

Improvement of mechanical properties of natural fiber–polypropylene composites using successive alkaline treatments

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ABSTRACT: The use of natural fibers (NFs) in polymer composites for structural applications has increased greatly in the last years, owing to their abundance and biodegradability. In this work, an innovative and simple successive alkali treatment has been developed to improve the mechanical properties of NFs/polypropylene (PP) composites. Three different cellulosic fibers (curauá, jute, and flax) were used, with a fixed proportion of 10 wt %. The fibers were immersed several times in a 5 wt % NaOH solution. Thermogravimetric analysis data showed an improvement in thermal properties of the fibers, as well as the increase of the crystallinity degree was measured by X-ray diffraction. By Fourier transform infrared spectroscopy, disappearance of characteristics peaks of hemicelluloses and lignin was observed. Finally, mechanical behavior of the NF/PP composites was examined, using dynamic mechanical analysis. The results revealed that the curauá/PP mechanical properties were significantly improved, showing the positive effect of the successive alkali treatments. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41710.

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INTRODUCTION

Natural fiber composites became an alternative to glass-reinforced composites in structural applications since 1990s. Such composites as hemp fiber–epoxy and flax fiber–polypropylene (PP) are particularly attractive in automotive applications because of low cost and low density. These materials are mostly produced by thermoforming, however, and can also be manufactured by large-scale continuous processes, such as extrusion, and can be molded into detailed parts such as good surface finish, when injected.^{1–3}

Use of lignocellulosic fibers derived from annually renewable resources as a reinforcing phase in polymeric matrix composites provides positive environmental benefits with respect to ultimate disposability and raw material use. Compared to inorganic fillers, the main advantages of lignocellulosic materials are^{4,5}: renewable nature; wide variety of fillers available throughout the world; nonfood agricultural-based economy; low energy consumption, cost, and density; high specific strength and modulus; comparatively easy processability owing to their nonabrasive nature, which allows high filling levels, resulting in significant

cost economy; and relatively reactive surface, which can be used for grafting specific groups.

Despite these attractive properties, lignocellulosic fillers are used only to a limited extent in industrial practice owing to difficulties associated with surface interactions. The inherent polar and hydrophilic nature of polysaccharides and the nonpolar characteristics of most of the thermoplastics lead to difficulties in compounding the filler in the matrix and, therefore, in achieving acceptable dispersion levels, which results in inefficient composites. Moreover, the processing temperature of composites is restricted to below 200°C because lignocellulosic materials start to degrade near 230°C. This limits the type of thermoplastics that can be used in association with polysaccharide fillers. Another drawback of lignocellulosic fillers is their high moisture absorption and the resulting swelling and decrease in mechanical properties. Moisture absorbance and corresponding dimensional changes can be largely prevented if the hydrophilic filler is thoroughly encapsulated in a hydrophobic polymer matrix and there is good adhesion between both components. However, if the adhesion level between the filler and the matrix is not good enough, a diffusion pathway can preexist or can be created under mechanical solicitation.^{4,5}

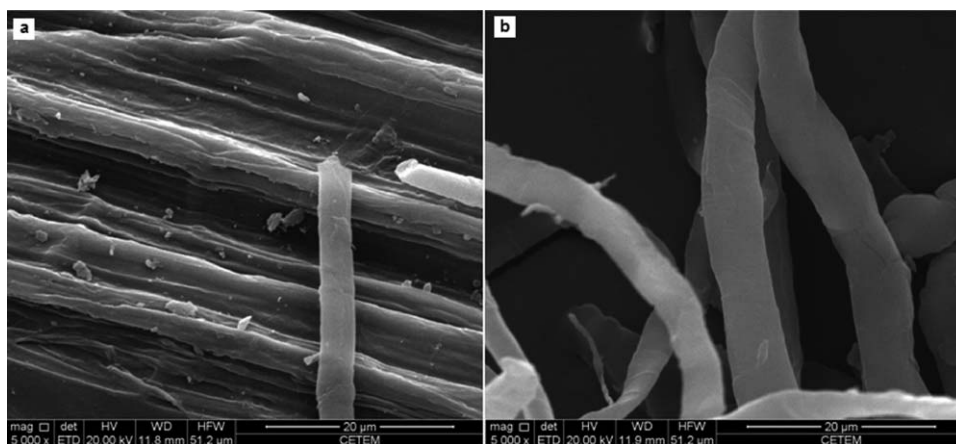


Figure 1. SEM micrographs of (a) untreated and (b) alkaline-treated curauá fibers ($\times 5000$).

The main components of natural fibers (NFs) are cellulose, hemicellulose, lignin, pectin, and waxes. Cellulose is a natural polymer consisting of repeating units of anhydrous D-glucose linked by β -1 linkages, 4-glycosidic bonds in positions C1 and C4. Degree of polymerization is around 10,000. Each repeating unit contains three hydroxyl groups and these, with the ease of performing hydrogen bonds, play a prominent role in the formation of the

crystal lattice and also govern the physical properties of cellulose. Hemicellulose comprises a group of polysaccharides consisting of a combination of a sugar rings by adding five and six carbons. Hemicellulose differs from cellulose in three aspects: first, it contains a number of different sugar units, whereas cellulose has only 1,4- β -D-glucopyranose. Second, it exhibits a considerable degree of branching containing pendant groups that provide an increase

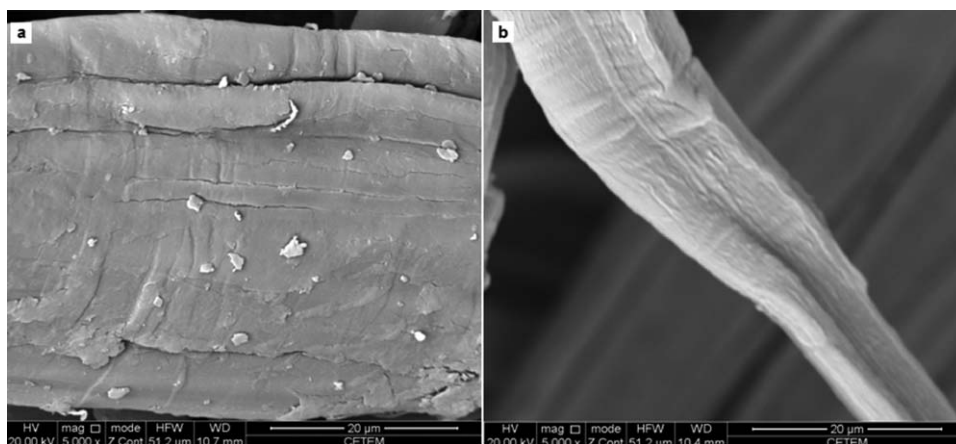


Figure 2. SEM micrographs of (a) untreated and (b) alkaline-treated jute fibers ($\times 5000$).

