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Macro and micro-mechanics behavior of stifness in alkaline treated hemp core fibres polypropylene-based composites

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ABSTRACT

Traditionally, glass fibre has been used as plastic reinforcement whenever mechanical properties of a matrix, like stiffness, do not meet the specifications. However, current tendencies try to replace glass fibres by more sustainable fibres to obtain ecofriendlier products. Natural fibres show comparatively good physical and mechanical properties and, unlike glass fibres, come from renewable resources and are recyclable and sustainable. In this work, hemp straw discarded from hemp manufacturing was used as reinforcement in polypropylene composites. One drawback associated to hemp straw is its high lignin content that reduces its reinforcing potential. Therefore, a soft alkaline treatment was employed to adjust the lignin contents. In this work, the evolution of the Young's modulus with the NaOH treatment is assessed and discussed. Intrinsic Young's moduli of hemp straw fibres at different alkaline conditions were determined by Hirsch model. Finally, Tsai-Pagano and Halpin-Tsai equations allowed the prediction of the theoretical Young's modulus of the composites. The results showed the competitiveness of a byproduct reinforced composite in front of commodity materials.

1. Introduction

The concern of the society towards the environment is nowadays promoting the development of eco-friendly materials [1–4]. In recent times, therefore, the use of natural fibres to substitute synthetic reinforcements like glass fibres has gained importance in the composites field [5–7].

The present work is part of a comprehensive study where hemp straw is being exploited as raw material to produce composites with significant tensile and flexural moduli, notable strength, and relevant acoustic and thermal properties. Hemp is an agricultural commodity crop applicable to a wide variety of uses like textiles, paper, building materials, foods … The global production of hemp was170.000 tons in 2014 [8]. Nonetheless, its production changes noticeably year to year, being 85.000 and 113.000 tons in 2013 and 2014, respectively in Refs. [8,9]. Once the hemp plants are treated to extract the bast fibers, 50–55% of the outputs are hemp core, considered as waste with little value. This hemp core is usually devoted to bedding for livestock, due to its high capacity to liquid abortion [1].

In the literature, there are examples of the integral exploitation of hemp straw used as filler for composite materials, but such materials showed uncompetitive mechanical properties despite the use of coupling agents. Good example for this is Vallejos et al. work [10] who reported that PP composites with 40 wt/wt% of hemp straw, in presence of maleated-polypropylene, improved by 20% the tensile strength of the polymeric matrix. This improvement can be defined as weak and the literature shows higher increments for natural-fiber or by-product fibres reinforced composites [11,12]. However, if hemp core is treated in alkaline conditions and defibrated, a byproduct turns into a valuable source of papermaking or reinforcing fibers. This is the case of a recent work by some of the authors [1] where PP composites reinforced with hemp core fibres gave significant improvements for matrix tensile strength. Moreover, these treatments agreed with the principles of green chemistry to minimize waste generation [13].

Nonetheless, stiffness is one of the most significant characteristics to attain competitive composites for structural and semi structural applications [14]. The stiffness evaluates the resistance of a body to deform under loads. More specifically, this property is related to the Young's modulus or modulus of elasticity, which is a numerical quantification of the stress increment over an increment of strain in the elastic region of the material. From an engineering point of view, a design has to sustain reasonable deformations under working conditions. However, a high percentage of polyolefin matrices show comparatively low rigidity, explaining the need to reinforce them with fibrous materials.

Industries like automobile and building are two examples where lignocellulosic fibres can be used as polymer reinforcements. Automobile applications include door panels, package trays, car roofs or load floors. The building sector uses lignocellulosic reinforced polymers for decking, railing, fencing, windows and doors [4,15–17]. In these products, the rigidity is more relevant than its ultimate strength. Therefore, the stiffness of the hemp core fibre reinforced polypropylene composite materials, where a by-product can replace a raw material, is worth studying. To the best of our knowledge, this has not yet been investigated.

