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Effect of chemical treatments and additives on properties of chicken feathers thermoplastic biocomposites

Casadesús M.², Macanás J.¹, Colom X.¹, Cañavate J.¹, Álvarez M.D.^{1, 2}, Garrido N.³, Molins G.¹, Carrillo F.^{1, 2}

¹ Universitat Politècnica de Catalunya, Department of Chemical Engineering. Colom 1, 08222 Terrassa, Spain.

² Universitat Politècnica de Catalunya, INTEXTER. Colom 15, 08222 Terrassa, Spain.

³ Universitat Politècnica de Catalunya, Department of Heat Engines. Colom 1, 08222 Terrassa, Spain.

Corresponding author and address:

Fernando Carrillo Navarrete (email: fernando.carrillo@upc.edu, Telf. +34 937398703)

Abstract:

The valorization of chicken feathers (CFs) waste was researched in this work through the preparation of composites using ground chicken feathers as a filler (20 % v/v) and polypropylene (PP) or low-density polyethylene (LDPE) matrices. In order to improve the compatibility between CFs and the matrixes two different strategies were followed. First, by the chemical modification of the CFs by either acetylation or silanization and, second, by the addition of adhesion promoters like maleated polypropylene (MAPP) and maleatead

polyethylene (MAPE). The effect of those treatments on the physical, mechanical and structural properties of the thermoplastic-CFs biocomposites, which are mainly related to the fibre–matrix compatibility, was analyzed. Results show that the addition of 20 % (vol/vol) of unmodified CFs to the thermoplastic matrices results in a significant decrease of the tensile strength associated to a weak interfacial adhesion was assessed by SEM. However, when the adhesion promoters were added to the mixture, a significant increase in the tensile strength was noticed, particularly when the composites were obtained by a process at 180 °C. On the contrary, acetylation and silane treatments of the CFs did not result in any practical improvement of the macroscopic properties of the biocomposites.

Keywords: Chicken feathers, keratin, thermoplastic composites, tensile properties, acetylation, silanization, maleated polypropylene, maleated polyethylene, biocomposites.

1. Introduction

Nowadays, there is a raising awareness regarding the use and management of plastics and this concern is reflected as a growing number of laws enacted in most countries. In this sense, the search for alternative environmentally friendly materials is being a priority these last years [1]. A common approach to increase the biodegradability of the materials is the use of natural fibres like hemp, flax, sisal, jute, bamboo or other plants as fillers or reinforcements in combination with a polymeric matrix [2-4]. However, regardless of the technical issues derived from the difficult processability of natural fibres with polymer matrices, the use of these fibres might not be so convenient from the environmental point of view since the production of natural fibres directly competes with food production for both land and water.

In order to avoid the depletion of natural resources, the valorization of biogenic residues obtained from sub-products of different processes can be advantageous both economically and environmentally. Following this idea, wood [5], corn stover [6] or waste textile fibre [7] are examples of biogenic waste which would end in a landfill unless they were reused somehow.

Among the myriad of by-products generated by the industrial processes, chicken feathers (CFs) are generated in large amount and they do not have any practical application. Considering that feathers are the 5-9 % of the total weight of chickens, it is estimated that 8.000.000 tons of CFs are produced in a year all over the world, due to the big consumption of chicken meat especially in the northern countries [8]. CFs, as well as blood, bones, etc. are considered as animal by-products not intended for human consumption (ABPs) by the standard CE 1069/2009 [9]. Consequently, all these by-products must be transformed in a technical plant, thrown in a landfill, transformed into compost or converted into animal nutrients with low properties. However, the EU regulation limits the use of feather waste for animal feed, due to the concerns on bovine spongiform encephalopathy [10]. Moreover, the use of CFs as nitrogen fertiliser has not been successful either, since the release of nitrogen from CFs is too slow and their difficult degradation could create an environmental problem [11]. In addition, incineration is not a suitable treatment method because the burning of keratin can lead to environmental pollution [12]. Hence, the idea of using CFs waste to fabricate more environmental friendly composite materials, by means of the partial substitution of the polymer with CFs, has attracted attention during last years [13,14]. In such scenario, CFs provide multiple advantages as they are inexpensive, non-abrasive, insoluble in organic solvents, biodegradable and have a low density [15].

Being made of keratin, CFs are reported to have a low density, approximately 0.9 g/cm^3 [16], and this fact opens the possibility of fabrication of light composite materials. In addition, CFs have demonstrated a thermal stability up to 190-205 °C due to the hydrogen bonds, S-S cross

linking, Van der Waals and electrostatic interactions that characterize its chemical structure [13]. Consequently, the processing of CFs combined with the majority of polymeric matrices is possible since most of the conventional thermoplastics melt below that temperature. Moreover, regarding to their mechanical properties, CFs have specific Young's modulus and tensile strength comparable to other natural fibres such as cotton.

Nevertheless, there is a general and important issue associated with the use of natural materials in composites linked to the existing lack of compatibility when mixing a hydrophobic matrix with a hydrophilic fibre [217]. Some solutions have been proposed to improve affinity of those components, resulting in an improvement of the mechanical properties. On the one hand, some chemical modifications can be performed in order to modify the surface properties of natural fibres creating groups that increase the adhesion to the matrix [13]. On the other hand, additives such as adhesion promoters based on the modification of polymer matrices with maleic anhydride have also been successfully used in order to improve mechanical properties of the composites [18].

Up to now, previous studies demonstrated that using CFs to prepare polymer composites results in composites with poor mechanical properties, such as low tensile strength and elongation at break, due to the lack of compatibility between CFs and polymeric matrices [12, 17]. So, the study of alternative strategies for improving their mechanical properties is still interesting regarding the performance of the materials.

Taking on board these premises, the main objective of this paper is to propose and study of different strategies aimed to enhance the compatibility between CFs and PP and LDPE matrices. Hence, two chemical modifications, namely acetylation [19] and silanisation [20], were carried out to modify the surface properties of CFs. Also, the addition of different percentages of adhesion promoters (MAPP and MAPE) into the mixture was considered, so as to include an intermediate component that would improve compatibility between the two

phases. Once the composites were prepared following the different procedures, characterization of their physical and chemical properties were carried out by using contact angle, tensile test, scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) techniques to find a relationship between the macroscopic properties, i.e. tensile strength, and microstructure. Finally, the properties of the CFs based biocomposites were compared in order to discern the conditions that provided better performance.

2. Methodology

2.1. Chicken feathers stabilization

Chicken feathers were kindly supplied from a slaughterhouse located in Catalonia (Spain). CFs from slaughterhouse are unstable, unsafe and biodegradable, so a pretreatment is mandatory to stabilize and sanitize the waste. Therefore, the CFs were first frozen at -20 °C and subsequently washed in a washing machine at 35 °C with a 3300 ppm H₂O₂ solution (hydrogen peroxide 35 % weight % solution, Chem-Lab NV, Belgium), in a 5/1 (vol/wt) liquor ratio for 50 min. After that, CFs were dried in an air oven at 60 °C for 24 h. Cleaned CFs were later chopped with a shredder (Retsch SM100, Germany) until each particle size was 2 mm or less. Finally, the CFs were air-dried at 105 °C for 4 h and kept under a dry atmosphere (desiccator) just before the composites were compounded.

2.2. Microbiology study

The efficacy of the aforementioned pretreatment was controlled by a microbiology test. About 0.5 g of different samples of CFs were introduced into 10 ml of deionised water and the mixture was sonicated in an ultrasonic bath during 5 min. Then the CFs were separated from the liquid, which were sown into Petri dish after appropriate dilution. Petri dishes were incubated during 18 h at 37 °C and the observed colonies were counted (cfu/g).

2.3. Chemical modification of chicken feathers

Acetylation and silanization [2] of CFs were carried out to modify the surface of the CFs with the purpose to improve fibre-matrix compatibility. Prior to the treatments, CFs were rinsed with methanol (J.T.Baker, UK) in a bath with magnetic agitation during 1 h and with a liquor

ratio of 1:15 in order to remove contaminants. Each treatment is described in the following sections.

2.3.1. Acetylation

Acetylation was carried out in accordance with the steps detailed elsewhere [19]. In brief, 25 g of CFs were added to a reactor containing 250 ml of glacial acetic acid (Panreac, Spain), 100 ml of acetic anhydride (Panreac, Spain) and 2.5 ml of sulphuric acid 95-98 % (Panreac, Spain). The reaction was carried out at 70 °C during 60 min. **Figure 1** shows two possible chemical reactions between acetic anhydride and either the hydroxyl groups or the primary and secondary amine groups [19]. After that, CFs were filtered and added to a water bath at standard ambient temperature. The mixture was carefully neutralized with NaOH solution with a weight concentration of 10 % (Laboratorios Riser, Spain) until the pH reached the value of 5. CFs were filtered again and rinsed with distilled water at 50 °C every 30 minutes during 2.5 h. Between each rinse, the solution of CFs and water was preserved in a bath at 50 °C. Finally, the CFs were dried during 24 h at 60 °C.

