GREEN COMPOSITES FROM *MUSACEAS* AGRO-INDUSTRIAL RESIDUES

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Abstract

Musaceas comestible fruit production generates a high amount of fibrous residues that can be useful as raw material for composite industry. In this study, green composite materials without synthetic matrix from Musaceas agro-industrial fibrous residues as rachis have been developed. Rachis samples have been treated using a thermo-mechanical process: the steam explosion. Several treatment conditions controlled by severity parameter and compression conditions (temperature and pressure) were analyzed. According with mechanical results, composite flexural behaviour is enhanced by higher compression conditions. However, as shown by FTIR spectroscopy analysis, atomic force microscopy (AFM), sugar analysis by HPLC and PVT (pressure-volume-temperature) measurements severity generates important variations on rachis chemical composition, associated with the reduction of hemicellulose as xylose that affects the mechanical and physical behaviour of this type of composites.

1. Introduction

Colombia is one of the most important *Musaceas* fruit exporter in the world. In this country, around 41,300 cultivated hectares of banana plants exist. This agricultural labor generates an important amount of residues as only 12 wt % of total plant corresponds to fruit. According with fibrous presence, banana residues are classified in: non-fibrous and fibrous. Fibrous samples include rachises, pseudtostems and leaf sheaths. In general, they are composted in the same crop area, but their degradation takes a long time and it can cause a lot of odour problems. These materials, as other lignocellulosic residues or fibers, have several advantages as raw materials for natural o green composite materials. Some of these include low cost, biodegradability, low density, high disposability, and cellulose content. Several biodegradable composites have been developed [1-2]. However, one of main drawbacks is associated with the cost of biodegradable matrices. For this reason, green composites without addition of synthetic matrices can be an interesting option [3]. In this type of materials, non-cellulosic components and amorphous cellulose of the cell-wall act as matrix. The self-bonding strength is improved only by activating the chemical components [3]. Chemical processes as oxypropylation or bezylation, enzymatic treatment using lacassa, or thermo-mechanical treatments including steam explosion have been used for this propose [3-7]. The steam explosion has several advantages that include low exposure time, non-chemical or additional products are required, and non-contaminant residues are generated. During this process, the hemicelluloses can be hydrolyzed [3] and a progressively depolymerization of lignin can take place [7]. Both phenomena affect the green composite material behavior. For better results, processing treatment conditions, as exposure time and temperature, as well as raw material size have to be controlled. Additionally, composite processing conditions can affect the mechanical and physical behavior of composite developed.

In this study, *Musaceas* agricultural residues were used to make green composites. The influence of steam explosion conditions on chemical composition and morphological aspects of treated samples has been analyzed by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM), respectively. Flexural properties of different composites have been evaluated. To

better analysis of steam treatment effect on banana rachis samples, additional physical and chemical characterizations have been included.

2. Experimental

2.1. Materials

Musaceas agricultural residues as rachis were used. Figure 1 shows their common disposition on soil plantation. Figure 2 shows a cross-section area where it is possible to see the vascular bundles (vb), parenchyma (pq) and cuticle (ct). All tissues of rachis samples were used. Samples were collected from *Musaceas* plants as banana (*Musa AAA, cv "Valery")*. They are cultivated in Colombia (Urabá region). Before thermo-mechanical treatment, the samples were conditioned until a moisture content around 90 wt %. Chemical composition of rachis samples is registered in Table 1.

Fig. 1. Rachis samples on soil plantation.