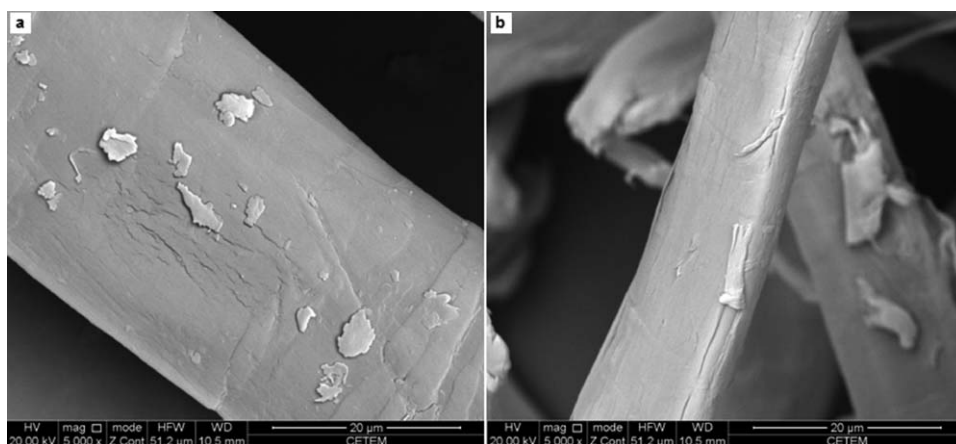


Figure 3. SEM micrographs of (a) untreated and (b) alkaline-treated flax fibers ($\times 5000$).

in its noncrystalline nature. Already cellulose is characterized by a linear polymer. Finally, the degree of polymerization of hemicellulose is around 50–300, 10 to 100 times smaller than the cellulose.

Lignin is characterized by a polymer complex formation with aliphatic and aromatic groups. It is completely insoluble in most solvents and cannot be broken in monomer units. Moreover, it is of amorphous nature and hydrophobic in its entirety, responsible for stiffening the plants. Hydroxyl, carbonyl, and methoxy groups are examples of groups that can be identified in the lignin, which contains five hydroxyl and methoxy groups by structural unit.^{6,7}

Pectin is the most structurally complex family of polysaccharides in nature, making up ~35% of primary walls in dicots and nongraminaceous monocots, 2–10% of grass and other commelinoid primary walls, and up to 5% of walls in woody tissue. Pectin is abundant in walls that surround growing and dividing cells, walls of cells in the soft parts of the plant, and in the middle lamella and cell corners.⁸

In relation to the treatments performed on NFs, alkaline treatment or mercerization is a chemical method commonly used when the application is directed to reinforce thermoplastic and thermoset polymers. The important change provided by the alkali treatment is the disruption of hydrogen bonds in the structure, thereby increasing its roughness. This treatment is able to remove some hemicellulose, lignin, waxes, and oils that cover the outer surface of the cell wall of the fibers, improving their thermal stability. Depending on the concentration of alkali, it is also able to depolymerize cellulose and expose some crystalline segments.⁹

Although NFs have been used to fill and reinforce thermosets, NF-reinforced thermoplastics, especially PP composites, have attracted greater attention owing to their added advantage of recyclability.¹⁰ Therefore, the aim of this article is to show the influence of successive alkali treatment on different plant fibers (curauá, jute, and flax), in terms of evolution of thermal stability and crystallinity, by successive immersions in a 5.0 wt % NaOH solution and the effect on mechanical properties of composites prepared with treated and untreated fibers using PP as matrix, with a 10 wt % content of fiber.

EXPERIMENTAL

Materials

Polypropylene homopolymer HP 550K, supplied by Braskem, with a melt flow index of 3.5 g/10 min (230°C/2.16 kg), was used as matrix. Jute and curauá fibers were purchased from Pamatec S.A. company (Pará, Brazil). Flax fibers were acquired from Vivabras (São Paulo, Brazil). Sodium hydroxide used for preparation of alkaline solution was provided by Vetec Química Fina S.A. Chemical treatments on vegetal fibers were performed using a liquor ratio of 1 : 30. PP/NF blends were prepared using 90/10 wt % proportion.

Chemical Treatment

In a first step, fibers were treated in a grinding knives mill. The aim of this procedure is to reduce the fiber size. Subsequently, the size separation is effected through a sieve with a mesh size of 200 (200 mesh/inch or 75 μm). After this step, hemicellulose and part of lignin were extracted out of cellulose by three

successive alkali treatments. In each treatment, the fibers were placed in a 5.0% solution of sodium hydroxide for 1 h at 80°C. Then, the fibers were washed with deionized water to remove excess NaOH until neutral pH. Finally, the fibers were dried at 20 mmHg and 80°C to constant weight for moisture removal.¹¹

Processing of Composites

For the preparation of composites with commercial PP, fibers were dried in an oven (treated and untreated) at 80°C for 12 h and mixed with the polymer in the proportion of 90/10 wt % in a mini-extruder twin-screw counter-rotating Haake Minilab at 180°C for 15 min and speed rotation of 60 rpm.

Characterization

X-ray Diffraction. The characterization by X-ray diffraction (XRD) to evaluate the crystallinity index of the pure fiber and the treated fibers was conducted in a diffractometer Rigaku, Miniflex model, working at a potential difference of 30 kV and tube electric current of 15 mA. The scanning was performed in the range of 2θ from 2° to 40°, with a goniometer speed of 0.05°/min.

Degree of crystallinity (X_c) can be calculated by fitting the areas under the XRD spectra [eq. (1)]:

$$X_c = \frac{A_{\text{cryst}}}{A_{\text{total}}} \times 100, \quad (1)$$

where A_{cryst} is the area from peak at $2\theta = 22.7^\circ$, associated to crystalline phase of fiber and A_{total} is the total area of diffraction peaks.^{12,13}

Thermogravimetric Analysis. The thermal stability was analyzed by thermogravimetric analysis (TGA) (Q500, TA Instruments). Samples were heated from room temperature to 700°C under nitrogen atmosphere at a heating rate of 10°C/min to determine the temperatures of degradation T_{0.05} (temperature with 5 wt % mass loss) and T_{max} [peak in derivative TGA—1st derivative of the TGA curve (DTG)].¹⁴

Table I. Thermal Properties of Untreated and Alkaline-Treated Natural Fibers

Fiber	Treatment	T _{0.05} (°C)	T _{max} (°C)
Curauá	Untreated	217	333/439
	First treatment	262	316/449
	Second treatment	265	319/427/455
Jute	Third treatment	263	316/430/458
	Untreated	267	344
	First treatment	263	305
Flax	Second treatment	263	305
	Third treatment	263	306
	Untreated	266	344/506
	First treatment	271	331/475
	Second treatment	286	336
	Third treatment	281	334/469

