USE OF CHICKEN FEATHERS WASTE FOR THE FABRICATION OF COMPOSITE MATERIALS

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Abstract
Chicken feathers (CFs), mainly discarded nowadays, are an alternative reinforcement to be applied in the preparation of composite materials (CMs). The effect of different sanitizing methods on the properties of both CFs and the corresponding CMs has been studied. Some characteristic parameters such as density have been found to be dependent on the treatment that CFs endure, whereas the mechanical properties of the CMs made of thermoplastics matrices (e.g. polypropylene and high density polyethylene) were only slightly affected by the treatment. The introduction of CFs decreased the tensile strength of the CMs compared with the neat polymers while other parameters (e.g. Young's modulus) were essentially unaffected.

1 Introduction
During the last years, researchers have focused their efforts in the fabrication of composite materials (CMs) made of thermoplastics and natural fibres such as wood, flax, hemp, jute or bamboo for their application in several industrial fields including, for example, the automotive sector [1,2] These natural fibres offer many advantages such as good strength properties, low cost, low density, high toughness, good thermal properties, non-abrasive behaviour and biodegradability [3]. Moreover, the use of these fibres for CMs has other intrinsic advantages including the reduction of synthetic polymers and, therefore, the decrease of petroleum consumption. However, cellulose fibres, which are the most typical natural fibres, also show some technical disadvantages being their incompatibility with hydrophobic polymer matrices a crucial issue [3]. In addition, the use of farmland for the cultivation of such fibres, which can compete with food production, is not free of public concern [4].
Having in mind the necessary compromise between the intensification of renewable resources use and the assurance of economical development, this communication report the use of a different type of natural fibres for the manufacturing of composites and biocomposite materials: chicken feathers [5,6] (CFs), which are a waste derived from the poultry industry.
CFs weight corresponds to 5-7% of the total weight of mature chickens (about 90g per 1 kg of chicken meat) [7,8]. Combining this datum with the rise chicken production around the world [9] (which achieved ca. 80,000,000 metric tons in 2010), it is clear that CFs valorisation as filler or reinforcement in CMs could be a better option than the current uses of feathers, which are nowadays disposed, incinerated or chemically hydrolysed to obtain pet food [10]. Similar

approaches have already been taken into account combining feather fibres with several polymers such as poly(methyl methacrylate) [3], epoxidized soybean oil [11], high-density polyethylene (HDPE) [12] or polypropylene (PP) [13], among others.
Chemically, CFs are made of about 95% keratin, which is an insoluble structural protein common in mammalian and avian species and it is found in claws, hoofs, horns, nails, hair, wool and, evidently, feathers [3,14,15]. Yet, even if keratin is a quite stable protein, CFs are biodegradable, so it is important to understand that CFs coming from the slaughterhouse must be sanitized/cleaned before their use as technical material. There are several procedures to carry out this sanitization/cleaning [16,17] (e.g. washing with surfactant, extraction with solvent…) and the effects of such treatments on the structure and properties of CFs need to be known. So the first step for properly valorising CFs is the accurate determination of CFs physicochemical properties in order to predict their behaviour and applicability. In this sense, in this work, several physicochemical parameters such as density, moisture regain and chemical stability have been evaluated for both untreated and treated CFs. In addition, mechanical tensile parameters of CFs-based CMs have been determined.

2 Materials and testing methods

2.1 Feather cleaning procedures.

Untreated CFs were kindly supplied by a waste management Spanish company. Four different treatments were carried out at laboratory scale:

- Ethanol method, consisting in a simple extraction with ethanol (96% v/v).
- Peroxide method, an oxidative treatment with an aqueous solution of H_2O_2 3300 ppm.
- Surfactant method, an aqueous washing treatment with a surfactant (Tetranyl BC-80 from Kao Chemical at a concentration of 0,7% v/v).
- Autoclave, a pressurized steam treatment at 135ºC during 20 minutes.

