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Additional Information

Estimation of the interfacial shears strength, orientation factor and mean equivalent intrinsic tensile strength in old newspaper fiber / polypropylene composites.

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Abstract

The present paper investigates the suitability of old newspapers (ONP) as a source of reinforcing fibers for composite materials. Different percentages of ONP fibers were compounded with polypropylene (PP). A coupling agent was added to the compound to improve the interface between matrix and reinforcing fibers. Tensile test were performed to obtain the mechanical properties of the composite materials. Micromechanics of the fibers were obtained using Hirsch model, Bowyer-Bader methodology and Kelly-Tyson equations. Due to the presence of a percentage of calcium carbonate in the obtained fibers (10%), the computed intrinsic characteristics were addressed as equivalent. The most important results were the mean equivalent intrinsic tensile strength of the ONP fibers, the mean orientation

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angle and the mean interfacial shear strength. The contributions of the matrix, the subcritical and the supercritical fibers to the tensile strength of the composite material were also computed.

Keywords: A: Fibres. B: Mechanical properties, Interface. C: Micro-mechanics.

1 Introduction

Due to environmental awareness, interest in natural fibers as an alternative to glass fibers as reinforcement in polymer composites has grown and generates a great deal of interest [1]. Advantages of natural fibers in composites are high availability, biodegradability, low cost, low density...

Currently the most used matrixes for natural fiber composites are thermoplastics, and the most common for this purpose are polypropylene, polyethylene and poly-vinyl chloride.

Lignocellulosic materials can be classified in three categories depending on its behavior inside the polymeric matrix [2]. The flours from wood and other low cost flours from agroforestry can be considered as particulate fillers that are able to increase the elastic moduli of the composite materials but have little influence on its strength. The virgin wood fibers and the cellulosic fibers from recycled papers had a higher aspect ratio (length by diameter ratio), and when are used as reinforcement with the adequate coupling agents, are able to increase both, the elastic moduli and the strength of the composite materials. The improvement of the elastic moduli is slightly superior to that obtained with particulate fillers [3-9]. The natural strands as jute, kenaf, flax, are the most effective cellulosic reinforcement fibers [2, 10-15].

A major problem which restricts reinforcing effect during the incorporation of lignocellulosic fibers into polymeric matrixes is the incompatibility between the hydrophilic fibers and the hydrophobic polymers. This fact normally results in poor interfacial adhesion and in restricted ability of stress transfer from the matrix to the reinforcement. Therefore, the enhancement of

1 compatibility between the hydrophobic thermoplastic polymer and the hydrophilic natural
2 fibers has attracted much attention of the researchers, and various techniques were
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4 evaluated in previous works [15-18]. Generally speaking, chemical modifications are used to
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6 decrease the polarity of the fibers surface in order increase its compatibility with the polymer
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8 surface. The treatments with short chain hydrophobic agents such as acetyls, isocyanates,
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10 or sylanols have proved insufficient to optimize the mechanical properties of the composite
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12 materials [19]. Actually, coupling agents, which react with the fiber's hydroxyl groups, but
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14 additionally are able to interlock with matrix chains are the best treatment to increase the
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16 mechanical properties of the composite. In this respect, the use of an interfacial coupling
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18 agent, such as Maleated polyolephines is the most commonly used method to improve the
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20 fiber-matrix interface, by means of – OH/maleic chemical interactions [16, 20]. More
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22 specifically the use of maleated polypropylene (MAPP) has yielded good tensile properties of
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24 the composites [9, 21]. In addition, an increase of the available –OH groups at fiber surface
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26 by NaOH treatment might enhance the reactivity at interface level [13], resulting in
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28 improvements of the mechanical properties of the natural fiber composites.
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34 The literature, on the application of newspaper recycled lignocellulosic fibers as
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36 reinforcement of polyolefinic thermoplastic matrixes, recognizes that it constitutes a valuable
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38 source of fiber [22, 23]. In spite of their advantages, the use of cellulose fibers from
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40 newspaper as reinforcement elements for thermoplastics has not been extensively
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42 investigated [1]. Some possible reasons include their limited thermal stability during
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44 processing, poor dispersion in the thermoplastic melt, and limited compatibility with the
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46 matrix, which contribute to unsatisfactory final properties of the composites [1]. Many years
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48 ago newspaper contained mostly mechanical pulp from softwood (pine, spruce, poplar) and
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50 inorganic fillers as mineral fillers, ink and process aid material [24]. Nowadays the
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52 mechanical pulp from soft wood has been replaced by a mixture of recycled paper and
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54 mechanical pulp, mostly from hardwood (poplar, beech...).