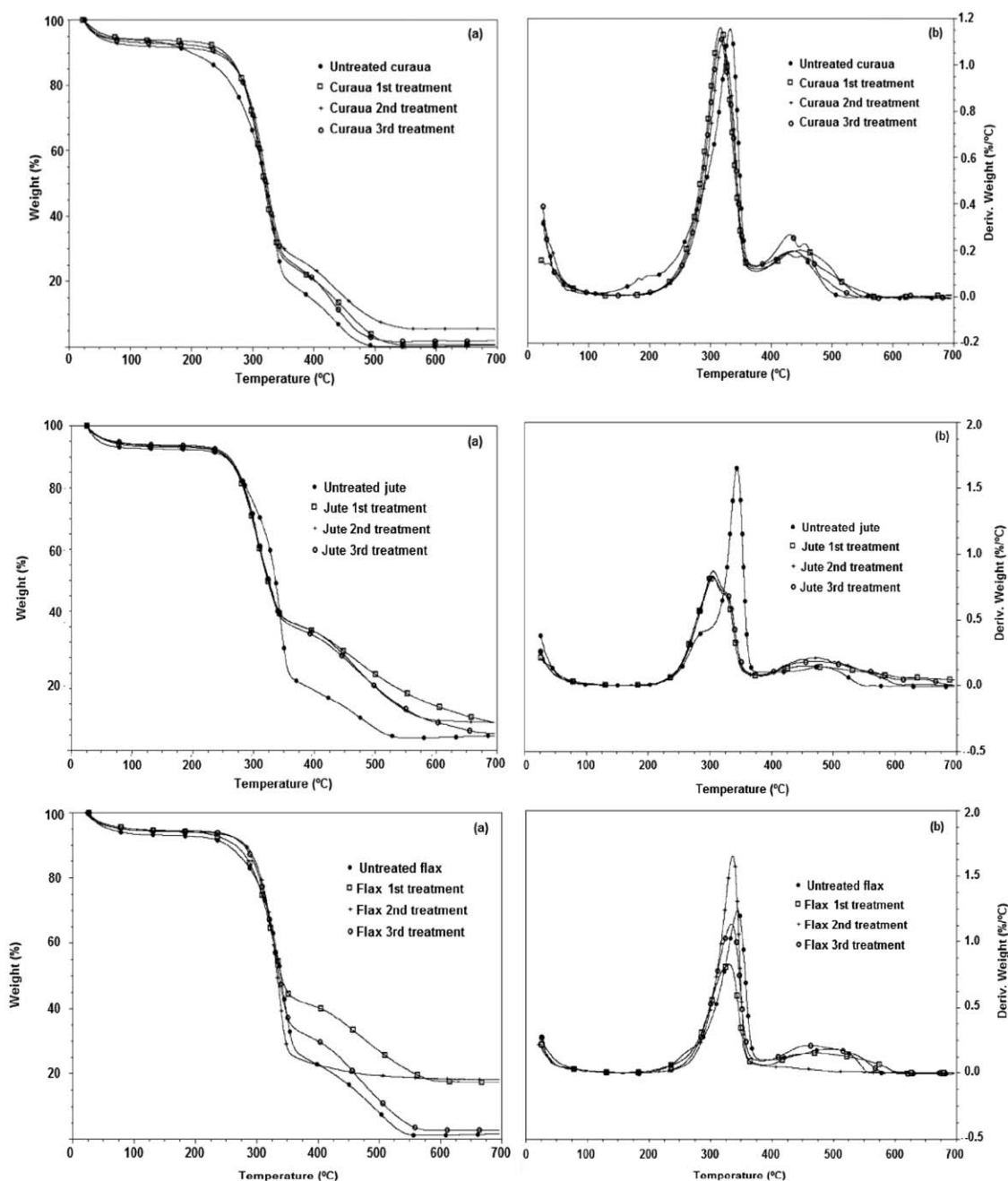


Figure 4. (a) TGA and (b) DTG curves of untreated and alkaline-treated natural fibers.

Infrared Spectroscopy. The characteristic absorption bands of the materials were analyzed by Fourier transform infrared spectroscopy (FTIR) (Excalibur 3100, Varian). The fiber (treated and untreated) spectra were obtained in the range of $4000\text{--}600\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} .

Dynamic Mechanical Analysis. After processing, films of the composites were prepared by compression molding at 200°C for 15 min and characterized by dynamic mechanical analysis (DMA) to evaluate the mechanical properties such as storage modulus (E') and loss (E'') as well as the glass transition temperature (T_g) and damping factor ($\tan \delta$).

The thermal DMA was performed using TA Q800 with a heating rate of $3^\circ\text{C}/\text{min}$, with a frequency of 1 Hz, and strain of 0.1% in the range of -40 to 150°C .

Differential Scanning Calorimetry. DSC tests were carried out using a DSC-TA instrument (model Q-1000), from room temperature to 200°C , at a constant heating rate of $10^\circ\text{C}/\text{min}$. Sample masses varied between 3.0 and 4.5 mg in all the tests. The degree of crystallinity was calculated according to eq. (2).

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \times 100, \quad (2)$$

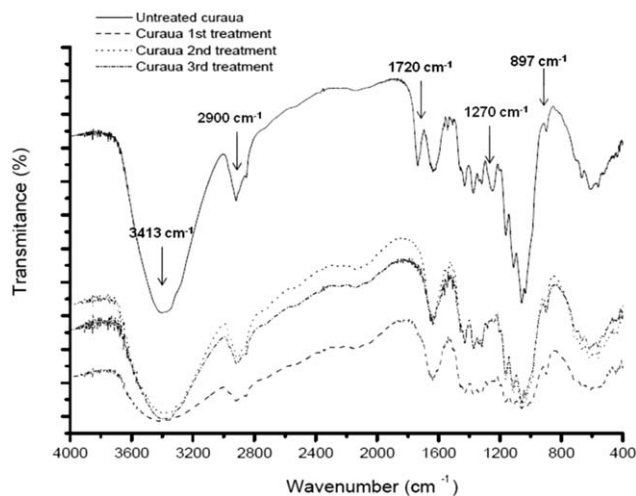


Figure 5. FTIR spectra of untreated and alkaline-treated curauá fibers.

where X_c is the degree of crystallinity (%); ΔH_m^a is the melting enthalpy of the sample (J/g); and ΔH_m^{100} is the melting enthalpy of 100% crystalline PP (J/g), which was considered to be 190 J/g.^{15,16}

Scanning Electron Microscopy. Scanning electron microscopy (SEM) observations were carried out in cryogenically fractured samples, in both transversal and surface directions. Analysis was performed using a FEI Company microscope model Quanta 200, using specimens coated with 300-nm gold (Au) particles applied by JEOL equipment model JFC 1500.

RESULTS AND DISCUSSION

The influence of the three successive alkaline chemical treatments in the fibers is presented in Figures 1–3, which shows SEM images of the fibers (curauá, jute, and flax), before and after the treatments. According to the micrographs, it can be observed a larger number of residues on the surface of neat curauá fibers [Figure 1(a)] than all other fibers. Possibly, for this reason, this fiber presents less thermal stability compared with jute and flax, as can be seen in Table I. Moreover, after alkalization, surfaces of the fibers are smoother, with extraction of external layer of the fibers, followed by fibers separation. This may be related to effect of successive alkaline treatments, responsible for the removal of low molar mass components such as hemicelluloses, pectins, and other polysaccharides.^{17–20}

Results of TGA of the fibers before and after the chemical treatments are presented in Table I and Figure 4. It is observed that for the curauá fibers the thermal resistance is greatly improved after the first treatment, with an increase of 45°C in degradation temperature between the untreated and treated fibers, which can be attributed to the removal of hemicellulose and other components of low molar mass, such as pectin and waxes, as evidenced by the disappearance of the characteristic shoulder at 275°C in DTG curve [Figure 4(b)].²¹ Similar behavior was observed in the flax fibers. However, the increase of thermal resistance only can be noted after the second alkaline treatment.

