Micromechanics of Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulp from Orange Tree Pruning as Polypropylene Reinforcement: A Comparative Study

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This work explores the use of mechanical (MP), thermomechanical (TMP), and chemi-thermomechanical (CTMP) pulps from orange tree pruning fibers (OPF) as reinforcing elements of polypropylene (PP) composites. Due to the nature of the natural fibers, the use of a coupling agent is needed to attain a good interface and to prevent fiber slippage from the matrix. The main objective of the present work was to investigate the orientation factor, the interfacial shear strength, and the intrinsic strength of the OPF. Coupled and non-coupled composites were formulated and tested, optimizing the coupling agent content with the objective of maximizing the tensile strength of the composites. Hirsch and Kelly-Tyson models and the Bowyer-Bader methodology were used to compute the micromechanic properties. The contribution of subcritical, supercritical fibers, and matrix were also calculated.

Keywords: Orange tree pruning; Mechanical pulp; Thermomechanical pulp; Chemi-thermomechanical pulp; Cationic demand; Interfacial shear strength; Orientation factor; Intrinsic tensile strength

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INTRODUCTION

Environmental awareness has been a popular topic during recent years. An example is the statement of the twelve principles of green chemistry (Anastas and Warner 1998). In regard to composite materials, the main concerns are related to the difficult degradability of plastics, the shortage of landfill space and the increase in the cost of its use, the emissions generated during incinerations, and the increase of cost and decrease of availability of fossil sources. Such considerations have led to interest in the use of fibers obtained from renewable sources as reinforcement for composite materials (Ardanuy *et al.* 2012; Satyanarayana *et al.* 2009). Although there are a lot of potential advantages in favor of that initiative (Satyanarayana *et al.* 2009), there are also some inefficiencies in the interface between natural fibers and polymers to deal with (El Mansouri *et al.* 2012; Vallejos *et al.* 2012).

Tree pruning is a farming practice consisting of removing or shortening some of the branches of the tree in order to facilitate its proper growth, regulate its production,

and improve its quality. Currently, the biomass produced by pruning is usually burned in fields, generating CO_2 emissions and increasing the risk of fire. Spain produces $1.15 \cdot 10^9$ kg/year of citrus pruning residues, which is about 10% of the total produced mass, taking into consideration the main sources of pruning (olive and almond trees, vines, and citrus). The use of orange tree pruning as reinforcement for composite materials can reduce the need for burning, provide low cost alternatives to wood fibers, and extend the value chain for the agricultural industry (Mishra and Sain 2009).

Mechanical pulp from wood fibers is primarily obtained from softwood (Lopez *et al.* 2012a). Although the most common application of that pulp is in the production of printing papers, newsprint, boards, and packaging papers, the MP can also be used as a polymer matrix reinforcing element (Lopez *et al.* 2011, 2012a,b; Mendez *et al.* 2007). On the other hand, depending on the production process and the obtained yield with respect to the raw material, the fibers can also be classified as mechanical pulp (MP), thermo-mechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP). The obtained products are fibers with different physic-chemical properties that can be used as a reinforcing element for composite materials.

The published literature on wood fibers reinforced polymer materials includes several studies on mechanical characterization of the composite materials (Bhattacharyya *et al.* 2003; Lopez *et al.* 2012a; Mendez *et al.* 2007; Zabhizadeh *et al.* 2011). There are also studies on the micromechanics of that kind of composite (Lopez *et al.* 2011, 2012b). Moreover, the influence of the coupling agents on the final mechanical characteristics of the composites has been widely researched (Bhattacharyya *et al.* 2003; Kazayawoko *et al.* 1999; Li and Sain 2003; Nygard *et al.* 2008; Sain *et al.* 2005). Specifically, the literature researching tree pruning as reinforcement for composite materials is scarce and is mainly related to the chemical characteristics of the pulps (Jimenez *et al.* 2004a,b, 2008, 2009; Requejo *et al.* 2012), or manufacture and testing of boards (Cuk *et al.* 2011; Hermawan *et al.* 2009; Pirayesh *et al.* 2011). To the best of our knowledge, there has been research on the production of pulp using OPF (Gonzalez *et al.* 2011), but there is not literature on the use of orange tree pruning fibers (OPF) as reinforcement in PP composites.