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In injection molded composites the orientation factor (χ_1) and the interfacial shear strength (τ) are key factors for the competitiveness of the product. Specifically, χ_1 is an empirical factor that accounts for fiber orientation and has a value of unity for aligned fibers, 3/8 for planar random configurations and 1/5 for three-dimensional random orientation. Nonetheless it is difficult to determine this factor for injection molded fiber-polymer systems [23]. The analysis of χ_1 and τ by means Bowyer-Bader methodology and the estimation of σ_t^F by means of Kelly-Tyson modified equation [25] proved to be valid to study micromechanics of composite materials [26-31].

The objective of this work is to evaluate the orientation factor (χ_1), the interfacial shear strength (τ) and the equivalent intrinsic tensile strength of the ONP fibers (σ_t^F) inside the PP matrix. The MAPP content was optimized to 6 wt% preparing composite materials with a 40% of ONP and 0 to 8wt% of MAPP. Composite materials with 20 to 50 wt% of ONP fibers content, with a 6wt% of MAPP, were formulated, compounded and tested. Hirsch model was used to obtain the intrinsic Young's moduli of the fibers, Bowyer-Bader methodology to compute the orientation factor (χ_1) and the interface shear strength (τ), and the Kelly-Tyson modified equation to calculate the equivalent intrinsic tensile strength (σ_t^F).

2 Materials and methods

2.1 Materials

The old newspaper, containing 85% of thermomechanical pulp from hardwood and 15% of calcium carbonate mineral filler, was supplied by Punt Diari, edited by Rotimpres (Spain).

The composites were prepared using homopolymer polypropylene (PP) (Isplen PP090 G2M) that was provided by Repsol –YPF (Tarragona, Spain) as the polymer matrix. Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) was acquired from Eastman Chemical Products (Spain) and used as coupling agent. Diethyleneglycol dimethyl ether (diglyme) was supplied by Clariant and was used as dispersing agent.

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Decahydronaphthalene (decalin) supplied by Fisher Scientific was used to dissolve the PP matrix in the fiber extraction from composites process. Figure 1 shows the chart flow we followed.

Figure 1

2.2 Disintegration of the old newspaper

Old newspaper was submitted to the disintegration process by means of a pilot scale pulper (Pucel Cell from Metrotech, France) equipped with an helicoidal rotor, deflectors, and with an effective volume of 20l. The disintegration was performed at 20 rev/s rotor speed, at a temperature of 50°C, and 10% consistency. The initial newspapers were cut into pieces of 10 x 10 cm, approximately and were soaked in water with a 1% of NaOH before starting the rotor. Afterwards the pulped material was filtered and oven dried at 80°C. Following ONP fibers were dispersed in a water-diglyme (1:3) mixture. The use of diglyme in the previous step limits the formation of hydrogen bonds between the cellulosic fibers [29] . A 5% of the CaCO₃ was lost during the disintegration and individualization processes.

2.3 Composites compounding

Composite materials comprising 20, to 50wt% PP/ONP fibers, were obtained. The materials were prepared in a Brabender[®] plastograph internal mixing machine. The working parameters were 80 rpm during 10min at a temperature of 180°C. The resulting blends were grounded with a knives mill, dried and stored at 80°C for at least 24h before processing. Composite materials with 40wt% of ONF fibers and 0 to 8% of MAPP were similarly obtained.

2.4 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, of each obtained composite blend,

1 were used for the experiment. Standard composite specimen samples (approx.
2 160x13.3x3.2mm) were obtained and used to measure the tensile properties in agreement
3 with ASTM D638 [26, 28].
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6 7 **2.5 Mechanical characterization**

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9 Prior to the mechanical test the specimens were stored in a Dycometal conditioning chamber
10 at 23°C and 50% relative humidity during 48 h, in agreement with ASTM D638. Results were
11 obtained from the average of at least 5 samples [26, 28].
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16 17 **2.6 Fiber extraction from composites**

18 Reinforcing fibers were extracted from composites by matrix solubization using a Soxhlet
19 apparatus and decalin as solvent. Once the fibers were extracted, they were rinsed with
20 acetone followed by distilled water in order to remove the solvent residue. Finally the fibers
21 were dried in an oven at 105°C for 24hours.
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28 29 **2.7 Determination of the fiber length and diameter**

30 Fiber's length distribution and diameter of the extracted ONP fibers were characterized by
31 means of a Kajanni analyzer (FS-300). A diluted aqueous suspension of fibers was analyzed
32 during 2 to 5 minutes, and the length of the fibers was evaluated considering an amount of
33 individual fibers in the range of 2500 to 3000 units.
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42 43 **2.8 Determination of the Young's modulus of the fiber (E_t^F)**

44 The intrinsic tensile modulus of the triticale straws was determined using the Hirsch model
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2.9 Determination of the interfacial shear strength (τ) and the fiber orientation factor (χ_1) and the intrinsic tensile strength of the fiber (σ_t^F)

With current standard processing techniques, perfect fiber alignment is almost impossible, and the orientation factor (χ_1) must be taken into account. The calculation of τ can be accomplished through the Kelly-Tyson modified equation (Eq. 1) [25, 33].