In spite of the removal of small fractions on the surface of jute fiber as observed by SEM analysis, no thermal improvement was

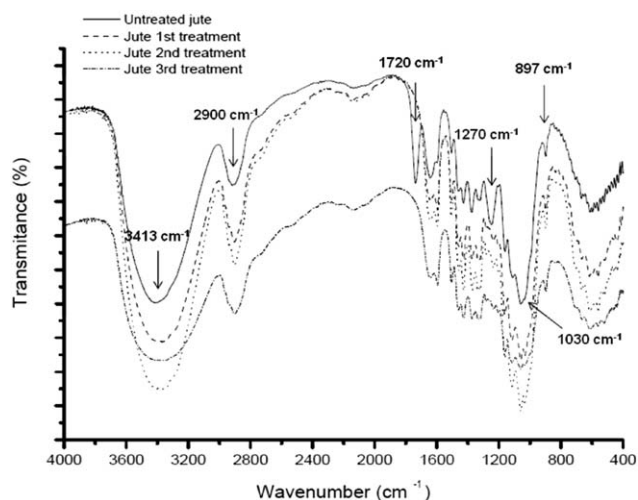


Figure 6. FTIR spectra of untreated and alkaline-treated jute fibers.

detected in jute fibers and this can be explained in terms of larger amount of lignin, which works as a strong adhesion component between the fibers, and difficult in the penetration of alkaline solution.^{22,23}

Three main mass loss stages can be observed in each curve in Figure 4(a). The first, up to about 150°C, can be attributed to evaporation of adsorbed water (whereas the curauá fiber is very hydrophilic). The second, in the range from 180 to 350°C, is attributed to the depolymerization of hemicellulose (untreated fiber), and the breaking of cellulose glycosidic bond (for all the fibers). Finally, the third stage, from ~250 up to 500°C, is related to the degradation of lignin (for all the fibers). These results are in agreement with the values reported in previous literature.^{24–30}

FTIR spectra of the pure and alkaline-treated fibers (Figures 5–7) reveal some important information about their characteristic absorption bands. The main peaks are located at: 3413 cm⁻¹ (stretching of the O–H bond), 2900 cm⁻¹ (stretch C–H bond), and 897 cm⁻¹ (stretch ring of glucose). This latter peak,

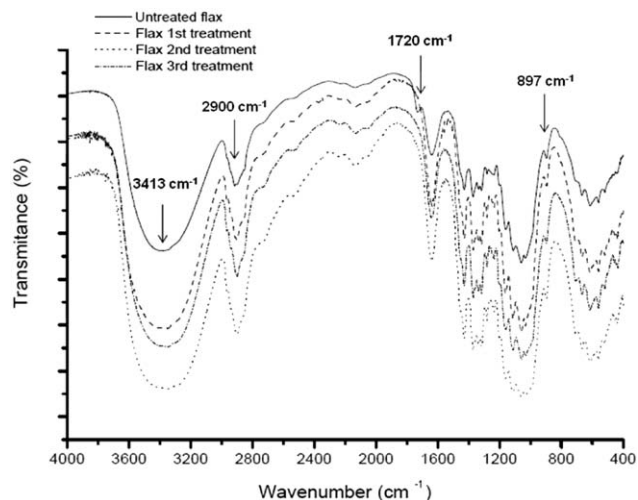


Figure 7. FTIR spectra of untreated and alkaline-treated flax fibers.

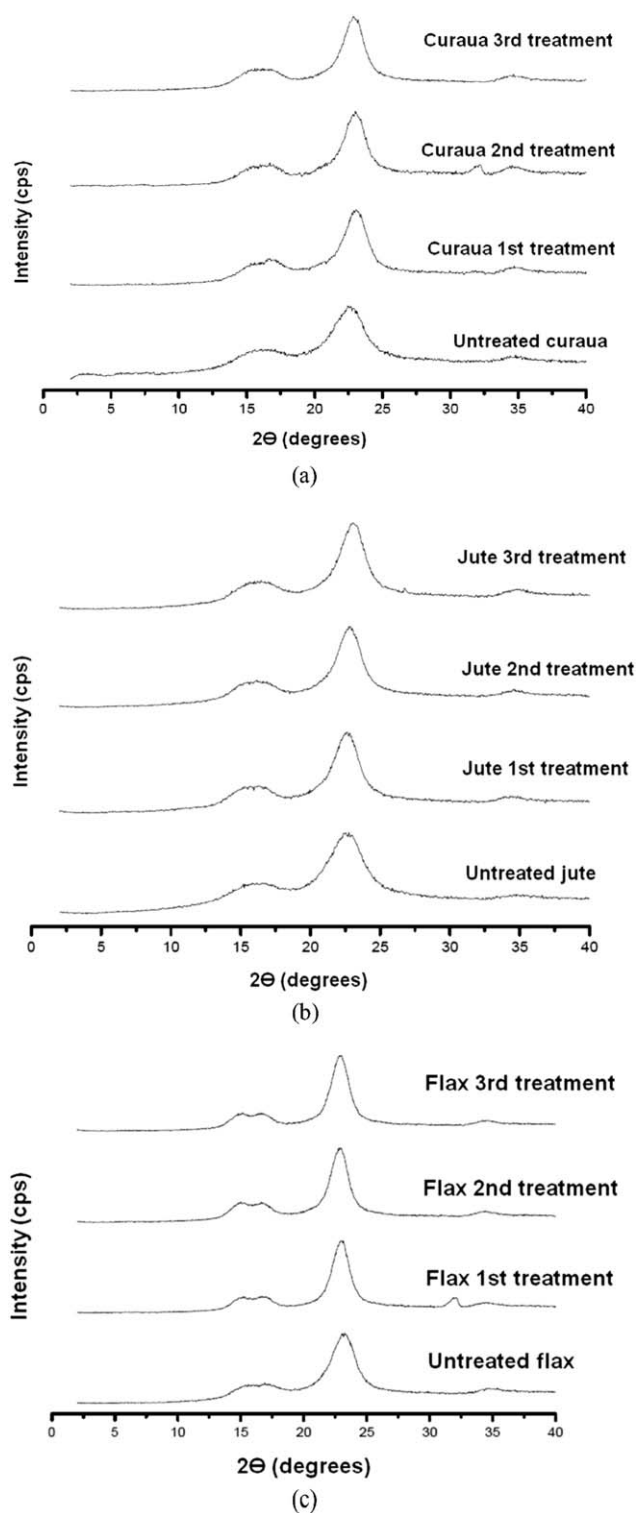


Figure 8. X-ray diffractograms of untreated and alkaline-treated natural fibers: (a) curauá, (b) jute, and (c) flax.

directly connected to the structure of the cellulose, remains unchanged even after the third chemical treatments, which shows that the cellulose is not degraded.^{31,32}