In this work, three different processes that generate few byproducts: mechanical, thermomechanical, and chemi-thermomechanical pulping, were tested in order to obtain mechanical pulp (MP), thermomechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP) from orange tree pruning. The produced fibers were morphologically characterized. The breaking length of the fibers was also evaluated according to a paper-making technique. Composite materials were formulated with a 30 wt% of MP, TMP, and CTMP as reinforcement of a polypropylene (PP) matrix. Different percentages of PP and maleated polypropylene (MAPP) were then tested to optimize the percentage of coupling agent in order to obtain the best tensile strength of the composite materials. Once the tensile strength of the composites was maximized, the micromechanic parameters (orientation factor, interfacial shear strength, and intrinsic strength of the fibers) were estimated. Finally, the contribution of the subcritical and supercritical fibers and the matrix to the composite strength were computed. The present research has the aim of providing agroforestry industry with alternatives for the use and valorization of their waste.

EXPERIMENTAL

Materials

The composites were prepared using polypropylene (PP) homopolymer (Isplen PP099 G2M) with an average melt flow rate (230 ºC; 2.16kg) of 55 g per 10 min and a density of 0.905 g/cm^3, kindly provided by Repsol-YPF (Tarragona, Spain). 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). Biomass from orange tree pruning fibers (OPF) obtained from seasonal tree pruning was supplied by Mas Clara de Domeny (Girona, catalonia, Spain). Other reactants were used: Diethyleneglycol dimethyl ether (diglyme) was supplied by Clariant and was used as dispersing agent. Decahydronaphthalene (decalin) (190 ºC boiling point, 97% purity) supplied by Fisher Scientific was used to dissolve the PP matrix in the fiber extraction from composites process. The reactants that were used for fiber treatment are summarized as follows: sodium hydroxide (Merck KGaA, Darmstadt, Germany), antraquinone (Badische Anilin & Soda Fabric AG, Germany) used without any further purification. Pes-Na (polyethene sodium sulfonate) is an anionic polyelectrolyte. Poly-DADMAC (polydimethyl diallyl ammonium chloride) is a cationic polyelectrolyte. Pes-Na 0.001N and Poly-Dadmac 0.001N were supplied by BTG Instruments GmbH (Germany).

Methods

Preparation of orange tree pruning derivatives

All the biomass from orange tree pruning was submitted to a crushing and classification process. Some OPF samples were submitted to a defibering process under cold aqueous conditions in a Sprout-Waldron equipment to obtain mechanical pulp (MP) with a higher aspect ratio. This process gave almost 100% yield with respect to the starting material (Ashori and Nourbakhsh 2009; Thamae *et al.* 2008). Another OPF sample was submitted to a thermo-mechanical process (vaporization followed by defibering). The OPF were heated to 160 ºC for 30 min, and the obtained pulp was rinsed with water and then passed through Sprout-Waldron equipment, resulting in thermo-mechanical pulp (TMP) with an increased reactant surface, and around 95% yield. For OPF chemi-thermomechanical fibers, the OPF were submitted to a sodium/ hydroxide/antraquinone (AQ) cooking process (5% NaOH: 0.1% AQ) in a liquid to fiber ratio of 4:1, working at 160 ºC for 20 min. Afterwards, the slurry was washed and shredded in Sprout-Waldron equipment, giving around 90% yield.

Preparation of paper handsheets for mechanical testing (papermaking route)

The handsheets for mechanical testing were prepared in a sheet former (ISP mod. 786 FH). Handsheets were made according to ISO 5269-2 and conditioned in a weather chamber at 25 ºC and 50% humidity for 48 h before mechanical testing.

Tensile Strength (TS)

Testing experiments were performed in a Housfield 42 universal testing machine, equipped with a 2.5 kN load cell. Testing was performed according to ISO standards 1924-2. The gap between clamping jaws was set to 150 mm, and the cross head speed was set to 20 mm/min. Preload was set at 2 N. Testing specimens were cut into paper strips 15 mm in width and 210 mm in length.

Density measurement

The density measurement of the composite (ρ^c) was carried out using a pycnometer. Distilled water was used as a reference liquid at 23 °C. The ISO 118-3 standard was respected throughout this experiment. The density of the fiber (ρ^f) was obtained from: $\rho^c = w^c/((w^m/\rho^m) + (w^f/\rho^f))$, where, were w^c, w^m, and w^f are the loads in weight of the composite, matrix, and fiber, and ρ^m is the density of the matrix.