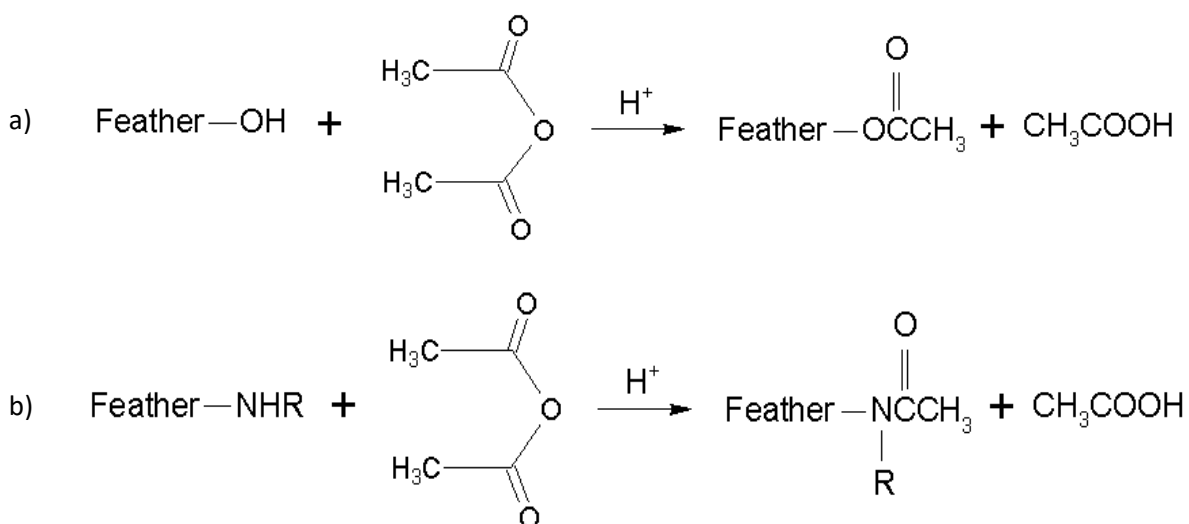


Figure 1. Possible acetylation reactions on functional groups present in feathers protein: a) esterification reaction on amino acid residues containing hydroxyl group; b) acetylation of an amino acid residues containing amine group.

2.3.2. Silanization treatment

Silane treated CFs were prepared by mixing 30 g of cleaned CFs with 337 ml of methanol (J.T. Baker, UK), 36 ml of distilled water, 76 ml of glacial acetic acid (Panreac, Spain) and 3 g of silane (A-174 NT, Grolman Group) in a bath with a liquor ratio of 1:15 (w/v). The reaction was carried out at pH 4 during 2 h and under magnetic agitation. After that, CFs were rinsed with water and dried first at 60 °C during 24 h and then at 120 °C during 2 h to promote the silanization reaction (**Figure 2**) [20].

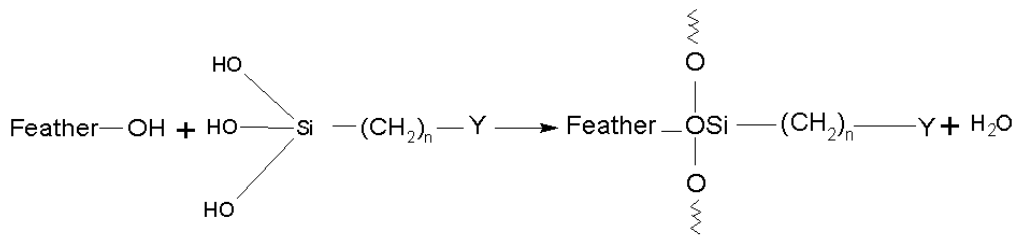


Figure 2. Silanization reaction.

2.4. Biocomposite preparation

LDPE (ALCUDIA® PE-022, Repsol-YPF, Spain) with a density of 0.915 g/cm³ and PP (Isplen® 099 K2M, Repsol-YPF, Spain) with density of 0.913 g/cm³ were used. Adhesion promoters Fusabond® M603 (maleated polyethylene, MAPE) with a density of 0.940 g/cm³ and Fusabond® P613 (maleated polypropylene, MAPP) with a density of 0.903 g/cm³ (Dupont, USA) were used in some experiments to substitute LDPE and PP, respectively. The substitution was performed with the purpose of improving compatibility between the fibre and the matrix through the presence of maleated groups in such additives. In this sense, the thermoplastic

portion of the MAPE or MAPP can entangle and cocrystallize with the unmodified matrix (LDPE or PP), while the maleic anhydride groups can bond to the some functional groups of the keratine fiber such as the hydroxyl group (-OH) of serine, the mercapto group (-SH) in cysteine and the terminal amino (-NH₂) and hydroxyl groups at the ends of the protein chains (**Figure 3**) [18].

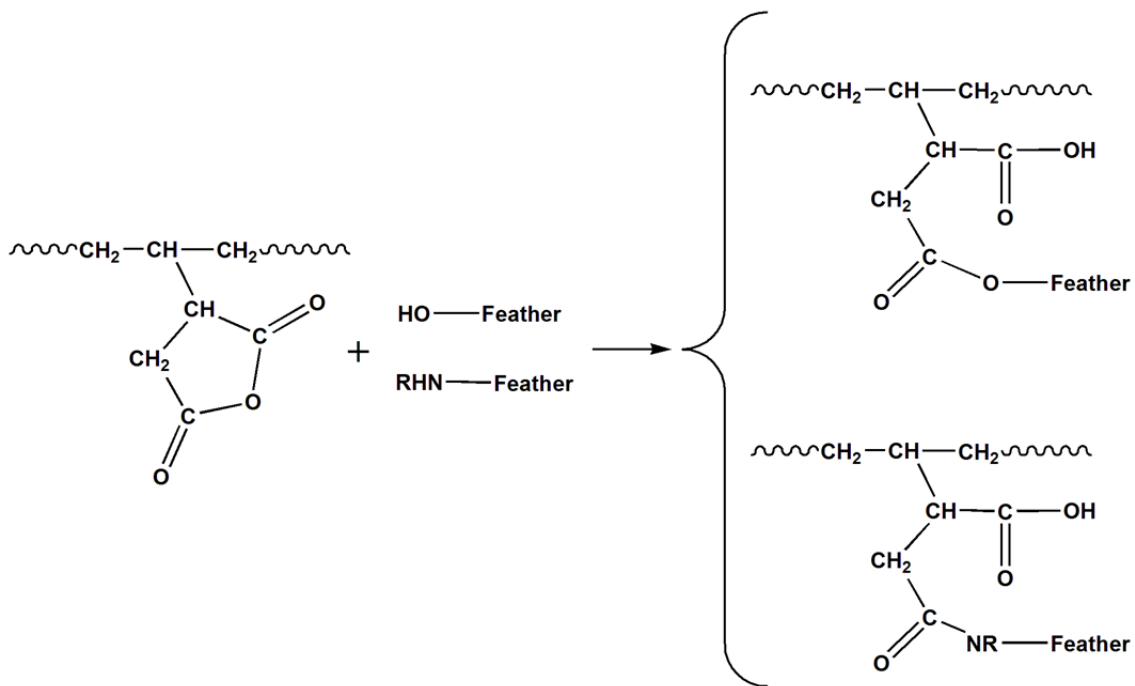


Figure 3. Reaction between the -OH and -NH groups of the CFs and the maleated polyethylene (MAPE).

For comparison purposes, a fixed amount of CFs (20 % v/v) was used in all the composites containing CFs since this value was proved in previous studies as a good compromise between the target of loading a maximal concentration of fibre and the drawback of significantly worsening the mechanical properties of the biocomposite [21].

Biocomposite specimens were obtained by mixing the previously shredded and dried CFs (always dried at 105 °C during 2 h, either modified or not) with dry LDPE and PP, including, if

that was the case, the corresponding amount of adhesion promoter. The polymer matrices were melted for 1 min and then the fibres were added and mixed for another 9 min with a mixing speed of 50 rpm.

As mentioned before, the percentage of CFs in the composite was constant (about 20 % $v/v_{\text{composite}}$) so, obviously, the inclusive polymeric part of the composite was fixed at about 80 % $v/v_{\text{composite}}$. However, in some cases a certain amount of adhesion promoters was used to substitute LDPE or PP polymers. Therefore, the composition of the polymeric matrix varied providing different percentages of adhesion promoters of about 1, 10, 20, 40, 70 % or 100 % v/v_{matrix} , where 100% stands for a complete substitution of the polymeric part (LDPE or PP) by pure maleated polymers (either MAPE or MAPP).

Components were mixed using a Brabender mixer type W 50 EHT PL (Brabender® GmbH & Co. KG, Germany) with cam blades. LDPE and PP matrices were melted first at 125 °C and 180 °C, respectively, and the corresponding amount of fibers were added later while mixing.

The effect of the mixing temperature on the final properties of the blend was studied when adhesion promoters were added. Therefore, some composites prepared at 120, 140, 160, 180 and 200 °C.

After that, the blend was then consolidated in a hot plates press machine type Collin Model P 200E (Dr. Collin GmbH, Germany) forming square plates, measuring 160 x 160 x 2.2 mm³. Consolidation was carried out at a pressure of 100 kN for 10 min at 105 °C for LDPE and 180 °C for PP. Finally, the square plates were cooled submerging the cast under water at room temperature. Some controls of pure matrices were also used as references.

The processing temperature, the exact volume/volume percentages of each component are shown in **Table 1** and **Table 2**, together with the additive:polymer ratio.

Table 1. Process temperature and composition of LDPE based biocomposites (A stands for acetylated CFs whereas Si stands for silanized CFs).