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

To solve the Kelly–Tyson modified equation it is necessary to know or estimate the values of E_i^F , E_i^m , and the characteristics of the reinforcing fibers: intrinsic strength (σ_i^F), orientation factor (χ_1), interfacial shear strength (τ), fiber diameter (d^F), and length (l^F). By previous extraction from the polymeric matrix, the fiber distribution can be empirically obtained. However, usually σ_i^F , χ_1 and τ are unknown.

In order to solve the equation, a Bowyer–Bader methodology was used [28, 29, 34] to evaluate χ_1 and τ [27].

3 Results and discussion

3.1 Composite Tensile properties

As mentioned above fibers contained 15% calcium carbonate, which in the process of disintegration lost 5%. Thus, the added reinforcement to the composite material was made up of 10% of CaCO_3 and 90% of ONP fibers.

The tensile strength of a composite is a combination of the properties of the matrix and the reinforcement and the ability of its interface to transfer shear strengths [30, 33]. Lignocellulosic fibers combined with hydrophobic thermoplastics as polypropylene (PP) needed to be modified because effective wetting of the fibers and strong interfacial adhesion

1 were required in order to achieve higher mechanical properties of the composite [23, 35-37].
2 To optimize the interface ONP fibers/PP different percentages of MAPP were tested. Figure
3 2 shows the behavior the 40% ONP fibers composite materials tensile strength. As it can be
4 observed the strength of the composite increased quickly with the percentage of MAPP until
5 the 4wt%. For the 4 to 8wt% of MAPP the strength was almost constant with a local optimum
6 value at 6wt% of MAPP. The decrease on the tensile strength at the higher coupling agent
7 content is attributed to self-entanglement among the coupling agent chains, rather than with
8 the polymer, resulting in slippage [20].
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19 Figure 2

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25 It was found that, for the currently tested formulations, the addition of 6wt% of MAPP
26 allowed the ONP fibers to develop the maximum reinforcing effect into the composite.
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30 Above we introduced the fact that the reinforcement was not 100% pure ONP fiber. Vallejos
31 et al [38] researched composites with a 40% of CaCO_3 and a 60% of PP, with a tensile
32 strength of 30 Mpa and a Young's modulus of 2.3 GPa. The equivalent content of a 40%
33 ONP fibers composite was to be 4% of CaCO_3 , 36% of ONP fibers and 60% of PP. Taking in
34 account that the tensile strength of the PP was found to be 27.6 Mpa and the additive
35 character of the rule of mixtures, the equivalent tensile strength of a 4% CaCO_3 , 96% PP
36 composite material had to be 27.84 Mpa, and the equivalent contribution of the CaCO_3 , 0.24
37 Mpa. Similarly if the Young's modulus of the PP was found to be 1.5 GPa and consequently
38 the equivalent Young's modulus for the same composite had to be 1.58 GPa, and the
39 equivalent contribution of the CaCO_3 was 0.08 GPa.
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53 Once established the 6wt% of MAPP we studied the influence of ONP fibers content. The
54 tensile properties of the ONP fiber-PP composites were influenced by the percentage of
55 ONP fibers, as shown in table 1. The tensile strength and the Young's moduli of the PP-
56 MAPP composites increased linearly with the ONP fibers content from 20 to 50 wt%.
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Meanwhile the tensile elongation at break of the composites decreased linearly from 4.1% to 2.2% when the ONP fibers content was increased from 20 to 50 wt%.

Table 1

3.2 Orientation factor and interfacial shear strength

The intrinsic tensile strength of reinforcing ONP fibers inside the PP composite is function of its intrinsic properties but also of its degree of adhesion with the polymer matrix and the mean orientation of the fibers inside the matrix. Fig. 3 shows the stress-strain curves for the tested reinforcement percentages, from 20 to 50 wt%, and for the PP matrix, reflecting the change of the σ_t^C in relation with the deformation ϵ_t^C . The curves correspond with the experimental outcome that was closed to the mean σ_t^C value. It was verified that σ_t^C increased when ϵ_t^C decreased, as a consequence of the rise in rigidity of the material. The composite shows a typical tensile stress-strain curve for a treated fiber composite.