Evaluation of the cationic demand

The cationic demand of the pulp suspension was determined with a streaming current detector, the Mütek (TM) Particle Charge Detector PCD-04 from BTG Instruments BmbH, (Germany). The streaming current method was used to detect the endpoint of a polyelectrolyte titration, which is related to the colloidal titration technique developed by Terayama (1952). The colloidal titration technique determines the polymer concentration added in excess in the supernatant. The weight of the cationic polymer adsorbed versus the dry weight of the sample in the suspension was calculated by measuring the difference with respect to the initial amount added (Carrasco *et al.* 1996; Rouger and Mutje 1984).

Compounding

Composite materials comprising 30 wt% PP/OPF 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 OPF during 10 min at a temperature of 180 ºC. 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 80 ºC for at least 24 h before processing.

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 190 ºC (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 (approx. 160 x 13.3 x 3.2 mm) 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 23 ºC and 50% relative humidity for 48 h, in agreement with the ASTM D638 standard. Afterwards, composites were assayed in a Universal testing machine (Instron™ 1122), fitted with a 5 kN load cell and operating at a rate of 2 mm/min. Tensile properties were analyzed by means of dog-bone specimens, according to the 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 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 h. 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 ºC for 24 h.

Determination of the fiber length and diameter

Fiber's length distribution and diameter of the extracted fibers were characterized by means of a MorFi Compact (Morfological fiber analyser), from Techpap SAS, (France). A minimum of two samples were analyzed.

Determination of Young's moduli of the fibers

The intrinsic tensile moduli of the MP, TMP, and CTMP from citrus pruning wood fibers were determined using the Hirsch model (Hirsch 1962; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Vilaseca *et al.* 2010).

Determination of the interfacial shear strength (τ) and the fiber orientation factor (χ_1)

With current standard processing techniques, perfect fiber alignment is almost impossible, and the orientation factor (χ_1) must be taken in account. The calculation of τ can be accomplished through the Kelly-Tyson modified equation (Eq.1) (Kelly and Tyson 1965; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Thomason 2002; Vallejos *et al.* 2012).

$$\sigma_t^C = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^f \cdot V_i^f}{d^f} \right] + \sum_j \left[\sigma_t^f \cdot V_j^f \left(1 - \frac{\sigma_t^f \cdot d^f}{4 \cdot \tau \cdot l_j^f} \right) \right] \right) + (1 - V^f) \cdot \sigma_t^{m*} \qquad (1)$$

In Equation 1, σ_t^C and σ_t^f represent the ultimate tensile strength of the composite and the reinforcing fibers. The σ_t^{m*} term is the contribution of the matrix at failure. The d^f and $l_{i,j}^f$ terms represent the fiber diameter and length, respectively. The V^f term is the volume fraction of reinforcement in the composite. In order to solve the equation, the Bowyer–Bader methodology was used (Bowyer and Bader 1972) evaluating χ_1 and τ.

Determination of the intrinsic tensile strength (σ_t^f)

Once the intrinsic tensile modulus, τ, and χ_1, were known, the intrinsic tensile strength was calculated applying the data for the ultimate failure point in Eq. 1. The Bowyer-Bader model, as an approximation, involves the following assumptions: that the stress transfer at the interface increases linearly from zero at the fiber end to a maximum value; that fiber-matrix debonding does not happen; that χ_1 is independent of strain and constant for all fiber lengths; that interfacial shear stress is independent of loading angle; that porosity in the composite is negligible; and that fiber and matrix stress *vs*. strain curves are linear (Li *et al.* 2009; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Vallejos *et al.* 2012).

RESULTS AND DISCUSSION

The tensile properties of a composite material usually depend on the nature of the reinforcement and the polymeric matrix, the dispersion grade of the reinforcement into the matrix, the aspect ratio of the reinforcement (ratio between length and diameter of the fibers l/d), the orientation of the fibers inside the composite, and the quality of the interface between the fibers and the matrix (Lopez *et al.* 2011; Thomason 2002; Vallejos *et al.* 2012; Vilaseca *et al.* 2010).