SAMPLE CODE	T (°C)	% CFs v/v _{composite}	% LDPE v/v _{matrix}	% MAPE v/v _{matrix}	additive/polymer ratio
LDPE-120-0-0	120	0	100	0	-
LDPE-120-20-0	120	20	100	0	-
LDPE-120-0-100	120	0	0	100	-
LDPE-120-20-100	120	19.8	0	100	-
LDPE-120-0-72	120	0	28	72	2.57
LDPE-120-20-72	120	20	28	72	2.57
LDPE-120-0-51	120	0	49	51	1.04
LDPE-120-20-51	120	20.1	49	51	1.04
LDPE-120-0-28	120	0	72	28	0.39
LDPE-120-20-28	120	20	72	28	0.39
LDPE-120-0-16	120	0	84	16	0.19
LDPE-120-20-16	120	20	84	16	0.19
LDPE-120-0-9	120	0	91	9	0.10
LDPE-120-20-9	120	19.9	91	9	0.10
LDPE-120-0-1	120	0	99	1	0.01
LDPE-120-20-1	120	19.9	99	1	0.01
LDPE-120-A20-0	120	18.6	100	0	-
LDPE-120-Si20-0	120	18.6	100	0	-
LDPE-140-20-9	140	20.1	91.1	8.9	0.10
LDPE-160-20-9	160	20.1	91.1	8.9	0.10
LDPE-180-0-0	180	0	100	0	-
LDPE-180-20-0	180	20.1	100	0	-
LDPE-180-0-100	180	0	0	100	-
LDPE-180-20-71	180	20	29.2	70.8	2.42
LDPE-180-0-71	180	0	29.1	70.9	2.44
LDPE-180-20-51	180	20	49.5	50.5	1.04
LDPE-180-0-51	180	0	49	51	1.04
LDPE-180-20-28	180	20	72	28	0.39
LDPE-180-0-28	180	0	71.9	28.1	0.39
LDPE-180-20-16	180	20	83.6	16.4	0.20
LDPE-180-0-16	180	0	83.7	16.3	0.19
LDPE-180-20-9	180	20	91.1	8.9	0.10
LDPE-180-0-9	180	0	91.1	8.9	0.10
LDPE-180-0-1	180	0	99	1	0.01
LDPE-180-20-1	180	19.8	99	1	0.01
LDPE-200-20-9	200	20.0	91.1	8.9	0.10

Table 2. Process temperature and composition of PP based biocomposites. (A stands for acetylated CFs whereas Si stands for silanized CFs).

SAMPLE CODE	T (°C)	% CFs v/v _{composite}	% PP v/v _{matrix}	% MAPP v/v _{matrix}	additive/polymer ratio
PP-180-0-0	180	0	100	0	-
PP-180-20-0	180	20	100	0	-
PP-180-0-100	180	0	0	100	-
PP-180-20-100	180	20	0	100	-
PP-180-0-72	180	0	28.4	71.6	2.52
PP-180-20-72	180	20	28.4	71.6	2.52
PP-180-0-50	180	0	49.7	50.3	1.01
PP-180-20-50	180	20.1	49.8	50.2	1.01
PP-180-0-29	180	0	71.2	28.8	0.40
PP-180-20-29	180	20.1	71.2	28.8	0.40
PP-180-0-17	180	0	83.2	16.8	0.20
PP-180-20-17	180	19.9	83.1	16.9	0.20
PP-180-0-9	180	0	90.8	9.2	0.10
PP-180-20-9	180	20.1	90.8	9.2	0.10
PP-180-0-1	180	0	99	1	0.01
PP-180-20-1	180	20	99	1	0.01
PP-180-A20-0	180	20	100	0	-
PP-180-Si20-0	180	20	100	0	-

2.5. Contact angle

Contact angle of materials was measured using a DSA 100B KRÜSS device (KRÜSS, Germany). Composite specimens were tested directly, but for pure CFs samples fibres were firstly compressed with a hydraulic press (Specac, USA) at 100 MPa to consolidate the formation of a pellet. Three water drops were released for each sample and the mean and the 95% confidence interval were reported.

2.6. Density

The experimental density of each composite was determined by the pycnometer method [22] using isopropyl alcohol as the test liquid. Three specimens were tested and mean and standard deviation were reported.

2.7. Water absorption

Rectangular specimens (25.4 x 12.7 mm²) from square plates were prepared and conditioned in a laboratory air dry oven at 60 °C for 24 h, cooled in a desiccator and weighed (w_o). Water absorption of composites was determined by immersion of such specimens in water at 25 °C for 24 h following an standard procedure [23]. The excess of water on the surface of the specimens was removed before weighing (w). Four specimens were tested for each sample and mean and standard deviation were reported. The percentage of water absorption (WA, in %) was calculated using equation (1):

$$WA = \frac{(w-w_o)}{w_o} \cdot 100 \quad (1)$$

2.8. FT-IR

Fourier-transform Infrared spectra were obtained by means of a Nicolet Avatar spectrometer with Csl optics (USA) in order to study the fibre-matrix-additives interaction and the effectiveness of the CFs surface treatments. A certain amount of the prepared composites was ground and dispersed into KBr (Merck, Germany) to reach a 1 % concentration. Mixtures were pressed at 100 MPa to consolidate the formation of the pellet. FTIR spectra were collected in the range of 4000-650 cm⁻¹ with 40 scans and a resolution of 4 cm⁻¹. Data were managed by using the Omnic software.

2.9. Tensile tests

Tensile tests were carried out in an Instron 3366 (Instron, UK) universal machine following the specifications of the ASTM-D-638-14 [24]. The test speed was set at 1 mm/min. Young's modulus, tensile strength, elongation at break and toughness were calculated using Bluehill

version 2 software. Five replicate specimens were analysed and the mean, standard deviation and 95% confidence intervals were calculated.

2.10. SEM

Those samples broken by the tensile test were analysed by SEM focusing into the fracture zone to qualitatively study the fibre/matrix compatibility. The microphotographs were taken in a Phenom G2 pro device (FEI company, USA) at an accelerating voltage of 15 kV. Previously, samples were coated with a fine layer of gold-palladium in order to increase their conductivity.

3. Results

First, the microbiology test confirmed that the best treatment to achieve the sanitization of CFs corresponds to the one that includes the steps of freezing and washing them with hydrogen peroxide (Table 3).

Table 3. Microbiology test of untreated and treated CFs.

Sample	Washing	Freezing	COLONIES (cfu/g)
A	No	No	$1.60 \cdot 10^{11}$
B	No	Yes	$1.08 \cdot 10^8$
C	Yes	No	$5.40 \cdot 10^6$
D	Yes	Yes	$2.68 \cdot 10^5$

Regarding the mechanical properties of the obtained biocomposites, **Figure 4** and **Figure 5** show the effect of the addition of CFs to pure thermoplastic matrices on the Young's modulus and tensile strength. On the one hand, it was corroborated that the addition of CFs produced a significant increase of the Young modulus with any of the tested materials and disregarding the processing temperature. Thus, the introduction of CFs to the biocomposite results in more rigid biocomposites compared to the pure matrices. It is noteworthy that the observed modulus increase was much more pronounced in LDPE (110 – 170 % of increase, depending on the temperature) than in PP biocomposites (about 20 % of increase) since the contribution of the modulus of the CFs is higher in less rigid matrices such as LDPE. On the other hand, the tensile strength (**Figure 5**) and elongation at break (**Figure 6**) were significantly reduced when adding CFs to the mixture, indicating low fibre-matrix compatibility, which is in agreement previous studies carried out by the authors [13]. However, it is worth to mention that the observed results differ from those obtained for Barone [25] who pointed up a significant increase of the modulus and tensile strength when adding CFs fibers to low crystallinity polyethylene matrix. Moreover, the effect of the temperature on mechanical properties of LDPE was studied in order to verify that any significant degradation of the LDPE matrix was not produced, what will be relevant when adhesion promoters were added to the mixture. Results

did not show any significant decrease of mechanical properties when processing LDPE based composites at 180 °C. This situation is a clear advantage over the processing of CFs and LDPE at 120 °C since the obtained composites show higher stiffness, less density, and comparable tensile strength that those of unfilled LDPE, without applying any expensive chemical treatment to the fibre. The reason for this result was previously reported by Barone et al. who proved that better mechanical performance of CFs/PE composites was achieved at higher temperatures (ca. 205 °C for high density PE) due to maximization of fibre/polymer interactions in the melt state [26].