The theoretical equivalent intrinsic Young's modulus of the ONP fibers, using Hirsch model, was evaluated to be 21.2 GPa as a mean value, close to the 18.2 ± 1.1 for stone groundwood fibers found by Lopez et al [28]. E_t^C for the 20 to 50 wt% of ONP fibers composites were 2.87, 3.83, 4.18, and 5.31GPa respectively.

Figure 3

The preparation of the composites and its injection resulted in a reduction of the fiber lengths [26, 27]. The diminution of the fiber lengths could be caused by the attrition happening during the composite fabrication [39, 40]. This is more relevant for coupled composites as the fiber is better tied to the matrix [28]. Hence it was necessary to obtain the length distribution of the fibers inside the composite (fig 4). It was observed that the average length of the fibers inside the composite decreased with the wt% of ONP fibers. The weighted fiber length experienced a substantial reduction when the percentage of reinforcement evolved from 20 to 50 wt% (table 1). This is consistent with the results of other investigations [26,

28]. At the same time the diameter of the strands was considered approximately constant and independent of the wt%, with a mean value of 21.6 μm . Consequently the aspect ratio (l^F/d^F) diminished at the same time as the wt% increased.

Figure 4

The next step was the evaluation of χ_1 and τ . The experimental data values required to apply Bowyer-Bader methodology are summarized in table 2.

Table 2

Strain levels at 1/3 and 2/3 of the breaking point were chosen as reference levels to perform the calculations. The values of the stress at levels 1 and 2 were obtained from the experimental data.

Table 3 shows the obtained results after Bowyer-Bader methodology and Kelly-Tyson equations were applied.

Table 3

The mean value of the orientation factor (χ_1) for the different composites (20 to 50 wt%) was 0.346. The obtained orientation factor implied a mean orientation angle of 39.9°, taking in account that $\chi_1 = \cos^4 \theta$ [41]. The angle is similar to the one obtained by Lopez et al. [28] with a mean orientation angle of 43° for stone groundwood and Vallejos et al. [26] with a mean orientation angle of 43° for hemp strands.

The critical fiber length (l_c^F) was calculated from $l_c^F = (d^F \cdot \sigma_t^C) / 2\tau$ [27].

The obtained value of the mean interfacial shear strength (τ) was 14.57MPa. The value stands in the interval of 15.95MPa and 13.8MPa, derived from the application of the Von Mises and Tresca criteria respectively [30, 42], considering the σ_t^m of the polypropylene. Consequently the result seems reasonable.

3.3 Mean equivalent intrinsic tensile strength of ONP fibers

When we used the Kelly-Tyson equation we do not contemplated the inclusion of fillers. Therefore, we perform calculations assuming that 100% of the reinforcing was ONP fiber. Although the contribution of the CaCO_3 was residual the result could not be considered as the intrinsic strength of the fibers, and consequently we referred to the intrinsic properties of the fibers as equivalent.

Once obtained the values for χ_1 and τ we used Kelly-Tyson modified equation (Eq. 1) to obtain a value of the equivalent σ_t^F for all the tested composites (Table 3). The mean value of the equivalent σ_t^F for 20 to 50 wt% composites was found to be 514.3 ± 34.7 MPa.

3.4 MAPP influence on τ , χ_1 and σ_t^F

We used the test results of the 40% ONP fibers composite with 0 to 8% of MAPP to study the influence of the MAPP on the micromechanics. To compute the interfacial shear strength, the orientation factor and the intrinsic fiber tensile strength we used Kelly-Tyson equations and the Bowyer-Bader methodology [25, 34]. The theoretical intrinsic Young's modulus of the ONP fibers was computed using Hirsch model [32]. It was observed that the addition of MAPP had little influence on the orientation factor. Figure 5 shows the interfacial shear strength, and the intrinsic strength of the ONP fibers when different percentages of MAPP were added. The intrinsic strength of the ONP fibers and the interfacial shear strength showed similar behaviors to that of the composite tensile strength. The fiber showed its capabilities as reinforcement in parallel with the increases of the interfacial shear strength. A good interface prevented fiber matrix slippage.