Nature of the reinforcement fibers

Table 1 shows the pulp and fiber parameters that can have significant influence on the competitiveness of composites. *Yield* refers to the ratio between dry raw material and processed matter, *TS* is the tensile strength of the paper sheet, *pDADMAC* evaluates the cationic demand of the fibers surface and is measured in microequivalents of polyDADMAC per gram of reinforcement, l_w^f and d^f are the mean weighted length and diameters of the fibers, *and* l_w^f / d^F is known as the aspect ratio.

Table 1. Pulps Experimental Parameters

	Yield (%)	*TS* (MPa)	*pDADMAC* (µeq/g)	l_w^f (*µm*)	d^f (*µm*)	l_w^f / d^f
MP	99.1	4.81	92.52	331	18.95	17.5
TMP	94.7	11.61	90.50	489	18.15	26.9
CTMP	90.1	13.80	88.06	485	18.70	25.9

In agreement with the principles of green chemistry (Anastas and Warner 1998), the processes to obtain fibers showed high yields (90% or more), consequently reducing the amount of byproducts. Obtaining fibers with such yields (90%) implied the use of more aggressive treatments. Thus, cold defibering (MP) presented a practically complete exploitation, taking in account the fiber barks. The chemical composition of MP can be considered almost equal to the orange tree pruning wood (Gonzalez *et al.* 2011). Fibers obtained by thermomechanical processes showed a lower yield due to the removal of extractives and some soluble hemicelluloses. In the case of chemi-thermomechanical pulp, in addition to removing hemicelluloses and extractives (Boras and Gatenholm 1999), the orange tree pruning wood was slightly delignified. The process yield was reduced to approximately 90%. The different processes modified the chemical composition of the fibers surfaces while increasing its bond capabilities. Consequently, as the yield decreased, the ability to create chemical bonds changed. The *TS* test outputs, increasing 141% from MP to TMP and 19% from TMP to CTMP, allowed for verification of this fact. In the papermaking field, *TS* is governed by three main parameters: the fibre strength, the fibre/fibre joint strength, and the number of efficient joints per volume (Marais and Wagberg 2012).

It is well known that the chemical composition of wood is mainly cellulose, hemicellulose, and lignin, and small amounts of other chemical components, such as resin and fatty acids, triglycerides, sterols, and steryl esters, usually classified as extractives (Johansson 2002). Despite different defibration and treatment techniques, the chemical percentage of carbohydrates and lignin of the whole pulps were approximately equal (Koljonen *et al.* 2003). However, differences were observed, both in the chemical

composition and morphology on the fiber surfaces (Boras and Gatenholm 1999; Koljonen *et al.* 2003). On the other hand, the surface composition could not be predicted from the bulk composition of the pulps (Boras and Gatenholm 1999; Johansson 2002; Koljonen *et al.* 2003). Results revealed that the surfaces of the fibers were covered by lignin and extractives. Figure 1, based on (Sundholm 1998) shows that the mean chemical bulk composition at the middle lamella level (middle lamella + primary wall) is essentially 19% cellulose and 23% hemicellulose, representing 42% of carbohydrates, and 58% lignin. These data are consistent with results of Koljonen *et al.* 2003, who found that 50 to 75% of the surface of the mechanical pulps (MP, TMP, and CTMP) was covered by lignin and extractives This is also consistent with the model of (Boras and Gatenholm 1999), with 50 to 55% of the surface covered by extractives and lignin and 49 to 45% by carbohydrates. The presence of lignin was also observed in the case of high temperature mechanical pulp (Bhattacharyya *et al.* 2003)

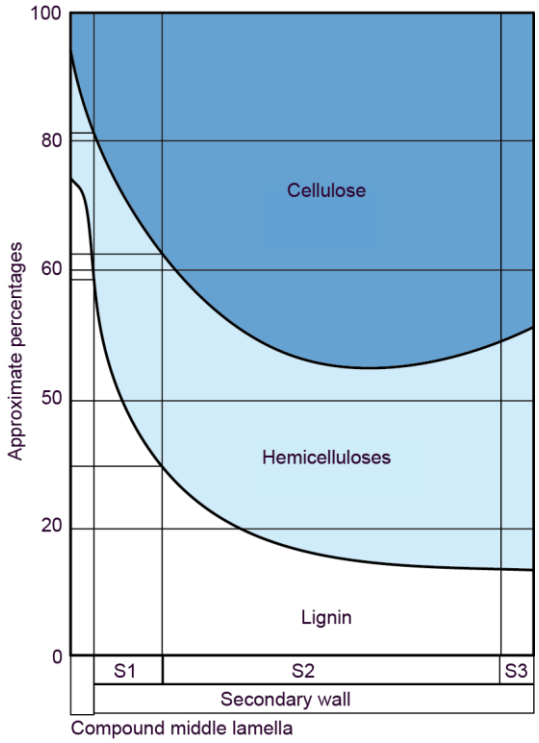

Fig. 1. Structure of wood fibers and chemical composition along its fibril structure. Figure created based on cited data in Sundholm (1998).

