Stem and Bunch Banana Fibers from Cultivation Wastes: Effect of Treatments on Physico-Chemical Behavior

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ABSTRACT: Much research related to the use of natural fibers in polymeric matrix composites has been developed. The presence of –OH groups in the chemical components of the natural fibers generates an important hydrophylic tendency that produces adhesion lacks with hydrophobic polymeric matrices. In this work natural fiber bundles mechanically extracted from both stem and bunch of cultivation banana wastes have been modified by both alkalization and silanization treatments. To evaluate the changes introduced by treatments on the chemical structure of fibers, Fourier-transform infrared spectrophotometry has been employed. The evaluation of advancing dynamic contact angles along with the determination of total surface free energy by using the Owens–Wendt method indicate that the treatments allow reduction of their hydrophilic tendency by alterations on the physicochemical characteristics of the fibers. This behavior is confirmed by the reduction of moisture uptake, analyzed by thermogravimetric analysis. Small differences on noncellulosic components of stem and bunch fiber bundles have been found. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1489–1495, 2004

Key words: banana fibers; surface treatments; hydrophilic behavior; surface free energy; infrared spectroscopy

INTRODUCTION

Much research related to the use of traditional natural fibers, such as sisal,[1–4] flax,[5,6] or jute,[7] as reinforcement for polymeric matrix composites has been developed around the world.[1–6] Some of this research has been motivated by the advantages and the potential approach for the development of nonstructural and recyclable composites, very important for automotive components, for which environmental friendly parts are currently being manufactured.[8,9] Some of these important advantages include: low density, low cost, medium stiffness, medium thermal resistance to processing conditions, high disposability and renewability, and low abrasion.[10]

In addition to those traditional fibers, many vegetable plants for producing adequate fibers as polymeric reinforcement exist. That is the case of banana fibers[11,12] and also of oil palm fibers.[13,14] Colombia is the third banana fruit producer in the world. In this country, around 41,300 cultivated hectares exist. This agricultural labor generates an important amount of wastes, since only 11.6 wt % of the total plant corresponds to fruit. The rest of the plant is constituted of fibrous and nonfibrous wastes. The main fibrous wastes correspond to bunch, stem, and leaf.[15] The most traditional fiber extraction process corresponds to mechanical means. The main compounds present in natural vegetable fibers correspond to cellulose, lignin, and hemicellulose. All of them contain –OH groups in their structure, thus leading to the strong hydrophilic tendency of natural fibers. This composition generally leads to problems of adhesion with polymeric matrices, due to their strong hydrophobic behavior. Moreover, the mechanical behavior of natural fiber based composites appears to be poor as the moisture uptake of composites is conditioned by the high hydrophility of natural fibers.

For enhancement of natural fiber/polymer adhesion, different alternatives, such as fiber modification,[16–18] matrix modification, or coupling agent addition, do exist.[19,20] Fiber modification may cause alterations on the physical and chemical characteristics of their structure, which includes variations on surface, chemical composition, and moisture uptake.[21] The surface behavior of natural fibers can be analyzed by using different techniques, such as: wetting measurements for determination of contact angle by Wilhelmy method (DCA)[21–24] or capillary technique by Washburn method[25]; photoelectron spectroscopy (XPS)[26]; and inverse gas chromatography (IGC).[27,28] In this work, the dynamic contact angle determination by the Wilhelmy method, due to its accessibility for the fiber bundles evaluated, has been employed to analyze sur-

face variations, in spite of studies developed by Barserg et al.,[22] who express controversy to the effective information submitted by this technique, due to the complex phenomena associated with fiber surface and probe liquid interaction. However, the Wilhelmy method can be useful when the results obtained are essentially employed to compare variations on the hydrophilic behavior between treated and untreated fibers.[21,23,24,28]

Fourier transform infrared (FTIR) spectroscopy and its variations, such as DRFT-FTIR (diffuse reflectance FTIR)[29] or ATR-FTIR (attenuated reflection FTIR),[21] have been employed to evaluate the variations introduced by surface treatment on the chemical structure of fibers. These methods can also be useful for evaluating the nature of fiber/matrix adhesion, mainly when a coupling agent is employed.