For the three first treatments, 2,5 g of untreated CFs were immersed in 100 ml of the corresponding solution (40:1 ratio) in closed vessels and located in a Linitest Original Hanau equipment, where they were agitated at constant speed during 1 h, at room temperature. Afterwards, CFs were filtered through a Büchner funnel and rinsed with 500 ml of distilled water. For the autoclave treatment, 150-240 g of untreated CFs were sterilized in an autoclave filled with 8.5 litres of distilled water. Finally, all the treated CFs where dried in oven during 48 hours at 60ºC before weighting. Several replicates were performed for each treatment method and average yields were calculated. The yield percentage (Y%) of each treatment was calculated by **Equation 1**, where w_0 is the initial mass of untreated CFs and w_i is the mass of treated CFs.

$$Y\% = 100 \cdot \frac{w_i}{w_0} \qquad (1)$$

2.2 Feathers classification

As a representative sample, about 10 g of CFs treated by the Autoclave method were measured and separated in different fractions depending on their length. Each fraction was weighted and the weight percentage of each fraction was calculated.

2.3 Microscopic characterization

CFs were observed by both Optical (Jenaval - Carl Zeiss) and Scanning Electron Microscopes (SEM) (JEOL-5610). In the last case, samples were gold-sputtered before analysis.

2.4 Density measurement

Liquid pycnometer method [18] was followed to determine the density of treated whole feathers as well as those of their separated parts: fibres and rachis. CCl_4 was used as solvent and at least 3 replicates of each type of sample were analysed.

2.5 Water uptake

CFs were dried at 105 ºC during 4 hours and weighted (w_d) before being immersed in distilled water at different temperatures (30, 50 and 70ºC). Then, wet CFs were centrifuged for 5 min and weighted again (w_w). Water uptake (WU%) was calculated according to **Equation 2**:

$$WU\% = 100 \cdot \left(\frac{w_w - w_d}{w_d} \right) \quad (2)$$

2.6 Moisture regain of untreated CFs

Untreated CFs were first stored in a desiccator containing P_2O_5, until total drying (w_D). Then, they were stored in a desiccator with a saturated solution of NH_4NO_3, which provides an atmosphere of 65% relative humidity [19] (HR), and weighted again ($w_{65\%}$). Moisture regain (MR%) was calculated as indicated by **Equation 3** [20]:

$$MR\% = 100 \cdot \left(\frac{w_{65\%} - w_D}{w_D} \right) \quad (3)$$

2.7 FTIR spectra acquisition

About 0.1 mg of grinded CFs (either whole feathers or their separated parts) were mixed with 300 mg of KBr to prepare solid pellets. Spectra in the range 400-4000 cm^{-1} were recorded by a Fourier Transform Infrared (FTIR) spectrophotometer Nicolett 510 M.

2.8 Mechanical resistance of feathers

Individual fibres were separated from CFs and mechanical properties (tensile force and elongation at maximum load) were tested with an universal tensile test machine (USTER Tensokid, Zwick-Roell). 25 replicates were performed for each fibre type.

2.9 CFs-based CMs fabrication and characterisation

CFs were first dried at 60ºC for 48 hours and kept under dry atmosphere and grinded (by using a Cutting Mill SM 100 (RETSCH). Composite specimens were obtained by mixing the previously ground and dried CFs mixing (up to 20% v/v) with HDPE (Alcudia 4810-B1, Repsol) and PP (Isplen PP-099-K2M, Repsol) matrices in a Brabender W50EHTPL mixer (Brabender GmbH & Co) heated at 160 ºC and 190 ºC for HDPE and PP, respectively. Mixing speed was fixed at 50 rpm. Mixing was performed for 6 minutes. Blends were consolidated at 100 kN and 180ºC (PP) and 160ºC (HDPE) for 3 minutes in a Collin Mod. P 200E hot plates press (Dr. Collin GmbH) forming square plates, measuring 184 x 184 x 2,2 mm^3. Control samples made of pure HDPE or PP were used as references.

Test samples were properly shaped according to the standard specifications to perform tensile test measurements and tensile tests were carried out in an Instron 3366 (Instron) universal machine [21,22]. Speed of the test was set at 20mm/min. From the stress-stain curves, Young's modulus, tensile strength and elongation at break were calculated using appropriated software. Five replicate specimens were analysed, and their standard deviation was calculated.