Natural fibres show high standard deviations in the value of their intrinsic modulus of elasticity [18,19]. Moreover, the experimental quantification of the Young's modulus in short fibres, such as hemp core fibres, is difficult, and due to its variability must be based in a large number of experiments. Besides, some researchers declare that the intrinsic properties of a single fibre outside and inside a composite can vary noticeably [20]. Nevertheless, the intrinsic elastic modulus of the fibres is an essential parameter to predict the stiffness behaviour of the composite material. This study proposes a specific methodology to analyse the Young's modulus of short-fibre reinforced composites. Such methodology is based on the use of Hirsch [21,22], CoxKrenchel [23,24] and Tsai-Pagano [25,26] models to solve the modified rule of mixtures (mRoM). The method has been used previously and has proved its usefulness to establish the intrinsic Young's modulus of the fibres and to predict the Young's modulus of the composites [12,27–31]. These models have allowed the determination of the intrinsic modulus of the fibres, the efficiency factor, orientation factor, length factor or the influence of the aspect ratio in the final properties of the composite.

In the present work, hemp straw was submitted to a chemo thermomechanical treatment under alkaline conditions to obtain hemp core fibres. Hemp core fibres/polypropylene composites were then prepared and their Young's modulus characterized. The composite materials were produced with percentages of reinforcement in the range from 20% to 50% wt%. A coupling agent was also added in some cases. The effect of alkaline treatments on the Kappa number and on morphological properties of the fibres is reported and discussed.

2. Experimental

2.1. Materials

Hemp straw of Cannabis Sativa was kindly provided by Agrofibra S.L. (Puigreig, Spain). The matrix was polypropylene (PP) ISPLEN® 090 G2M kindly provided by Repsol-YPF (Tarragona, Spain). Maleic-grafted polypropylene (MAPP) Epolene® G30 15, with an acid number of 15 mg KOH/g and Mn of 24800 Da, which was acquired from Eastman Chemical Products (Middelburg, The Netherlands) was used as coupling agent where necessary.

Chemical reagents, sodium hydroxide (NaOH) and anthraquinone (AQ), both were supplied by BASF (Tarragona, Spain), were used for fibres digestion. Decahydronaphtalene (decalin), provided by Sharlab S.L. (Sentmenat, Spain), was employed to dissolve the polymeric matrix in the fibre extraction process. All the reactants were used as received.

2.2. Preparation of hemp core fibres

The hemp core straw was submitted to a chemo thermomechanical process during 30 min at 160 °C in a 15 L batch reactor. Three different digestions, containing 5%, 7.5% and 10% of NaOH based on the fibre content (wt%), were produced. The liquid/solid ratio was set at 10. A 0,1% of AQ based on the fibre amount was added to catalyse the cooking process. Following, the resulting treated hemp straw was water rinsed and passed through a SproutWaldron equipment to obtain defibrated fibres from the hemp core bundles. Finally, the slurry was filtered and dried for at least 24 h at 80°C in a Dycometal oven (Viladecans, Spain) to obtain dry hemp core fibres.

2.3. Compounding and injection moulding

PP composites comprising 20–50% wt% hemp core fibres (HCF) contents were compounded in a Gelimat multikinetic mixer model G5S by Draiswerke (Mahaw, New Jersey, USA). The process parameters were 2500 rpm for 2 min until a discharge temperature of 210°C was reached. Previous researches showed that the fibre length remained longer with Gelimat multikinetic mixer than with other mixing processes like twin screw extruders or Brabender mixers. Longer lengths promote better strengthening capabilities to the fibres and improve the final tensile properties of the composites [32].

The resulting blends were ground in pellet shape by means of blade mill equipment and, dried and stored for at least 24 h at 80 °C in a Dycometal oven (Viladecans, Spain) before processing.

The standardized samples for stress-strain test were prepared with a Meteor 40 injection-moulding machine Mateu & Solé (Barcelona, Spain). The processing temperatures of the three heating zones were 175, 175, and 190 °C, respectively. The first and the second pressures were 120 and 37.5 kgf/cm^2, respectively. Normalized samples (approximately 160 × 13.3 × 3.2 mm) in accordance with ASTM D638 were produced.

2.4. Mechanical characterization

The specimens were conditioned during 48 h at 23 °C and 50% of relative humidity as required by ASTM D618 standard. Following, the specimens were tensile tested using a universal testing machine DTC-10 supplied by IDMtest (San Sebastian, Spain), fitted with a loading cell charge of 5 kN and working at a speed rate of 2 mm/min. Results were obtained from the average of at least 5 samples. An extensometer MFA2 (Velbert, Germany) was used in agreement with ASTM D638.

