CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECT OF CHEMICAL TREATMENTS ON THE PROPERTIES OF HDPE COMPOSITES WITH *Luffa cylindrical* FIBER

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In this study, we examined the effect of the addition of *Luffa cylindrical* (LC) fiber on the properties of high-density polyethylene (HDPE) composites. The fibers were subjected to acetylation and alkylation reactions. The composites were then examined in terms of their mechanical properties, morphology and water absorption. HDPE/LC composites containing 3.75, 7.5 and 15 wt% LC were prepared in an extruder and were subsequently injected into specimens. The properties of composites with untreated fibers and those with treated fibers were determined according to their compositions. The composites were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy, thermal analysis and tensile testing. The maximum improvement in mechanical properties was obtained for the composites with treated fibers. Morphological studies demonstrated that better adhesion between the fiber and the polymer matrix resulted from the alkylation treatment. The differences observed between the various composites are explained by different adhesion mechanisms. Interdiffusion takes place in untreated composites; multiple mechanisms of adsorption-wettability, interdiffusion and, to a lesser extent, chemical bonds occur in acetylated fiber composites; and finally, the adhesion in composites modified with octyl bromide is primarily due to a chemical mechanism based on covalent bonds.

Keywords: *Luffa cylindrical*, vegetable fiber composite/HDPE, chemical treatments, compliance

INTRODUCTION

Vegetable fibers are found virtually all over the world in abundance, particularly, in the tropics. Their biodegradability can contribute to a healthy ecosystem, and their low cost and reasonable performance in building materials can meet economic needs in various industries.[1-3]

Natural fiber obtained from leaves, seeds or coir exhibiting reasonable performance in building include Liberian, sisal, jute and sponge (*Luffa cylindrical*). These materials are composed of fibrils bonded with resin materials in natural plant tissue.[4] While some fibers have been widely investigated and used as building materials and for medical purposes, many other lesser known fibers have limited applications, for example, in making rope, mats, bags and wall hangings. One of the difficulties encountered in finding new uses for these natural fibers is the lack of scientific data on their structures and properties.[5] Natural fibers demonstrate little resistance to the environment and show an intrinsic variability in their properties.[4-6] *Luffa* fiber possesses good qualities as it is cheap, abundant and non-toxic. Although *Luffa* fiber has many advantages, it is rarely used industrially.

The bushing plant (LC), of *Curcubitacea* family, is shown in Figure 1.[7] The fruit of the plant is shown in Figure 1a, and the ripe fruit is shown in Figure 1b. The plant has a hard shell and an inner spongy region, with a multidirectional array of fibers forming a natural carpet. The plant also has an inner fiber core (Figure 1c) and an outer core mat (Figure 1d).[7]

The ripe fruit has a thick rind with a multidirectional array of fibers forming a type of natural carpet. The fruit has a thick rind fiber core and external core fibers.[6] The sponge gourd, the fruit of *Luffa cylindrical*, has a ligneous netting system in which the fibrous cords are disposed in a multidirectional array forming a natural mat. This fibrous vascular system is composed of fibrils glued together with natural resinous materials from the plant tissue.[8]

Among the varieties of sponges found in Brazil, the vast majority are used as bath sponges and for medicinal purposes.[7]

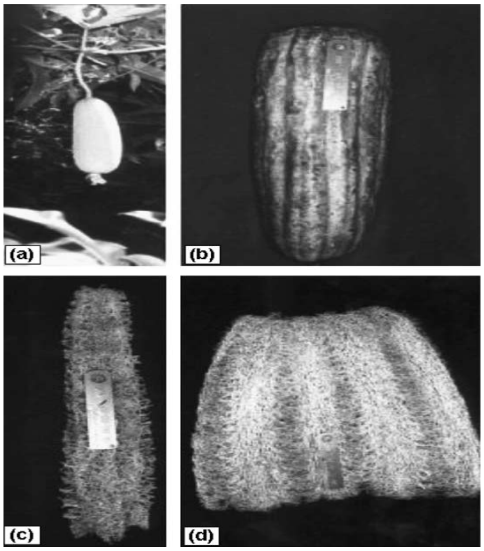


Figure 1: LC plant (a), fruit (b), inner core of the fiber (c) and outer core as an open mat (d)[7]

