A NEW NATURAL FIBER: TOQUILLLA STRAW A POTENTIAL REINFORCEMENT IN THERMOPLASTIC POLYMER COMPOSITES

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Toquilla straw (*Carludovica palmata*) obtained from the Manabí province in Ecuador has been used traditionally for weaving the Panama hat. Due to its importance and high disposability as a renewable source and the methodological characterization which is required to understand its physical and chemical properties. To this end, sections of treated and untreated specimens were studied to analyze the mechanical, thermal, spectral and morphological properties. From thermal and mechanical analysis's that were carried out on the Toquilla straw fibers revealed a temperature onset of about 230°C before the degradation and Young's modulus as well as stress in the range of natural fibers used as reinforcement in thermoplastic polymer composites. Possible changes in their composition and structure were monitored using Fourier Transform Infrared spectroscopy as well as the morphology by means of a scanning electron microscope.

Keywords: natural fibers, reinforcement polymer composites, mechanical properties

INTRODUCTION

Nowadays, agriculture is playing an important role in the bio-based economy, providing feedstocks for the production of liquid fuels, chemicals and advanced materials (FAO 2013), such as natural fiber composites for industry. The mechanical properties of several natural fibers (Delgado *et al.*, 2012; Gupta *et al.*, 2012) or hybrid materials (Noorunnisa Khanam *et al.*, 2010) are attracting much attention to produce composite materials in the automotive industry (Bledzki *et al.*, 2006), aeronautical and civil buildings (Nguyen *et al.*, 2009). Natural fibers have the advantages of low cost, low density, biodegrability, abundance and cause less environmental impacts than man-made fibers. Vegetable fibers are classified according to their origin as well as the part of the plant (i.e., leaf, seed, bast, fruit, grass and stalk) and their properties which can be affected by factors such as climate, maturity, harvesting or physical or chemical treatments (Kalia *et al.*, 2009).

Carludovica palmata grows in the rainforest ranging from Guatemala to Bolivia and is considered a member of the *Cyclanthaceae* family and is a close relative to the Palmae (*Arecaceae*) family (Lopez *et al.*, 2008). This plant is sometimes referred to as Jipijapa or Montecristi when made into Panama hats to remember the names of villages in Ecuador where the finest hats are made. Other names used to refer to this plant are iraca, lucaina, lucua, palmiche, cestillo, nacuma, rabihorcado, murrapo, alagua and rampira to refer to this plant (Solano, 1997).

In this study, we report the mechanical, thermal, spectral and morphological characterization of the *Carludovica palmata* or Toquilla straw fibers. These fibers are the fundamental element of the most traditional Ecuadorian product recently inscribed in the Representative List of the Intangible Cultural Heritage of Humanity and widely known as the Panama Hat (UNESCO, 2012). For a better understanding and use of the treated natural fibers, in particular toquilla straw, information on the different properties is also required. An attempt to describe the changes occurring in the structure of toquilla straw fiber due to this process is presented. Treated and untreated fibers were characterized by using mechanical testing, differential scanning calorimeter, thermogravimetric analysis, infrared spectroscopy and scanning electron microscopy.

METHODS

Bundles of Toquilla straw were obtained from Manabí province in Ecuador with and without any pre-sizing, chemical and physical treatment for this study. Two kinds of specimens were studied. The first one, treated Toquilla straw following the traditional process in which the strands are boiled in a water bath for 10 h and then dried under the sun. In addition, the bleaching process with sulfur vapors to whiten the plant was carried out. Toquilla straw was arranged in fiber bundles as reported in another cases (i.e., hemp, jute, arundo) (Elkhaoulani *et al.*, 2013; Fiore *et al.*, 2014) the main chemical components being cellulose, hemicelluloses, lignin and pectin which make the morphological structure of the plant fibers. In spite of the different diameters of the Toquilla straw for three different sections, an estimation of area and diameters of about 0.61 mm^2 and 400μm was a possible measure. The apparent density of the fiber (in bulk) of 1.06 g/cm^3 was estimated using hexane (ρ=0.760 g/cm^3) as a solvent under the Archimedes method.

Weights of a bundle of strands and the apparent density (in bulk) were measured in air and solvent by a procedure detailed below (Mwaikambo and Ansell, 2001).

$$\rho_A = \frac{\rho_s \cdot Wf_a}{Wf_a - Wf_s} \qquad (1)$$

where ρ_s is the density of hexane; Wf_a and Wf_s are the weights of the strands in air and hexane, respectively.

EXPERIMENTAL

The universal machine (Instron-5582) at a constant speed of 3mm/s was employed for tensile strength measurements, according to ASTM C (1557-03) standard test. All samples for tensile strength testing were selected from the same stem.

Toquilla straw specimens were obtained by sectioning in three different parts of the leaf for mechanical characterization, as shown in figure 1a. The first section is named as the basis, the second one the central section and lastly a final section of the leaf. Afterwards, ten samples from each section of the raw single straw each having the length (100mm) and the treated straw were selected for testing of their elongation at break, Young's modulus, stress and thermal properties. Morphology of the Toquilla straw is shown in figure1b which revealed a spiral design. The fiber-cells with a polygonal shape were observed with a light microscope and SEM experiments showing variability in diameter in the cross section area images. It is shown along the specimen the morphology is like other natural fibers.

