Micro-Mechanics Mercerization Analysis on the Tensile Strength and Interphase Quality of Stipa Stem Fiber-Reinforced Polypropylene Composite Materials

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Abstract- the Production of greener composite materials by substituting glass fibers with natural fibers is a current field of research. If such natural fiber reinforcements come from agro-industrial side streams, as stipa stem fibers (SSFs) come from the extraction of stipa strands for the textile industry, an additional advantage can be identified. Nonetheless, such by-product fibers show some drawbacks, such as high lignin contents, which can make it difficult to obtain a good interphase between the fibers and the matrix and to obtain good fiber individualization. A digestion treatment at different NaOH contents is proposed to eliminate soluble lignin and extractives from the surface of the fibers. At the same time, the use of a coupling agent solves incompatibilities between the fibers and the matrix. The composites were tensile tested and the impact of the proposed treatments was evaluated and discussed. Later, the Kelly-Tyson modified equation and a modified rule of mixtures—the micro-mechanic models—were used to study the impact of such treatments on the quality of the interphase between the polymer and the reinforcement. Both treatments showed a high impact on the tensile strength and the quality of the interphase, obtaining competitive composite materials reinforced with SSFs derived from a by-product.

Indexed Terms- Stipa Fiber, Polypropylene, Tensile Strength, Bio-Composites, Micro-Mechanics, Mercerization, Interphase

I. INTRODUCTION

Environmental concern has constantly increased in the past years. The field of research of composite materials responds to this concern by researching substitutions for materials with high environmental impacts, mainly mineral reinforcements and oil-based matrices (Rivera-Gómez et al, 2014). In this sense, in the recent years, the literature on the use of natural fibers as a replacement for mineral fibers such as glass-fibers includes a high increase of publications as well as a high increase in reporting on the mechanical properties of the formulated materials ((Delgado_Aguilar et al, 2017), (Dicker et al, 2014)) .

Important factors for choosing a natural source for a reinforcement are its availability, proximity, cost and the need for complementary processes. Then, it is important to bear in mind that there are some natural fibers, such as hemp or abaca, which have higher costs than glass fiber ((Koronis et al, 2013),(Bledzki et al, 2015)). Nonetheless, fibers show high intrinsic properties, although some processing is needed to obtain fibers with industrial value. The processes used to obtain such fibers produce a quantity of by-products in the lower-quality fibers. The process used to obtain plant fibers had been shown by((Delgado Aguilar et al, 2016), (Vallejos et al, 2006)).

After harvesting, hemp plants are treated to extract the hemp strands that are used in the paper and textile industries. The hemp stems are constituted by 30% to 35% hemp strands, 10% to 15% waste and 50% to 55% hemp core. Once the plants are fragmented, a

mixture of hemp strands and hemp core fibers (HCFs) is obtained. Such a mixture is submitted to separation processes, in which HCFs are separated from the hemp strands. Hemp strands are submitted for further cleaning processes to obtain the final high-quality fibers. On the other hand, the hemp core remains a byproduct of low value (Vallejos et al, 2006).

Hemp core is usually used as bedding for livestock, principally because of its high capacity toadsorb liquids. One of the main drawbacks of hemp core is its high lignin content (Barbera et al, 2011). Nonetheless, there are treatments, such as NaOH pulping, that allow for the obtaining of chemi-thermo-mechanical pulps with an increased presence of celluloses on their surface and enhanced individualization (Granda et al, 2016).

Plant fiber has already drawn the attention of researchers intending to design more environmentally friendly composites (La Rosa et al, 2013), and the studies present promising mechanical properties and the ability of such composites to replace glass fiber-based composites. HCFs have also drawn the attention of researchers, and there is literature on their use as reinforcements for different polymeric matrices (Lopez et al, 2012). However, to the best knowledge of the authors, this is the first time that SSFs as a by-product have been used as reinforcement.

In this work, SSFs, obtained as a by-product of the fragmentation of stipa stems to produce stipa strands for the paper making and textile industries, were used to produce polypropylene (PP)-based composites. Composites containing 40% *w/w* SSF were produced and tensile tested. In order to obtain high strength properties, the stipa fiber were cooked with different percentages of sodium hydroxide (NaOH), and chemi-thermo-mechanical pulps with a reduced presence of lignin on their surface were obtained. At the same time, different amounts of coupling agent were tested to solve the incompatibilities between the hydrophobic matrix and the hydrophilic reinforcements. The effect of both treatments on the tensile strength of the composites were reported and discussed. Following this, a micro-mechanics analysis was conducted to assess the impact of the

mentioned treatments on the quality of the interphase between the SSFs and the PP. A modified rule of mixtures for the tensile strength and the modified Kelly-Tyson equation with the solution provided by Bowyer and Bader were the models used to perform the micro-mechanics study.

II. MATERIALS AND METHODS

2.1 Materials
The untreated stipa fibers were provided. A PP ISPLEN 090 G2M was used as the polymeric matrix. Some composites added Epolene, a maleic-grafted polypropylene (MAPP), as coupling agent. The other reactants used included decahydronaphtalene to dissolve the matrix in the fiber extraction during the composite process, and NaOH and anthraquinone used to prepare the fibers. The reactants were used without any further purification.

2.2 Stipa Fiber Treatment
The stipa fibers were treated for 120 minutes at 98 $\pm$ 2 $^{\circ}$C in a 15 L batch reactor. Three different batches containing 5%, 7.5% and 10% NaOH were prepared. In addition to the NaOH, the reactor included 0.1% anthraquinone. The liquid/solid ratio was set at 10. Following this, the digested fibers were washed and dispersed by using a pulp disintegrator. Then, the pulp was defibrated using single-disk Sprout-Waldron equipment. Finally, the fibers were dried for 48 h at room temperature.