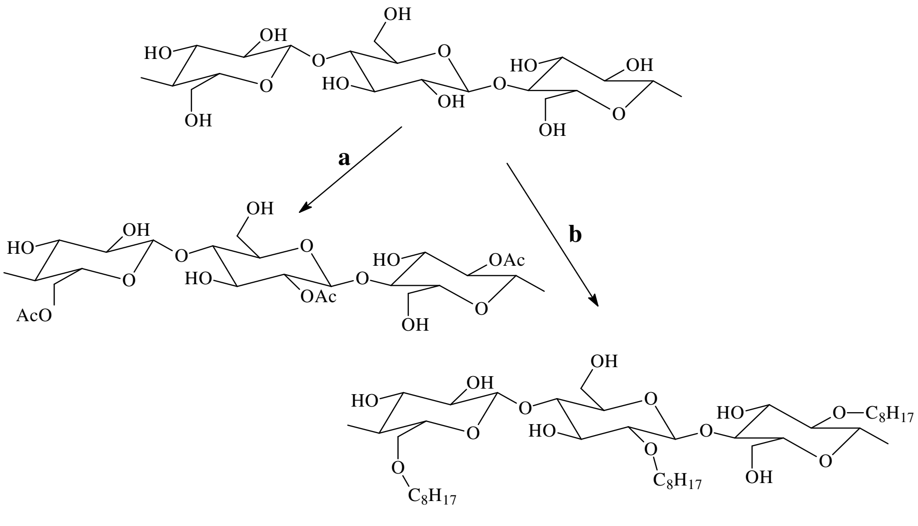


Figure 2: Scheme of the partial acetylation and alkylation of cellulose; (a) H_2SO_4, Ac_2O, AcOH; (b) KOH, benzene, DMF

To develop new applications for materials, complete characterization is required. In polymer composites, surface components are responsible for many interfacial phenomena, such as adsorption and adhesion, and the characterization of fibers before and after any treatment is necessary to characterize the final composite.[7,9]

The poor adhesion between natural fibers and polymer matrices is the main drawback to the direct use of lignocellulosic fibers in polymer composites. Lignocellulosic fibers are hydrophilic, while the polymers commonly used as matrices are hydrophobic.[10] Consequently, the generated interface between the fiber and polymer matrix is weak, resulting in an ineffective transfer of stress to the polymer fibers. Numerous physical and chemical treatments have been proposed to improve this feature and to therefore increase the performance of composites made from natural fibers.[3,11-18]

In the case of LC, a simple alkali treatment may improve the fiber-matrix interface, although previous studies have not reported significant effects.[13,19] Among the possible chemical treatments for this type of fiber, esterification reactions and acetylation reactions have great advantages in terms of cost and efficiency and have been extensively used in the treatment of wood fibers.[20]

This work presents the preparation and characterization of HDPE composites reinforced with LC. The fibers were chemically modified in the composites and were extruded and injected. The composites were characterized by FTIR, and their morphology was characterized by scanning electron microscopy (SEM). The effects of chemical treatments and fiber concentration on the mechanical properties, morphology and water absorption of the composites were characterized.

EXPERIMENTAL

Materials

Octyl bromide was obtained from Aldrich Chemical Co. Dimethyl formamide (DMF), toluene, acetic acid, acetic anhydride, potassium hydroxide, sodium hydroxide and sulfuric acid were all obtained from Vetec Fine Chemicals. All solvents were used as received.

Treatment of LC fibers

The LC fibers were washed with water at 30 °C to remove any adhered materials. Then, the fibers were dried in an oven at 50 °C for 24 h. After drying, they were cut into 20 mm pieces. Next, the fibers were agitated in a solution of 100 mL sodium hydroxide (0.5 M) at room temperature for 20 min. Finally, the fibers were washed in water until a neutral pH was achieved and were dried in an oven at 50 °C for 24 h.

Acetylation reaction of LC fibers

In a 250 mL flask equipped with a reflux condenser and a magnetic stirrer, 30 g of LC fiber, 75 mL of acetic anhydride, 50 mL of acetic acid and 10 drops of sulfuric acid were stirred for 3 h at 70 °C. Then, the fibers were separated by filtration, washed until a neutral pH was achieved and dried in an oven at 50 °C for 24 h.

Alkylation reaction of LC fibers

In a 250 mL flask equipped with a reflux condenser and a magnetic stirrer, 30 g of LC fibers, 50 mL of toluene, 50 mL of DMF, 6 g (0.11 mol) of potassium hydroxide and 13.4 mL (0.078 mol) of octyl bromide were refluxed for 4 h. After cooling, the fibers were separated by filtration, washed with alcohol (3 x 100 mL) and dried in an oven at 50 °C for 24 h.