The thermal stability of raw and treated Toquilla straw was investigated within a dynamic range from 25°C to 900°C and rate of 10°C/min with a purging N_2 gas stream of 200mL/min. The thermo gravimetric analyzer (TGA/SDTA 851 Toledo Mettler, Columbus, OH) and the controlled environment with an inert gas (Ar, 50mL) were employed. The thermograms were recorded using 7.03mg and 4.41mg of treated and untreated specimens, respectively.

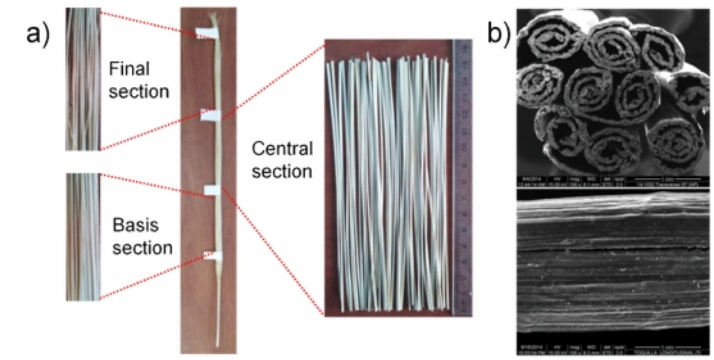

Figure 1. Toquilla straw a) corresponding to basis, central and final sections and several strands from the central section of experiments are shown. (b) Morphology of the Toquilla straw for cross section and longitudinal was recorded by SEM

Infrared spectroscopy experiments were performed using FTIR spectrometer (Perkin Elmer PC 1600). A series of 20 scans were collected for each measurement over the 4000 to 400 cm^{-1} spectral range and 4cm^{-1} of resolution.

The morphology of the central section of Toquilla straw was investigated by a scanning electron microscope (SEM, FEI-Quanta Inspect). Before SEM analysis, samples were coated with a thin layer of metallic platinum using a sputter coater (SC7620 sputter, Emitech). Moreover, cross-section areas of the Toquilla straw and thickness less than 5 μm and longitudinal sectioning were prepared by means of a Micron HM 360 Microtome for viewing with a light microscope (Micros Austria, Crocus 2).

RESULTS AND DISCUSION

Table 1. Mechanical properties of the Toquilla straw for three different sections using the Weibull distribution

Sections	Parameters	Treated fiber	Standard error	Untreated fiber	Standard error
Final	Tensile stress [MPa]	20.69	2.31	73.5	5.28
	Young Mod. [GPa]	3.43	0.40	3.09	0.08
Central	Tensile stress [MPa]	134.4	10.1	127.9	2.55
	Young Mod. [GPa]	4.79	0.11	4.06	0.07
Basis	Tensile stress [MPa]	47.13	4.65	131.8	9.28
	Young Mod. [GPa]	3.95	0.21	4.30	0.01

Young's modulus of about 4.1±0.7GPa and 3.8±0.6GPa were estimated for sixty samples both treated and untreated fibers, respectively. By comparing the tensile modulus and tensile strength values of raw fibers with treated ones, it revealed that the sulfur treatment reduced the mechanical properties of sectioned zones named basis and final by almost 30% (see Table 1). Untreated and treated specimens of the central section revealed a tensile strength of about 130±10 MPa. The different sections of the Toquilla revealed a similar mechanical response as reported for other lignocellulosic fibers (De Rosa *et al.*, 2010). Due to the dispersion in dimensions of fibers, a statistical treatment using a two parameter Weibull distribution to estimate the tensile strength and the Young's modulus was used, as shown in figure 2.

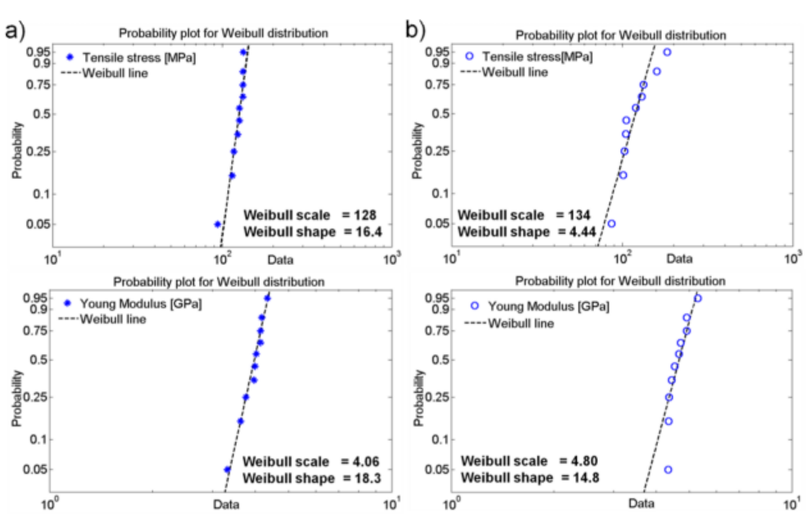

Figure 2. Statistical treatment using the Weibull distribution to mechanical properties for a) raw Toquilla straw and b) treated fibers of the central section

These mechanical properties were associated to scale parameter after fitting experimental data using the Weibull distribution method widely used to analyze natural fibers (Andersons *et al.*, 2005; Peponi *et al.*, 2008). Tensile stress calculated in Toquilla straw reveals its potential uses as reinforcement in polymeric composites which is higher than 40MPa reported for some polymers.