In alkaline-treated jute fiber, it can also be noticed the disappearance of the absorption peak at 1030 cm^{-1} , corresponding

Table II. Degree of Crystallinity of Untreated and Alkaline-Treated Natural Fibers

Sample/Fiber	Degree of crystallinity (%)		
	Curauá	Jute	Flax
Untreated	62	64	75
First treatment	70	67	79
Second treatment	70	68	75
Third treatment	73	68	77

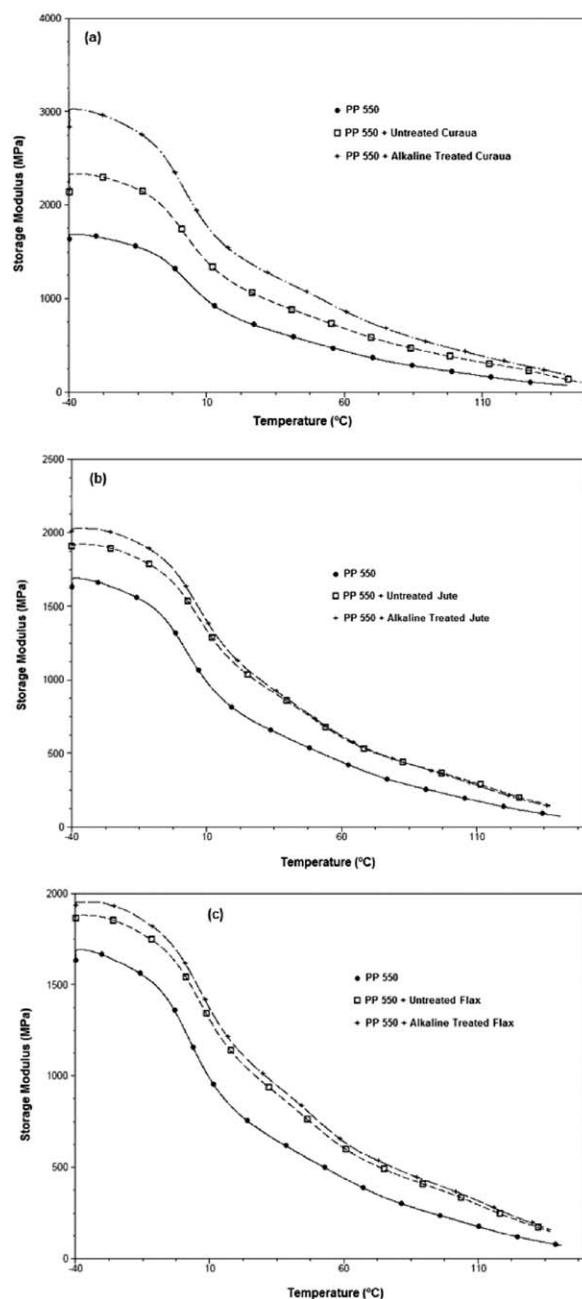


Figure 9. Storage modulus of polypropylene (PP 550) and their composites with untreated and treated fibers: (a) curauá, (b) jute, and (c) flax.

Table III. DMTA Results of Composites of Polypropylene/Natural Fibers (10% wt/wt)

Sample	Fiber	Description	E' at -40°C (MPa)	E' at 25°C (MPa)	E'' at 25°C (MPa)	T_g by $\tan \delta$ ($^{\circ}\text{C}$)	Tan δ damping factor
PP-550P	-	Processed pure polypropylene	1941	811	45	8.7	0.07322
PP-550P-C1	Curauá	PP550 + untreated curauá	2334	1083	50	7.1	0.06688
PP-550P-C2		PP 550 + alkaline-treated curauá (third treatment)	3022	1393	63	5.9	0.06453
PP-550P-J1	Jute	PP550 + untreated jute	1914	1039	45	10.9	0.05601
PP-550P-J2		PP 550 + alkaline-treated jute (third treatment)	1996	1073	507	10.9	0.05904
PP-550P-F1	Flax	PP550 + untreated flax	1837	1028	43	10.4	0.05414
PP-550P-F2		PP 550 + alkaline-treated flax (third treatment)	1897	1077	51	10.8	0.05982

to C—O stretching of hemicellulose and lignin. On the other hand, in treated curauá, the disappearance of the peak at 1270 cm^{-1} occurs, corresponding to C—O stretching of hemicellulose and lignin, indicating that most of the hemicellulose and lignin has been removed.³³

For all fibers, an absorption band at about 1720 cm^{-1} was vanished in the alkaline-treated fibers. The first alkaline treatment was enough to remove a substantial portion of uronic acid, a constituent of hemicellulose xylan, which resulted in the disappearance of the corresponding peak. Hemicellulose contained groups that absorbed in the carbonyl region, which are soluble in aqueous alkaline solutions.³⁴

XRD patterns of untreated and treated NFs and those submitted to different treatments are presented in Figure 8 and Table II, as well as the crystallinity degree, measured by the amorphous and crystalline areas of each diffractogram. Treated and untreated fibers showed three main reflection peaks at $2\theta = 15.6^{\circ}$, 22.7° and 34.6° relative to the cellulose crystalline structure. As a result of alkaline treatment, narrower and more intense crystalline peaks were observed for the treated fibers, particularly for curauá, leading to higher degree of crystallinity.^{30,33} For fibers with higher cellulose content, like flax, two peaks around 16° are observed; nevertheless, for curauá fibers, owing to the presence of amorphous cellulose, hemicelluloses, and lignin, only one broad peak is noted. These components cover the two peaks.^{30,35–37}

Regarding the diffractogram, it is clear that the amorphous peak owing to the presence of lignin and the various hemicelluloses present in the untreated fiber is decreased in intensity as soon as the alkaline treatment has been performed. In any case, crystallinity is not strongly affected by all these treatments, except for the curauá fiber, which shows a strong increase of X_c . It has also been reported that the thermal expansion of cellulose

is related to the crystallite size and crystallinity index. Less crystalline cellulose with small crystallites, such as wood cellulose, expands when subjected to a small amount of heat. Although the mechanism of this process is not well understood, the crystallite size, crystallinity index, and degree of polymerization may be important factors for the transfer of heat in the decomposition of cellulose.

Mechanical properties of the NF/PP composites were analyzed by DMA. During the DMA investigation, a sample is subjected to a sinusoidal deformation force at small amplitudes, determining a wide temperature range, both the elastic (E') and the loss (E'') moduli. The ratio between these effects, $\tan \delta$ (or damping factor), is a parameter that characterizes the viscoelasticity of the material, indicating a relaxation process. In the proximity of the glass transition temperature (T_g) the modulus E' decreases and both E'' and $\tan \delta$ curves reach a maximum.