The changes in the chemical composition of the fibers surface, which led to the noticeable increase of the *TS*, can be explained as being a consequence of a higher accessibility to the chemical components able to generate hydrogen bonds or Van der Waals interaction. In that sense, it was expected that the MAPP also took advantage of the higher accessibility, improving the fiber-matrix interface.

Moreover, the evaluation of the cationic demand was performed by means of the colloid titration technique TTC (Carrasco *et al.* 1996; Rouger and Mutje 1984; Terayama, 1952). Table 2 shows the outcomes in microequivalents of polyDADMAC per gram of reinforcement. The gradual removal of the extractives by the treatments led to an increase of the hydrophilicity of the surfaces. In agreement with Lopez *et al.* (2012a), the cationic

demand decreased slightly with the insensitivity of the treatments. Probably the main contribution to surface charge density shown by the fibers is due to the presence of extractives in addition to lignin. In comparison to MP, TMP, and CTMP, the surface charge density displayed by bleached hardwood kraft pulps (19.20 µeq/g) is very low, probably due to the relative absence of extractives and lignin (Lopez *et al.* 2012a).

Taking into account that all the fibers were mechanically defibrated, it was observed that the weighted length of the fibers increased as the defibering benefited from the fibers treatments (cold water, steam, and NaOH 5% + steam). The changes in length were especially noticeable from MP to TMP, while they were minor from TMP to CTMP; this was probably due to the softening of lignin, a fact that facilitated the defibration (Flandez *et al.* 2012). Nonetheless, as a result of the loads during the composite preparation, the fibers experienced a reduction of their lengths, and the length distribution outside and inside the composite were not related (Karmaker and Youngquist 1996; Li *et al.* 2009; Vallejos *et al.* 2012).

As can be found in Table 1, the diameter of the fibers can be considered almost constant. Nevertheless, and as a consequence of the weighted length variation, the aspect ratio of the fibers increased with the intensity of the treatments form MP to TMP and remained similar from TMP to CTMP.

Interface, optimization of the composite tensile strength

Lignocellulosic fibers combined with hydrophobic thermoplastics as PP needed to be modified because effective wetting of the fibers and strong interfacial adhesion in order to achieve higher mechanical properties of the composite (Colom *et al.* 2003; de Carvalho *et al.* 2012; Osman *et al.* 2010). Different coupling agents exist, but in the research of PP reinforced with natural fibers (Li and Sain 2003), it is shown that the best results are obtained with the use of MAPP. The use of MAPP coupling agent promotes the interaction between OPF fibers and PP matrix at the interface due to the increase in the accessibility to OH groups. The proposed coupling mechanism is hydrogen bonding and also covalent ester linkage generated by the chemical reaction of the anhydride groups of the MAPP and the hydroxyl groups of the fiber surface (Mendez *et al.* 2007). In order to evaluate the micromechanics tensile properties of OPF, PP composite materials containing 0 to 8% MAPP content were prepared. In fact, the optimization of the MAPP percentage against composite strength, prevents the premature fiber slippage from the matrix by ensuring an enhanced anchorage of the fiber to the matrix and the exploitation of the reinforcing capabilities of the fiber (Lopez *et al.* 2011). In papermaking, and as demonstrated by Davison (1972), the weak link in paper dry strength is very often the fiber/fiber joint strength, and not the fiber itself. Additionally, the stoichiometry of the interaction between the fibers and the MAPP is discussed by Lopez *et al.* (2011).

Figure 2 shows the evolution of the tensile strength of the composites against the MAPP content. The tensile strength increased somehow linearly with the MAPP content, up to 6 wt% in the case of MP and TMP, and up to 4 wt% in the case of CTMP. It appeared that the accessibility of MAPP to OH groups and the ease for creation of hydrogen and ester bonds increased from MP to CTMP. The lower percentage of MAPP needed by CTMP composites to increase the tensile strength could be a consequence of the higher accessibility and extend of reaction.