Figure 5

3.5 Contribution of the matrix and the subcritical and supercritical fibers to the composite strength

Eq. 1. could 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 calculated from Eqs. 2, 3 and 4 respectively. To estimate the final contribution to the composite X and Y must be multiplied by χ_1 .

$$X = \sum_i^{l_i^F < l_c^F} \frac{\tau \cdot l_i^F \cdot V_i^F}{d^F} \quad (2)$$

$$Y = \sum_j^{l_j^F > l_c^F} \sigma_t^F \cdot V_j^F \left(1 - \frac{\sigma_t^F \cdot d^F}{4 \cdot \tau \cdot l_j^F} \right) \quad (3)$$

$$Z = (1 - V^F) \cdot \sigma_t^{m*} \quad (4)$$

Figure 6 shows that the contribution of the subcritical fibers remains minimum, but not negligible for the composites with bigger amount of reinforcement. Thus for the case of 50 wt% it represent the 16 % of the total and approximately half of the contribution of the polymeric matrix. In the 40 wt% case the contribution represents an 13.1% contribution and more or less 1/3 of the contribution of the matrix. The contribution of subcritical fibers in the cases of 30% and 20 wt% composites was 10.3% and 9% respectively. In all the cases it is clear the contribution of supercritical fibers, representing respectively the 33.9%, 46%, 54.2% and 59.8%. Taking in account the cumulative contribution of the fibers (X+Y) the amount increases respectively to 43.3%, 56.4%, 67.3% and 75.7%. This behavior could be due the increase in the relative presence of MAPP in respect to PP and consequently the probability of creation of hydrogen bonds in the interface.

Figure 6

4 Conclusions

The old newspaper fibers, once coupled, showed its potential as reinforcement for polypropylene composites when a 2 to 6wt% of MAPP was added.

The Bowyer-Bader methodology, as analytical method to solve Kelly-Tyson equation, showed its usefulness when applied on the mechanical properties of ONP fiber reinforced polypropylene composites.

The equivalent mean intrinsic tensile strength of the ONP fibers at failure was defined and found to be 514.3 ± 34.7 MPa.

The mean orientation factor for the ONP/PP/MAPP composites was found to be 0.346 ± 0.02 representing a mean orientation angle of 39.9° .

The mean interfacial shear strength of the ONP/PP/MAPP composites was found to be 14.57 ± 0.63 MPa.

The improvements in the interfacial shear strength where directly related with the efficiency of the ONP fibers as reinforcement.

The contribution of the supercritical fibers to the tensile strength of the composite increased quickly with the fiber content. At the same time the contribution of the matrix descended and the contribution of the subcritical fibers increased slowly.

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Table 1. Tensile mechanical properties of composite reinforced with ONP with 6 wt% of MAPP. Inside the parenthesis is the standard deviation.

Reinforcement (wt%)	Volume Fraction V^F	Old newspaper		
		With 6% MAPP		
		σ_t^c (MPa)	E_t^c (GPa)	ε_t^c (%)
0	0	27.6 [0.5]	1.5 [0.1]	9.3 [0.2]
20	0.148	38.7 [1.1]	2.8 [0.2]	4.1 [0.5]
30	0.222	43.9 [1.3]	3.8 [0.1]	3.6 [0.3]
40	0.296	45.2 [1.2]	4.2 [0.2]	2.5 [0.2]
50	0.370	49.6 [1.3]	5.3 [0.2]	2.2 [0.1]

Table 2. 20 to 50% ONP fiber Composite with a 6wt% MAPP properties. Stress-Strain input data and parameters

Reinforcement content (%)	Average length (μm)	Weighted average length (μm)	Average diameter (μm)	Composite strength (Mpa)	Composite modulus (Gpa)	Fiber modulus (Gpa)	Elongation at break (%)
20%	237	1094	21.6	38.7	2.87	21.2	4.1
30%	265	664	21.6	43.9	3.83	21.2	3.6
40%	260	526	21.6	45.2	4.18	21.2	2.5
50%	198	416	21.6	49.6	5.31	21.2	2.2
Reinforcement content (%)	Strain level 1 analyzed (%)	Composite stress at strain level 1 (MPa)	Strain level 2 analyzed (%)	Composite stress at strain level 2 (MPa)	Matrix stress at strain level 1 (MPa)	Matrix stress at strain level 2 (MPa)	Matrix stress at break (Mpa)
20%	1.37	24.66	2.73	37.22	15.1	22.3	25.6
30%	1.2	26.26	2.4	40.11	13.68	21.01	24.7
40%	0.84	22.06	1.67	36.43	10.33	17.12	21.4
50%	0.73	22.95	1.47	38.68	9.3	15.75	20.1

Table 3. 20 to 50% ONP fiber Composite with a 6wt% MAPP output data

Reinforcement content (%)	Orientation factor χ_1	Interface shear strength (Mpa) τ	Fiber's tensile strength (Mpa) σ_t^F	Critical length (μm) l_c^F
20%	0.373	14.5	500	372
30%	0.356	14.45	554	413
40%	0.327	15.42	529	369
50%	0.329	13.91	474	366