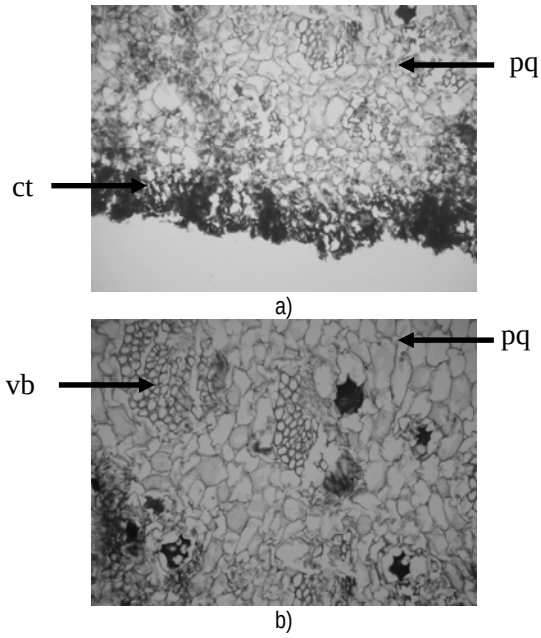


Figure 2. OM micrographs of cross-section of rachis. a) outer region, b) central region. 200x

Table 1. Chemical composition of rachis samples

Parameter	Weigh percentage (%)
Water extractive	14.81
Organic extractives	2.76
Klason lignin	14.28
Cellulose	51.05
Hemicellulose	17.10

2.2. Steam explosion treatment

The samples were submitted to high pressure saturated water steam explosion at temperatures between 190 ºC and 210 ºC and 4 and 8 min residence time. Temperature (T) and time (t) of thermal treatment are related by one variable. severity (R_0) parameter, as follows:

$$R_0[\text{min}] = \int_0^{t[\text{min}]} \exp(T[^\circ C]\cdot 100/14.75)dt \qquad (1)$$

Steam explosion treatment was performed in a batch pilot plant equipped with two vessels: reactor and expansion vessel. After explosion, treated materials were washed with fresh water, filtered and dried up. The equilibrium moisture of samples was around 7 wt %.

2.3. Composite fabrication

Treated and untreated samples were molded in a Polystat-200 hydraulic press using different temperatures (T_C) between 150 and 200 ºC for 15 min. Compression pressure (P_C) applied range was between 6 to 12 MPa. Samples were 150x50x3 mm^3. An orthogonal experiment design involving 23 experiments was performed. The studied variables have been severity and compression conditions. Table 2 summarizes all experiments carried out.

2.4. Test methods

Mechanical and physical properties were tested according with UNE EN 310-94.

Morphological changes have been analyzed using an AFM NanoScope IIIa, Multimode™ from Digital InstrumentS. All samples have been imaged in tapping-mode.

FTIR spectroscopy, Perkin Elmer PC1600, has been employed for analyzing the variations on fiber chemical composition after treatment. KBr samples were prepared under a pressure of 80 kN/cm^2 for 5 min. All spectra were taken in transmission mode at a resolution of 4 cm^{-1} and twenty scans were carried out for each specimen.

Table 2. Experimental design for composite samples.

Test	Log(R_o)	P_C (MPa)	T_C (°C)
1	4.0	9.0	217.045
2	4.0	3.95462	175.0
3	4.0	9.0	175.0
4	4.0	9.0	175.0
5	3.5	6.0	150.0
6	4.8409	9.0	175.0
7	4.0	9.0	175.0
8	4.5	6.0	150.0
9	3.5	12.0	200.0
10	4.0	9.0	175.0
11	3.5	12.0	150.0
12	4.0	9.0	175.0
13	4.0	9.0	175.0
14	4.0	9.0	175.0
15	4.0	9.0	132.955
16	4.5	12.0	150.0
17	4.5	6.0	200.0
18	3.5	6.0	200.0
19	3.1591	9.0	175.0
20	4.0	9.0	175.0
21	4.5	12.0	200.0
22	4.0	14.04540	175.0
23	4.0	9.0	175.0

Additionally, xylose content of untreated and treated samples were evaluated using HPLC with a Bio-Rad HPX-87H chromatograph.

For PVT (pressure-volume-temperature) analysis a SWO/Haake PVT 100 has been employed. The specific volume of samples has been evaluated in 50-200 ºC temperature range and 1-800 bar pressure range with 200 bar steps. Several isobaric scans have been carried out to measure specific volume along the time.