Preparation of the pellets

HDPE/LC composites with different fiber concentrations (3.75, 7.5 and 15 wt% of fiber) were prepared using an ORYZON model OZ-E-EXL22 extruder. The composite was processed in heating zones at different temperatures: Zone 1 (165 °C), Zone 2 (175 °C), Zone 3 (185 °C) and Zone 4 (195 °C). A rotation speed of 60 rpm was used. After extrusion, the pellets were dried in an oven at 50 °C for 24 h.

Injection of the test specimens

After drying, the pellets were subjected to processing by injection in a mold to produce test samples according to ASTM D-638. In this work, we used an injector model HIMACO LHS 15080.

Structural characterization

FTIR spectra were collected in the 4000 to 650 cm^{-1} range using a Shimadzu Prestige-21 Model Spectrometer. Scanning electron microscopy was performed using a JEOL JSM-6390LV apparatus, with secondary electrons and an accelerating voltage electron beam of 15 kV. The thermal stability was studied using a high-resolution thermobalance (TA instrument, TGA-Q500 V20.10 build 36); 10 mg samples were scanned from 25 to 700 °C at a heating rate of 10 °C/min under a 50 ml/min nitrogen flow, and the corresponding weight loss was recorded.

Mechanical property characterization

The hardness of the material was determined by a Shore A hardness test, Zwick Materials Testing 3100 (ASTM D 2240, DIN 53505, ISO 868). This process was performed according to ASTM D2240-03. Tensile tests of the HDPE/LF composites were performed under ambient conditions in a universal testing machine with a load cell of 5 kN and a strain rate of 50 mm/min on a traction machine EMIC. This process was performed according to ASTM D412-98. For increased result reliability and to perform an appropriate statistical treatment, at least five samples were tested and the average values are reported.

Physical-chemical characterization – water absorption

The injected samples were subjected to a water absorption test. The standard procedure followed the

Standard Test Method for Water Absorption of Plastics D 570-98. Initially, the samples were dried at 70 °C for 6 h until a constant weight was achieved. Then, the samples were immersed in a static distilled water bath at a temperature of 25 °C to observe the absorption of water. The samples were left in this condition for 24 h. Afterward, they were dried with paper towels and weighed. The water absorption of the composites was calculated using the following equation:[21]

$$\text{Water absorption (\%)} = [(M - M_D) / M_D] \times 100 \qquad (1)$$

where: M is the final mass of the sample after water absorption,

M_D is the initial mass of the sample before water absorption.