Thermogravimetric analysis (TGA) for the treated natural fiber reveals that thermal decomposition occurred in four stages (see figure 3a). The first range characterized with a rapid weight loss of about 12% up to 90°C of temperature due to the moisture caption and water evaporation. In this same range, untreated fibers show a low percentage of weight loss, less than 5% also observed in DTG curves in (b). *C. Palmata* samples which were not previously dried for this study. This fact suggests that volatile contents after treatments with sulphur vapors degrade below 90°C. For a range from 200°C to 350°C, both thermograms show similar behavior, with a weight loss of 40% and 50% for treated and untreated specimens, respectively.

A closer inspection in DTG curve shows a light peak of about 250°C prior to major decomposition occurring from 270 to 400°C, with a maximum temperature of decomposition around 330 and 340°C for treated and untreated fibers, respectively. Inset in Figure3b, revealed a displacement of temperature onset of about 10°C for treated samples. In this range of temperature, several natural fibers such as jute, curua, ramie and kenaf have shown an increase thermal stability after drying at 105°C for 1 h

(Ornaghi *et al.*, 2014). Above 350°C up to 475°C, the percentage weight losses are around 25%. Degradation of cellulose and lignin contents is associated for this range of temperature. In higher temperatures (800°C), the weight loss is less than 10% and associated to ash. The use of the Toquilla straw as reinforcement is assumed as retardant effect to thermal degradation within the composite material.

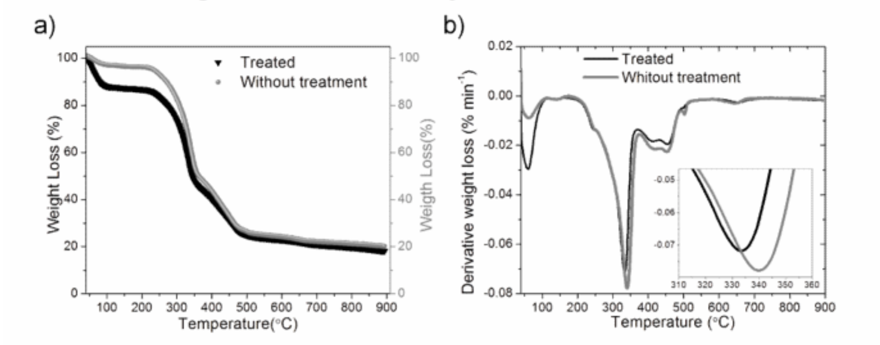

Figure 3. a) Thermogravimetric (TGA) and b) differentiate thermogravimetric (DTG) analysis curves of treated and untreated Toquilla straw specimens

From spectral analysis shown in figure 4, the spectral region from 3500 cm^{-1} to 2500 cm^{-1} is related to the stretching vibration of O-H, C-H and CH_2 group of lignin/cellulosic and hemicellulosic component of natural fibers.

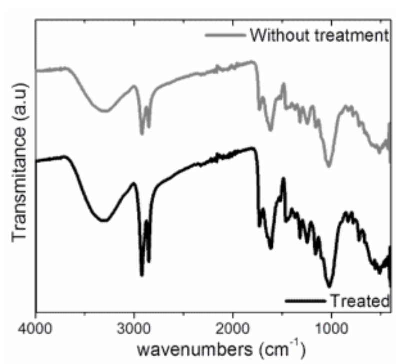

Figure 4. Fourier Transform Infrared spectra measured for untreated and treated Toquilla straw fibers

The stretching vibration of the hydroxyl group in lignin and cellulose correspond to the broad absorption band around 3300cm^{-1}. The band around 1729 cm^{-1} region may be attributed to C=0 stretching vibration of the acetyl group in hemicellulose. The peaks at 1650 cm^{-1} and 1616 cm^{-1} are attributed to non-esterified pectins. A closer inspection, the light shoulder around 1650 cm^{-1} in the treated specimen spectra is not present for untreated specimen spectra. The stretching vibration at 1515 cm^{-1} is assigned to aromatic skeleton vibration in lignin. By comparing both treated and untreated samples few changes were observed. This fact can suggest that the different mechanical response of both specimens is due to structural changes or crystalline effects.

CONCLUSIONS

The Toquilla straw revealed degradation temperature of about 350°C showing its potential uses as thermoplastic reinforcement in composite materials. The tensile strength measured on the central section showed higher values than most common polymeric compounds. Spectral analysis did not show relevant changes of treated and untreated samples that allowed us to conclude the origin of variability of the mechanical responses calculated in the sections.

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