2.5. Kappa number determination

Kappa number is a method used to determine the lignin content in a sample of pulp. The Kappa number determination of hemp core fibres was realized in line with the standard ISO 302:2004-Determination of Kappa number.

2.6. Fibres extraction and morphological characterization

Reinforcing fibres were extracted from the composites by polymeric matrix dissolution using a Soxhlet equipment. Decalin was employed as solvent. Small portions of material were cut and introduced into a specific cellulose filter and placed inside the Soxhlet apparatus. The fibre extraction was finished after 24 h. Then, the extracted fibres were cleaned with acetone and water to eliminate the residual solvent. Lastly, the extracted fibres were dried at 105 °C for 24 h.

Fibre morphological properties were determined and characterized by Morfi Compact analyser by Techpap SAS (Grenoble, France). Length and diameter distributions were achieved processing close to 30000 images. A minimum of 4 samples were analysed for every test.

2.7. Density measurement

The density determination of the composites (ρ^c) was performed using a pycnometer. The temperature conditions were 23 °C and distilled water was utilized as reference liquid. The method followed was the ISO 1183-1. The

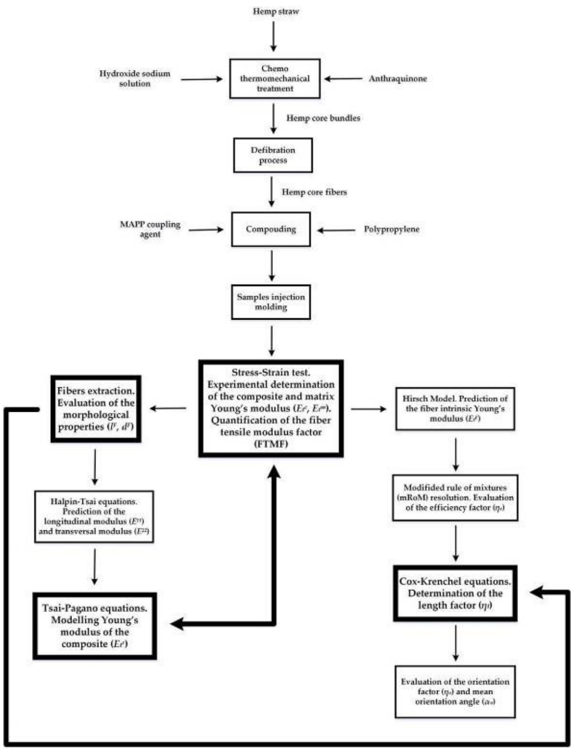

Fig. 1. Flow chart to determine the macro and micromechanical characteristics of the HCF/PP composites

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identity used to calculate the density of the composite was $\rho^c = w^c/((w^m/\rho^m) + (w^F/\rho^F))$ where w^c, w^m and w^F are the contents in weight of the composite, the polymeric matrix and the fibre, respectively. On the other hand, ρ^m and ρ^F represent the densities of the polymeric matrix and the fibre, respectively.

3. Micro-mechanical models

Previous works have reported that the most influent factors that determine the Young's modulus of a semi aligned short fibre reinforced composite are: fibre content, fibre and matrix stiffness and, fibre orientation and morphology [33]. Moreover, the aspect ratio of the fibre, the ratio between its mean lengths and diameter, also plays a role and may significantly vary the magnitude of this property. Fig. 1 illustrates the methodology used to calculate the macro and micro-mechanics properties of the HCF/PP composites.

3.1. Modified rule of mixtures

One of the most common micro-mechanical models used to predict a composite Young's modulus is a modified rule of mixtures (mRoM) [33,34]:

$$E_t^c = \eta_e E_t^F V^F + (1 - V^F)E^m \qquad (1)$$

$$\eta_e = \eta_l \eta_o \qquad (2)$$

Where η_l and η_o are the length factor and the orientation factor, respectively.

According to the literature, the efficiency factor can be expected in a range from 0.4 to 0.6 [25,27,28]. η_l is a parameter linked to the fibre morphological properties and η_o is related with the processing conditions and the machinery parameters [35].