2.3 Composite Preparation
The composites with 40% w/w SSF were prepared in a Gelimat kinetic mixer (model G5S,Draiswerke, Mahaw, New Jersey, USA). The mixture was prepared at 2500 rpm for 2 min until a discharge temperature of 210 $^{\circ}$C was achieved. Whit necessity, as a result of the composite production, the coupling agent mixed with the PP was added. The composites were granulated in a blade mill equipped with 10 mm mesh and were kept in an oven at 80 $^{\circ}$C to prevent moisture absorption.

2.4 Sample Configuration
The normalized samples for the tensile test were injection-molded by means of a Meteor 40 injection machine (Mateu & Solé, Barcelona, Spain). At least 10 test samples from each composite blend were

injection-molded. The processing temperatures of the three heating areas were 175, 175, and 190 ^{o}C, the last of these corresponding to the injection nozzle. The first and second pressures were 120 and 37.5 kgf/cm^2, respectively. The dog bone samples (approx. 160×13.3×3.2 mm^3) were used to measure the tensile properties, in agreement with the ASTM D638.

2.5   Strength Characterization

According to the ASTM D638 standard, the samples were stored in a Dycometal conditioning chamber at 23 ^{o}C and 60% relative humidity for 48 h prior to the strength testing. Following this, the composites were tensile tested in a universal testing machine (InstronTM 1122, Mark-10 Corporation, Copiague, New York, NY, and USA) fitted with a 5 kN load cell and operating at a rate of 2 mm/min, according to the ASTM D638 standard. Results were obtained from the averaging of at least five samples.

2.6   Fiber Extraction from the Composites

A Soxhlet apparatus was used to extract the reinforcing fibers from the composites by matrix solubilization, using decalin as the solvent. Small parts of the composite were cut, placed inside a cellulose filter and set into the Soxhelt equipment. The fiber extraction lasted for 24 h. The fibers were extracted and rinsed with acetone and then distilled water in order to remove the solvent residue. Finally, the fibers were dried at room temperature for 48 h.

2.7   Morphologic Analysis of the Fibers

The length and diameter distributions of the extracted fibers were characterized by means of a MorFi Compact instrument (Morphological fiber analyzer, Techpap SAS, Grenoble, France). The equipment measured between 25,000 and 30,000 fibers. Four samples of each type of fiber were analyzed.

III.   MICRO-MECHANICS MODELS

All the micro-mechanics used to model the behavior of the tensile properties of the composites were linear. The literature endorses the use of such models mainly in the case of good interphases between the reinforcement and the matrix (Oliver-Ortega et al, 2016)

3.1   Modified Rule of Mixtures

One of the most simple but elegant ways to model the contribution of the phases to a property of a composite is the use of a rule of mixtures. The literature shows a diversity of formulations for such equations, but all are based on a combination of the contribution of the phases, equalized by their volume fractions and, in some cases, by a number of efficiency factors (Thomason et al, 2002). An accepted formulation of a modified rule of mixtures (mRoM) for short-fiber semi-aligned composites is

$$\sigma_t^C = x_1 . x_2 . \sigma_t^F . V^F + (1 - V^F) . \sigma_t^{M*} \qquad (1)$$

where σ_t^C is the ultimate tensile strength of the composite, σ_t^F is the intrinsic tensile strength of the reinforcement, V^F is the volume fraction of the reinforcement, and σ_t^{M*} is the contribution of the matrix at the ultimate strain of the composite; x_1 and x_2 are the orientation and the length factors, respectively, used to equalize the contribution of the semi-aligned short-fiber reinforcement. Usually, a coupling factor f_c is obtained by multiplying such factors ($f_c = x_1 . x_2$). It is accepted that well-bonded composites show coupling factors ranging from 0.18 to 0.2 ((Lopez et al, 2011), Lopez et al, 2012)). The values for the matrix and the composite are easily acquired experimentally, but the intrinsic tensile strength of the reinforcement and the coupling factor are not so easily acquired. Because of their length, testing the reinforcing fibers is difficult or sometimes impossible. Additionally, there is controversy on the use of experimental values of the fibers to model the behavior of a composite (Shah et al, 2016). Therefore, the use of additional models is required to achieve the intrinsic tensile strength of the reinforcement.

3.2   Modified Kelly-Tyson Equation

Kelly and Tyson developed a new formulation for the rule of mixtures (Kelly et al, 1965). These authors divide the reinforcements into sub- and super-critical categories, depending on their lengths. The tensile loads of the composite are transferred from the matrix to the surface of the fibers via shear stress.

Then, the stresses are accumulated from both ends of the fiber toward its middle. The longer the fiber, the

higher its final accumulated load, up to the moment at which the intrinsic tensile strength of thereinforcement is reached and the reinforcement breaks, which coincides with the critical length (Vallejos et al, 2012). The original Kelly-Tyson equation was formulated for aligned reinforcements, but later on, a modified version adding an orientation factor (x_1) was proposed [14,33,34]:

$$\sigma_t^C = x_1(X + Y) + Z \qquad (2)$$

Where X, Y and Z, are the contributions of the subcritical fibers, the critical fibers and the matrix, respectively. Then, such contributions are defined by

$$X = \sum_{l=0}^{l=l_c} \left[\frac{\tau.l.V_1^F}{d^F}\right] \qquad (3)$$

$$Y = \sum_{l=l_c}^{\infty} \left[\sigma_t^F.V_l^F.\left(1 - \frac{\sigma_t^F.d^F}{4.\tau.l}\right)\right] \qquad (4)$$

$$Z = (1 - V^F).\sigma_t^{M*} \qquad (5)$$

whereτ is the interfacial shear strength that defines the maximum shear load transfers allowed by theinterphase between the reinforcement and the matrix; and d^F and l are the diameter and the length of the fibers, respectively. The length is a variable

that is defined by the morphological analysis, when a length distribution is obtained and the volume fraction of such a length (V_1^F) is also defined. The rest of the parameters are already defined for the mRoM (Equation (1)).