3. Results and Discussion

Table 3 summarizes the mechanical behaviour of banana green composites at different severities and compression conditions, and Figure 3 and 4 show estimated response surface strength at break (σ_b). and modulus (E), respectively. According with these results, flexural properties have a strong dependence on compression conditions. A better behavior is obtained when there is a combination of high temperature and pressure, as observed in samples 9, 21-23. This behaviour can be associated with higher homogeneity inside of material. The mechanical behaviour of these green composites from *Musaceas* agro-resiudes are comparable with those reported by other authors as Nemli et al. [5] for kiwi materials.

Table 3. Mechanical behaviour of bunch composites.

Sample	Log(R_o)	σ_b (MPa)	E (MPa)
1	4.0	14.29	1790
2	4.0	20.52	1875
3	4.0	23.50	2379
4	4.0	20.10	2104
5	3.5	10.43	1321
6	4.8409	12.80	1746
7	4.0	14.45	1774
8	4.5	15.23	1681
9	3.5	16.12	2819
10	4.0	15.06	1805
11	3.5	12.34	1465
12	4.0	8.46	1202
13	4.0	21.59	2112
14	4.0	18.34	2048
15	4.0	16.51	1790
16	4.5	16.6	2025
17	4.5	13.29	2492
18	3.5	24.14	2478
19	3.1591	15.75	2364
20	4.0	24.14	2478
21	4.5	20.03	3063
22	4.0	20.22	2860
23	4.0	22.67	2811

A severity value around 4 offers a better mechanical behaviour. This optimized condition can be associated with several modifications that happen during the treatment, including chemical and morphological variations on samples. It is possible that at severity lower than 4, lignin still has a high molecular weight and low reactivity that affects the matrix behavior inside of the composite. While at higher severity, thermal degradation of lignin and cellulose and other non-cellulosic structures happen, thus affecting the composites homogeneity. Additionally, at higher severity, an important reduction on the sample size is observed.

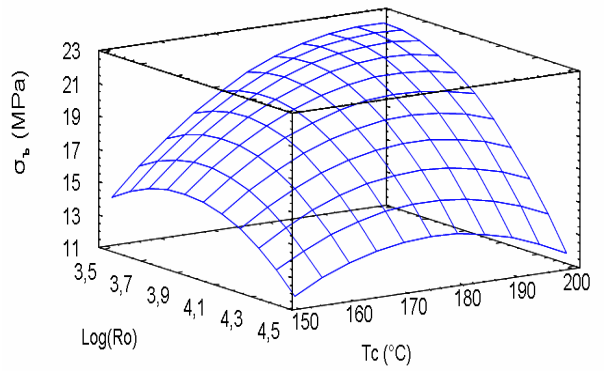


Fig. 3. Estimated response surface for σ_b at different severities conditions.

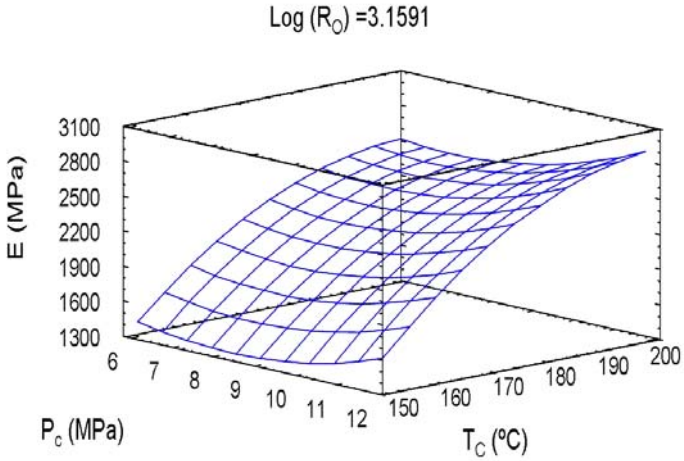


Fig. 4. Estimated response surface for **E** at different compression conditions.