In this study, different untreated and treated banana fiber bundles extracted from stem and bunch cultivation wastes of banana plants have been analyzed. Surface treatments, such as alkalization and silanization with γ-glycidoxypropyltrimethoxy-silane (GLYMO), have been used. FTIR spectrophotometry has been employed to establish variations between both stem and bunch fiber bundles and also to analyze the changes after treatments. Surface free energy has been determined by the Owens–Wendt method. Thermogravimetric analysis (TGA) has also been used to characterize the variations on water uptake as well as the thermal stability of fibers after treatments.

EXPERIMENTAL

Materials

Banana fiber bundles were mechanically extracted in the Mechanical Laboratories of UPB (Medellín/Colombia) from cultivation wastes of stem and bunch of the *Valery* species, the main banana plant cultivated in Colombia (Urabá region). The chemical agent used for silanization was γ-glycidoxypropyltrimethoxy-silane (GLYMO), kindly supplied by Degusssa-Hülls (Karlsruhe, Germany).

Fiber surface modification

Previous to the treatments, all fibers were dried at 105 ± 5°C. For alkalization (M), fiber bundles were immersed in a 20 wt % sodium hydroxide solution for 1 h. The fibers were repeatedly washed with distilled water with a few drops of acetic acid, then washed with distilled water until neutral pH was established. The fibers were dried for 24 h at 105 ± 5°C. For silane treatment, the fibers were immersed in a 5 wt % silane methanol solution for 1.5 h. Then, the fibers were dried at 105 ± 5°C for 24 h.

TABLE I
Surface Parameters of Probe Liquids

| Liquid	Polar component (mJ/m^2)	Total surface free energy (mJ/m^2)
Water	50.8	72.4
Ethyleneglycol	21.3	47.0
α-Bromonaphthalene	—	44.4

Test methods

FTIR spectroscopy, Perkin–Elmer PC1600, was employed for analyzing the variations on fiber chemical composition after treatments. The spectra were taken at a resolution of 4 cm^{-1}, and twenty scans were carried out for each specimen.

Dynamic contact angles were measured in a Krüss K14 dynamic contact angle analyzer using the Wilhelmy plate technique.[21] In this method, single fiber bundles are dipped into the probe liquids up to a depth of 2 mm with a speed of 50 μm.s^{-1}. During the test, it is possible to obtain the advancing and retrocessing angles.[21] The advancing angle has been employed due to its reproducibility. The probe liquids used for contact angle determination were water, ethyleneglycol, and α-bromonaphthalene at 24°C. The surface energy parameters of probe liquids employed are registered in Table I. Ten fiber bundles were investigated for each treatment. The surface free energy was calculated using the Owens–Wendt method.[30] Thermogravimetric analysis of untreated and treated fiber bundles was carried out in helium atmosphere at a heating rate of 10°C/min, using a thermoanalyser, Setaram 92–12.