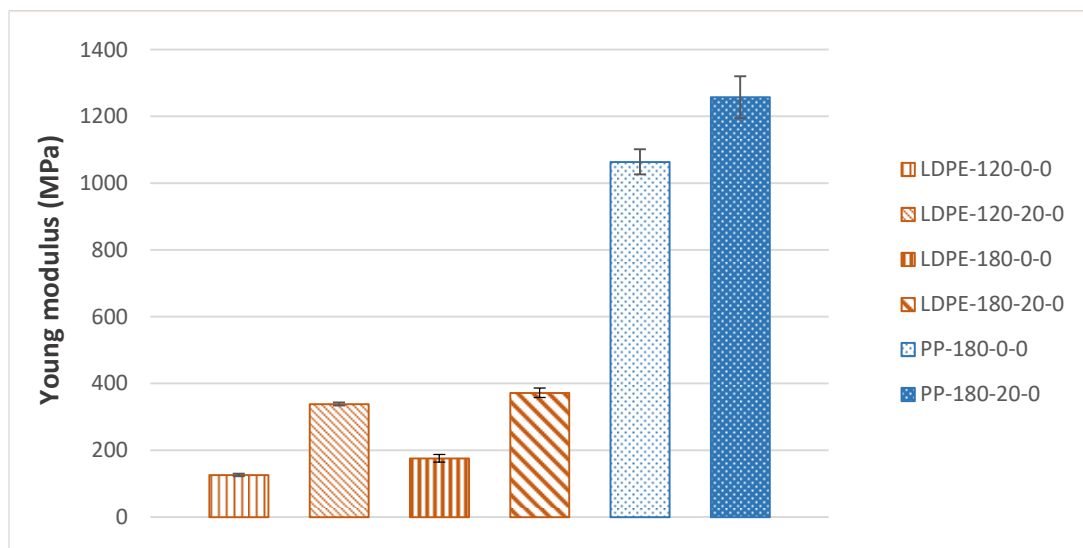


Figure 4. Young's modulus of CFs/LDPE and CFs/PP biocomposites

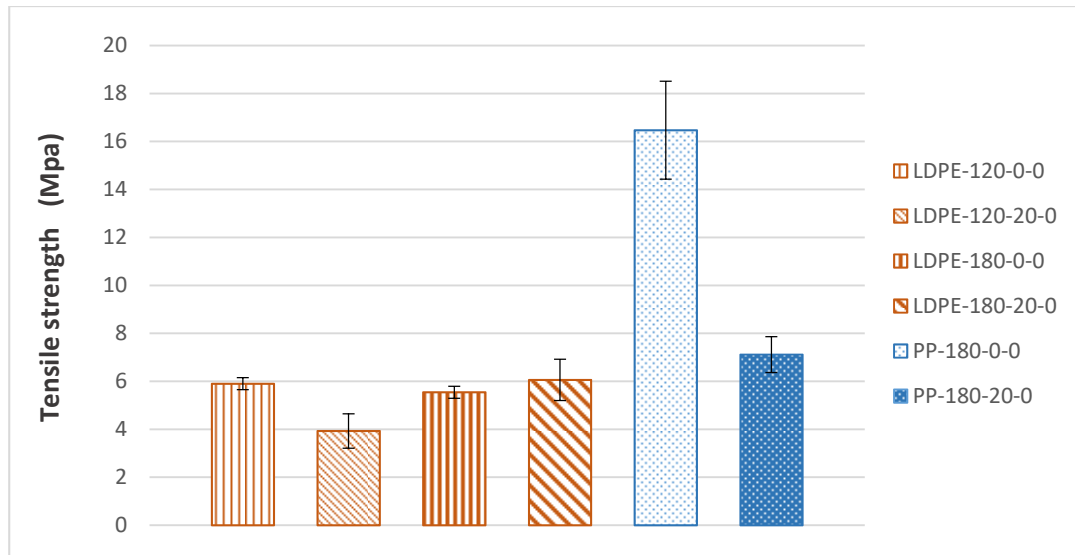


Figure 5. Tensile strength of CFs/LDPE and CFs/PP biocomposites

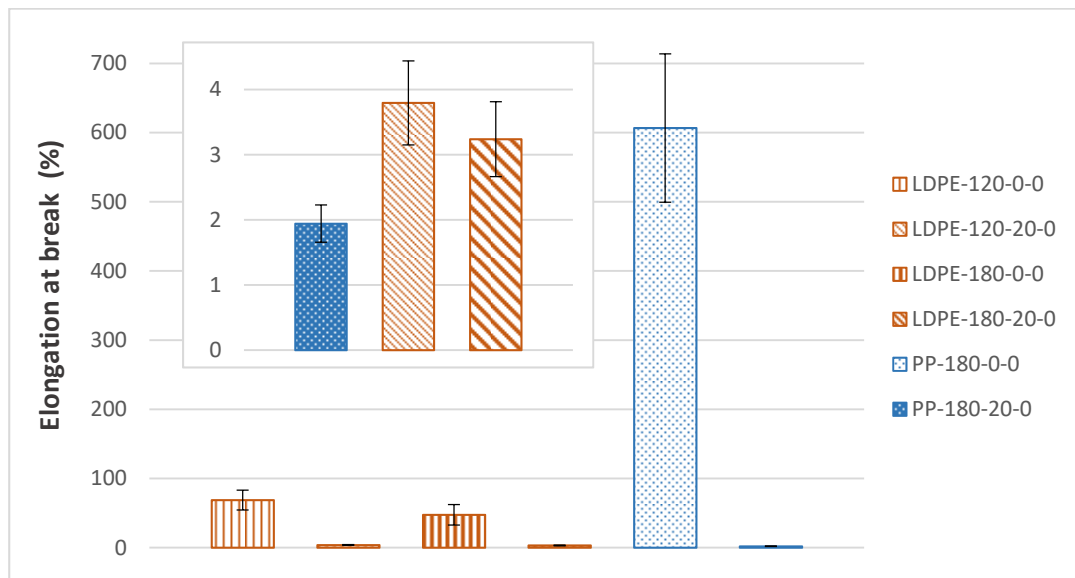


Figure 6. Elongation at break of CFs/LDPE and CFs/PP biocomposites

The aforementioned lack of compatibility between fibres and matrices was also corroborated by SEM. As it is shown in **Figure 7**, for the LDPE, the CFs appeared loose without any kind of interaction with the polymeric matrix, while for PP, there were holes with the shape of the fiber indicating detachment from matrix due to weak interaction between both components. Despite images do not show the same magnification, both are useful to determine the lack of compatibility between fibres and matrices.

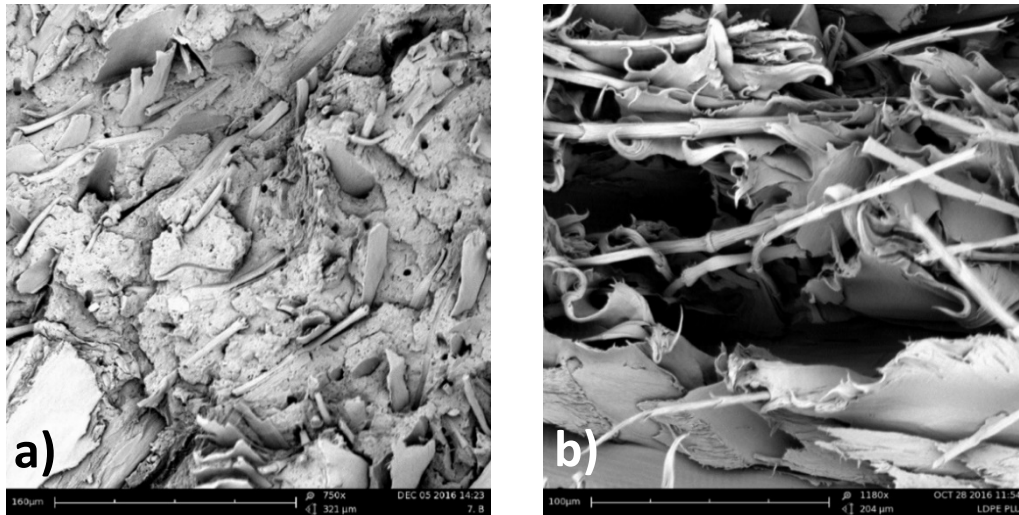


Figure 7. SEM images of the fracture surface of composites: a) LDPE-180-20-0 and b) PP-180-20-0 respectively

Contrary to what might have been expected due to the presence of polar groups (-OH, -NH₂) in the chemical structure of keratin that are absent in nonpolar thermoplastic matrices, by contact angle measurements the hydrophobicity of the CFs turned to be higher than that of matrices although the obtained values were comparable and close to 100 ° (**Figure 8**). Consequently, and taking into account the similar hydrophobicity between materials, a better performance of biocomposite in terms of mechanical properties would be expected.

	CFs	LDPE-180-0-0	PP-180-0-0
mean contact angle (°)	115.7	95.4	93.4
95% confidence interval	3.7	1.6	2.2

Figure 8. Contact angle measurements of CFs, LDPE and PP.

Taking on board the aforementioned results, some strategies for enhancing compatibility between CFs and thermoplastic matrices were studied based on either making them more hydrophobic by chemical treatments (acetylation or silanization) or by the addition of adhesion promoters into the mixture.

After acetylation or silanization, contact angles values were found comparable to the non-treated CFs [18] (**Figure 9**), so the expected increase of hydrophobicity of CFs was not achieved by these means and, consequently, the mechanical properties of the prepared biocomposites should not improve by using these routes. Actually, the tensile strength (**Figure 10**), the Young modulus and the elongation at maximum load (values not shown) of the biocomposites prepared with treated CFs did not change compared to the obtained using unmodified CFs.

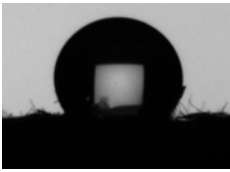
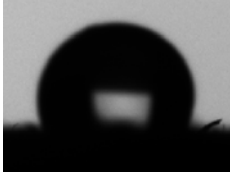
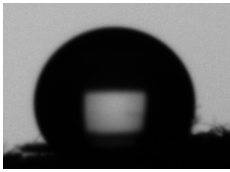
	CFs	Acetylated CFs	Silanized CFs
			
mean contact angle (°)	115.7	119.5	112.6
95% confidence interval	3.7	12.5	8.4

Figure 9. Contact angle of CFs and treated CFs.