To quantify the neat contribution of the reinforcement to the Young's modulus of the composite materials, a fibre tensile modulus factor (FTMF) [28] was computed by isolating the fibre contribution on the Young's modulus of the composite in the mRoM.

$$FTMF = \frac{E_t^c - (1 - V^F)E_t^m}{V^F} = \eta_e E_t^F \qquad (3)$$

FTMF can be directly computed from the experimental data. FTMF is a function of the fibre volume fraction, represented by a linear regression. The slope of such line is the FTMF. Nevertheless, the use of additional models is necessary to obtain the length and the orientation factors. The length factor was computed in agreement with Cox-Krenchel's model [24,27,28].

$$\eta_l = 1 - \frac{\tanh\left(\frac{\xi L_{ww}^F}{2}\right)}{\frac{\xi L F_{ww}^F}{2}} \qquad (4)$$

With

$$\xi = \frac{1}{r}\sqrt{\frac{E_t^m}{E_t^F(1 - \nu)\ln\left(\frac{\pi}{4V^F}\right)^{1/2}}} \qquad (5)$$

Here, L_{ww}^F is the fibre's mean double weighted length, r the fibre's mean radius, v the Poisson's ratio of the matrix and ξ expresses the stress concentration rate at the ends of the fibres. Accordingly to the bibliography, 0.36 was used as polypropylene's Poisson's ratio [36].

An interesting study performed by Fukuda and Kawata [37], enabled the connection between the orientation factor (η_o) and the mean orientation angle (α_o), assuming a square packing distribution of the fibres inside the composite.

Then, the mean orientation angle can be obtained from Equation (6).

$$\eta_o = \frac{\sin(\alpha_o)}{\alpha_o}\left(\frac{3-\upsilon}{4}\frac{\sin(\alpha_o)}{\alpha_o} + \frac{1+\upsilon}{4}\frac{\sin(3\alpha_o)}{3\alpha_o}\right) \quad (6)$$

3.2. Fibres intrinsic Young's modulus: Hirsh's model

The measurement of the intrinsic Young's modulus of a fibre is difficult and requires very specialized equipment as nano indenters [38,39]. Furthermore, there is discrepancy on the value of single fibre properties measurement to be used in composite micro-mechanics [20]. Nonetheless, the intrinsic tensile properties play an important role to predict and evaluate the Young's modulus of a composite. Hopefully, there are several mathematical models which allow estimating the mechanical properties of the fibres. In this sense, Hirsch's model (Equation (7)) was used to estimate the intrinsic Young's modulus of HCF [21,25,27].

$$E_t^c = \beta(E_t^f V^F + E_t^m V^m) + (1-\beta)\frac{E_t^f E_t^m}{E_t^m V^F + E_t^f(1-V^F)} \quad (7)$$

V^m is the matrix volume fraction (where $V^F + V^m = 1$). The factor β equalizes the parallel and perpendicular contributions of Reuss and Voigt models, respectively [40]. It is assumed that β is a parameter which evaluates the stress transfer between the fibre and the polymeric matrix. The literature exposes that the parameter β is mainly affected by the reinforcement orientation, fibre length and stress impact at the fibre ends [41]. It has been reported that a value close to β = 0.4 accurately reproduces the experimentally obtained results for natural fibre composites [42,43].

3.3. Modelling of composite Young's modulus: Tsai Pagano equations

The literature presents a variety of models used to predict the Young's modulus of short fibres reinforced composites [12,29,44]. One of the most cited is the Tsai-Pagano model [26]. This model considers fibres morphology and combines the contribution of the expected longitudinal and transversal elastic modulus terms. The model can be expressed by Equation (8):

$$E^c = \frac{3}{8}E^{11} + \frac{5}{8}E^{22} \quad (8)$$

Here, E^{11} and E^{22} are the longitudinal and transversal Young's modulus, calculated by the Halpin-Tsai equations (Equations (9) and (10)) [45].

$$E^{11} = \frac{1 + 2\left(\frac{L_{ww}^F}{d^F}\right) z_l V^F}{1 - z_l V^F} E_t^m \quad (9)$$

$$E^{22} = \frac{1 + 2\, z_t V^F}{1 - z_t V^F} E_t^m \quad (10)$$

Being the parameters z_l and z_t

$$z_l = \frac{\left(\frac{E_t^F}{E_t^m}\right) - 1}{\left(\frac{E_t^F}{E_t^m}\right) + 2\left(\frac{L_{ww}^F}{d^F}\right)} \quad (11)$$

$$z_t = \frac{\left(\frac{E_t^F}{E_t^m}\right) - 1}{\left(\frac{E_t^F}{E_t^m}\right) + 2} \quad (12)$$

Where d^F is the fibre's mean diameter. All the other parameters were previously defined.