Experimental results of storage modulus are presented in Figure 9 and Table III. Addition of 10 wt % of treated curauá fibers increases E' and E'' up to 50% with respect to the values of neat PP. On the other hand, treated jute and flax seem not to have any influence in the mechanical behavior of the composites, when compared to those prepared with untreated fibers. The modulus of PP is determined by two factors: strength of intermolecular forces and, ultimately, by packaging of polymer chains. When fibers are inserted into the resin, the increasing of the modulus is observed owing to the stiffness imposed by fibers.^{38,39}

Tan δ values and curves are presented in Figure 10 and Table III, respectively. In a composite, damping factor takes place owing to the nature of the matrix and fiber materials; friction generated from the slip in interface resin/fiber; energy dissipation at cracks and delaminations produced at damaged locations; and viscoplastic and thermoelastic damping.⁴⁰ For pure

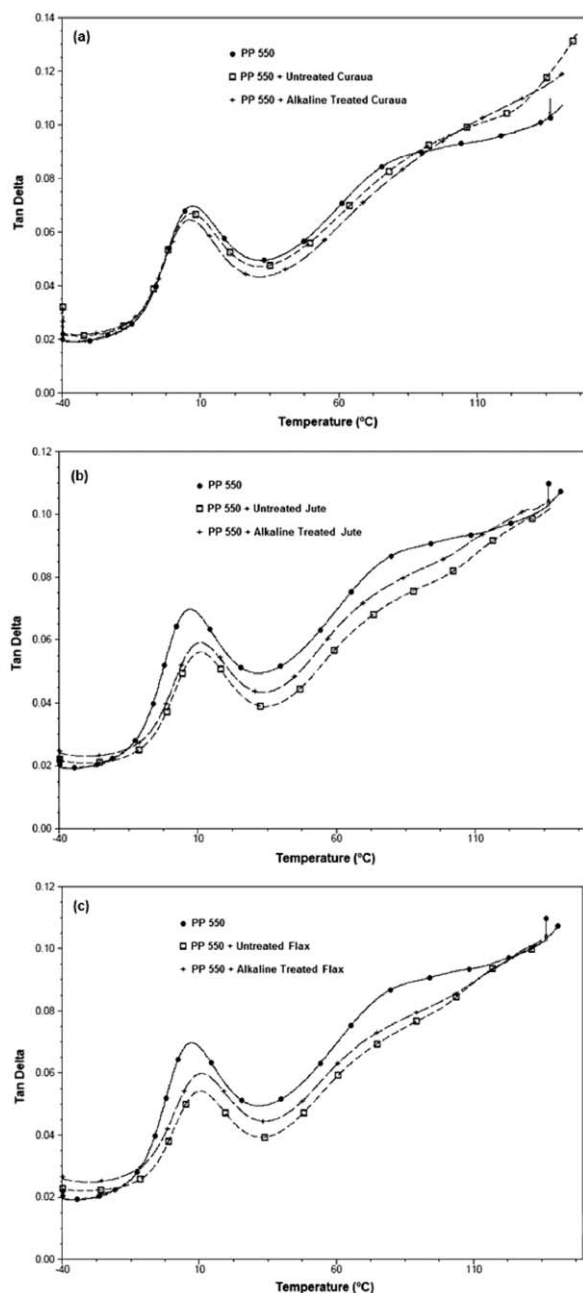


Figure 10. $\tan \delta$ of polypropylene (PP 550) and their composites with untreated and treated fibers: (a) curauá, (b) jute, and (c) flax.

PP, with increasing of temperature, $\tan \delta$ initially increases until α -transition peak temperature and then decreases. The position of peak can represent the α -relaxation temperature of 82°C for PP. Addition of fibers onto PP, treated or untreated in any case, did not cause significant changes in α -relaxation temperatures of the composites. This is in correlation with the literature,^{40–42} in which the position of α -relaxation was not significantly altered upon incorporation of natural short fibers.

Thermal properties of pure PP and their composites were investigated by DSC and the results are shown in Table IV and Figures 11 and 12. When fibers were added to PP matrix, both crystallization temperature (T_c) and degree of crystallinity increased, indicating the ability of NFs as nucleating agents. Consequently, crystallization process of matrix becomes faster.^{43,44} It can be also observed a slight decrease in melting temperature of composites compared to pure PP, possibly owing to the formation of more defecting crystals that can be confirmed by slight enlargement of their endothermic peaks in second heating DSC curves (Figure 12). Looking to thermal behavior of composites, both the degree of crystallinity and melting enthalpy of the composites prepared with treated fibers are higher than those of composites with untreated fibers, in all cases. However, composite with treated curauá fibers shows improved mechanical properties than all other composites in terms of elastic modulus. So, it means that the enhanced distribution and adhesion of treated curauá fibers in PP matrix is the most important parameter to be considered than the increase of crystallinity of composites.

Morphology of NF/PP composites was analyzed by SEM (Figures 13–15). The SEM evidences why composites with treated curauá fibers show better results in terms of elastic modulus than other fibers. It can be observed a large number of voids in cross-sectional fractures in composites of PP 550 with untreated curauá fibers [Figure 13(a)], resulting in a poor interaction adhesion with resin. This leads to a poor mechanical behavior compared with a composite prepared with treated curauá [Figure 13(c)]. In this case, the number of voids is drastically reduced and, consequently, better fiber distribution onto PP matrix, leading to less fiber agglomerations. Therefore, in this case, successive chemical treatments were able to improve adhesion between short curauá fibers and PP matrix. However, it is important to notice a presence of fiber pull-out in both cases [Figure 13(b,d)], mainly for composites with untreated curauá fibers, with higher diameter, and less distributed than treated ones.

Table IV. DSC Results of Composites of Polypropylene/Natural Fibers (10% wt/wt)

Sample	Fiber	Description	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PP-550P	–	Processed pure polypropylene	111.7	164.2	75.1	39.9
PP-550P-C1	Curauá	PP550 + untreated curauá	116.3	160.3	71.1	41.0
PP-550P-C2		PP 550 + alkaline-treated curauá (third treatment)	118.7	161.3	78.1	45.6
PP-550P-J1	Jute	PP550 + untreated jute	118.1	161.3	64.3	37.6
PP-550P-J2		PP 550 + alkaline-treated jute (third treatment)	118.0	161.7	78.0	45.6
PP-550P-F1	Flax	PP550 + untreated flax	119.5	160.0	60.2	35.2
PP-550P-F2		PP 550 + alkaline-treated flax (third treatment)	119.6	159.6	74.5	43.5

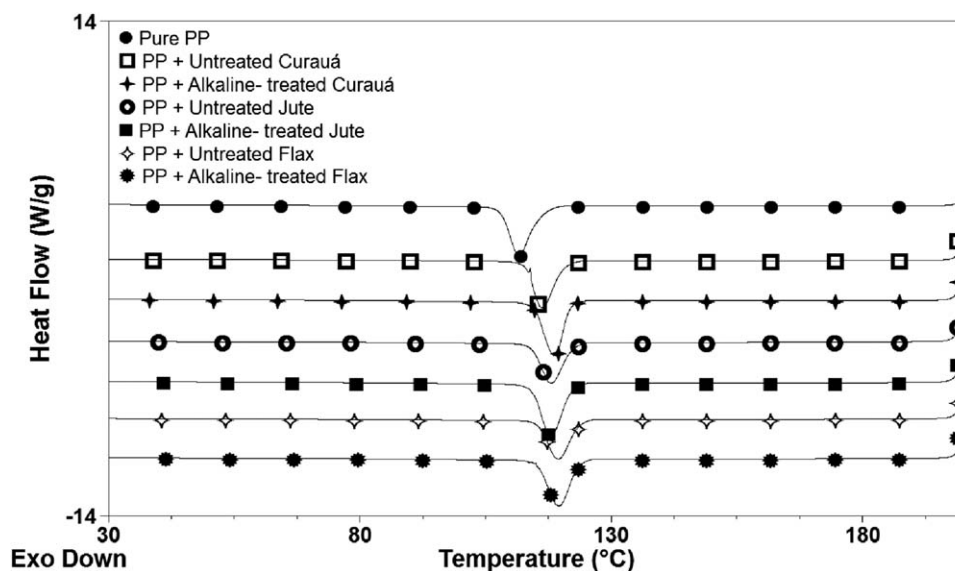


Figure 11. DSC curves of composites—first cooling.