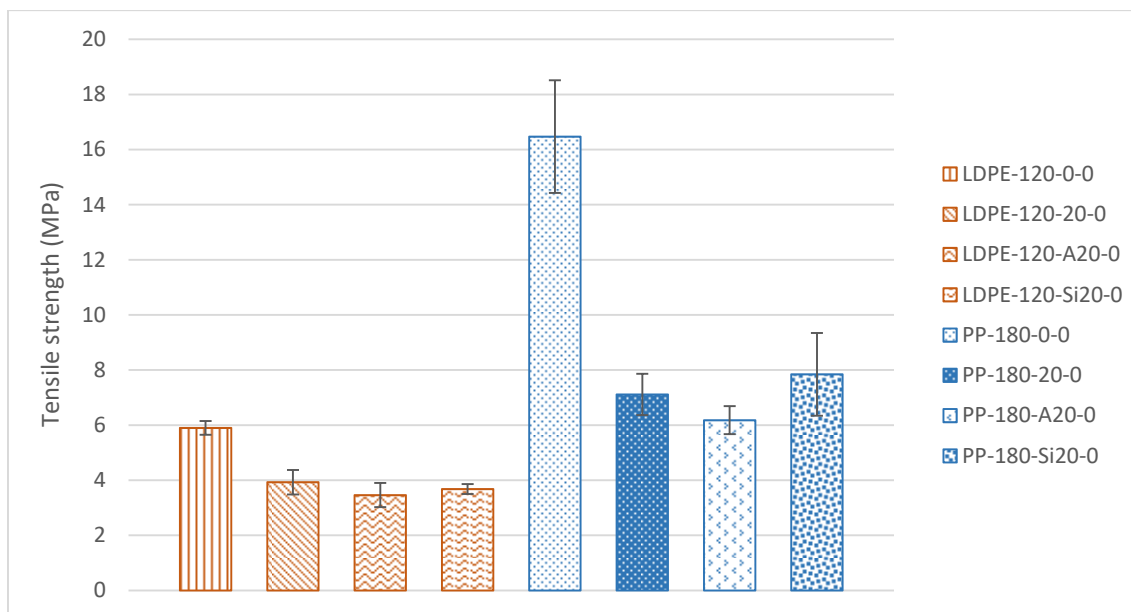


Figure 10. Tensile strength for LDPE and PP composites prepared with untreated, acetylated (ACF) and silanized (SiCF) CFs.

Nevertheless, the evidence that acetylation occurred was corroborated by FTIR (**Figure 11**), where the shoulder peak at 1732 cm^{-1} , belonging to the stretching of the ester carbonyl C=O group, was observed in the FTIR of acetylated CFs but not in CFs treated with hydrogen peroxide or the combination of hydrogen peroxide treatment and methanol washing. Other changes in the spectra were detected and interpreted according to the literature ([19] and references therein). For instance, it is possible to observe an increase in the intensity of the amide III peak at 1226 cm^{-1} due to the stretching of the C–N group in the secondary amides. A modification of the peak intensities at $2880\text{--}2970\text{ cm}^{-1}$ region was also noticed which could be assigned to asymmetric and symmetric vibrations of the CH_3 group. Finally, the peak at 1040 cm^{-1} , characteristic of esters, was larger and sharper for the acetylated CFs.

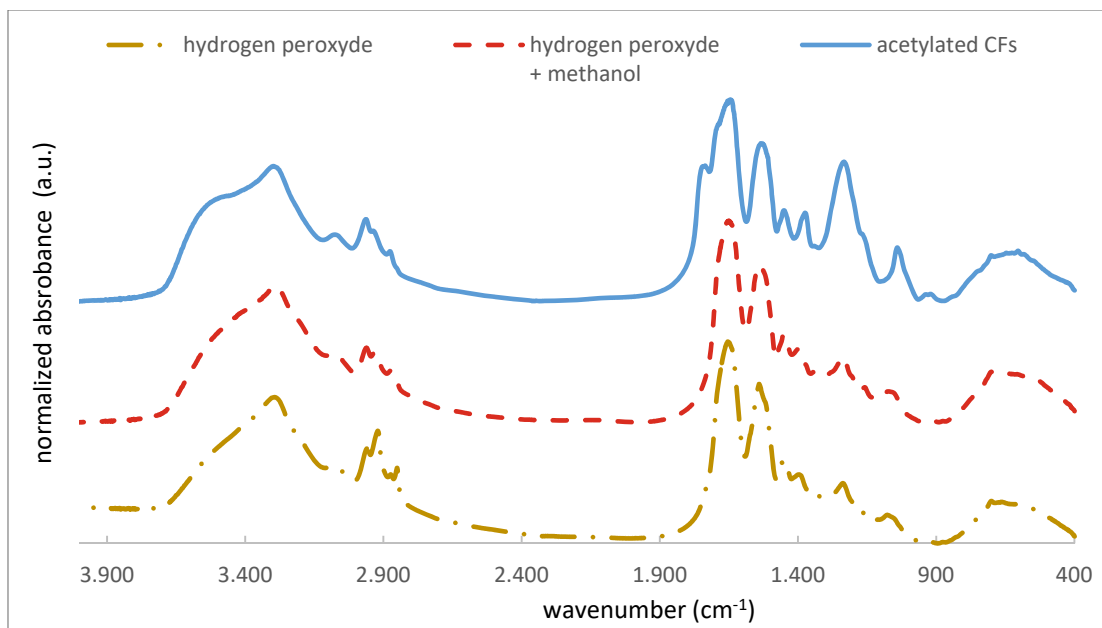


Figure 11. FTIR of washed and acetylated CFs.

As an alternative to the modification of CFs, the effect on the tensile properties caused by the substitution of thermoplastic matrices by the corresponding maleic anhydride based adhesion promoter (MAPE or MAPP) was studied. In this case, the adhesion promoter acted as intermediate simultaneously interacting with the matrix and the CFs. So, the thermoplastic portion (LDPE or PP) of the adhesion promoter can entangle and co-crystallize with the unmodified matrix, while the maleic anhydride groups can bond to the amino acids groups of the keratin fiber. The results obtained for LDPE based biocomposites shown that it was possible to increase the tensile strength of the biocomposites by substitution of pure LDPE matrix with MAPE (**Figure 12**). Moreover, such increase was highly affected by the processing temperature showing a continuous rise up to 180 °C. This limiting value is coherent since it is known that application of temperatures greater than 205 °C for a long time can degrade CFs, worsening the mechanical properties [26]. The main conclusion of this test is that the lower performance provoked by the inclusion of CFs can be balanced by increasing the processing temperature during the mixing up to a limiting temperature. By this strategy, not only the aforementioned lowering is balanced but the final mechanical properties (exemplified by the

main parameter tensile strength) can be improved reaching a value higher than 7.5 MPa compared with 6 MPa of pure LDPE. For this reason, further experiments with MAPP were carried out at the optimal temperature of 180 °C.

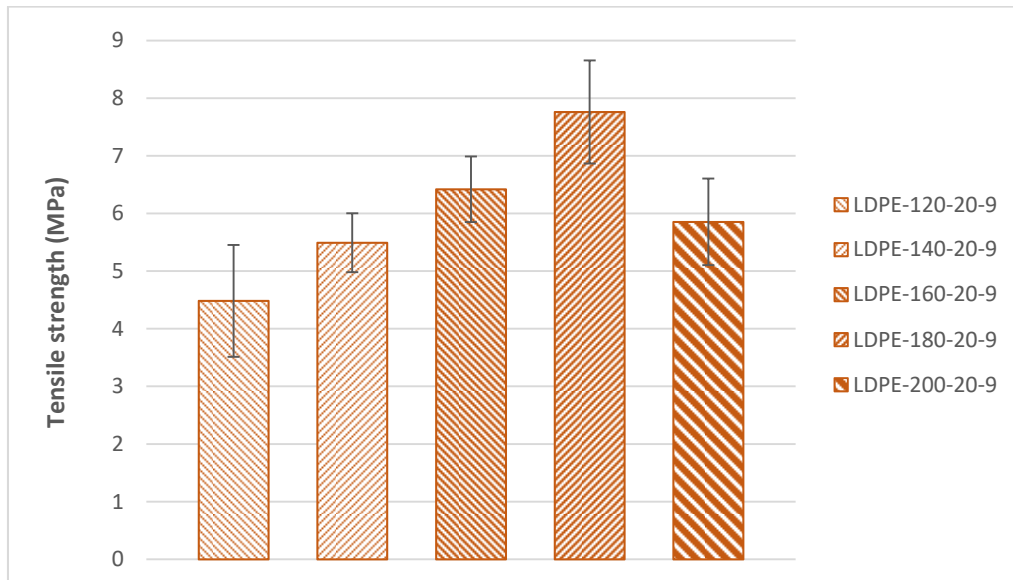


Figure 12. Tensile strength of CFs/LDPE composites obtained using MAPE as adhesion promoter at different temperatures.

It is worth to mention that the increase of the tensile strength with temperature (from 120 to 180 °C) can be correlated using an analogy with the Arrhenius equation. Thus, plotting the logarithm of the evaluation property (tensile strength) versus the reciprocal of the temperature, the points adjust to a straight line indicating a good fitting (**Figure 13**). This situation allows to establish a relationship between the temperature of mixing and the chemical reactions/interactions that occurs when adding the corresponding adhesion promoter to the mixture. Continuing with the analogy, from the linear equation, it was possible to calculate a pseudo activation energy of 5784 J/mol.

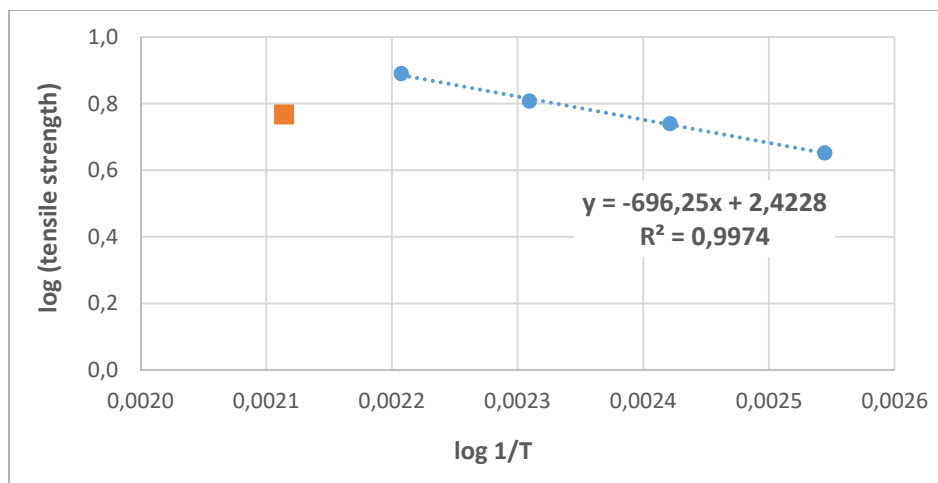


Figure 13. Relationship between the reciprocal of the temperature and the logarithm of the tensile strength.