4. Results and discussion

4.1. Effect of the alkali treatment

The purpose of the soft NaOH treatment catalysed with AQ was removing the vast majority of extractives, soluble lignin, a portion of hemicellulose and non-soluble lignin from the fibre surface. Fibres with less amount of lignin will exhibit higher proportion of cellulose, which is the most crystalline compound and it is expected to increase the stiffness of the composite [25].
The Kappa number was measured for every alkali condition (Table 1).

As expected, the Kappa number decreased with the severity of the NaOH treatment. Particularly, the Kappa number of the 10% NaOH treated fibres was 5% and 16% lower than that for the ones treated at 7.5% and 5% NaOH, respectively. Nonetheless, the yield, defined as the ratio between the raw material and the reinforcing fibres, was reduced with the amount of NaOH used. Accordingly with the principles of green chemistry the production of by-products must be limited, and if possible, the by-product must be recycled [13]. In the present case, the raw material is already a by-product, and the used processes minimize the production of further by-products. All the used treatments showed yields close to 70%, which are acceptable yields in pulp production [46].

The reduction of lignin content produced a slight increment of the fibre lengths. However, the aspect ratios were similar in all cases, and superior than 10, indicating good strengthening and stiffening capabilities of the resulting fibres [40,47].

4.2. Macro-mechanics

According to the literature, the quality of the fibre-matrix interface is not critical for the measurement of the Young's modulus. The role of

Table 1
Impact of NaOH treatment on HCF characteristics.

NaOH (wt. %)	Yield (wt. %)	Kappa number	l_{wwF} (µm)	d_F (µm)	l_{wwF}/d_F
5%	78.6	73.2	655	23.7	16.0
7.5%	76.4	68.1	665	24.5	15.8
10%	66.9	57.0	684	24.6	16.1

Table 2
Young's modulus PP-HCF at diff erent fibre content and NaOH uncoupled comp treat ıents, for MAPP coupled

NaOH (wt.%)	HCF (wt.%)	V_F (%)	E_{tc} (GPa)	ε_{tc} (%)	E_{tc} (GPa)	ε_{tc} (%)
			0% MAPP		6% MAPP	
PP	–	–	1.5 ± 0.08	9.3 ± 0.17	1.5 ± 0.06	9.3 ± 0.17
5	20	0.139	3.0 ± 0.09	4.6 ± 0.19	3.0 ± 0.11	5.2 ± 0.09
	30	0.217	3.9 ± 0.11	3.0 ± 0.21	4.0 ± 0.14	3.9 ± 0.16
	40	0.301	4.8 ± 0.14	1.6 ± 0.18	4.8 ± 0.13	3.1 ± 0.21
	50	0.393	5.9 ± 0.11	1.2 ± 0.22	5.6 ± 0.15	2.6 ± 0.25
7,5	20	0.139	3.0 ± 0.07	4.8 ± 0.16	3.0 ± 0.07	5.7 ± 0.06
	30	0.217	4.0 ± 0.9	3.2 ± 0.13	4.0 ± 0.08	4.7 ± 0.17
	40	0.301	4.8 ± 0.12	2.1 ± 0.17	4.8 ± 0.11	3.6 ± 0.19
	50	0.393	5.8 ± 0.15	1.7 ± 0.27	5.7 ± 0.14	2.7 ± 0.22
10	20	0.139	3.1 ± 0.06	5.1 ± 0.18	3.2 ± 0.08	6.1 ± 0.17
	30	0.217	4.1 ± 0.11	3.5 ± 0.21	4.1 ± 0.11	4.3 ± 0.19
	40	0.301	4.9 ± 0.09	2.4 ± 0.24	4.9 ± 0.12	3.8 ± 0.23
	50	0.393	6.0 ± 0.13	2.0 ± 0.14	6.0 ± 0.15	3.6 ± 0.22

the coupling agent MAPP is to enhance the bonding ability between both components at the interphase. In particular, the maleic unities of MAPP can react with the hydroxyl groups at fibre surfaces, promoting covalent bonds between them, and also favouring the number of hydrogen bonds. The experimental values of the modulus and strain at break for composites at different compositions are found in Table 2.