In any case, the Kelly-Tyson equation has three unknowns,σ_t^F,τ and x_1. Fortunately, Bowyer and Bader developed a method to solve the equation (Bowyer et al, 1972).

3.3 Bowyer and Bader Method

The solution proposed by Bowyer and Bader is based on several assumptions, the most relevantbeing that the strain of all the phases is the same: $\varepsilon_t^M = \varepsilon_t^F = \varepsilon_t^C$(the strains of the matrix, the reinforcement and the composite, respectively). Then, in the elastic section of the stress-strain curve, it is fulfilled that $E_t^F = \varepsilon_t^M + E_t^F$, where E_t^F is the intrinsic Young's modulus of the reinforcement. Bowyer and Bader proposed the use of the experimental data of two strain points (Figure 1).
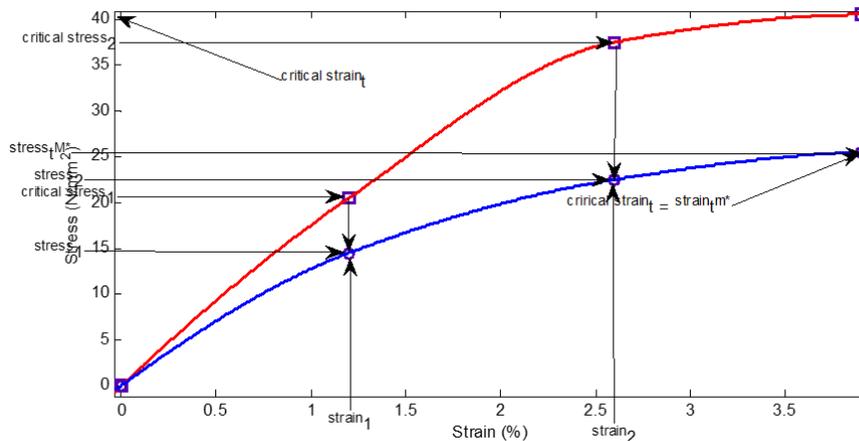

Fig. 1: Bowyer and Bader Two Strain Fits

Then, Equation 2 can be expressed, for the two intermediate strains, as

$$\sigma_i^C = Z_i = x_1(X_i + Y_i) \qquad (6)$$

The left-hand side of the equation refers to available experimental data; the right-hand sidedepends on the value of the critical length and is computed by using Equations (4) and (5). Then, the ratio for Equation (6)

expressed for the points 1 and 2 is proposed; deleting the orientation factor, we obtain

$$R = \frac{\sigma_1^C - Z_1}{\sigma_2^C - Z_2}; \quad R^* = \frac{X_1 + Y_1}{X_2 + Y_2} \qquad (7)$$

By numerical methods, it is possible to obtain a solution in which R = R*.

3.4 Hirsch's Model

As for the intrinsic tensile strength of the fibers, the intrinsic Young's modulus of short fibers is also difficult to obtain experimentally. Thus, the use of a micro-mechanic equation is proposed. Hirsch's model is a combination of the Voigt and Reuss models that equalizes the orientation effects of the fibers in the Young's modulus of the composite ((Hirsch et al, 1962), (Reixach et al, 2013)). The equation can be expressed as

$$E_t^C = \beta . \left(E_t^F . V^F + E_t^M . (1 - V^F) \right) + (1 - \beta E t F . E t M E t M . V F + E t F . 1 - V F$$

(8)

where E_t^C, E_t^F, and E_t^M are the elastic modulus of the composite, the reinforcement, and the matrix, respectively. The factor β equalizes the parallel and perpendicular models and it has been reported that, for natural fiber composites, a value of $\beta = 0.4$ adequately reproduces the results obtained experimentally ((Kalaprasad et al, 1997), (Vilaseca et al, 2010)).

IV. RESULTS AND DISCUSSION

4.1 Sipa Stem Fiber Characteristics after NaOH Treatments

The NaOH soft treatments had the objective of cleaning the surface of the fibers form extractives, soluble lignin and insoluble lignin and to ease fiber individualization. The virgin HCFs, as straws and mechanical pulps (0% NaOH), were impossible to properly individualize, showing high percentages of fiber bundles. For the 5% NaOH treatments, it was not possible to obtain properly individualized SSFs. These treatments also had some impact from hemicelluloses mixed with the lignin contents. As a direct consequence of the reduction of the lignin contents in the fiber surfaces, the percentage contents of celluloses and hemicelluloses increased, and as did the availability of OH groups. This was reflected by the Kappa number (Table 1).

Table 1: Stipa Fiber By-Product NaOH-Treated Fiber Experimental Parameters

NaOH (%)	Yield (%)	Kappa	l_w^F (μm)	d^F (μm)	l_w^F / d^F
5.0000	68.1000	63.2000	469.0000	13.8000	13.9000
7.5000	66.4000	58.1000	589.0000	14.7000	17.9000
10.0000	56.9000	47.0000	619.0000	14.6000	19.2000

The kappa number of the 7.5% NaOH-treated fibers was found to be 7% lower than that of the 5%NaOH-treated sample. The 10% NaOH-treated pulp showed a Kappa number 28% and 19% lowerthan the 7.5% and 5% NaOH treated pulps, respectively. Thus, the NaOH treatment responded well tothe objective of increasing the presence of the OH content at the surface of the fibers. Certainly, the increases in the severity of the NaOH treatments produced decreases in the yield of the process, understood as the amount of treated fibers against the initial biomass. Nevertheless, all the treatmentsshowed yields in the spectrum of chemi-thermo-mechanical or semi-chemical processes high enough to consider them as being in the low range of the high-yield treatments. These yields ensure the minimum creation of by-products from a by-product, being in line with the principles of green chemistry (Anastas et al, 1998).