In order to analyze morphological changes introduced by steam explosion treatment on rachis samples, AFM micrographs are shown in Figure 5 for untreated and treated composites. An important presence of extractives is observed on untreated sample surface. However, when the severity increases, a progressive reduction is observed. At higher severity as 4.5, it is possible to see cellulose microfibrils, thus indicating a reduction on non-cellulosic component. This suggests that the reduction of non-cellulosic compounds could improve the mechanical behavior of composites, which is observed in samples 21-23 in table 3.

FTIR spectrophotometry has been employed to analyze variations introduced by steam explosion treatment on chemical structure of rachis samples. Figure 6 shows spectra of untreated and treated materials at different severities. Rachis as other vegetable sources is mainly composed by cellulose, hemicellulose and lignin [8-9]. Table 4 resumes some of their characteristic vibrations.

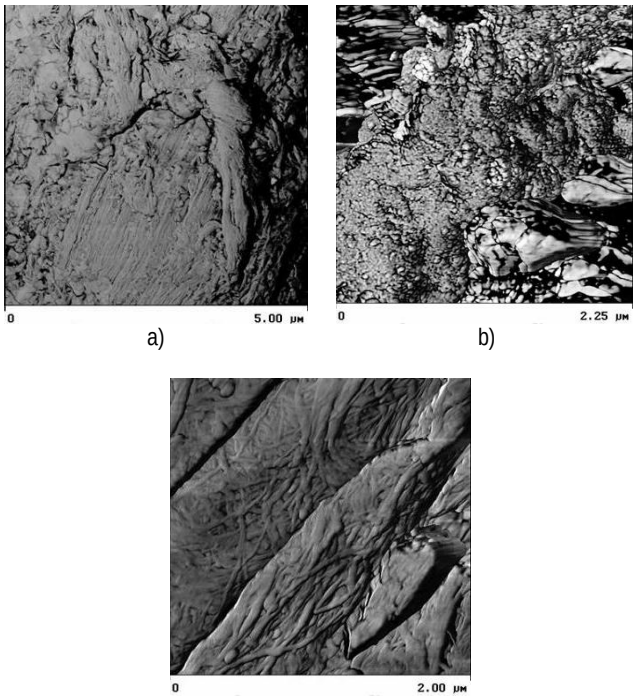


Fig. 5. AFM phase images of bunch composites for different severities: a) untreated sample, b) 3.5 c) 4.5.

When the severity treatment conditions increase a progressive removal of hemicellulose stretching at 1724 and 1649 cm^{-1} takes place. Moreover, at higher severity conditions, a high reduction of 1724 cm^{-1} peak happens, and it is possible to observe clearly the lignin stretching in the 1707 cm^{-1} region. This reduction corresponds to the elimination of one of the most important component of hemicellulose as xylose. Authors as Sun et al. [10-11] report comparable results on non-woody plants as straw. This tendency confirms the AFM results commented above.

Other significant modifications on FTIR spectra of treated samples are associated with variations of stretching at 1321 cm^{-1}. It can be associated with variations on lignin reactivity that affect the mechanical internal bond inside of the composite.

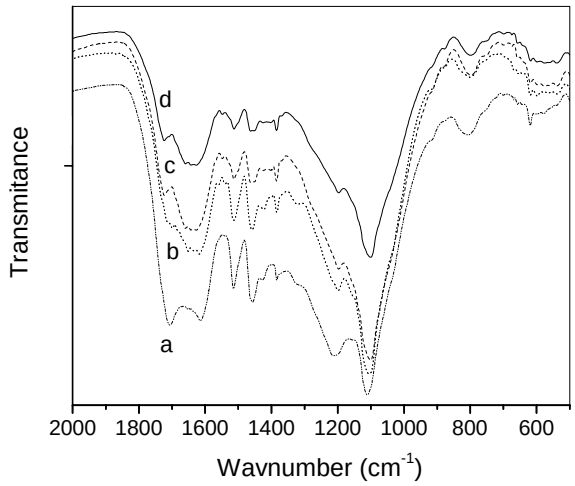


Fig. 6. FTIR spectra of composite samples at different severities: a) untreated; b) 3.5; c) 4; d) 4.5.