The presence of the MAPP coupling agent showed little effect on the Young's modulus. Hence, this fact corroborates that the interfacial adhesion between the fibre and the polymeric matrix has little influence on the stiffness of the composite [28,48,49]. However, the addition of coupling agent resulted in materials able to sustain larger deformations (Fig. 2), which means that the composites with MAPP become less fragile. As a consequence, this issue implies a competitive advantage related to the uncoupled composites.

The Young's moduli of the composites increased linearly with the fibre content (Fig. 2). The improvement of the Young's modulus indicates a higher stress transfer between the polymer and the natural fibre [50].

The improvement of Young's modulus against reinforcement content is explained by the diminution of the matrix mobility in its amorphous regions due to the addition of stiffer fibres [51,52]. In the present work, the incorporation of HCF fibres produced on average increments in Young's modulus of 100%, 166%, 225% and 300%, for compositions of 20%, 30%, 40%, and 50% wt of reinforcement, respectively.

The obtained results were compared with other experiences where the same polymeric matrix was used. Table 3 displays the Young's modulus of PP composite materials reinforced with hemp strands (HS), stone groundwood (SGW), old newspaper fibres (ONF) and glass fibre (GF) [12,22,28]. In order to compare the obtained values with the literature, PP-HCF composites treated with 5% of NaOH were taken as reference, because the production of this fibre generated less amounts of waste [13].

Table 3
Young's modulus and specific Young's modulus of different composite materials.

Composite	Reference	Fibre content (wt.%)	ρ_C (g/cm^3)	E_{tc} (GPa)	E_{tc}/ρ_C (GPa/g·cm^{-3})
PP-SGW	[28]	30	1.00	3.5 ± 0.1	3.5
PP-ONF	[22]	30	1.00	3.8 ± 0.1	3.5
PP-HS	[12]	30	1.02	3.8 ± 0.1	3.7
PP-HCF	Present study	30	1.01	3.9 ± 0.1	3.9
PP-GF [3]	[28]	30	1.12	5.6 ± 0.1	5.0

Composite materials reinforced with GF were the stiffer. However, GF is a manufactured product that involves high energy costs during its production, and comes from non-renewable resources becoming a less environmentally friendly material than those coming from renewable resources. Instead, hemp core fibres come from a waste of natural fibres, which presumably make them of environmental interest. Moreover, HCF fibres were found to be in line with the stiffening capabilities of other natural fibres. There are differences in the nominal values, but with little statistical significance. Specific Young's moduli of natural reinforced composites were below the specific property of glass fibre composites, for the same content by weight.

By using the mRoM, it is possible to predict the volume fractions of reinforcement for a precise Young's modulus. If the objective is the modulus obtained with the GF-based composites, Table 4 shows the needed fibre contents in composites with the different natural fibres. All-natural composites needed close to 50 wt% to achieve 5.6 GPa, compared to the 30 wt% for the PP-GF composite.

When a new composite material is developed, there is an interest to obtain a parameter which allows determining the reinforcing capacity of the fibre. In this respect, the fibre tensile modulus factor (FTMF), defined in section 3.1, is considered as a good candidate. Fig. 3 shows the computed FTMF for all the discussed composites.

The PP-HCF composites showed a FTMF of 12.448 GPa. This value was very similar to the one of all the other natural fibre-based composites. The FTMF values for the PP-SGW and the PP-ONF composites were 10.331 and 11.321 GPa, respectively. The FTMF obtained with hemp strands-based composites was 13.840 GPa, slightly higher than our PP-HCF. The stiffening capabilities of HCF are in line of the other natural fibres, showing the competitiveness of a by-product in front of virgin raw materials. On the other hand, the FTMF value of PP-GF was evaluated to be 32.667 GPa, above twice the natural based reinforcements'.