Conversely, for the case of PP it is not possible to take advantage of increasing the processing temperature since PP cannot be processed neither under 180 °C (melting temperature of the polymer) nor above 205 °C (to avoid CFs degradation). Accordingly, experiments including MAPP were also carried out at 180 °C.

The effect of the incorporation of the corresponding adhesion promoter on macroscopic mechanical properties can be observed in **Figures 14-17** where target properties were represented vs the fraction of maleated polymer included in the polymeric part of the composite

On the one hand, the Young's modulus of biocomposites was not significantly affected when an amount of either MAPP or MAPE was added to the mixture. The observed increase in the modulus (ca. 60 % for LDPE and ca. 20 % for PP) was mainly caused by the presence of CFs that rigidize the composite, regardless the amount of adhesion promoter added. Even in those cases when the total polymeric part consisted of pure maleated polymers, no significant differences were stated.

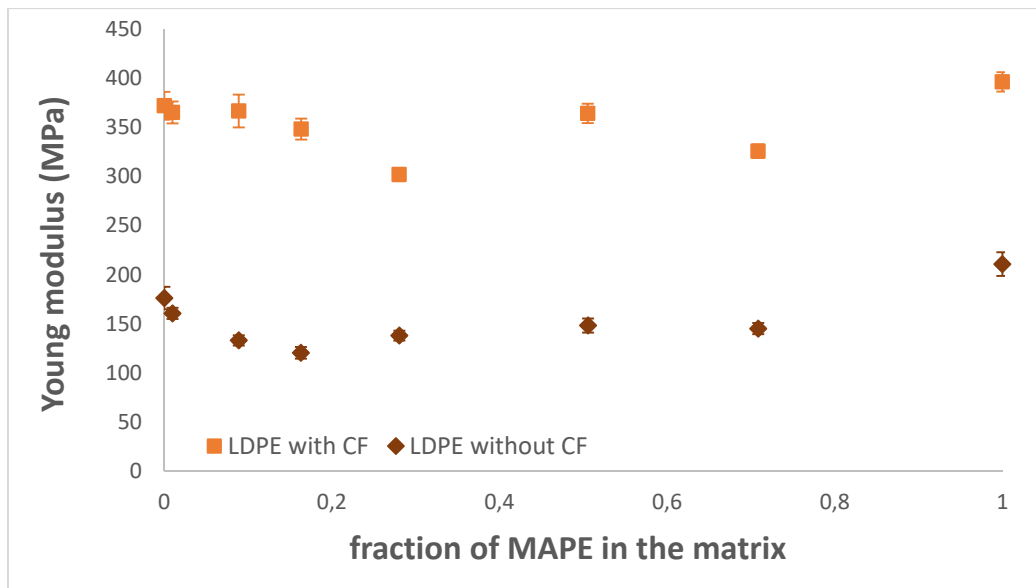


Figure 14. Young's modulus of CFs/LDPE composites resulted from the substitution of the matrix by MAPE at 180 °C.

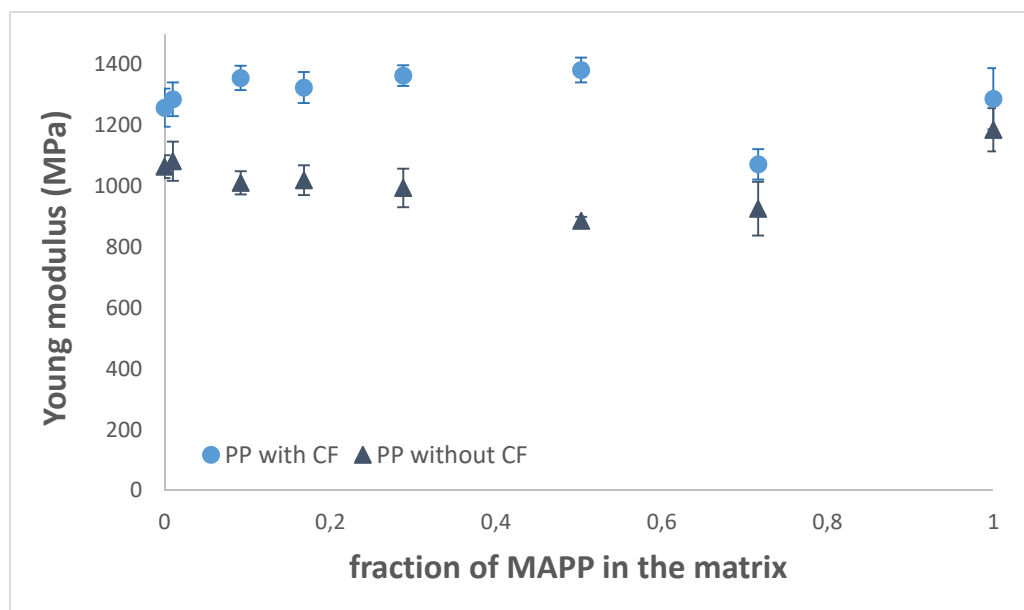


Figure 15. Young's modulus of CFs/PP composites resulting from the substitution of the matrix by MAPP at 180 °C.

On the other hand, the substitution of LDPE matrix by MAPE does produce in all cases an increase of tensile strength (from 6 MPa to >7 MPa) when biocomposites were processed at

180 °C, obtaining the highest values when the fraction of MAPE were either 1 % or 100 % (Figure 16). These results confirmed the improvement of compatibility when MAPE was included in the formulation and, from the technical point of view, it was remarkable that such a low amount of MAPE (1 %) improved so highly the target property, achieving a tensile strength increase of up to 30 %. In general terms, the observed trends of tensile properties agree with the results obtained by Ghani et al. for LDPE/CFs composites, prepared using polyethylene grafted maleic anhydride, which pointed out an improvement of the modulus and tensile strength as well as a decrease of the elongation at break when increasing the CFs concentration up to 10 % wt [27].

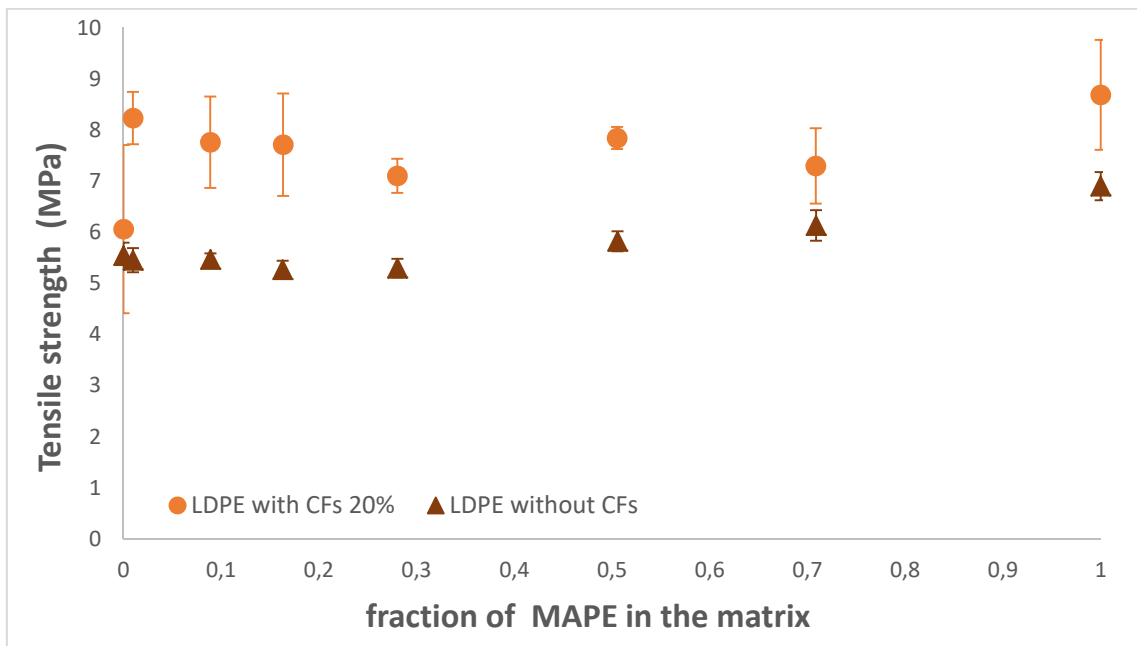


Figure 16. Tensile strength of CFs/LDPE composites resulting from the substitution of the matrix by MAPE at 180 °C.

Regarding to PP based biocomposites, the general behaviour was rather different since the final tensile strength highly depended on the fraction of MAPP and a general trend can not be assumed. First, the incorporation of CFs into pure PP caused a decrease of the tensile strength

but that can be compensated by the addition of a certain amount of MAPP (**Figure 17**). In this sense, a progressive increase of the tensile strength was observed when the substitution of matrix by MAPP was in the range from 1 % to about 30 %. However, the values of tensile strength never exceeded the values obtained for materials prepared without CFs (for 30 % error overlapped). Afterwards, no significant differences were observed between those composite with and without CFs and the tensile strength continuously decreased due to the lower tensile strength of pure MAPP.

Hence, the incorporation of about a 30 % of MAPP allowed to overcome the decrease of tensile strength caused by the addition of CFs but a further improvement was not achieved.