It was found that for higher MAPP contents, the tensile strength tended to decrease. The decrease in tensile strength at the higher coupling agent contents is

attributed to self-entanglement among the coupling agent chains, rather than with the polymer, resulting in slippage (Beg and Pickering 2008). This result is in agreement with previous research, where it was found that, for different reinforcement fibers, although the optimum percentage of MAPP varied with the fiber content, a 6 wt% of MAPP delivered the best mean outputs (Lopez *et al.* 2011; Mendez *et al.* 2007; Vallejos *et al.* 2012).

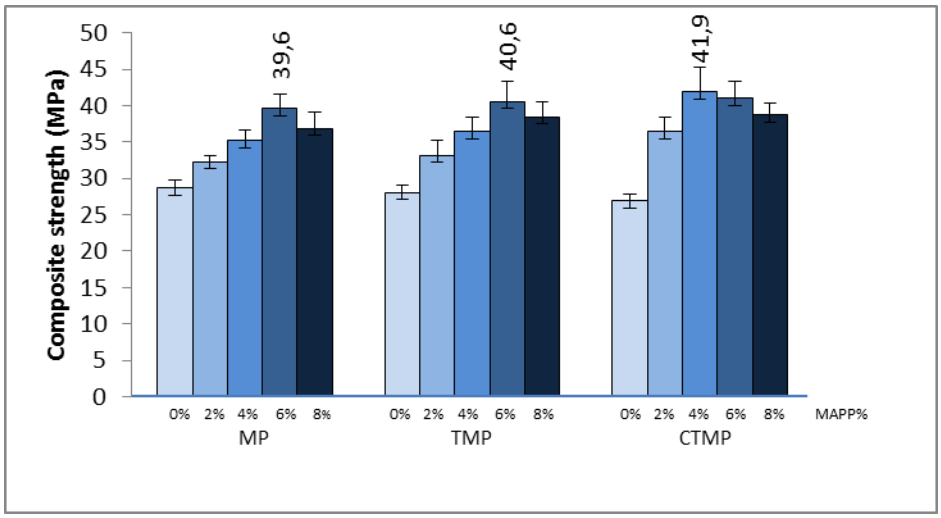

Fig. 2. Evolution of the 30 wt% CPF/PP composites strength against the MAPP content

Once the percentage of MAPP for the different PP/OPF composites was established, it was found that the obtained maximum σ_t^C were slightly different. In fact, the highest value of σ_t^C increased from MP to TMP by 2.5% and from TMP to CTMP by 3.2%, showing a high correlation with the behavior of the cationic demand that also changed slightly. If the results are compared with a 30% stone groundwood (SGW)/PP composite with 6% of MAPP (Lopez *et al.* 2011, 2012a), it is found that the SGW composites show 18% higher σ_t^C (46.7 MPa). The difference could be explained by the fact that SGW came from softwood and MP from hardwood. Usually the intrinsic strength of softwood fibers is higher than that of hardwood. On the other hand, the fibers surface chemical composition is also different, leading to a different extension of the reactions between the MAPP and the fibers surface.

Orientation factor, interfacial shear strength, and mean intrinsic tensile strength

Once the nature of the fibers was established and the understanding of the interface mechanism was improved, it was possible to initiate the evaluation of the micromechanics; in fact, this was the main objective of the present research. To solve the Kelly-Tyson equation by means of the Bowyer-Bader methodology, it was necessary to establish all the necessary input data (Eq. 1).

The Young's moduli of the composites were computed by the Hirsch model (Hirsch 1962) applied to the experimental values of the analyzed composites. Table 2 shows all of the input data needed to compute the moduli of the fibers. In all cases, the density of the matrix was 0.905 g/cm^3, and the factor β, that determines the transference of the stress between the fiber and the matrix, was 0.4 (Kalaprasad *et al.* 1997).