RESULTS

Infrared spectroscopy

FTIR spectrophotometry is an appropriate technique to establish the variations introduced by the different treatments on the chemical structure of natural fibers. FTIR spectra of untreated and treated banana fiber bundles are shown in Figure 1. Both stem and bunch fiber bundles present the typical vibration bands of the components of other vegetable fibers, such as fique[21] or sisal,[23] mainly corresponding to cellulose, hemicellulose, and lignin. Every band is very similar for both types of fiber bundles, indicating a close similarity on their chemical compositions. All vibrations are summarized in Table II. The hydrophilic tendency of these natural fibers is reflected in the broad absorption band in the 3700–3100 cm^{-1} region, which is related to the –OH groups present in their main components. In the 1600–900 cm^{-1} region, it is possible to appreciate in both bundles vibrations of chemical components of the lignin at frequencies of 1514 cm^{-1} for guaiacyl[31]
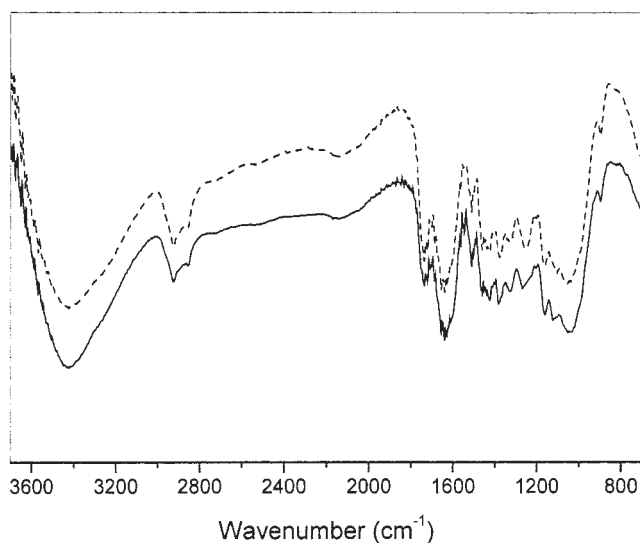
Figure 1 FTIR spectra of banana fiber bundles: (——) stem and (- - -) bunch.
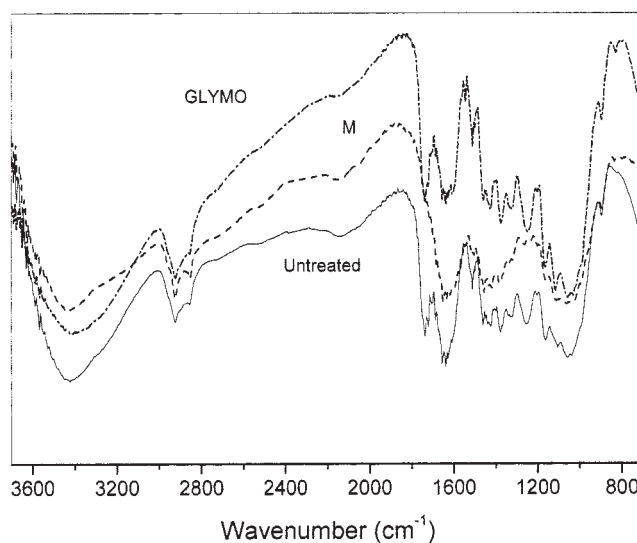
Figure 2 FTIR spectra of bunch banana fiber bundles: (——) untreated, (- - -) alkalized, and (– - –) silanized.

and 1468, 1433, and 1214 cm^{-1} associated with syringyl.[31] On the other hand, the small band at 1554 cm^{-1}, nonexistent in the bunch spectrum, could indicate that small variations on fatty acid contents exist among both banana bundles. The intense band around 1260 cm^{-1}, associated with hemicellulose, appears clearly higher for bunch fibers. This fact, along with the higher absorption band centered around 1730 cm^{-1}, clearly shows that fiber bundles from bunch origin get a higher hemicellulose content than that for the corresponding stem ones.

The variations introduced in chemical composition after treatments on both banana fibers are shown in Figures 2 and 3. Possible mechanisms of fiber modification are shown in the following lines:
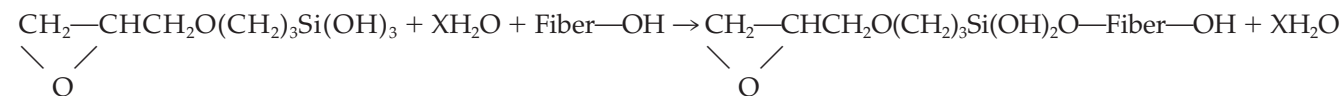
• For alkali treatment

Authors such as Bisanda and Ansell[32] and Sheekala et al.[33] proposed the reaction scheme:

TABLE II
FTIR Vibrations Observed in Both Banana Fiber Bundles

	Band wavenumber (cm^{-1})	
	Stem	Bunch
OH bonds stretching in cellulose and lignin	3454	3452
C—H stretching present in lignin and waxes	2937, 2873	2927, 2873
Carbonyl groups present in fatty acids	1743	1737
C=O bonds of non-conjugated ketone present in hemicellulose	1731	1730
C=O bonds of hemicellulose	1658, 1639	1656, 1635
Aromatic skeletal vibration and C=O stretching of lignin	1606	1606
C=C stretching present in fatty acids	1554	1554
Aromatic skeletal vibration present in lignin	1514	1512
C—H asymmetrical deformation of cellulose and lignin ring	1465	1462
C=C aromatic ring of lignin	1433	1429
C—H symmetrical deformation of cellulose	1385	1382
C—O stretching associated with syringil ring	1338	1342
C—O stretching of primary alcohol present in guaiacyl lignin and also in hemicellulose and cellulose	1268–1219	1259–1219
O—H stretching of cellulose	1203	1201
C—O—C asymmetrical glucose rings and xylane groups of hemicellulose	1169	1167
C—H stretching of lignin	1125	1103
C—O of secondary alcohol	1053	1064
C—H stretching of guaiacyl	1043	1042
β-glycosidic linkages of glucose ring of cellulose	900	900
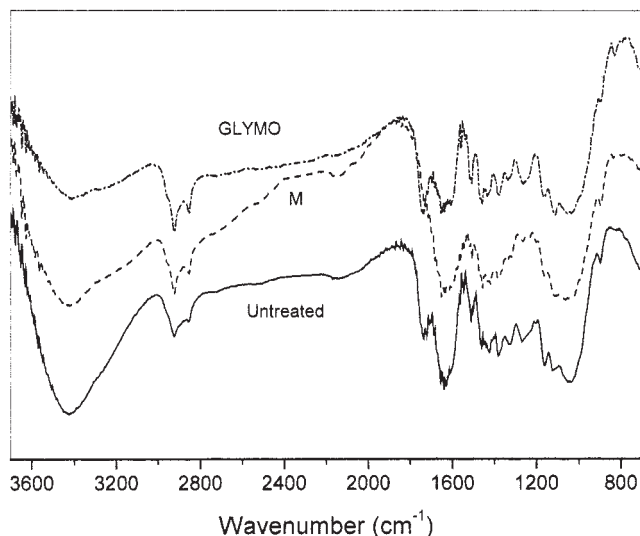
Figure 3 FTIR spectra of stem banana fiber bundles: (——) untreated, (- - -) alkalized, and (– – –) silanized.

$$CH_2—CHCH_2O(CH_2)_3Si(OH)_3 + XH_2O + Fiber—OH \rightarrow CH_2—CHCH_2O(CH_2)_3Si(OH)_2O—Fiber—OH + XH_2O$$
$$\diagdown \diagup$$
$$O$$

The most significant effect introduced by alkali treatment is associated with the attenuation of vibrations around 1745–1725 cm^{-1}, which corresponds to the reduction of carbonyl groups present into fatty acids of fiber and C = O of nonconjugated ketone present in hemicellulose. However, as noted in previous work[21,34] and also by other researchers,[35–37] the slight intensity decrease of the band around 1510 cm^{-1} is evidence that some lignin amount can be removed, but this compound still remains on fiber bundles after alkalization. Vibrations in the region between 3000 and 2850 cm^{-1}, associated with the C-H stretching of lignin, hemicellulose, and cellulose,[36] slightly decrease upon alkalization.

With respect to silane treatments, the main variations are observed at nearly 836 cm^{-1} and around 1100–1150 cm^{-1}. These vibrations are associated with Si-C bonds and Si-OH, respectively. The presence of these vibrations indicates the effectiveness of this treatment process, as the silane was effectively deposited on the fiber surface.

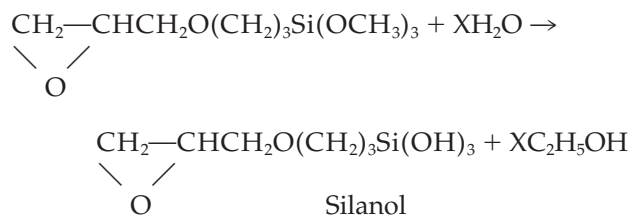### Advancing contact angles and surface free energy

To analyze the hydrophilic behavior of treated and untreated banana fibers, the contact angle technique has been used. The surface free energy of probe liquids must be different to evaluate the polar and dispersive components of the total free surface energy of fibers by the Owens–Wendt method. In this method, a semiempirical equation, referred to as a geometric mean, was developed:

$$Fiber—OH + NaOH \rightarrow Fiber—O^-Na^+ + H_2O \quad [28]$$

However, the presence of Na$^+$ on fiber surface is negligible, and it does not introduce significant alterations on the elemental composition of fiber.

• For silane treatment

Considering the mechanism proposed by the same authors,[32,33] silane molecules are chemisorbed on the fiber. The silanol formed by moisture presence can react with hydroxyl groups of natural fibers, forming stable covalent bonds to the cell wall:

$$CH_2—CHCH_2O(CH_2)_3Si(OCH_3)_3 + XH_2O \rightarrow$$
$$\diagdown \diagup$$
$$O$$

$$CH_2—CHCH_2O(CH_2)_3Si(OH)_3 + XC_2H_5OH$$
$$\diagdown \diagup$$
$$O \qquad Silanol$$

$$\sigma_{sL} = \sigma_s + \sigma_L - 2*((\sigma_s^d * \sigma_L^d)^{0.5} + (\sigma_s^p * \sigma_L^p)^{0.5})$$

where σ_s is the fiber–liquid interfacial surface free energy, and σ_L the surface free energy for the probe liquid, each parameter containing dispersive (d) and polar (p) components.[30]