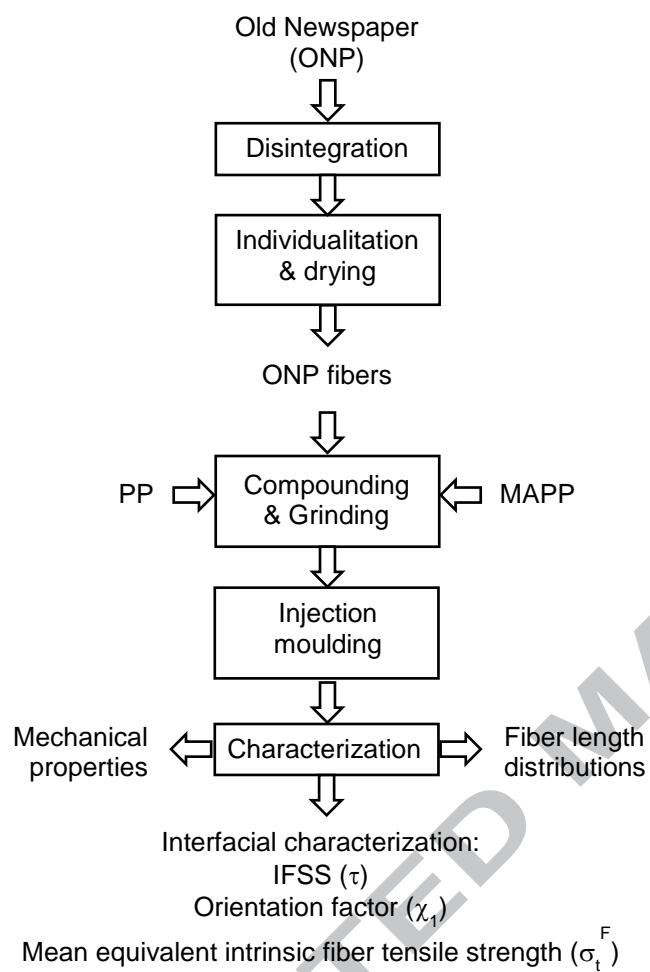


Figure 1: Flow chart of the experimental procedure

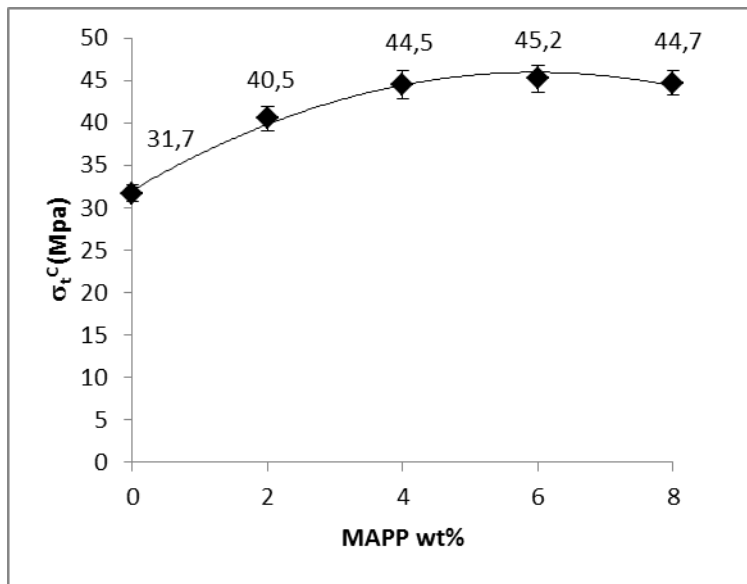


Figure 2: Evolution of the Composite tensile strength (σ_t^C) of the 40wt% ONP fibers composite materials against the MAPP wt%.