Table 2. Fiber and Composite Properties

	Weight (%)	ρ^f (g/cm^3)	V^f ($^o/_1$)	E_t^C (GPa)	E_t^m (GPa)	E_t^f (GPa)
MP (6% MAPP)	30	1.25	0.237	3.8	1.5	23.1
TMP (6% MAPP)	30	1.29	0.230	3.1	1.5	16.3
CTMP 4%(MAPP)	30	1.365	0.220	2.94	1.5	15.3

Composite compounding and processing entails a reduction of the fibers lengths (Li *et al.* 2009; Vallejos *et al.* 2012). The shortage is probably attributable to the attrition that happens during the compounding and processing of the composites (Bourmaud and Baley 2007; Karmaker and Youngquist 1996). Hence it was necessary to obtain the length distributions of the fibers inside the composites (Fig. 3). In fact, the values of the mean weighted lengths inside the composite were 256, 310, and 331 µm for the MP, TMP, and CTMP, respectively. The corresponding percentages of shortening were 22%, 36%, and 32%, respectively.

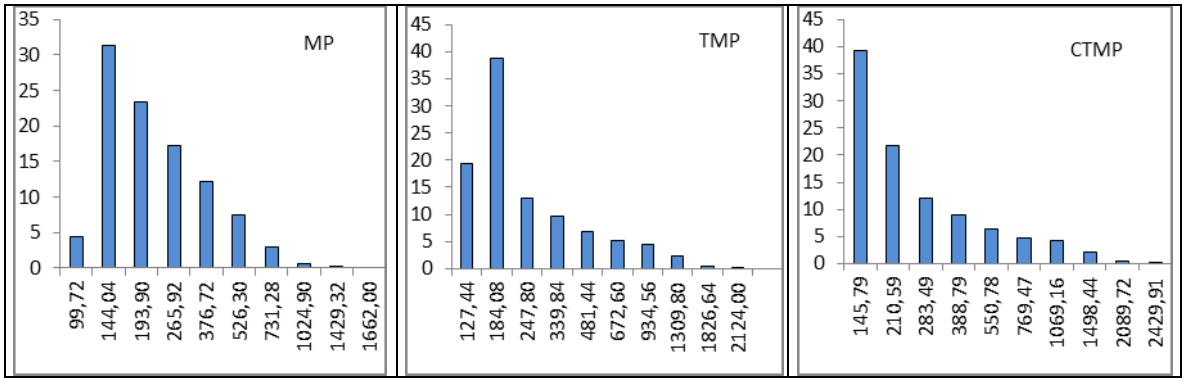

Fig. 3. Fiber length distributions inside the composite material. Length percentage against fiber weighted length

From the experimental results, and once the fiber distributions were known, it was possible to apply the Bowyer-Bader methodology. Table 3, in which ε_t^C is the strain at composite failure, summarizes the mean experimental data outputs. The values of the properties for the two strain levels (a quarter and a half from breaking point), needed to apply Bowyer-Bader methodology, were obtained from the experimental outputs.

Table 3. Experimental Composite Mechanical Properties at Breaking Point and at One-Quarter and One-Half of the Breaking Point

	ε_t^C (%)	σ_t^C (MPa)	σ_t^{m*} (MPa)	$\varepsilon_t^C{}_{(1/4)}$ (%)	$\sigma_t^{m*}{}_{(1/4)}$ (MPa)	$\sigma_t^C{}_{(1/4)}$ (MPa)	$\varepsilon_t^C{}_{(1/2)}$ (%)	$\sigma_t^C{}_{(1/2)}$ (MPa)	$\sigma_t^{m*}{}_{(1/2)}$ (MPa)
MP	4	39.6	25.7	1.00	12.0	22.6	2.00	33.9	19.2
TMP	4.3	40.6	26.3	1.08	13.2	19.8	2.15	31.2	20.0
CTMP	4.6	41.9	27.0	1.15	14.2	20.6	2.30	31.9	20.5

Once the Bowyer-Bader methodology was applied, the values for τ, χ_1, and l_c were obtained, as shown in Table 4. Taking into account that $\chi_1 = \cos^4\theta$, the obtained

orientation factors (χ_1) for the different OPF, implied mean orientation angles of 40.5º, 43.1º, and 42.9º for the MP, TMP, and CTMP, respectively. The found angles were similar and showed that fiber treatments slightly affected the orientation angle.

The critical fiber length (l_c^f) was calculated from $l_c^f = \left(d^f \sigma_t^C\right) / 2\tau$ (Li *et al.* 2009).

The obtained values of the interfacial shear strength (τ), considering the σ_t^m of the PP (28.4 MPa), were within or close to the range derived from the application of Von Misses and Tresca criteria (16.4 MPa and 14.2 MPa, respectively (Pegoretti *et al.* 1996; Vilaseca *et al.* 2010). The interfacial shear strength increased slightly with the intensity of the OPF treatments.