Tables III and IV show the dynamic contact angles and surface free energies of both stem and bunch fiber bundles, respectively. Both kinds of fibers present comparable contact angles with each probe liquid. These natural fibers present a similar chemical distribution of their polar and dispersive components in their surfaces. The contact angles observed with water and α-bromonaphthalene show that these fibers get both polar and dispersive components. However, the high contact angles obtained with ethyleneglycol ratify the strong polar ten-
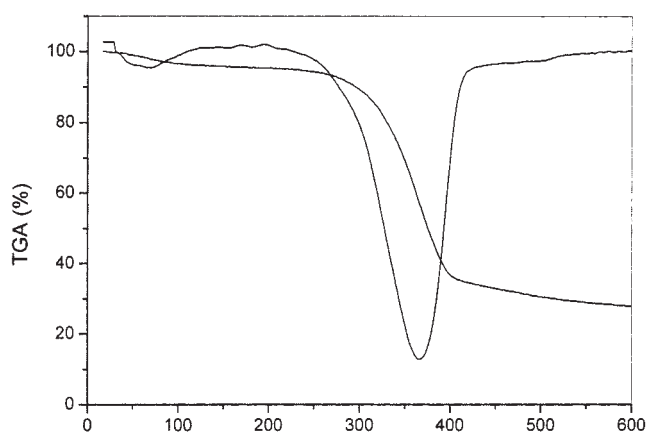
TABLE III
Advancing Contact Angles of
Treated Banana Fiber Bundles

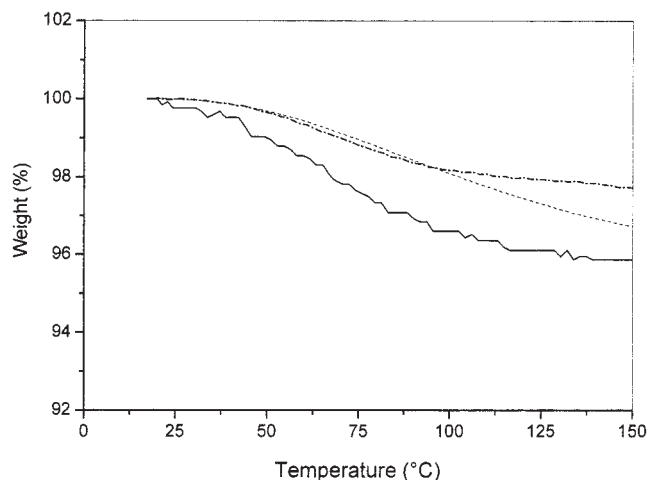| Fiber	Water	α-Bromonaphthalene	Ethyleneglycol
Stem			
Untreated	45.3	46.1	55.7
M	63.9	37.1	50.8
GLYMO	70.6	33.3	44.5
Bunch			
Untreated	42.6	47.5	55.9
M	62.4	38.1	52.9
GLYMO	72.9	35.2	44.6

TABLE IV
Polar Component and Total Surface Free Energy
Calculated by Owens Method for
Treated Banana Fiber Bundles

Fiber	Polar component (mJ/m^2)	Dispersive component (mJ/m^2)	Total surface free energy (mJ/m^2)
Stem			
Untreated	24.3	23.0	47.3
M	16.2	24.1	40.3
GLYMO	10.3	28.5	38.8
Bunch			
Untreated	26.4	22.1	48.5
M	16.8	22.0	38.8
GLYMO	10.0	26.9	36.9

Figure 5 First weight decomposition region for treated stem fiber bundles: (——) untreated, (- - -) alkalized, and (– - –) silanized.

dency of surfaces of the banana fibers studied. The wettability analysis by the Owens–Wendt method confirms this observation, since the polar component contribution is near to 50% of the total surface free energy. This behavior is associated with the presence of –OH groups in chemical structures such as cellulose and hemicellulose. The contact angles in water of the treated fibers increase with respect to the values of untreated fibers, while they decrease with ethyleneglycol. These results indicate a reduction of hydrophilic behavior, represented by an increment of affinity with low polar component liquids such as ethyleneglycol. Alkalized fiber bundles present dynamic contact angles in water between 62 and 64 grades. Gassan et al.[28] reported the values of water contact angle for both untreated jute fibers and lignin around 75, whereas the water contact angle for cellulose is 33.[28] In accord with this, it is possible that alkalization alters the distribution of chemical components on the surface fibers, and thus lignin could be present in a high concentration in the surface layers of both banana fibers after alkalization, contributing to the reduction of the hydrophilic behavior of fibers.