Consequently, higher percentages of NaOH were discarded as lower yields were obtained.

The weighted length of the fibers increased with the intensity of the NaOH treatments. This wasnot surprising because, as the percentages of lignin decreased, the ease of individualizing the fibers increased. Thus, the attrition of the fibers during the individualization process also decreased. The 10% NaOH-treated fibers were 26.3% longer than the 5% NaOH-treated fibers. The diameters of the fibers showed slight variations from one treatment to another. In all the cases, the aspect ratio was higher than 20, ensuring a priori good strengthening

capabilities of HCFs. Additionally, the prepared pulps were readily usable in the papermaking industry for the production of brown line papers, that is, fluting and liners.

4.2. Impact of NaOH and Coupling Agent Contents on the Tensile Strength of the Composites

Next, composite materials with 40% w/w SSF were prepared and tensile tested. The obtained properties are shown in Table 2. It was found that the impact of the NaOH treatments of the reinforcements on the tensile strength of the uncoupled composites was modest.

Table 2: Tensile Strength, Strain at Break and Work to Fracture of the Stipa Stem Fiber (SSF)-Reinforced Polypropylene (PP) Composites.

Composite Configuration			0% MAPP			6% MAPP		
VF (%)	SSF (wt%)	NaOH (wt%)	σ_t^C (N/mm^2)	ε_t^C (%)	W_F (MJ/m^3)	σ_t^C (N/mm^2)	ε_t^C (%)	W_F (N/mm^2)
0	0	-	17.6±0.50	8.3[*]±0.20	157.51±0.20	16.8±0.20	8.2[*]±0.20	-
0.301	40	5.0	18.86±0.16	0.64±0.16	09.46±0.78	35.77±1.23	2.12±0.23	29.78±1.16
0.301	40	7.5	13.34±0.86	1.13±0.23	14.54±1.01	48.86±1.86	2.63±0.26	39.60±2.39
0.301	40	100.0	12.81±0.50	1.43±0.31	16.68±1.57	50.83±0.50	2.84±0.35	45.75±3.48

*The strain for the matrix was measured at the point of maximum strength.

The tensile strengths of the composites with added 0% MAPP slightly increased in all the casesbut remained close the value of the neat matrix. This behavior was likely due to the diffusion of the polymer on the surface of the fibers and due to a mechanical anchoring. Thus, the presence of a higher amount of OH groups on the surface of the fibers did not promote increases of the tensile strength of the uncoupled composites. Similar behaviors are reported in the literature, where, for low amounts of plant fiber reinforcement, the tensile strength of the composite is lower than that of the matrix (Pracella et al, 2010).

The addition of a 6% MAPP to the matrix slightly changed its properties. Its tensile strength was reduced by 3% and its strain maximum strength increased by 1%. On the other hand, the impact of adding MAPP in the composite formulation was clearly visible (Figure 3).

It is well known and reported in the literature that the different nature of hydrophobic thermoplastics and hydrophilic natural fiber surfaces leads to bad-quality interphases. Thus, chemical modifications can be used to decrease the polarity of the fiber surface. Treatments with acetyls, isocyanates or silanes have been reported as useful and effective but insufficient to provide a good interphase (Serrano et al, 2014). The use of MAPP as a coupling agent is one of the most recurrent solutions to these problems. While the NaOH treatments allowed for a higher presence of OH groups on the surface of the fibers, MAPP takes further advantage of the presence of such groups. The maleic anhydride groups of the MAPP create hydrogen bonds and covalent ester linkages with the hydroxyl groups of the fiber surface. At the same time, the PP chains of the MAPP entangle with the PP matrix ((Mendez et al, 2007), (Birnin-Yauri et al, 2017)).
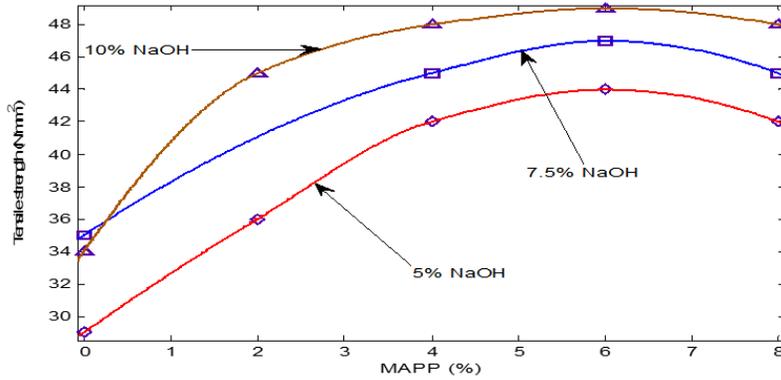
Fig. 2: Evolution of the Tensile Strength of the Composites against the Coupling-Agent Contents

Table 3: Analysis Table for Composites Tensile Strength Evolution against Coupling-Agent Contents