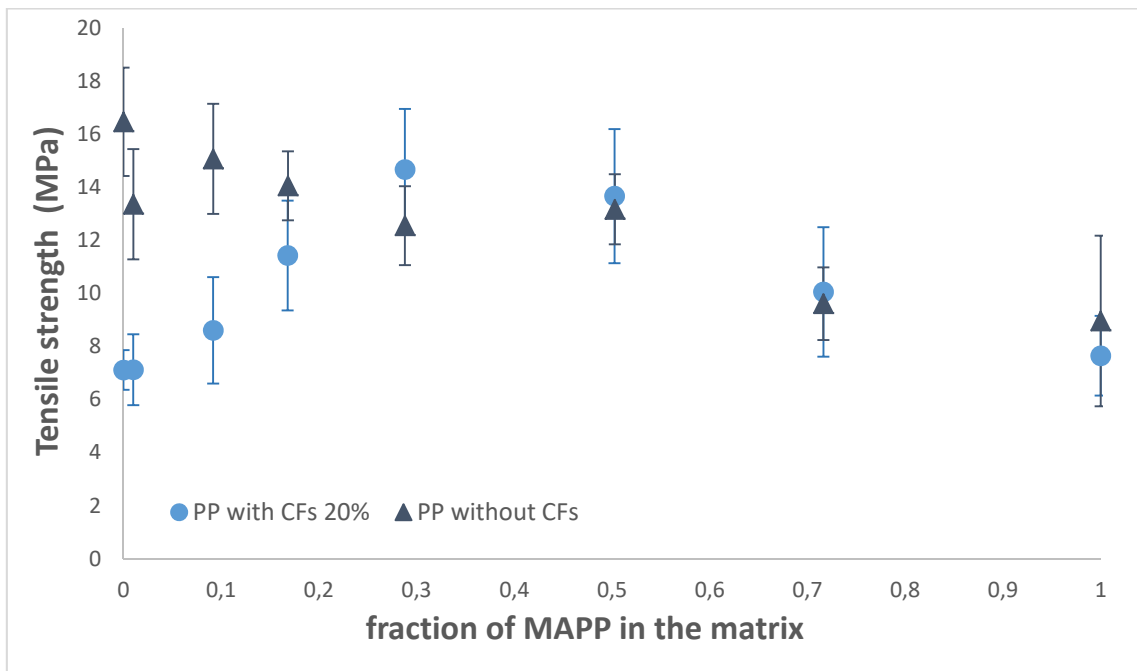


Figure 17. Tensile strength of CFs/PP composites resulting from the substitution of the matrix by MAPP at 180 °C.

The aforementioned results indicated that the use of MAPE and MAPP improved the compatibility between the CFs and the matrices up to certain limits: 1) for LDPE the increase

due to MAPE was limited to a 25 % of tensile strength and 2) for the best scenario of PP the use of MAPP only overcame the performance decrease due to the inclusion of CFs.

In order to provide the benchmarking of composites made of either LDPE/CFs or PP/CFs against other typical materials, **Figure 18** shows the global picture of common materials in terms of Young's modulus and tensile strength. Data for constructing the plot were obtained from CES-EduPack database, avoiding estimated records [28], and from references of other authors [25,27,29-35]. As it can be seen, the experimental value for both LDPE/CFs and PP/CFs composites from this work exhibit higher performance than the pure polymer but lower performance than other natural fibre reinforced composites obtained by combination of either flax, hemp, jute or hardwood with PP or High Density Polyethylene (HDPE) [35]. Also, it is worth to note that Modulus and tensile strength of the LDPE/CFs material are close to the values reported by other authors although they are slightly lower than some of the published ones [25,27]. The most interesting fact might be that the PP/CFs material behaves better than the composites obtained using PP and just the quill fraction of feathers [29]. In addition, CFs based materials behaves better than most of the elastomeric materials and rigid foams but worse than most of the common technical polymers and reinforced composites.

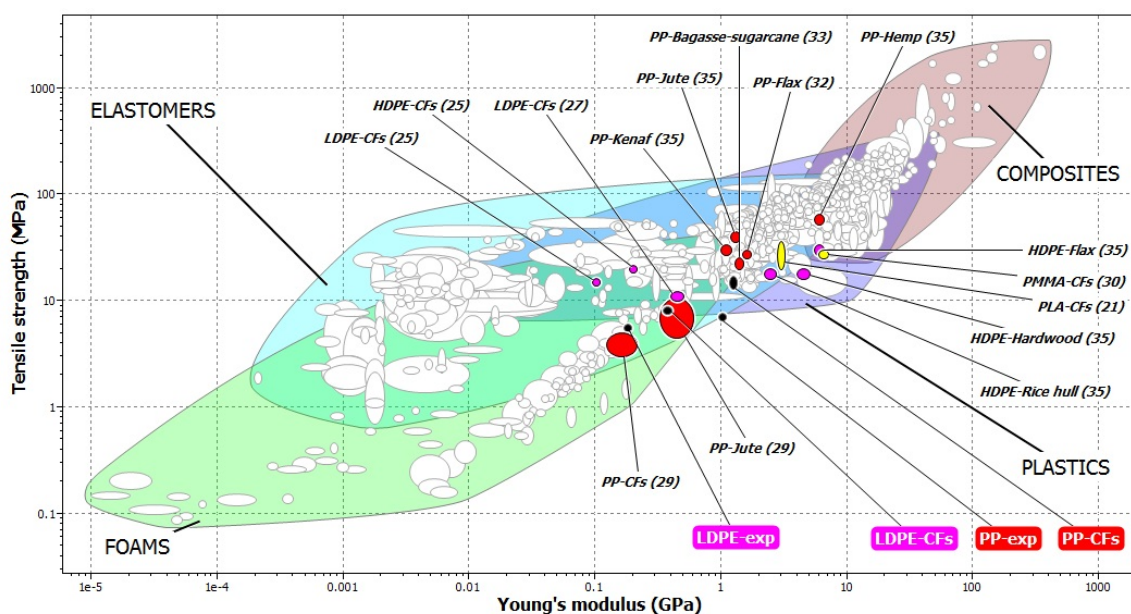


Figure 18. Comparison chart of the target properties (tensile strength and Young's modulus) for the developed materials (LDPE-CFs, PP-CFs), the original polymers (LDPE-exp, PP-exp) and other reference materials from the literature and the CES-EduPack database. PLA stands for Poly(lactic acid) and PMMA stands for Poly(methyl methacrylate).

When analysing the obtained results in the regard of complementary techniques, a weak interaction was observed by SEM analyses of the fracture surface (**Figure 19**), which confirmed that less fibres on the surface because they are not separated from the matrix. By FTIR spectra no significant changes in chemical structure were noticed, mainly due to the overlapping of signals and the broad peaks due to CFs. (**Figure 20**). Accordingly, the reaction between CFs and MAPE/MAPP (**Figure 3**) can not be proved nor discarded.

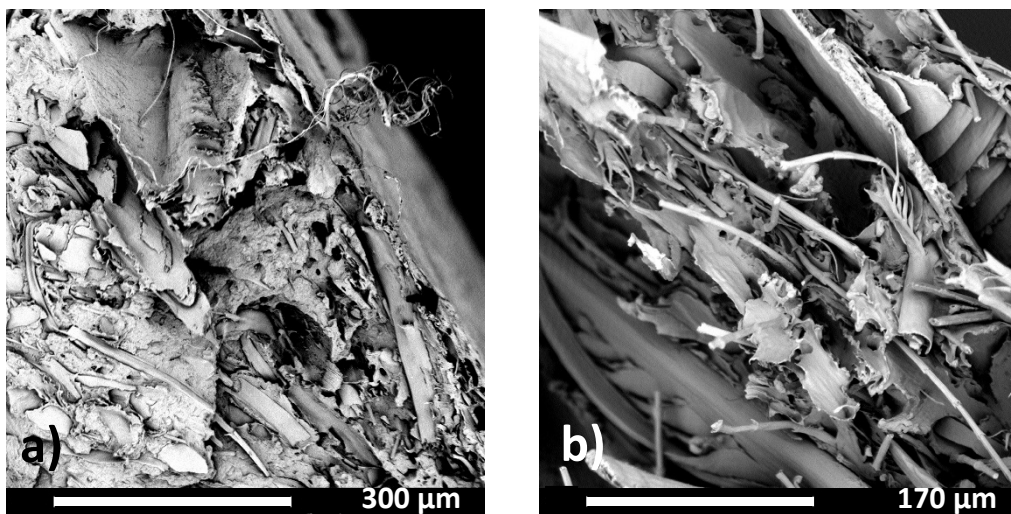


Figure 19. SEM images of fracture surfaces biocomposites: a) LDPE + 20 % CFs + 10 % MAPE, b) PP + 20 % CF + 10 % MAPP.