With respect to the silanized fibers, it is possible to observe the increment on the water contact angle and the reduction of α-bromonaphthalene contact angle for both stem and bunch fiber bundles. This behavior indicates an effective reduction of the hydrophilic tendency of the fiber bundles. With respect to the surface free energy, the reduction on the polar component of all treated fibers with respect to the untreated one appears to be evident. These results confirm the diminution of the hydrophilic tendency of the banana fiber bundles analyzed. Alkalization has a slight influence on the dispersive component of the surface free energy. However, the dispersive component of silanized fibers is higher than that of untreated fibers, as a consequence of the new groups deposited in the fiber surface, as shown above by FTIR spectroscopy.

The variations observed on surface free energy for untreated and treated banana fibers are comparable with values reported by other authors with natural fibers such as jute by using methods of analysis such as inverse gas chromatography (IGC).[38] The estimated surface tension values for other fibers such as flax[39] or sisal[38] get values in the range from 25.5 mN/m to 50 mN/m. On the other hand, the similarity on surface behavior for both stem and bunch fibers is remarkable, which can be related to their similar surface chemical composition, shown above by FTIR analysis as well.

Thermogravimetric analysis

Thermogravimetric analysis by dynamical assay provides information related to the regions of loss weight of fibers. Figure 4 presents the TGA analysis for untreated stem fiber bundles, and Figure 5 presents the moisture uptake in the first decomposition region, while Table V summarizes the thermal behavior of untreated and treated banana fibers. The natural fibers

Figure 4 Thermogravimetric analysis of untreated stem banana fiber bundles.

TABLE V
Thermal Behavior of Treated Banana Fiber Bundles

Fiber	Weight loss in first region 30–125°C (%)	Maximal decomposition temperature (°C)
Stem		
Untreated	5.5	353
M	2.9	370
GLYMO	2.0	392
Bunch		
Untreated	3.2	358
M	3.2	375
GLYMO	2.0	390

present two main weight loss regions: the first one in the 50–125°C region and the other in the 210–450°C region. The first decomposition region is associated with moisture desorption. Both untreated stem and bunch fibers show moisture losses in amounts between 3 and 5 wt % in the 50–125°C region. However, the treated fibers show an important decrease of these values. This behavior is related to the reduction on hydrophilic tendency of fibers, which in the case of alkalized fiber bundles is associated with the reduction of hemicellulose components such as xylans. The higher reduction of moisture sorption for all banana fibers studied has been obtained with silanization treatment. These results are in agreement with previous work.[21] In the second weight loss region, it is possible to observe that the main decomposition process occurs in the 300–400°C range, where cellulose decomposition takes place. Maximal decomposition temperatures of treated fiber bundles are higher than those observed for both untreated banana fiber bundles. These results indicate an increase on thermal stability by the effect of surface treatment, which can be associated with the reduction of fiber components with low thermal behavior such as xylans, as for alkalinized fibers, or with the presence of new groups as in the case of silanization. A comparable result has also been reported for fique fibers.[21] The reduction of xylans, the hydrophilic component of hemicellulose, in the alkalized fibers also contributes to reduce the moisture uptake.

CONCLUSION

Banana fiber bundles, extracted by mechanical means from agricultural wastes such as stem and bunch, present small differences in chemical composition as a function of their position in the plant. A high similarity of surface behavior has been found for both stem and bunch fibers, thus indicating that both parts of plants get a similar chemical composition in their surfaces with a high lignin content. With implementation of surface treatments it becomes possible to reduce the hydrophilic behavior of the fibers to enhance their compatibility with polymeric matrices. Both alkalization and silanization treatments introduce alterations on chemical composition, leading to the reduction of the polar component of the free surface energy and affecting the hydrophilic tendency of fiber bundles. Thermogravimetric analysis of both banana fiber bundles has confirmed that all treatments employed allow the reduction of water uptake of fiber bundles and increase their thermal stability.

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