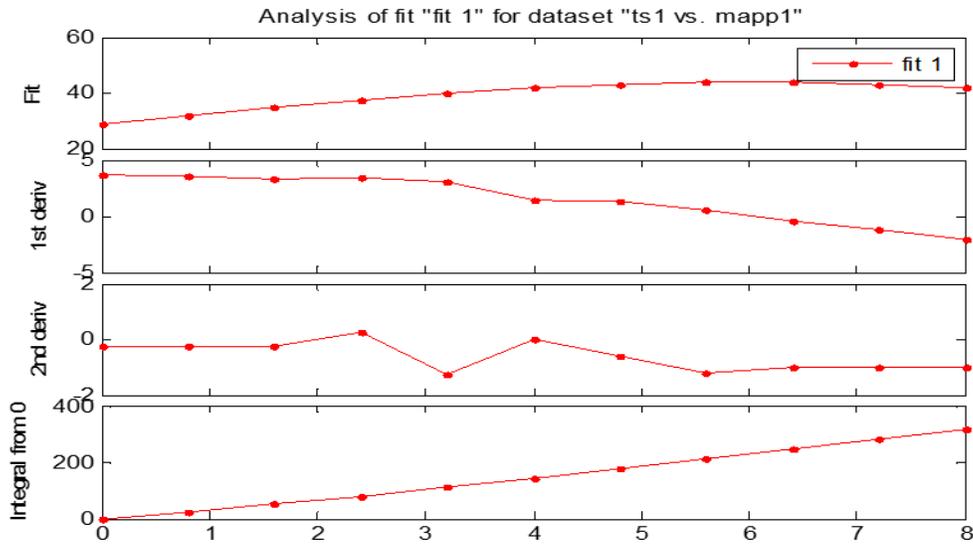| X_i	$f(X_i)$	$df(X_i)/dX$	$d^2f(X_i)/dX^2$	integral $f(X_i)$
0	29	3.75	-0.230769	0
0.8	31.9237	3.55615	-0.253846	24.3798
1.6	34.6849	3.34385	-0.276923	51.0346
2.4	37.3551	3.49385	0.276923	79.8406
3.2	40.0763	3.10615	-1.24615	110.834
4	42	1.5	0	143.75
4.8	43.136	1.26	-0.6	177.817
5.6	43.888	0.54	-1.2	212.665
6.4	43.92	-0.4	-1	247.839
7.2	43.28	-1.2	-1	282.762
8	42	-2	-1	316.917

Fig. 3: Analysis Fit for Composites Tensile Strength Evolution against Coupling-Agent Contents

As the percentage of MAPP was increased, the tensile strength of the composites, regardless of theamount of NaOH used in the cooking process of the SSFs, increased up to a local maximum identified for the 6% MAPP contents. Higher MAPP contents were derived for slight decreases in the strength of the materials. The literature reports a main cause of such behavior as the coupling agent chains self-entangling instead of reacting with the PP, resulting in slippage (Beg et al, 2008).

The composites with 6% w/w MAPP clearly showed the combined effect of NaOH treatments and coupling agent addition. These composites, when compared with the matrix, showed tensile strengths with 65%, 80% and 88% increases, for the 5%, 7.5% and 10% NaOH treatments, respectively (Tables 2 and 3). Compared to the uncoupled composite with the same NaOH treatment, the increases were by 58%, 50% and 57%, respectively. Thus, in both treatments, the NaOH cooking and the addition of coupling agents promoted the increase of the tensile strengths of the composites. Such notable increases indicated the possibility of well-dispersed fibers; however, SEM images are needed to guarantee such a hypothesis.

Regarding the strain at break of the composites (Tables 2 and 3), an increase that was associated withthe presence of MAPP and with the harshness of the NaOH treatment was observed. The composites showed strains at break 3 times lower than those of the matrix but that was usable and comparable to glass fiber-based composites (Lopez et al, 2012).

The work to fracture (WF) showed that the composite materials increased the ability to endureenergy without breaking, while deforming plastically, by the addition of a 6% MAPP and 10% NaOH treatment. The WF of such materials was 4.5 times higher than that of an uncoupled composite treated with 5% NaOH.Other similar natural fiber-reinforced composites, such as chemi-thermo-mechanical pulp from orange tree prunings treated with 5% NaOH, obtained a tensile strength of 46.5 MN/mm^2 (Reixach et al, 2015), which was very similar to SSF-based composites (Table 2 and 3). The strain at break was the same for the SSF- and the pruning-based composites. By comparison, another by-product, old newspaper-based composites, obtained a tensile strength of 45.2 MN/mm^2, which was also very similar to that obtained with SSF-based composites (Serrano et al, 2014).

Therefore, the experimental data show that adding MAPP has a direct effect on the tensile strength of the materials, and a NaOH treatment on fibers makes sense only for coupled composites. This research was followed up to investigate if such conclusions were also valid for the quality of the interphase.

4.2   Morphology of the Fibers

As has been mentioned in the modeling section, the Kelly-Tyson model uses the morphology of the fibers as an input to predict the micro-mechanic properties. However, the initial morphologic data of the fibers could not be used (Table 1). It is known that during composite preparation and sample injection-molding, the reinforcing fibers suffer decreases in their length (Karmaker et al, 1996). Table 4 shows the morphologic properties of the SSFs extracted from the composite. The weighted and double-weighted lengths were computed and are in agreement with those of the literature (Granda et al, 2016).

Table 4. Morphologic Properties of the Fibers Extracted from the Composites.

$NaOH(\%)$	$d^F(\mu m)$	$l_a^F(\mu m)$	$l_w^F(\mu m)$	$l_{ww}^F(\mu m)$
5	13.7	107	280	555
7.5	14.5	113	286	565
10	14.6	121	297	584

It was observed that the length of the fibers, compared with the initial treated pulps, decreased from 50% to 70%. Thus, the aspect ratios decreased in parallel but remained higher than 10%. The diameter of the fibers decreased slightly but remained almost equal.

It was observed that all the distributions were similar and had slight changes in the percentages ofshort fibers, indicating a higher ratio of fiber shortening in the case of the fibers treated with milder NaOH percentages. It was explained in the introduction to the Kelly-Tyson equation that the fibers were divided into subcritical and supercritical sets. The equation defining the critical length is

$$l_C = \frac{d^F . \sigma_t^F}{2.\tau} \qquad (9)$$

The diameter of the fibers and the intrinsic tensile strength of the fibers are quasi-invariantsbecause they depend on the phase. Therefore, the interfacial shear strength (τ) defines the critical length that decreases with higher values. Thus, the composites with a higher quality interphase are able to take advantage of a higher amount of supercritical fibers. Hence, the 10% NaOH-treated SSF had a slight advantage, as shown by higher mean lengths.