4.3. Micro-mechanics

The intrinsic Young's modulus of reinforced composites was calculated by means of the Hirsch's model. Table 5 shows the modelled values for each fibre content and NaOH treatment.

It was proved that the intrinsic Young's modulus of HCF was almost not affected by the presence of the coupling agent. However, the use of

Fig. 2. Young's modulus and deformations of PP-HCF composites at different fibre content, with and without MAPP coupling agent and with different amount of NaOH. a), b) and c) cases have been treated with 5%, 7.5% and 10% wt. NaOH content, respectively.

Table 4
Reinforcement needed for achieving the same Young's modulus as glass fibre composites.

Composite	Reference	Fibre content (wt.%)	E_{tc} (GPa)	E_{tF} (GPa)
PP-SGW	[28]	57.5	5.6	18.2
PP-ONF	[22]	55.9	5.6	22.8
PP-HS	[12]	45.3	5.6	27.4
PP-HCF	Present study	48.4	5.6	–
PP-GF	[28]	30.0	5.6	71.6

Fig. 3. Fibre tensile modulus factor of different composite materials.

Table 5
Intrinsic Young's modulus of the HCF at different NaOH treatments.

NaOH (wt.%)	HCF (wt.%)	V_F (%)	E_{tF} (GPa) 0% MAPP	E_{tF} (GPa) 6% MAPP
5	20	0.139	26.2	25.6
	30	0.217	26.2	27.6
	40	0.301	26.1	25.5
	50	0.393	25.9	24.1
7.5	20	0.139	26.3	26.2
	30	0.217	27.0	28.2
	40	0.301	26.2	25.5
	50	0.393	25.4	25.1
10	20	0.139	27.8	28.7
	30	0.217	28.4	28.8
	40	0.301	26.7	26.3
	50	0.393	26.4	26.8

Table 6
Mean intrinsic Y g's modulus of the H

NaOH (wt. %)	Kappa number	Yield (wt. %)	E_{tF} (GPa) 0% MAPP	E_{tF} (GPa) 6% MAPP
5	73.2	78.6	26.1 ± 0.2	25.7 ± 1.4
7,5	68.1	76.4	26.3 ± 0.7	26.2 ± 0.7
10	57.0	66.9	27.3 ± 0.9	27.6 ± 1.3

chemo thermomechanical treatments tended to improve the intrinsic Young's modulus of the fibres. . The mean values of the intrinsic Young's moduli of HCF at different NaOH treatments are shown in Table 6.

In short fibre composites, the reinforcing fibres show a distribution of fibre lengths and orientations [43]. In order to determine the implication of such morphology, the efficiency factor, and the fibre length and fibre orientation factors can be calculated. The computed values for the present case appear in Table 7.

It was noticed that the length factor (η_l), was not affected by the alkaline treatment; explained by the small alterations of the mean fibre lengths (Table 1). Moreover, since the efficiency factor (η_e) was also invariable the fibre orientation factor (η_o, Equation (2)) remained constant at each NaOH treatment.

Table 7
Micromechanical aspects of PP-HCF composites.

Treatment	0% MAPP				6% MAPP			
NaOH (wt.%)	$\square_{\square}$	$\square_{\square}$	$\square_{\square}$	α_o (°)	$\square_{\square}$	$\square_{\square}$	$\square_{\square}$	α_o (°)
5	0.46	0.91	0.51	54.7	0.45	0.91	0.50	55.56
7.5	0.46	0.91	0.51	54.7	0.46	0.91	0.51	54.7
10	0.47	0.91	0.52	53.8	0.48	0.91	0.53	53.0

On the other hand, the mean orientation angles for the coupled composites were found to be between 55.56° and 53°, for the 10% and 5% treatments respectively, calculated according to the square packing distribution. Another way for determining the mean orientation angle is from $\chi_1 = \cos^4(\alpha_o)$; where χ_1 is the orientation factor used in the modified Kelly and Tyson equation [53]. In a previous research, the authors found an orientation factor (χ_1) of 0.29 for an equivalent angle of 42,87°. The mean angles obtained from the Young's modulus and tensile strength micromechanics showed noticeable differences. Anyhow, other studies also showed similar behaviours of the mean orientation angles [12,54].