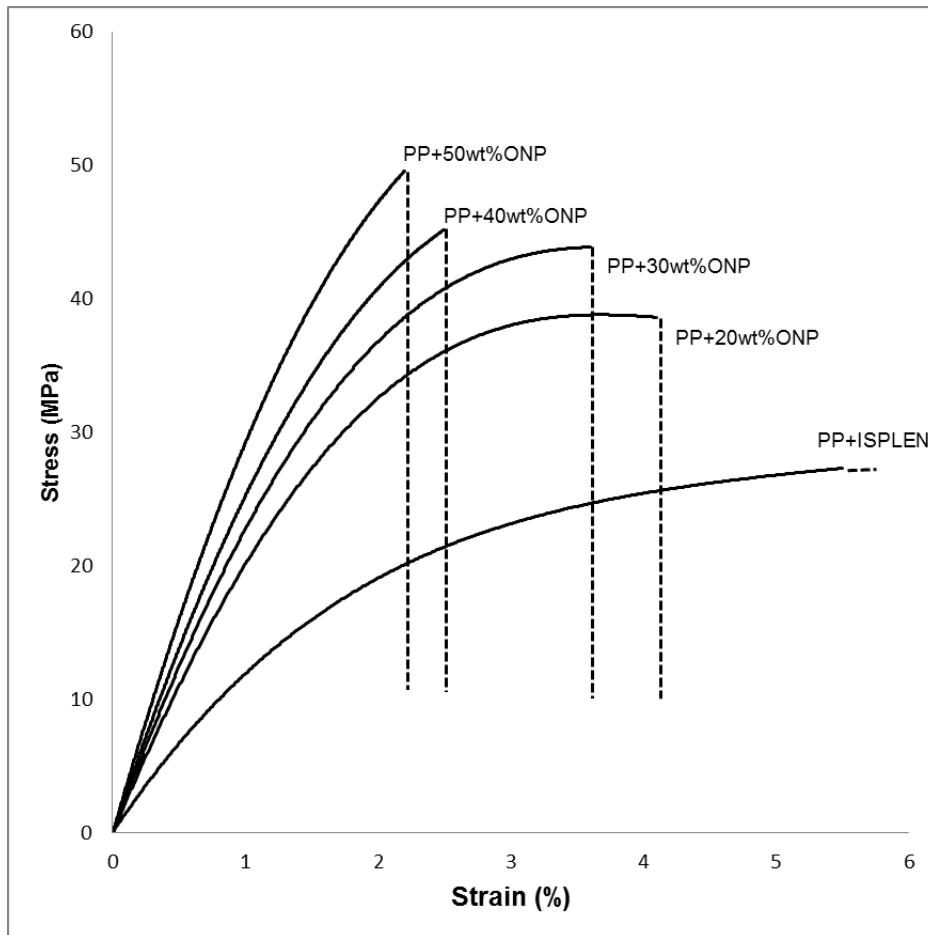


Figure 3: Stress-Strain curve for the tested PP-MAPP-ONP composites

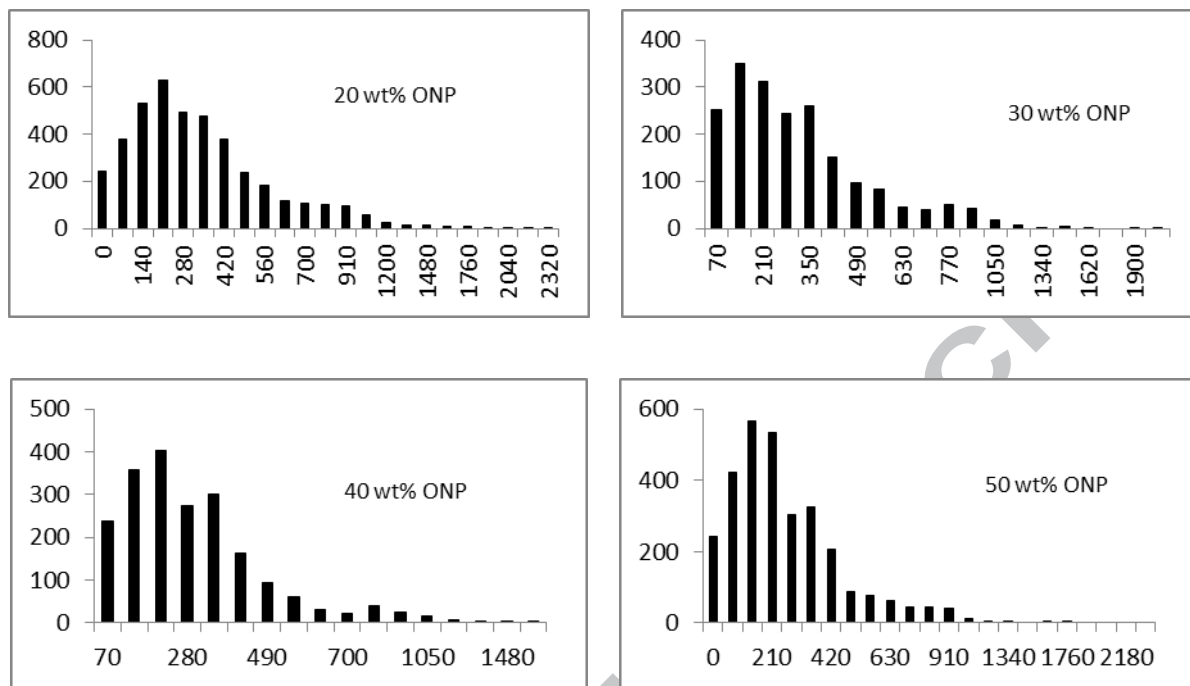


Figure 4: Fiber length distribution for the tested PP-MAPP-ONP composites.