4.3 Micro-Mechanics

The micro-mechanic analysis had the objective of assessing the influence of the properties of thephases and their contents on the properties of the composites. Table 4 shows the initial data used to solve the Kelly-Tyson modified equation with the solution provided by Bowyer and Bader.

Table 4: Data used to solve the Kelly-Tyson Modified Equation with the Method supplied by Bowyer and Bader.

Property	Unit	5.0%	7.5%	10.0%
E_t^F	(N/mm^2)	15.7	16.3	17.6
σ_t^{M*}	(N/mm^2)	13.5	14.7	15.2
ε_1	(%)	0.7	0.8	0.9
σ_1^M	(N/mm^2)	9.7	11.0	11.5.
σ_1^C	(N/mm^2)	12.1	15.2	17.2
ε_2	(%)	1.5	1.7	1.8
σ_2^M	(N/mm^2)	15.4	17.0	17.6
σ_2^C	(N/mm^2)	27.6	31.9	34.7

The contribution of the matrix was computed by approximating the stress-strain curve of thematrix to a 4th degree polynomial:

$$\sigma_t^{M*} = -0.0159.(\varepsilon_t^C)^4 + 0.3712.(\varepsilon_t^C)^3 - 3.3674.(\varepsilon_t^C)^2 + 14.8953.\varepsilon_t^C.0.0493 \qquad (10)$$

The intrinsic Young's modulus of the composites was computed by using the Hirsch model (Equation 8). Figure 5 shows the experimental strength and strains, final and intermediate, of the composites and the matrix, used to solve the Kelly-Tyson equation. The Young's moduli of the composites were very similar: 4.7, 4.7 and 4.8 GPa for the 5%, 7.5% and 10% NaOH-treated composites, respectively. This is clearly shown by the stress-strain curves of the composites, which show few deviations on their initial section slope.
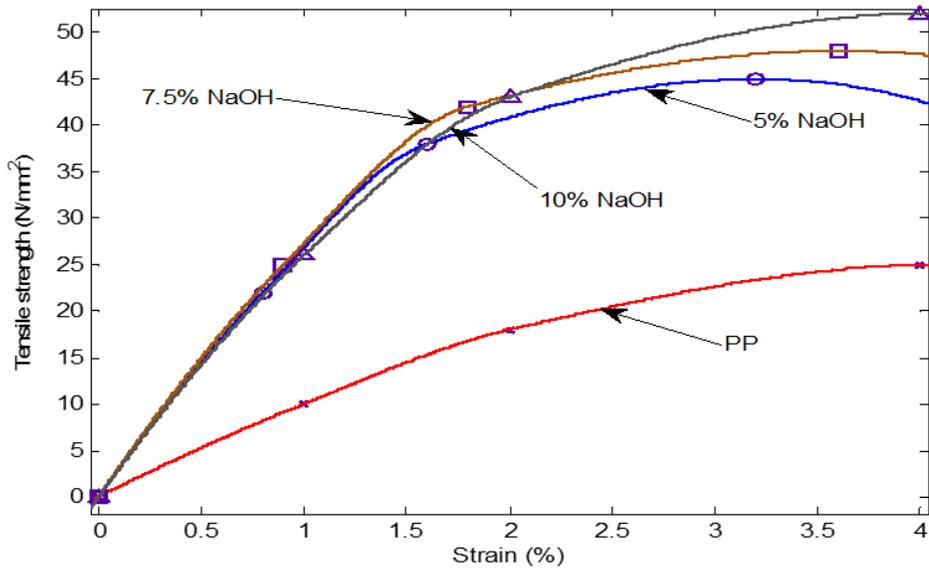
Fig. 4: Mean Stress-Strain Curves of the Composites and the Matrix

Table 5: Analysis Table for Mean Stress-Strain Curves of the Composites and the Matrix.

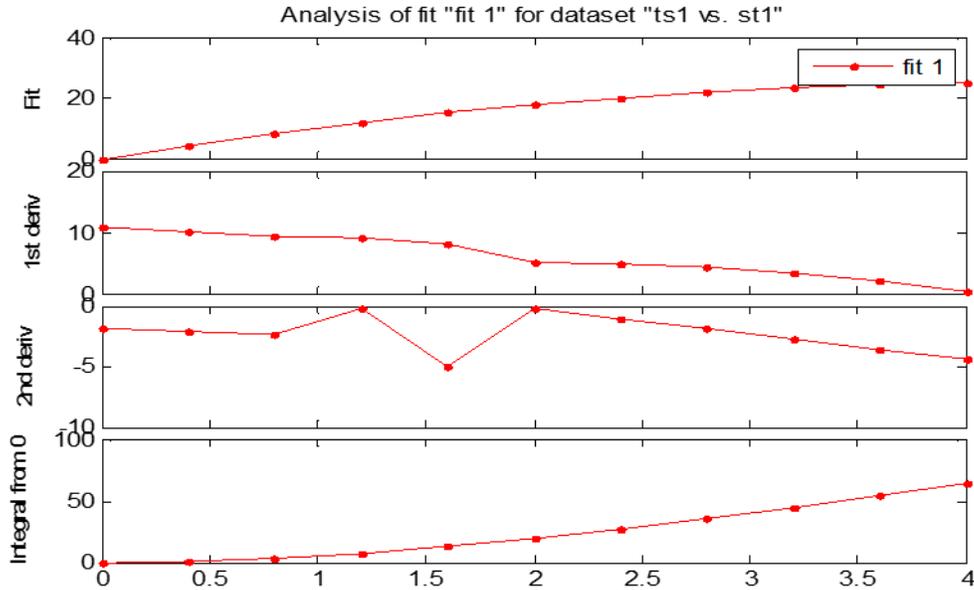| X_i	$f(X_i)$	$df(X_i)/dX$	$d^2f(X_i)/dX^2$	integral $f(X_i)$
0	0	11	-1.77778	0
0.4	4.25067	10.2356	-2.04444	0.860326
0.8	8.17422	9.36444	-2.31111	3.35692
1.2	11.8069	9.09899	-0.161616	7.35591
1.6	15.3042	8.06465	-5.0101	12.7919
2	18	5.09091	-0.181818	19.4924
2.4	19.9993	4.84909	-1.02727	27.0955
2.8	21.8342	4.26909	-1.87273	35.4699
3.2	23.3695	3.35091	-2.71818	44.5229
3.6	24.4698	2.09455	-3.56364	54.1075
4	25	0.5	-4.40909	64.0227