3 Results

3.1 Pretreatment yields and CFs classification

The yields for the four cleaning procedures tested are reported in **Table 1**. As it observed, about 40% of the initial mass of CFs is preserved after three of the treatments. For Autoclave

treatment, a higher yield was obtained. However, when classifying autoclave treated samples about a 4% of total weight were residues (e.g. dust, soluble mater) would have been removed by any of the other liquid phase methods. The CFs classification also showed that the 9.5% of weight corresponded to CFs longer than 10 cm (a quite inappropriate size for CMs fabrication without grinding) whereas about a 22% were shorter than 3 cm. The rest (64.3%) corresponded to CFs between 3 and 10 cm long.

Pre-treatment	Yield (%)
Ethanol	40 ± 4
Peroxide	41.2 ± 1.8
Surfactant	39.4 ± 1.7
Autoclave	47.7 ± 1.3

Table 1. Yield for the different treatment methods tested. Error corresponds to standard deviation of 3 replicates.

3.2 Density

Density measurement of whole feathers and separated parts (see **Figure 1**) showed clear differences between fibre and quill fractions for each treatment and also for untreated CFs. The found values are close to a two-fold ratio. Whole feathers density is closer to fibre density in almost all cases but values for untreated CFs show a notably higher dispersion due to the fact that they are inhomogeneously soiled. On the contrary, no significant differences were found for CFs coming from different treatments, regardless of the considered fraction (fibre or quill). Fibre density values were lower than 1 g/cm^3 except for untreated and autoclave CFs, which is a lower value compared with the density of cellulosic fibres [11]. In general terms, the experimentally found values for CFs fibres are in agreement with those mostly reported in the literature 0.8 g/cm^3 [11] and 0.89 g/cm^3 [5,12,13].

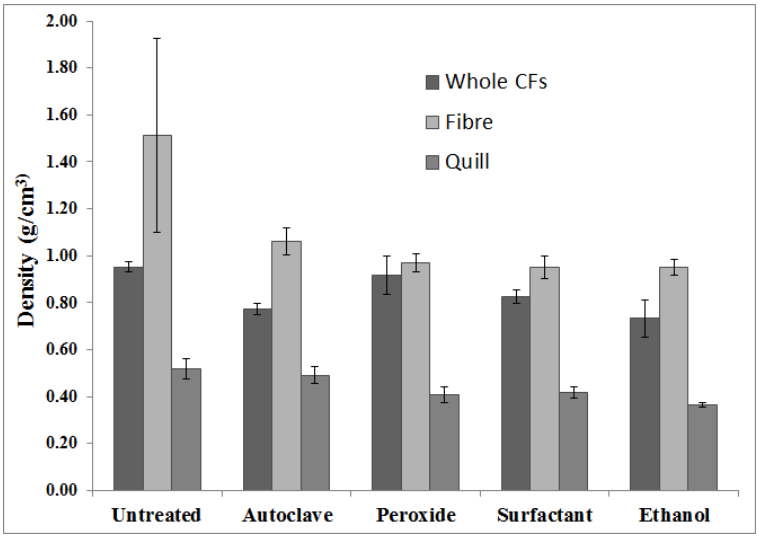

Figure 1. Density values for whole feathers and separated parts for treated and untreated CFs.

In order to explain the differences between the densities of fibres and quill, it is noteworthy to mention that both their chemical composition and their morphology are different. Like this, CFs fibres consist of a higher concentration of α-helices whereas the quill or rachis is mainly composed by ß-sheets and/or disordered structures [14]. SEM micrograph of the cross section of a quill (**Figure 2**) shows an open cell porous structure, which, very probably, is responsible for the low-density values of this part. On the other hand, fibre image by optical microscopy allows the identification of typical feather barbs, barbules and hooklets [5].