RESULTS AND DISCUSSION

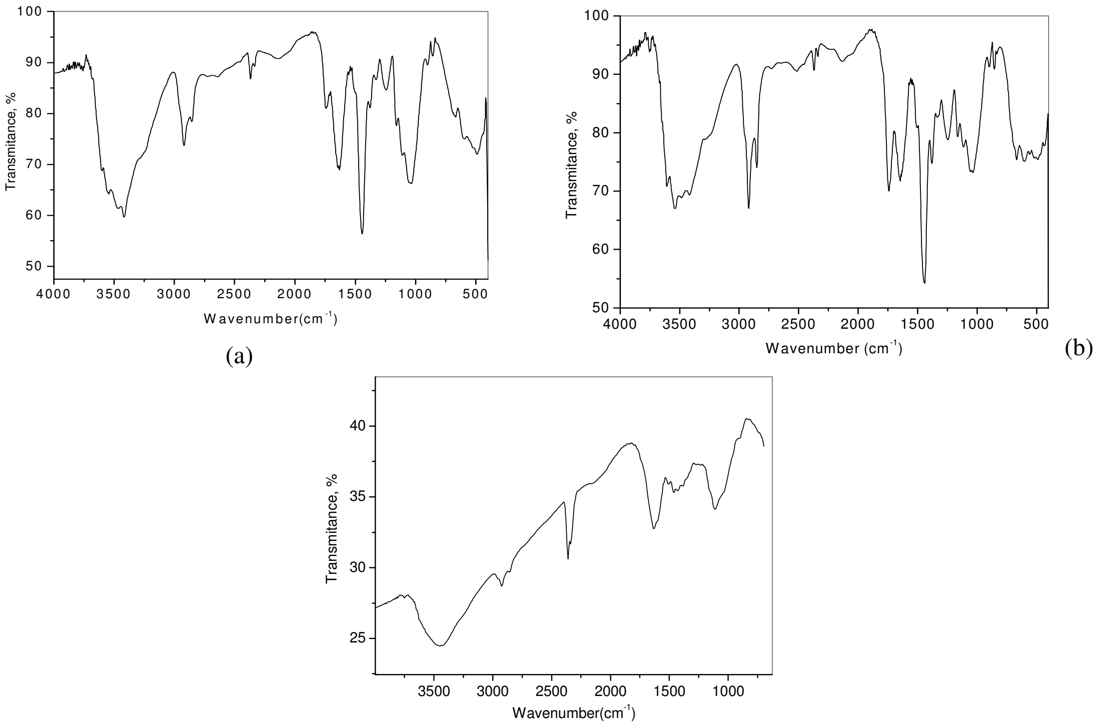
Preparation of the composites

The chemical treatments used in this work, both the acetylation process and alkylation process, led to changes in fiber color, and the samples exhibited yellowing. In the production of pellets, we also observed a change in the pellet color according to the fiber concentration. The same behavior was observed in the specimens produced by the injection process.

HDPE/LC composites with different fiber concentrations (3.75, 7.5 and 15 wt% of fiber) were prepared using an ORYZON model OZ-E-EXL22 extruder. A rotation speed of 60 rpm was used. Composites from extrusion were ground to obtain pellets suitable for injection molding. The injection molding conditions employed for the composite materials studied in this research were based on a previous study determining the range of conditions suitable for injection molding with this type of composite. The injection molding conditions used were: cylinder temperature profile (three heating zones), 180-185-190 °C; cycle time, 60 s; mold temperature, 40 °C.

FTIR characterization

FTIR spectroscopic analysis was used to characterize and compare the chemically modified fibers against untreated fiber. Fig. 3 shows IR spectra in the 4000 to 500 cm^{-1} range for the different composites.



(a)

(b)

(c)

Figure 3: FTIR spectra of fiber pretreated with sodium hydroxide (a), acetylated fiber (b) and alkylated fiber (c)

The NaOH fiber treatment resulted in the loss of the C=O (carbonyl) peak at 1725 cm^{-1} attributed to the removal of reducible hemicelluloses found on the fiber's surface.[22] The change in the 1235 cm^{-1} peak associated with the C-O stretching of the acetyl groups of lignin indicates that lignin is partially removed from the fiber surface after alkali treatment.[22] A signal was also observed at 3417 cm^{-1}, which is characteristic of the axial vibration of the hydroxyl group (hydroxyl groups of carbons 2, 3 and 6) of glucose.

The spectrum of acetylated fiber can be easily distinguished from that of untreated hydrolyzed by the increased intensity of the C=O (carbonyl) peak at 1741 cm^{-1} and the significant reduction in the hydroxyl signal. The presence of hydroxyl groups on the treated fiber is demonstrated by the presence of a signal at 3541 cm^{-1}, indicating that the acetylation reaction was not complete.

In the infrared spectrum of the alkylated fiber, there is a significant reduction in the signal at 3487 cm^{-1}, corresponding to the hydroxyl group. Although the esterification reaction did not reach 100% efficiency, the partial reaction is still interesting because it reduces the hygroscopicity of the fibers, which increases in the fiber-polymer phase interaction. One can also observe an increase in both the 1420 cm^{-1} band attributed to the CH_2 symmetric bending and the 873 cm^{-1} band assigned to the symmetric in-phase ring stretching mode.[22] Both of these bands are associated with grafting of the octane chain. In addition, the carbonyl stretching shoulder at 1741 cm^{-1} vanishes, which was previously attributed to the presence of noncellulosic impurities in the native fibers.[22]

Mechanical properties

Tensile tests were performed to assess the fiber-polymer phase interaction. The results are shown in Table 1. In general, the tensile strength of the composites formed by the polymer-fiber phase depends on the pretreatment and the fiber content. However, the mechanical properties are greatly enhanced in the composites composed of treated fibers, as shown by this study. Table 1 summarizes the tensile strength values obtained for the composites in this work.

We observed an increase in the yield stress for composites formed with both treated fiber and untreated fiber. The yield stress also increases with increasing fiber concentration in the composite. Similar trends were observed for the elastic modulus, toughness and maximum stress.

However, the deformation decreases with increasing fiber concentration, particularly for the samples subjected to chemical treatment. These results also corroborate the efficiency of the treatment process performed on the fiber, which is responsible for altering the efficiency of the interaction between the fiber and polymer matrix by restricting the deformation and increasing the hardness and strength of the material.