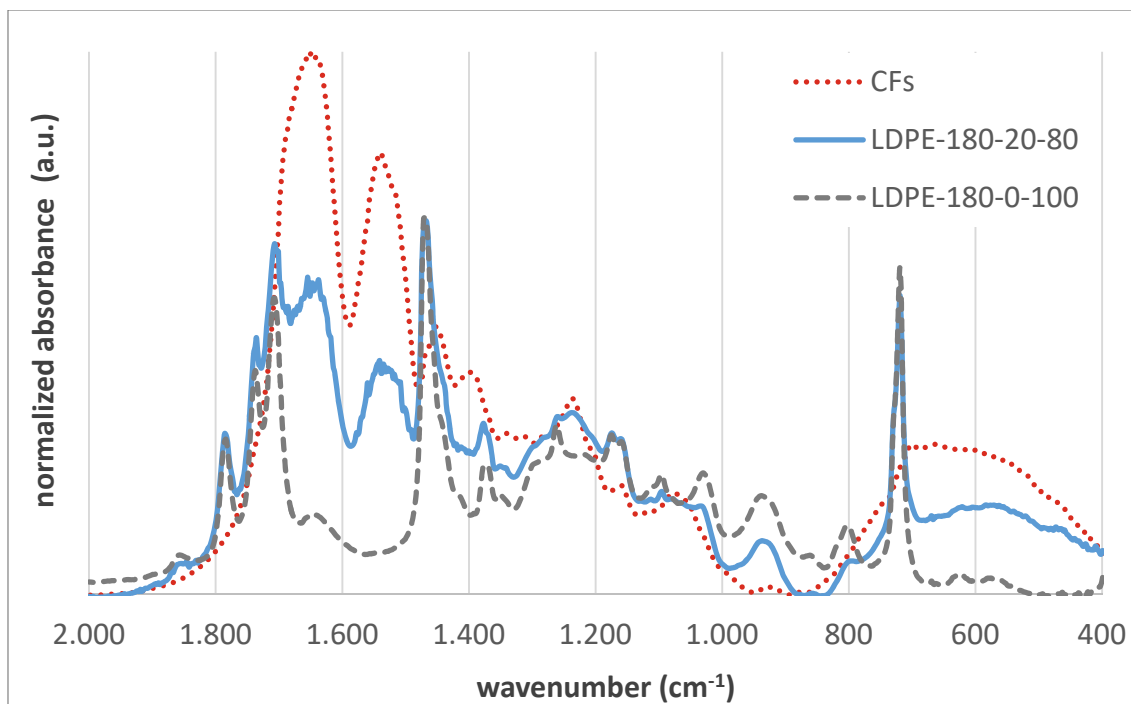


Figure 20. FTIR spectra of CFs, MAPE and composite prepared by mixing MAPE and CFs at a temperature of 180 °C.

So as to provide a general overview of the manufactured composites, density and dimension stability (measured as water absorption) were also researched. The density of the biocomposites is shown in **Figure 21** and the incorporation of CFs to the mixture did not cause any significant increase of their density with values around 0.92 g/cm^3 , regardless the amount of adhesion promoter included (data plotted limited to 20 and 50 % of MAPE or MAPP). Consequently, these results confirm the possibility to obtain light materials when mixing CFs with thermoplastic matrices. On the contrary, dimensional stability worsened when CFs were added since the absorption of water was much higher for those composites containing CFs, reaching values of 1 % (**Figure 22**), 10-fold higher than the absorption observed in pure polymers.

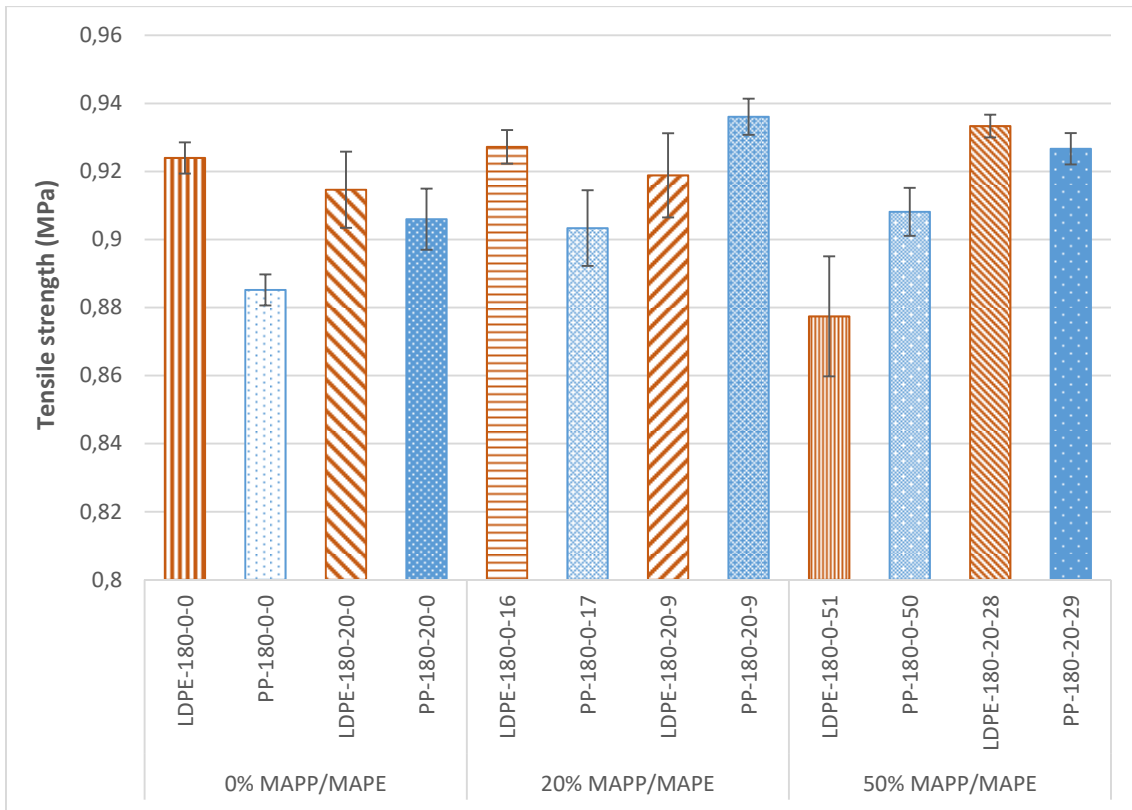


Figure 21. Density of the CFs thermoplastic composites.

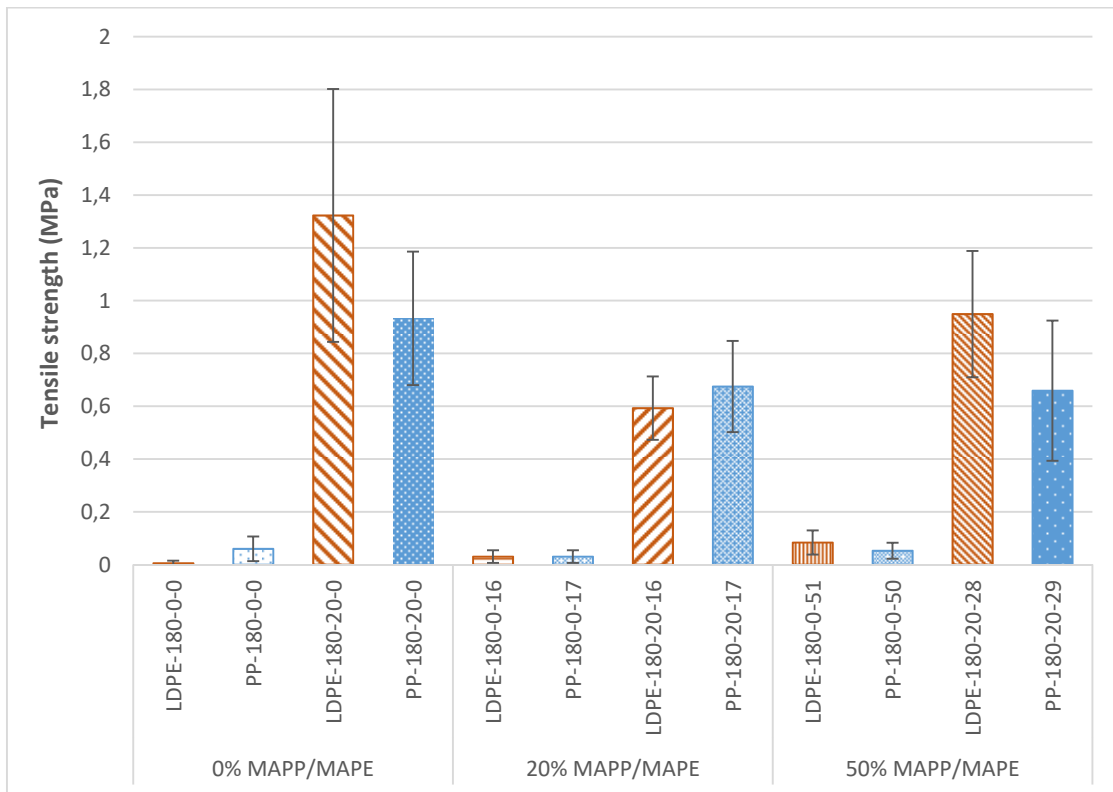


Figure 22. Water absorption of the CFs thermoplastic composites.

4. Conclusions

Preparation of biocomposites made of LDPE or PP and including CFs as a filler has been postulated as a technical solution to valorize CFs waste. It was demonstrated that tensile strength of the matrices suffers a significant decrease when CFs (either washed or chemically modified) were added. Consequently, the first strategy consisting in acetylation or silanization of CFs was discarded and the use of adhesion promoters such as MAPP and MAPE was proposed. This last strategy was crucial to balance the lower performance of composites as by using maleated polymers it was possible to maintain or even improve the mechanical properties of the resulted composites. In this sense, processing LDPE with MAPE ($\geq 1\%$) at 180 °C improved a 30 % the tensile strength, whereas for the PP biocomposite the addition of CFs maintained the tensile strength if the ratio of MAPP to matrix is higher than ca. 0.5. When this ratio was reached, the composite containing CFs perform as those without CFs. Summing up, of all the strategies studied to enhance the compatibility between CFs and thermoplastic matrices, the use of adhesion promoters is the best compared to silanization and acetylation. In spite of the results obtained, SEM and FT-IR results do not showed any remarkable interaction between fibres and the matrix. In addition, the use of CFs in composites allowed obtaining lightweight materials although some worsening of their stability was observed.

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