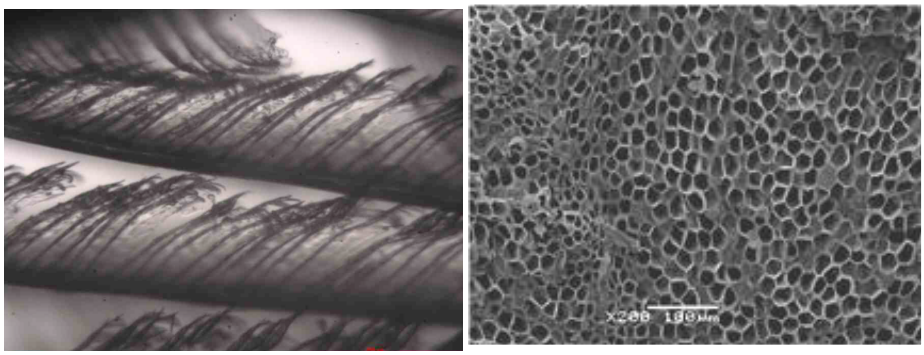

Figure 2. Left: Optical microscopy image of CFs fibres. Right: SEM image of a quill cross-section.

3.3 Moisture regain and water retention

The moisture content of CFs is an important factor that can influence their weight and mechanical properties [2]. Chicken processing methods include CFs wetting in hot water before plucking, so CFs from the abattoir are wet. Reported values (10-15%) [19,23,24] were slightly lower than the experimental data obtained at 65% HR for untreated CFs.: 16.5%. On the other hand, very similar values for water retention were found for all samples regardless the water temperature and the cleaning method. The average value was: 41.15 ± 0.02%.

3.4 Chemical composition by FTIR

FTIR spectra of treated and untreated CFs are shown in **Figure 3**, avoiding overlapping. The typical signals for keratin corresponding to peptide bonds (C=O at 1650 cm^{-1}, N-H and N-C=O_{st} at 1540 cm^{-1}, C-N_{st} at 1240 cm^{-1}) can be observed in all the spectra together with signals corresponding to OH groups from water or radical groups of amino acids (3200-3650 cm^{-1}) [25]. No significant differences in these signals can be observed among the samples.

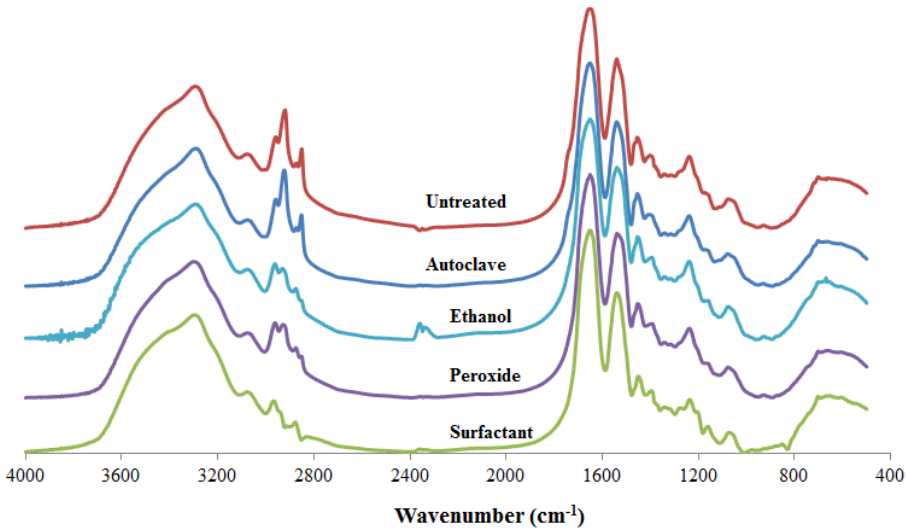

Figure 3. Comparison of FTIR spectra of natural and treated CFs.

Though, in **Figure 4** (left), clear differences can be observed for alkyl chains signals (C-H_{st}, CH_{2d}, CH_3) at to different regions: 2800-3000 cm^{-1} and 1300-1500 cm^{-1}. These signals can be attributed to alkyl chains of both radical groups of amino acids and, more probably, to natural fats. The last hypothesis was confirmed by the comparison of the a FTIR spectrum of CFs fats extract (obtained by Soxhlet extraction) with the subtraction of the FTIR spectrum corresponding to CFs cleaned by surfactant to that of untreated CFs (**Figure 4**, right). According to this, the treatment with surfactant is able to remove fats from CFs at a higher

extend, whereas the autoclave method did not significantly remove fats as the peaks for autoclaved samples coincide with those of untreated feathers.