4.4. Modelling of the Young's modulus

Tsai-Pagano model and Halpin-Tsai equations (Equations (7)–(11)) were used to compute the theoretical Young's modulus of the composites (Table 8). In opposition to Hirsh model, Halpin-Tsai equations have into account the morphological properties of the fibres. In Table 8, the modelled and the experimental Young's moduli for the PP-HCF composites are shown, and the error column indicates the difference in percentage between the experimental (E_t^c) and the modelled (E^c) Young's moduli.

It was found that both Tsai-Pagano model and Halpin-Tsai equations were suitable to estimate the Young's modulus of PP-HCF composites. Hence, the models were consistent and did approximate rather well the Young's modulus of the composites. Undoubtedly, if Tsai-Pagano model and Halpin-Tsai equations were used to predict the intrinsic Young's moduli of the fibres, slightly lower values than those for the Hirsch model would be obtained. The little differences are representative of the effect of the morphological properties of the fibres in the results. Consequently, while Hirsch equations reported good results, the use of other models is advisable to know the possible deviations due to morphological properties.

Table 8
Tsai-Pagano modelled elastic modulus and experimental Young's modulus for PP-HCF at different NAOH treatment and fibre content.

		0% MAPP			6% MAPP		
NaOH (wt.%)	□□ (%)	E_c (GPa)	E_{tc} (GPa)	Error (%)	E_c (GPa)	E_{tc} (GPa)	Error (%)
5	0.139	2.9	3.0	4.1	2.9	3.0	3.5
	0.217	3.8	3.9	3.2	3.8	4.0	6.9
	0.301	4.7	4.8	1.0	4.7	4.8	0.4
	0.393	6.0	5.9	1.7	5.9	5.6	6.3
7.5	0.139	2.9	3.0	4.1	2.9	3.0	3.8
	0.217	3.8	4.0	4.8	3.8	4.0	7.7
	0.301	4.7	4.8	1.2	4.8	4.9	0.4
	0.393	6.0	5.8	3.5	6.0	5.8	3.6
10	0.139	2.9	3.1	5.4	3.0	3.2	6.8
	0.217	3.8	4.1	6.3	3.9	4.1	6.5
	0.301	4.8	4.9	1.5	4.8	4.9	0.2
	0.393	6.1	6.0	2.9	6.2	6.0	2.7

5. Conclusions

It was possible to formulate and manufacture composites reinforced with a by-product and obtain competitive composite materials. These materials agreed with the principles of green chemistry as allowed recycling a byproduct and minimized the production of further by-products. Hemp straw was submitted to a chemo thermomechanical process with NaOH to obtain hemp core fibres. Polypropylene-hemp core fibres green composites were prepared and their stiffness was measured and studied.

An increment of NaOH during the pulping process showed little improvement on the Young's modulus of the composites, with a slight advantage for the harsher treatments. Nonetheless, the processing yield decreased with the harshening of the treatment. The increase of NaOH contents during the cooking treatments facilitated the individualization of the hemp core fibres, reducing the attrition during the individualization process and allowing obtaining fibres with longer mean fibre lengths.

The addition of the coupling agent had little effect on the Young's modulus of the composites. Therefore, the interfacial adhesion between the polymeric matrix and the natural fibre did not interfere on the composite stiffness although the coupling agent improved the deformation of the material.

The fibre tensile modulus factors showed the neat contribution of the fibres reinforcement to composite's Young's modulus. This contribution was similar to other natural fibres used as reinforcement of the same matrix. The efficiency factors calculated from the Young's modulus were found within the range from 0.45 to 0.48, in line with values found by other researchers. The Tsai-Pagano model, as well as the Halpin-Tsai equations, worked fairly well in adjusting the behaviour of Young's modulus of polypropylene-hemp core fibres composites. The fibre morphological properties little affected the predicted values, with a 4% mean discrepancy between experimental and theoretical values.

Polypropylene-hemp core fibres reinforced composites showed a realistic potential for the substitution of polypropylene-glass fibre composites. This can result in positive effects on the environment. However, a life cycle assessment should be performed to corroborate this hypothesis.

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