Fig.5: Analysis Fit for Mean Stress-Strain Curves of the Composites and the Matrix

The intermediate strain points used to solve the Kelly-Tyson equation are marked above the corresponding curve. The composites did not show a clearly defined elastic region, but it could be observed that theintermediate points were positioned at the almost-linear sector. The intermediate strain locations were defined as 1/3 and 2/3 of the strain at break of the composites. Once the solution provided by Bowyer and Bader was implemented, the results shown in Tables 6 and 7 were obtained.

Table 6: Micro-Mechanic Properties of the Reinforcing Fibers and the Interphase

$NaOH(\%)$	x_1	τ	σ_t^F	L_c^F
5.0	0.18	12.03	472	297.7
7.5	0.18	12.73	548	354.8
10.0	0.18	12.06	584	376.1

It was found that the orientation factors coincided at 0.29. Such a value is in line with those obtained in the past and already published in the literature (Espinach et al, 2017). Such literature shows that the value of the orientation factor depends, among other parameters, on the equipment used to injection-mold the specimens (Sambale et al, 2017). In the cited bibliography, the orientation factor was always found to be inside the range from 0.25 to 0.35.

The interfacial shear strength, as a measure of the quality of the interphase, increased with theintensity of the NaOH treatments. All the values were near that defined by the von Mises criteria (15.9 MPa). If such a value is considered as an upper bound for the theoretical values of , then all the interphases could be considered as very good to almost optimal (Vallejos et al, 2012).

As for the rest of the parameters, the intrinsic tensile strength of the SSFs increased with the intensity of the NaOH treatment, indicating a better exploitation of the strengthening abilities of these reinforcements. The values were in line with those of the literature, where similar reinforcements obtained intrinsic tensile strengths in the range from 550 to 900 MPa (Lopez et al, 2012). It must be taken in account that the higher values corresponded to high-quality hemp fibers.

As it was abovementioned, the critical length was computed with Equation (9). The increasesof the critical lengths of the SSFs against the NaOH treatments were highly defined by the quality of the interphase and by the higher values of the intrinsic tensile strengths. This was of specialimportance when applying the Kelly-Tyson modified equation. As can be seen in Figure 4, the fiber length distributions are presented as discrete sets and not as continuous curves. Thus, depending on the value of the critical length, a complete set of fibers could pass from supercritical to subcritical, altering the results. Figure 6 shows the cumulative contribution of the subcritical and supercritical fibers and the matrix to the tensile strength of the composite.
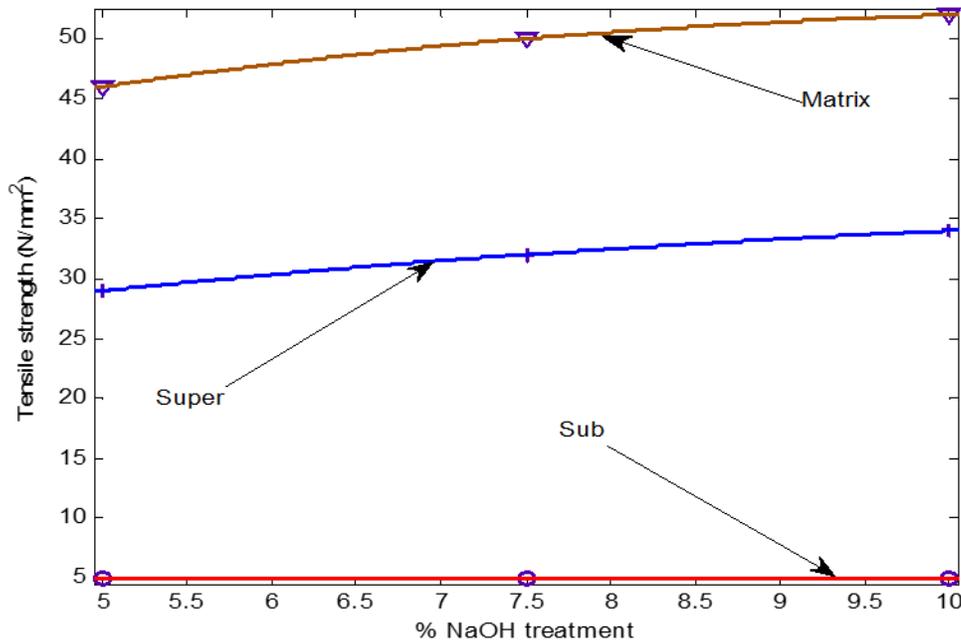

Fig. 6: Subcritical-Supercritical Fibers and Matrix Contributions to Composite Tensile Strength

Table 7: Subcritical-Supercritical Fibers and Matrix Contributions Analysis to Composite Tensile Strength