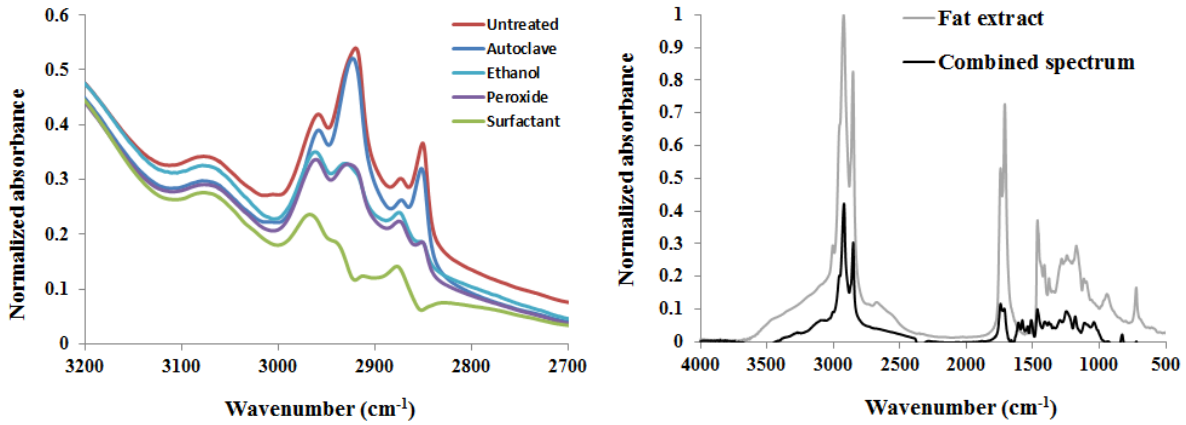

Figure 4. Left: FTIR spectra in the 2700-3200 cm^{-1} range corresponding to alkyl chains. Right: FITR spectrum of extracted fats and combined spectrum (untreated CFs minus CFs washed with surfactant).

It is worth to mention that the FTIR spectra of separated parts of feathers showed very similar peaks and it was not possible to distinguish between α-helix and ß-sheet structures. Raman spectroscopy has been reported to be a better analysis technique for this purpose [14].

3.5 Mechanical tensile properties of feathers

Tensile force at maximum load values were found to be very similar (in the range of 28 to 34 cN) for all the treatments. Elongation at maximum load was 0.3-0.5 mm for samples treated by autoclave and surfactant methods and close to 1 mm for those processed by ethanol and peroxide. Such differences are not easy to explain as peroxide cleaning is, *a priori*, a more aggressive cleaning method than washing with surfactant so the first was more likely to be capable to weaken the resistance of CFs fibres.

3.6 CFs-based CMs mechanical characterization

The obtained results regarding the mechanical properties of the CFs-based CMs prepared with CFs cleaned and sanitized by different methods can be seen in **Figures 5**. The most relevant conclusion of these plots is that, in rough numbers, all the treatments provide similar values for Young's modulus, tensile strength at maximum load and elongation at break, although with some small differences. Secondly, when comparing the properties of specimens made of neat polymer with those containing a 20% (v/v) of CFs, it is found that the performance of pure polymer samples is better for all the parameters excluding the Young's modulus. Thus, the inclusion of CFs globally reduces the tensile properties of the materials being elongation at break the parameter that changes more dramatically. Note that Young's modulus parameter is very often not correlated with interfacial interactions, so it is expected to be less influenced by the addition of filler. Slight differences can be observed between CMs made of PP or HDPE so one may conclude that there is not a better compatibility of CFs with any of these thermoplastics. Only the tensile strength at maximum load seems to be less decreased in the case of HDPE CMs. Taking into account the exact values of each parameter, and having in mind that differences are not outstanding, it is possible to say that the mechanical resistance decrease for the treatment methods following this sequence: ethanol, autoclave, surfactant and peroxide. Accordingly, ethanol-cleaning method would be the preferred process although its industrial application would imply some safety risks.