In the case of the composites prepared with jute and flax (Figures 14 and 15), micrographs show a similar behavior, with a large number of gaps and voids, as well as fibers pullout, mainly for composites prepared with treated flax fibers [Figure 15(c,d)]. It can be also observed, in Figure 15(d), presence of fractures on the surface of treated flax fiber, which certainly contributes to poor adhesion between treated fiber and PP matrix, resulting in decrease of mechanical properties. Moreover, a factor that can also contribute to nonenhance of mechanical properties is the different fiber lengths and diameters across the surface of composites, resulting in a nonuniform distribution of fibers in resin, avoiding an increase of mechanical properties of treated fibers compared with untreated ones. Therefore, it can be concluded that successive chemical treatments were not enough to improve elastic modulus of composites.

CONCLUSIONS

In this work, an innovative and simple successive alkali treatment has been developed to improve the mechanical properties of NF/PP composites. Three different cellulosic fibers (curauá, jute, and flax) were used as reinforcing material in PP matrix, with a fixed proportion of 10 wt %.

The fibers were immersed several times in a 5 wt % NaOH solution. The successive alkaline chemical treatments seemed to be efficient, mainly for curauá fibers, because amorphous fraction of low molar mass (mainly hemicelluloses) have been completely removed, as observed by SEM, TGA, and DTG curves. FTIR confirmed that removal owing to the disappearance of the bands at 1270 and 1720 cm^{-1} , characteristic of groups present in hemicellulose and lignin. Also, the disappearance of characteristic peaks of hemicelluloses and lignin was observed, while

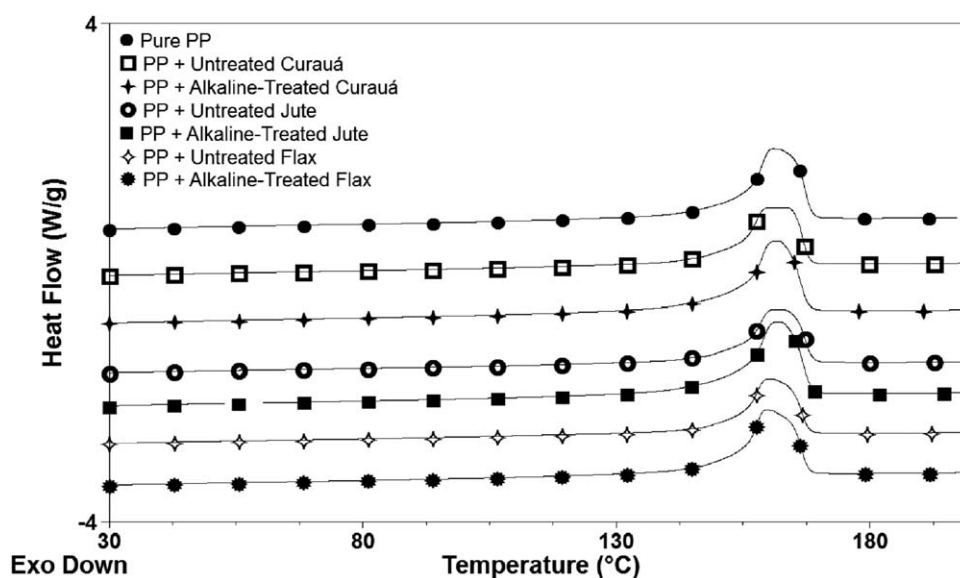


Figure 12. DSC curves of composites—second heating.

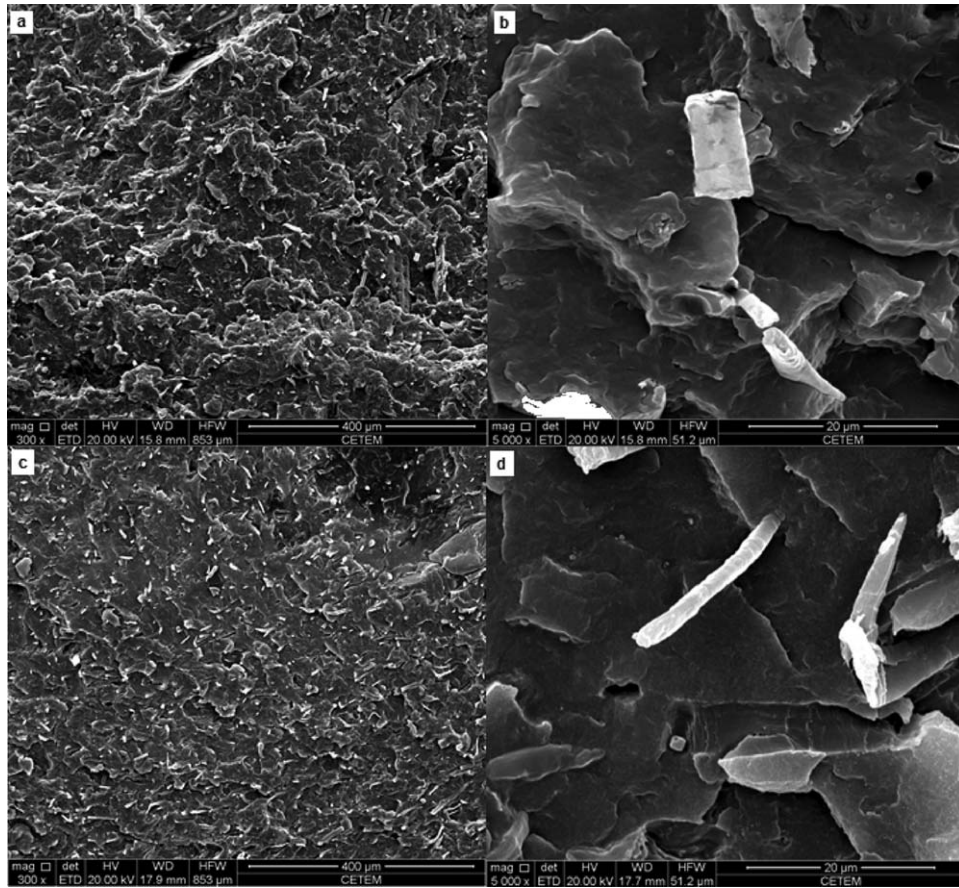


Figure 13. SEM micrographs of PP 550 composites with (a) untreated curauá fibers ($\times 300$), (b) untreated curauá fibers ($\times 5000$), (c) treated curauá fibers ($\times 300$), and (d) treated curauá fibers ($\times 5000$).