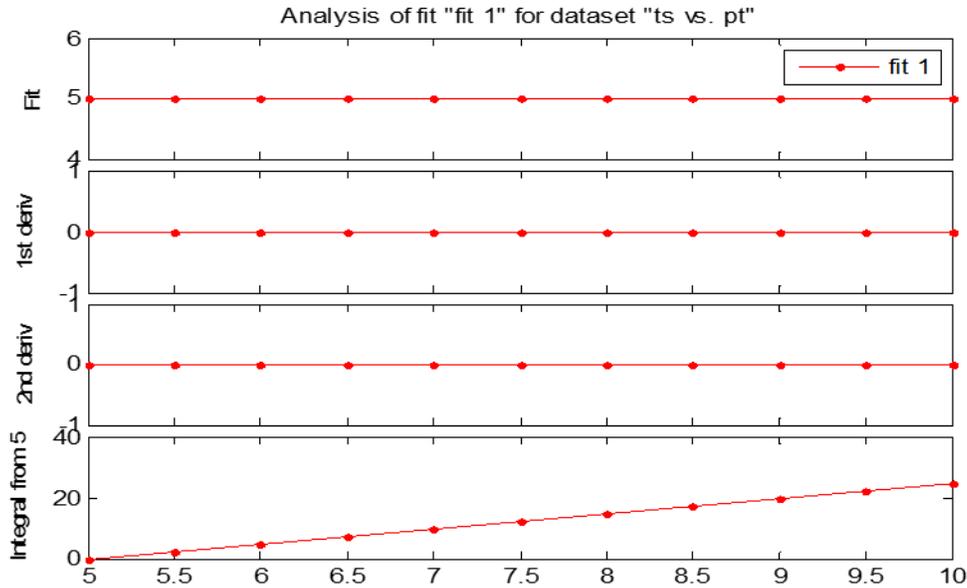| X_i	$f(X_i)$	$df(X_i)/dX$	$d^2f(X_i)/dX^2$	integral $f(X_i)$
5	5	0	0	0
5.5	5	0	0	2.5
6	5	0	0	5
6.5	5	0	0	7.5
7	5	0	0	10
7.5	5	0	0	12.5
8	5	0	0	15
8.5	5	0	0	17.5
9	5	0	0	20
9.5	5	0	0	22.5
10	5	0	0	25

Figure 7: Subcritical-Supercritical Fibers and Matrix Contributions Analysis Fit to Composite Tensile Strength

It was observed that the main contributions were obtained for the supercritical fibers in all the cases, followed by the matrix. In all the cases, the contribution of the subcritical fibers was modest. Table 6 shows the percentage contributions. It was found that the contribution of the supercritical fibers amounted to more than 50%, the matrix amounted to around 34%, and the subcritical fibers amounted to around 8%.

Table 8: Percentage Contribution of the Phases to the Tensile Strength of the Composite.

NaOH	5.0 %	7.5 %	10.0 %
Subcritical	11.1	9.6	10.0
Supercritical	55.0	57.7	58.1
Matrix	36.9	35.7	34.9

With the objective of verifying the obtained values, the mRoM (Equation (1)) was solved. The value of the intrinsic tensile strength was then obtained as in Table 5, and the rest of the values are shown in Tables 2 and 4. Then, the values of the coupling factor were obtained. The equation was also solved for the uncoupled composites (Table 8).

Table 9. Coupling Factors obtained by solving a Modified Rule of Mixtures for the Tensile Strength of the Composites.

NaOH (%)	0% MAPP	6% MAPP
5.0	0.104	0.204
7.5	0.116	0.195
10.0	0.100	0.191

As expected, the coupling factors of the composites when adding 6% MAPP lead to a couplingfactor of around 0.2, indicative of good interphases. On the other hand, the uncoupled composites delivered coupling factors of around 0.1, 50% less than the coupled factors.

Using the mRoM, a correlation between the intensity of the NaOH treatment and the quality ofthe interphase was not observed, but the solution was highly ballasted by the higher intrinsic tensile strength values.

V. CONCLUSIONS

Bio-composites with stipa stem by-product fiber-reinforced PP were prepared and tensile tested. The stipa stem fibers were subjectedted to a cooking process under 5%, 7.5% and 10% NaOH contents. To the composites were added percentages of a coupling agent ranging from 0% to 8%.

The coupling agent contents had a direct and visible impact on the tensile strength of the composites, solving the incompatibility between the hydrophobic matrix and the hydrophilic fibers. Higher tensile strengths were found for the composites when 6% w/w MAPP was added.

The cooking of the fibers showed little effect on the tensile strength of the composites withouta coupling agent, increasing the value only slightly. Nonetheless, when percentages of MAPP were added to the composites, the materials reinforced with the fibers and treated with the most intensive NaOH process showed noticeably higher tensile strengths. Hence, a combination of the coupling agent and intensive cooking of the fibers had a noticeable impact on the tensile strength of the composites. It was possible to obtain competitive natural fiber by-product-reinforced composites, thus adding value to stipa stem fibers. The preparation of the chemi-thermo-mechanical hemp core fibers produced low percentages of new by-products, which was in line with the principles of green chemistry.

The cooking process stimulated the individualization of the fibers, resulting in longer fibers as the percentages of NaOH used during the preparation of the reinforcements were increased.

The Kelly-Tyson model showed a high impact of the presence of MAPP and the treatment of the fibers on the quality of the interphase between the fibers and the matrix. The more intensive the NaOH treatment, the higher the quality of the interphase. The mRoM was unable to bring about increases in the quality of the interphase against the harshness of the NaOH treatment. The quality of the interphase of the uncoupled composites was half of those coupled with 6% w/w MAPP.

The notable increases in the tensile strength of the coupled composites indicated a good dispersion of the fibers in the composite, but more research is needed to guarantee such a hypothesis. A good dispersion of the reinforcement is one of the main parameters for ensuring good tensile properties.

In the future, obtaining suitable SSFs by using a higher yielding process may be of interest, thus minimizing the creation of by-products and further aligning with the principles of green chemistry.

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