Thermal decomposition analysis – TGA

Figure 6 shows the TGA results of the composite with acetylated fibers at the three LC fiber concentrations used in this work.

Table 1
Mechanical properties of composites with LC fiber

	Without treatment			Acetylated fiber			Alkylated fiber		
Composition (wt%)	3.75	7.50	15.00	3.75	7.50	15.00	3.75	7.50	15.00
Flow stress (MPa)	5.44 ± 0.36	6.12 ± 0.79	6.16 ± 0.03	8.74 ± 0.72	11.71 ± 0.42	21.60 ± 3.72	9.00 ± 0.35	12.08 ± 0.41	24.83 ± 1.50
Elastic modulus (MPa)	127.22 ± 13.42	130.47 ± 4.02	133.68 ± 16.52	186.97 ± 4.27	287.68 ± 5.97	493.98 ± 144.38	196.52 ± 6.33	269.73 ± 12.08	539.25 ± 85.98
Deformation (%)	61.40 ± 11.73	40.26 ± 0.79	39.04 ± 4.66	7.54 ± 1.19	4.05 ± 0.33	2.38 ± 1.65	4.15 ± 1.08	6.37 ± 3.16	2.57 ± 0.57

We see the beginning of mass loss at 250 °C for the composites with 7.50 wt% and 15.00 wt% fiber. The composite with 3.5 wt% exhibits a mass loss that is very similar to that of polymer

PE. This behavior is attributed to fiber decomposition that occurs at temperatures below the polymer resin decomposition. Figure 4a (top) shows the TGA spectra obtained for the composite with 3.5 wt% compared with pure PE, and Figure 4b (bottom) shows the TGA spectra obtained for the composite with acetylated fibers.

Water absorption

Figure 5 shows the water absorption of composites obtained with different treatments of the LC fiber. We observed that the alkylation and acetylation treatments reduce the water absorption by reducing the number of hydroxyl units that are free to interact with the water molecules.

The formation of hydrogen bonds between the free hydroxyl group in the cellulose molecules and water molecules is largely responsible for the absorption of water in the cellulose fibers' hydroxyl group. Another reason for the decreased water absorption of the composites is the expansion caused by the fiber-polymer interaction. The processes of alkylation and acetylation increase the lipophilicity of fiber and improve the adhesion between the fiber and matrix, which decreases the gaps between the fiber and polymer matrix and reduces the absorption capacity of the composite.

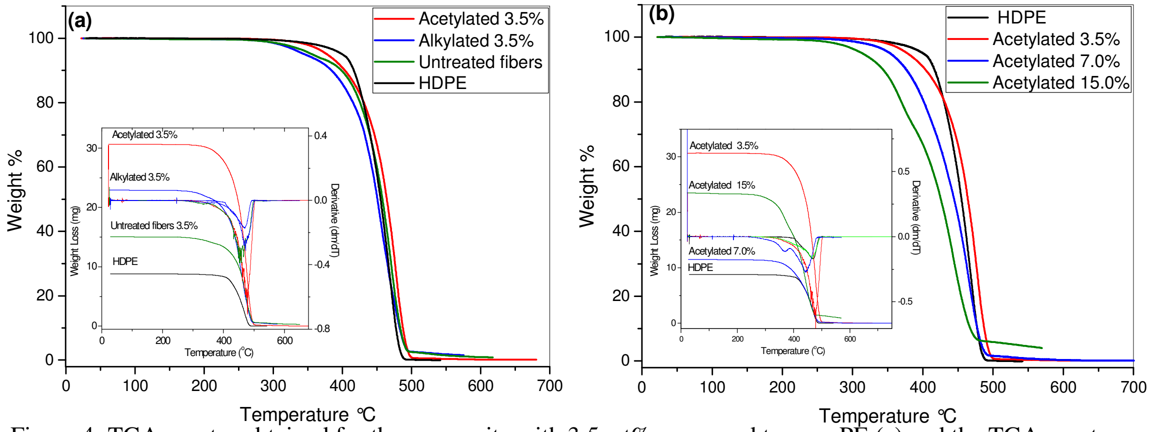


Figure 4: TGA spectra obtained for the composite with 3.5 wt% compared to pure PE (a) and the TGA spectra obtained for the composite with acetylated fibers (b)