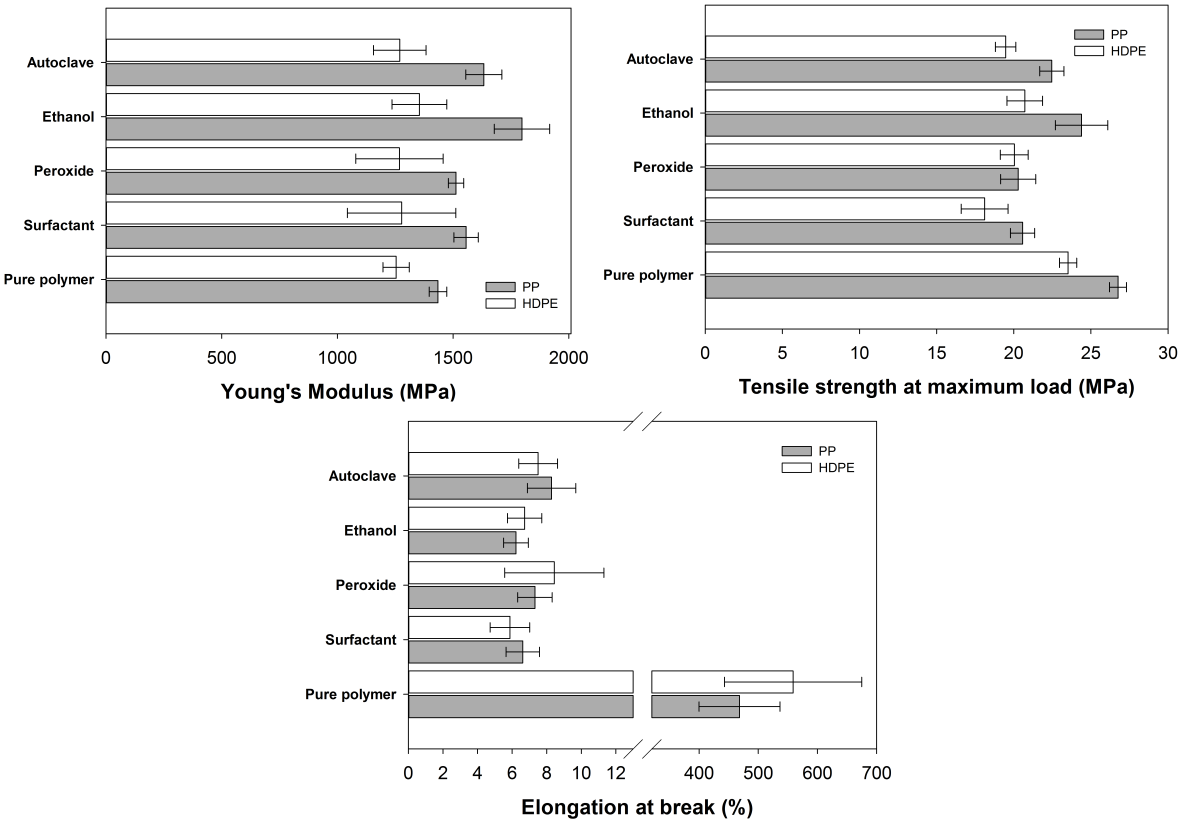

Figure 5. Comparison of mechanical properties for the different CFs-based CMs and neat polymers.

4 Conclusions

The density of whole CFs fibres was found to be lower than 1 g/cm^3 except for untreated CFs and lower than 0.81 g/cm^3 for CFs cleaned by ethanol or autoclaved. These values predict a density reduction in CFs-bases CMs compared with those reinforced with cellulosic fibres. More interesting is the two-fold ratio found for the density of fibres and quill fractions. On the other hand, thanks to FTIR it has been proved that cleaning procedures (except Autoclave) highly remove fatty acids form CFs. In this sense, the most effective treatment was washing with surfactant, followed by ethanol and peroxide treatments. Water retention seems to not be affected either by the treatment method used nor the temperature and pointed an average value of about 40%, much higher than the value for moisture regain of untreated CFs at 65% RH. Regarding the mechanical properties of CFs-CMs, most of the characteristic parameters are reduced by the addition of a 20% v/v of CFs.

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