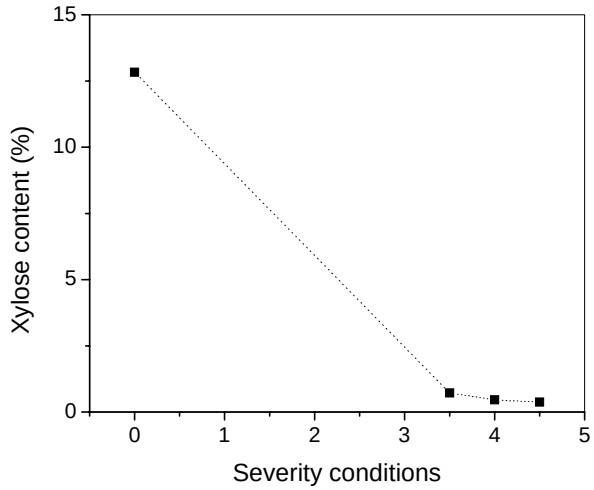
On the other hand, non-significant variations are observed on cellulose vibrations. This suggests that steam exposition conditions used in this study do not affect the cellulose structure and changes mainly occur in non-cellulosic components.

Additional chemical analysis using HPLC to determine the variation of xylose content in treated and untreated samples have been carried out. As Figure 7 shows, an important reduction of xylose content is observed for all thermo-mechanical treated samples. Results confirm FTIR observations shown above.

Table 4. FTIR vibrations in *Musaceas* rachis samples.

Vibration	Wavenumber (cm^{-1})
COO groups in fatty acid, hemicellulose	1724
COO group in lignin	1707
C=O groups related to hemicellulose	1649
Aromatic skeletal of lignin	1606
Aromatic skeletal of lignin	1513
C-H asummetrical deformation of cellulose and lignin ring	1464
Aromatic ring of lignin	1424
C-H symmetrical deformation associated with crystalline cellulose	1383
CO stretching syringil and guaicyl groups of lignin	1321
OH bonds of cellulose	1198
Aromatic C-H out of plane bending	810

Fig. 7. Xylose content for untreated and treated rachis samples.



On the other hand, PVT tests on samples treated at different severities have also been done. Figure 8 shows the variation of specific volume V as a function of temperature in the range between 25 and 200 C at 200 bar (atmospheric pressure). Table 5 summarized specific volume values at 1 bar. These results indicate than for low severity conditions the specific volume is lower than for the other conditions. It is possible that for mild severity, as 3.5, low molecular weight components can be distributed along the material at higher temperature. The progressive reduction of non-cellulose components, added to potential changes on lignin structure affecting the interfacial behavior [12], promotes the observed increase on specific volume. However, a more detailed study about this topic is required, specially considering the changes on lignin structure as potential crosslinking phenomena.

Table 5. Specific volume for treated samples at different severities.

Severity condition	V 1bar (cm^3/g)
3.5	0.7557
4.0	0.7626
4.5	0.7762

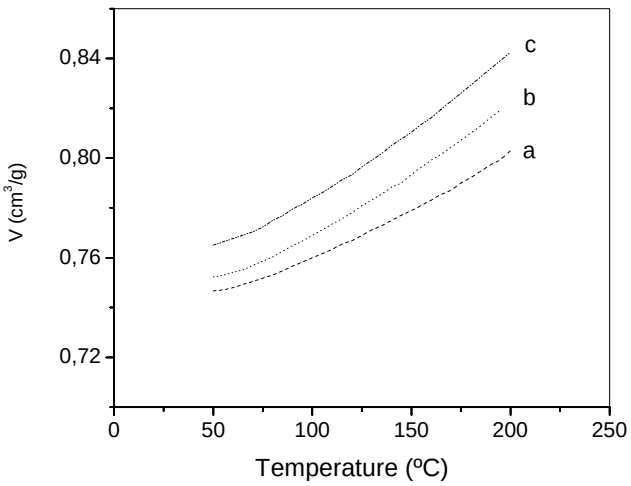


Fig. 8. Temperature dependence of the specific volume at 200 bar for several severities: a) 3.5; b) 4; c) 4.5.

