Joseph, K., and Thomas, S. (1997). "Theoretical modelling of tensile properties of short sisal fibre-reinforced low-density polyethylene composites," *J. Mater. Sci.* 32, 4261-4267.
- Méndez, J. A., Vilaseca, F., Pèlach, M. A., López, J. P., Barberà, L., Turon X., Gironès, J., and Mutjé, P. (2007). "Evaluation of the reinforcing effect of groundwood pulp in the preparation of polypropylene-based composites coupled with maleic anhydride grafted polypropylene," *J. Appl. Polym. Sci.* 105(6), 3588-3596.
- Michell, A. J., and Willis, D. (1978). "Cellulosic fibres for reinforcement," *Appita* 31, 347-354.
- Mutjé, P., Vallejos, M. E., Gironès, J., Vilaseca, F., López A., López, J. P., and Méndez J. A. (2006). "Effect of maleated polypropylene as coupling agent for polypropylene composites reinforced with hemp strands," *J. Appl. Polym. Sci.* 102, 833-840.
- Neagu, R. C., Gamstedt, E. K., and Berthold, F. (2006). "Stiffness contribution of various wood fibers to composite materials," *J. Compos. Mater.* 40, 663-699.
- Oksman, I., Matherw, A.P., Langstrom, R., Nystrom, B., and Joseph, K. (2009). "The influence of fibre microstructure on fibre breakage and mechanical properties of natural fibre reinforced polypropylene," *Compos. Sci. Technol.* 69, 1847-1853.

- Pegoretti, A., Della Volpe, C., Detassis, M., and Migliaresi, C. (1996). "Thermomechanical behaviour of interfacial region in carbon fibre/epoxy composites," *Composites Part A*, 27, 1067-1074.
- Roberts, D., and Constable, R. D. (2003). "Chemical coupling agents for filled and grafted polypropylene composites," In: *Handbook of Polypropylene and Polypropylene Composites*, 2<sup>nd</sup> Edition, Haruntun G. Karian. New York. ISBN: 0-8247-4064-5.
- Rodríguez, M., Rodríguez, A., Bayer R., J., Vilaseca, F., Gironès, J., and Mutjé, P. (2010). "Determination of corn stalk fibers' strength through modeling of the mechanical properties of its composites," *BioResources* 5(4), 2535-2546.
- Sundholm, J. (1998). *Mechanical Pulping*, J. Sundholm (ed.), Published by Finnish Paper Engineers Ass. and TAPPI., ISBN: 952-5216-22-5.
- Terayama, H. (1952). "Method of colloid titration (a new titration between polymer ions)," *J. Polym. Sci.* 8, 243-253.
- Thomasom, J. L. (2002). "Interfacial strength in thermoplastic composites – At last an industry friendly measurement method?" *Composites: Part A* 33, 1283-1288.
- 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," *Bioresour. Technol.* 101, 387-395.

Article submitted: August 5, 2011; Peer review completed: October 13, 2011; Revised version received and accepted: October 20, 2011; Published: October 23, 2011.