Once the values for χ_1 and τ were obtained, the Kelly-Tyson modified equation was used (Kelly and Tyson 1965; Lopez *et al.* 2011; Vallejos *et al.* 2012) to obtain a value for σ_t^F for all the tested composites (Table 4). The obtained values of σ_t^F for MP, TMP, and CTMP composites increased with the intensity of the treatments, noticeably from MP to TMP and slightly from TMP to CTMP.

Table 4. Micromechanics Properties of the Formulated Composites

	τ (MPa)	χ_1	l_c (µm)	σ_t^f (MPa)
MP	16.00	0.335	303	512
TMP	16.03	0.284	309	547
CTMP	16.74	0.288	307	549

The values of the orientation factor were around 0.3, which is very similar to the corresponding value for SGW (Lopez *et al.* 2011). The critical length of the fibers was similar. The interfacial shear strength increased slightly from MP to CTMP and had a value around 16 MPa, which is very similar to that of SGW (15.71 MPA). At the same time, the intrinsic tensile strength increased with the intensity of the treatments, and as expected, due to the above-mentioned differences between fibers from hardwood and softwood, was 20% smaller than the mechanical pulp from SGW's mean intrinsic tensile strength (612 Mpa) (Lopez *et al.* 2011).

Equation 1 can be simplified to $\sigma_t^C = \chi_1(X + Y) + Z$ where *X*, *Y*, and *Z* are the contribution of the subcritical fibers, supercritical fibers, and the matrix to the composite strength (σ_t^C). Values for *X*, *Y*, and *Z* were deduced from Eq. 2. To estimate the final contribution to the composite, *X* and *Y* must be multiplied by χ_1.

As it can be observed in Table 5, the contribution of the matrix remained almost constant, with a value around the 50% of the total for all the materials. It was also observed that the contributions of the subcritical fibers were the less relevant. The contribution of the subcritical fibers decreased from 18.5% to 11.1% from the MP to the TMP. Its value was similar for the case of TMP and CTMP.

Table 5. Nominal and Percentage Contribution of the Subcritical (*X*) and Supercritical (*Y*) Fibers, and the Matrix (*Z*) to the Strength of the Composite Materials

	$X \cdot \chi_1$ (MPa, %)	$Y \cdot \chi_1$ (MPa, %)	Z (MPa, %)
MP	7.35 18.5%	12.64 32.0%	19.61 49.5%
TMP	4.51 11.1%	15.87 39.1%	20.22 49.8%
CTMP	4.75 11.3%	16.13 38.6%	21.02 50.1%

It was observed that the contribution of the matrix remained almost constant and equivalent to the 50% of the final composite strength. The contribution of the subcritical fibers decreased noticeably from MP to TMP and remained almost constant from TMP to CTMP. Consequently, the relative contribution of the supercritical fibers increased.

CONCLUSIONS

In this work, the micromechanical parameters of mechanical, thermomechanical, and chemi-thermomechanical pulps from orange tree pruning, as reinforcement of a polypropylene matrix, were characterized. From the results it was found that:

1. The treatments used to obtain mechanical pulp (MP), thermomechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP) from orange tree pruning fibers (OPF) caused changes in the chemical composition of the fiber surfaces. The changes were made evident by the tensile strength of the paper (papermaking route), but not so much by the extent of the compatabilizer/fiber surface reaction. The research allowed a better understanding of the bonding mechanism in the interface between matrix and reinforcing fibers.
2. The tensile strength increased from MP to CTMP composites, but the process yield decreased. The slight increments of the tensile strength hardly justify the use of CTMP processes with OPF.
3. The mean orientation factor for the injection-molded composite materials was about 0.3 with a 42.3º mean orientation angle, configuring a short fiber semi-aligned composite
4. The interfacial shear strength values stand within or close to the interval derived from the application of the Von Misses and Tresca criteria, and are similar to those of mechanical pulp from softwood (SGW).
5. The intrinsic tensile properties of the fiber for the coupling agent-enhanced composite materials are similar for MP, TMP, and CTMP and inferior to that of SGW.
6. The use of MP from OPF is shown as a source to add value to agroforestry waste, extending the value chain for the agricultural industry, providing low cost alternatives to wood fibers, and reducing the need for burning.

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