4. Conclusiones

Green composites from *Musaceas* agro-industrial residues were developed. Steam exploded treatment is necessary to improve the mechanical behaviour of composites because it reduces the non-cellulosic components of treated samples. Compression processing conditions affect the mechanical behaviour of composites more than severity conditions.

Acknowledgments

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5. References

[1] Braun B., Dorgan J. R. and Knauss D. M. "Reactively Compatibilized Cellulosic Polylactide Microcomposites". *Journal of Polymer and the Environment*, Vol. 14, No. 1, pp 49-58, 2006.

[2] Cyras V. P., Iannace S., Kenny J. M. and Vázquez A. "Relationship between Processing and Properties of Biodegradable Composites Based on PCL/Starch Matrix and Sisal Fibers". *Polymer Composties*, Vol. 22, No. 1, pp 104-110, 2001.

[3] Widyorini R., Xu J., Watanabe T. and Kawai S. "Chemical changes in steam-pressed kenaf core binderless particleboard". *Journal of Wood Science*, Vol. 51, No. 1, pp 26-32, 2005.

[4] Velásquez J. A., Ferrando F. and Salvadó. J. "Effects of kraft addition in the production of binderless fiberboard from steam exploded *Miscanthus simensis*. *Industrial Crops and Products*, Vol. 18, No. 1, pp. 17-23, 2003.

[5] Nemli G., Kirci H., Serdar B. and Ay N. "Suitability of kiwi (*Actinidia sinensis* Planch.) prunings for particleboards manufacturing". *Industrial Crops and Products*, Vol. 17, No. 1, pp 39-46, 2003.

[6] García-Jaldon, C., Dupeyre D. and Vignon. M. R.·"Fibres from semi-retted hemp bundles by steam explosion treatment". *Biomass and Bioenergy*, Vol. 14, No. 3, pp 251-260, 1998.

[7] Anglés M. N., Reguant J., Montané D., Ferrando F., Farriol X. and Salvadó. J. "Binderless composites from pretreated residual softwood". *Journal of Applied Polymer Science*, Vol. 73, No. 12, pp 2485-2491, 1999.

[8] Gañán P., Cruz J., Garbizu S., Arbelaiz A. and Mondragon I. "Pseudostem and rachis banana fibers from cultivation wastes: Effect of treatments on physico-chemical behavior". *Journal of Applied Polymer Science*. Vol 94, No 4, pp 1489-1495, 2004.

[9] Singh B., Verma A. and Gupta M. "Studies on adsorptive interaction between natural fiber and coupling agents". *Journal of Applied Polymer Science*. Vol 70, No.9, pp 1847-1858, 1998.

[10] Sun X. F., Xu F., Sun R. C., Fowler P. and Baird M. S. "Characteristics of degraded cellulose obtained from steam-exploded wheat straw". *Carbohydrate Research*. Vol 340, No.1, pp 97-106, 2005.

[11] Sun R. C., Sun X. F., Fowler P. and Tomkinson' J. "Structural and physico-chemical characterization of lignins solubilized during alkaline peroxide treatment of barley straw", *European Polymer Journal*, Vol. 38, No. 7, pp 1399-1407, 2002.

[12] Maximova N., Ôsterberg M, Laine J. and Stenius P. "The wetting properties and morphology of lignin adsorbed on cellulose fibres and mica", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 239, No. 1-3, pp 65-75, 2004.