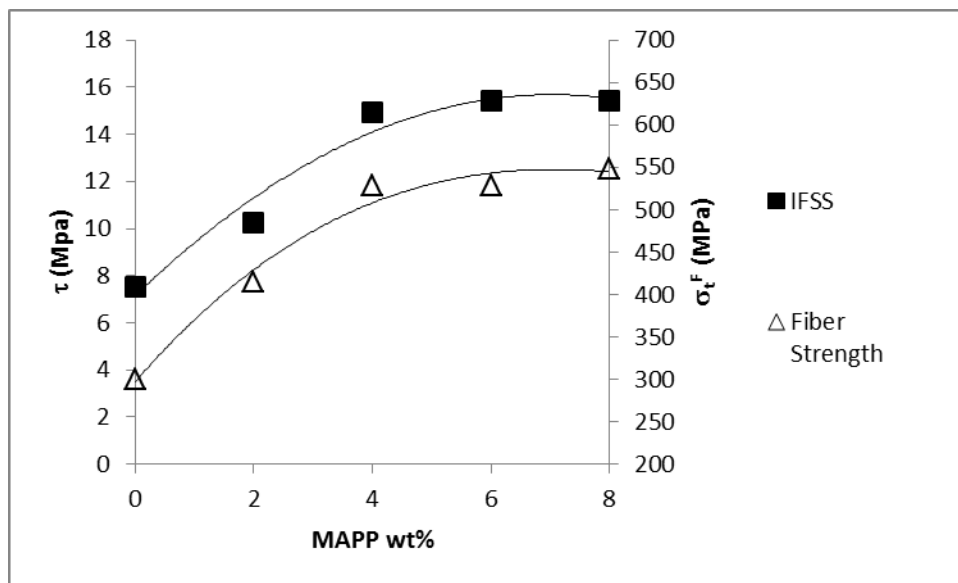


Figure 5: Evolution of the Composite interfacial shear strength (τ) and the intrinsic strength of the ONP fibers (σ_t^F) of the 40wt% ONP fibers composite materials against the MAPP wt%.

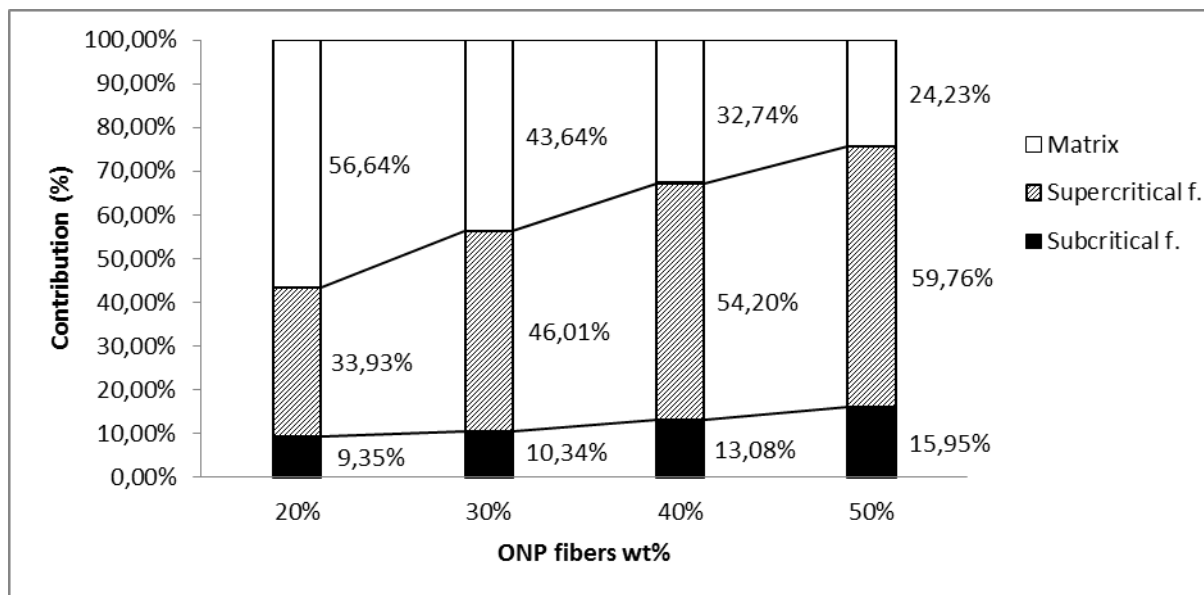


Figure 6: Contribution of the subcritical, supercritical and matrix to the tensile strength of the composite materials.