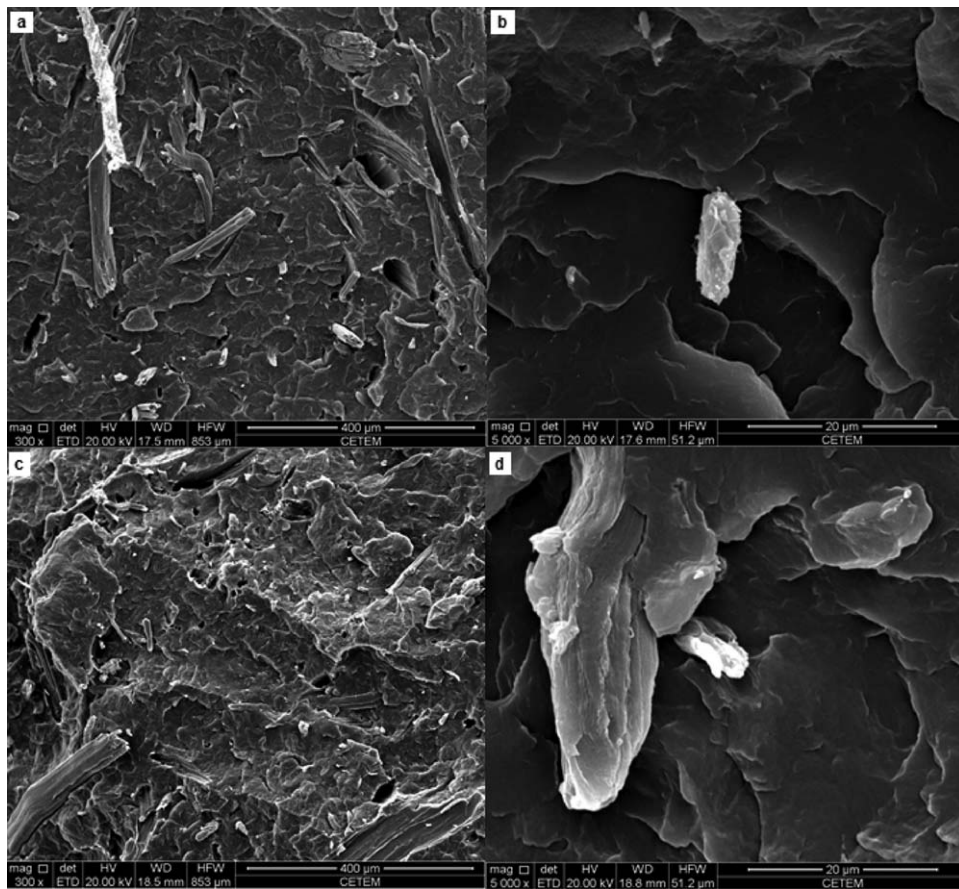


Figure 14. SEM micrographs of PP 550 composites with (a) untreated jute fibers ($\times 300$), (b) untreated jute fibers ($\times 5000$), (c) treated jute fibers ($\times 300$), and (d) treated jute fibers ($\times 5000$).

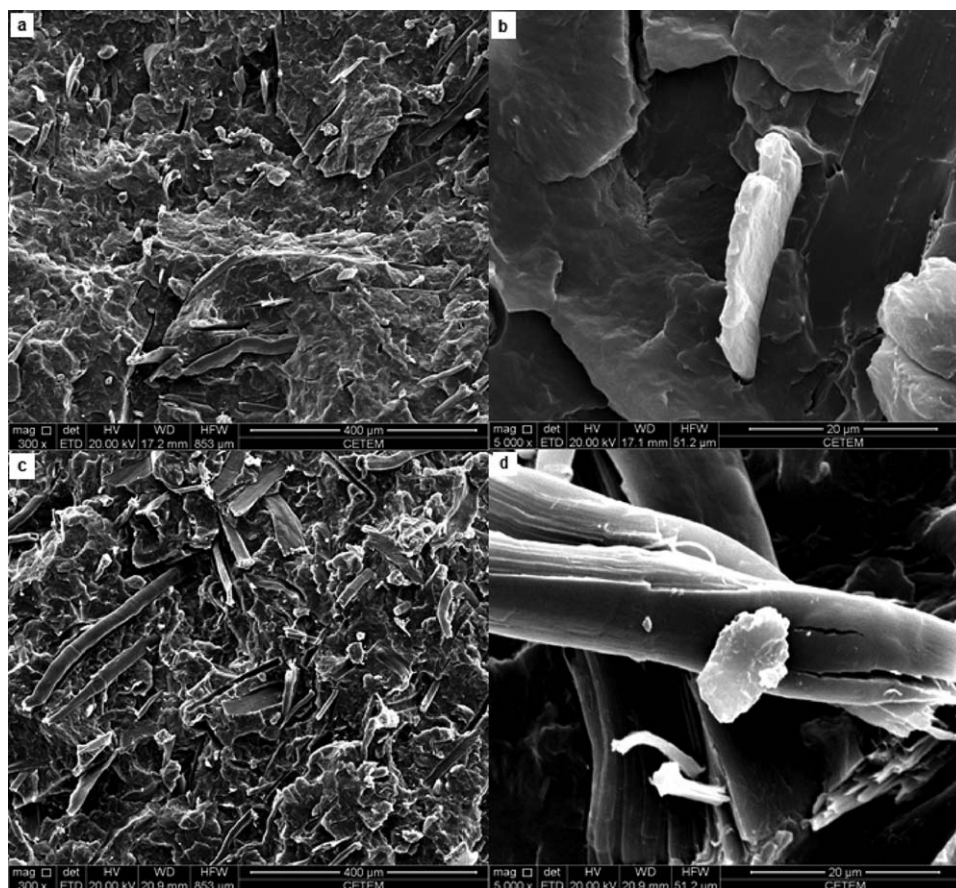


Figure 15. SEM micrographs of PP 550 composites with (a) untreated flax fibers ($\times 300$), (b) untreated flax fibers ($\times 5000$), (c) treated flax fibers ($\times 300$), and (d) treated flax fibers ($\times 5000$).

the characteristic peak of cellulose (897 cm^{-1}) remained unchanged in all the fibers. As a result, the degree of crystallinity increased with alkaline treatments, which could be noticed by the XRD patterns obtained. It can be observed that the addition of 10 wt % of treated curauá fibers increases E' and E'' up to 50% with respect to the values of neat PP.

As degree of crystallinity and melting enthalpy of the composites prepared with all treated fibers are higher, the better distribution and adhesion of treated curauá fibers in PP matrix is the most important parameter to be considered than the increase of crystallinity of composites, as could be seen by SEM micrographs. Moreover, the thermal resistance of curauá fibers has strongly increased after the chemical treatments compared with the other fibers, which could also be responsible for the sharp increase of mechanical properties of PP–curauá fiber composites.

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