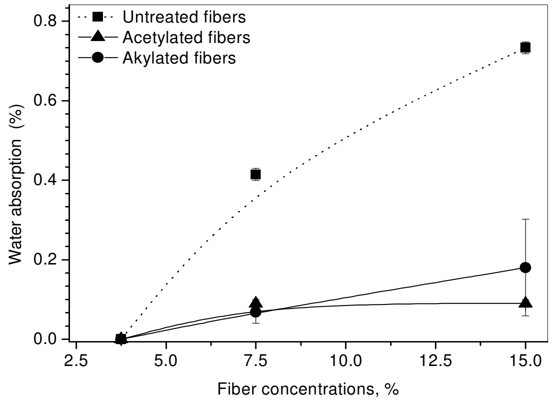


Figure 5: Water absorption of composites with different fiber concentrations, untreated fibers (■), acetylated fibers (▲) and alkylated fibers (●)

Figure 6 shows SEM images acquired to study the morphological aspects of the composites with acetylated fiber (3.5 wt%, Figure 6a) and the composites with alkylated fiber (3.5 wt%, Figure 6b). We observed that the interfaces are fully immersed in the fibrous polymer phase, which indicates a strong fiber-polymer interaction.

The mechanical tests and SEM clearly show the feasibility and the interaction between the fiber and the polymer in both treatments. The mechanical properties and the results obtained by

FTIR and SEM clearly demonstrate the existence of interactions among the components of the composites (i.e., the HDPE matrix and fibers). The differences observed between the various composites can be explained by their particular adhesion mechanisms. The untreated composites present a very weak physical-mechanical adhesion. In the composites with modified fibers, the presence of groups that can be self-hydrolyzed introduces multiple mechanisms of adsorption-wettability, interdiffusion and, to a lesser extent, chemical bonds primarily formed by secondary bonding. The composites treated with octyl bromide display a chemical adhesion mechanism, with the formation of covalent bonds as well as hydrogen bridges, although neither interdiffusion nor adsorption-wetting mechanisms can be excluded.

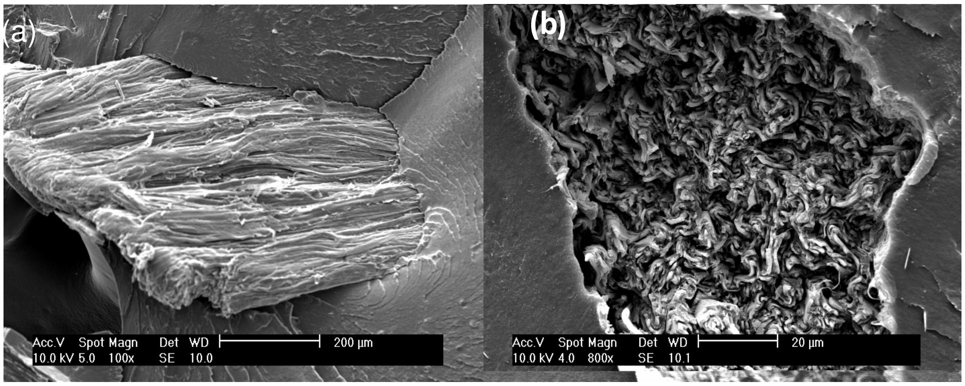


Figure 6: SEM images of the composite with 3.5 wt% acetylated fibers (a) and the composite with 3.5 wt% alkylated fibers (b)

CONCLUSION

The experimental results show that the interaction between vegetal fibers and polymers can be improved by chemical treatments. Two methods (acetylation and alkylation) were used to alter the lipophilicity of the fiber and, therefore, the interaction between the fiber and the polymer. The chemical alteration of the fiber was confirmed by infrared spectroscopy. The composites were prepared by the extrusion technique followed by sample injection.

The composites were analyzed for mechanical strength, water absorption and thermal stability. It was observed that the chemical change increased the tensile strength of the fiber-polymer composite and consequently reduced the material deformation. These results were particularly pronounced for the composites with alkylated fibers.

We also observed a significant reduction in water absorption in the polymer-fiber composites after chemical treatment, with no significant differences between the chemical processes used.

The differences observed between the various composites in this work are explained by their different adhesion mechanisms. Interdiffusion occurs in untreated composites; multiple mechanisms of adsorption-wettability, interdiffusion and, to a lesser extent, chemical bonds take place in acetylated fiber composites, and finally, the adhesion occurring in composites modified with octyl bromide is primarily a chemical mechanism of covalent bonds.

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