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Article

Biocomposites from dwarf-green Brazilian coconut impregnated with cashew nut shell liquid resin

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Abstract

The dwarf-green coir fibers treated with sodium hydroxide 10% produced the best set of properties of the biocomposites generated: greater roughness and exposure of intrafibrillar cavities, providing better adhesion with the matrix, higher rigidity, increased resistance to traction and better interface properties, making them better as structural materials. The best results reported in the thermal behavior of biocomposite fibers were found in fibers treated with sodium hydroxide 10%. These showed a single stage of decomposition, which occurs at a higher temperature (300°C). It was observed that the natural fibers were more resistant to the action of the microorganisms due to the presence of more lignin and hemicellulose, while fibers treated with 5 and 10% sodium hydroxide showed different degradation degree.

Keywords

Dwarf-green coir fibers and biocomposites, cashew nut shell liquid resin, biodegradability, mechanical and thermal properties

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Introduction

The uncertain price availability of petroleum and growing environmental concerns over its use have prompted the investigation of new, more environmentally friendly, products and processes not relying on fossil fuels. In this context, composite materials based on natural fibers are expected to be important alternatives to petroleum-based materials, with significant benefits for society.[1–14]

The use of these fibers is also justified by its low cost, low density, easy biodegradability, nontoxicity

and its capacity of being recycled. Brazil has a great potential to produce and trade different types of fibers. However, many of them, such as coconut, pineapple and banana are discarded and treated as agricultural waste. If used properly, they provide countless applications, especially in the North and Northeast of Brazil, where they are usually grown.[15]

The coconuts (*Cocos nuciferas L.*) are one of the most diffuse agricultural activities in tropical countries. According to Faostat,[16] Brazil is the fourth leading producer and the Northeast region is the largest Brazilian producer of coconut. The increasing production of green coconuts from dwarf trees and of tourism in northeastern Brazil is causing environmental consequences due to the large amount of discarded material and its slow decomposition rate.

For this reason, the development of alternatives to enable reducing the high number of the green coconut shells sent to waste disposal sites is very important to reduce their environmental impact. The use of green coir fibers as reinforcement in resin–matrix composites could be a useful and immediate application. These biocomposites have successfully been employed in the aerospace, construction and automotive industries, making these initiatives of great importance for the environment because these natural polymers act as neutralizers of CO_2.[12,17]

The main objective of this paper is to report the synthesis of new biocomposites from dwarf-green coir fibers impregnated with a polymeric matrix from cashew nut shell liquid (CNSL), as well as their structural, thermal and mechanical properties. The biodegradability of the dwarf-green coir fibers, raw and obtained through chemical treatment (alkali solution), was also investigated.

Experimental

Materials

The fibers were supplied by Embrapa Agroindústria Tropical (Fortaleza, Brazil) in yarn form. The CNSL used in this work was kindly provided by Amêndoas do Brazil Ltda (Fortaleza, Brazil). Sodium hydroxide (NaOH; 99%), sodium hypochlorite (NaClO; 97%), formaldehyde (37%), ammonium hydroxide (30%), 2-(dimethylamino)ethyl benzoate (99%) and sodium sulfate (99%) were obtained from Sigma-Aldrich and used without prior treatment. Resin epoxy was obtained from Epoxiglass (São Paulo, Brazil).

Alkaline treatment in dwarf-green coir

The fibers were previously cut (40 cm × 35 cm in length) and washed with water and neutral detergent for residue removal. After that, these fibers were washed with distilled water at room temperature. The fibers were dried and kept away from moisture. They were treated with 5 and 10% NaOH solutions, at temperature intervals of 60–70°C for 6 h. This procedure partially removed lignin, hemicellulose and other residues from the surface of the fibers. After this period, to remove the excess of NaOH on the surface of the fibers, they were washed several times with distilled water. To perform the bleaching, the fibers were kept in a solution of NaClO/H2O (1 : 1) under heating (60–75°C) for 4 h. The bleaching was performed after alkali treatment. At this point, the fibers showed a strong bleaching effect (see Figure 1), being subsequently washed several times with distilled water. The active bleaching agent is the hypochlorite ion and the reactions are as follows[15,18,19]

$$\mathbf{NaOCl + H_2O \rightarrow NaOH + HOCl} \quad (1)$$

$$\mathbf{HOCl \rightarrow H^+ + {}^-OCl} \quad (2)$$

$$HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O \quad (3)$$

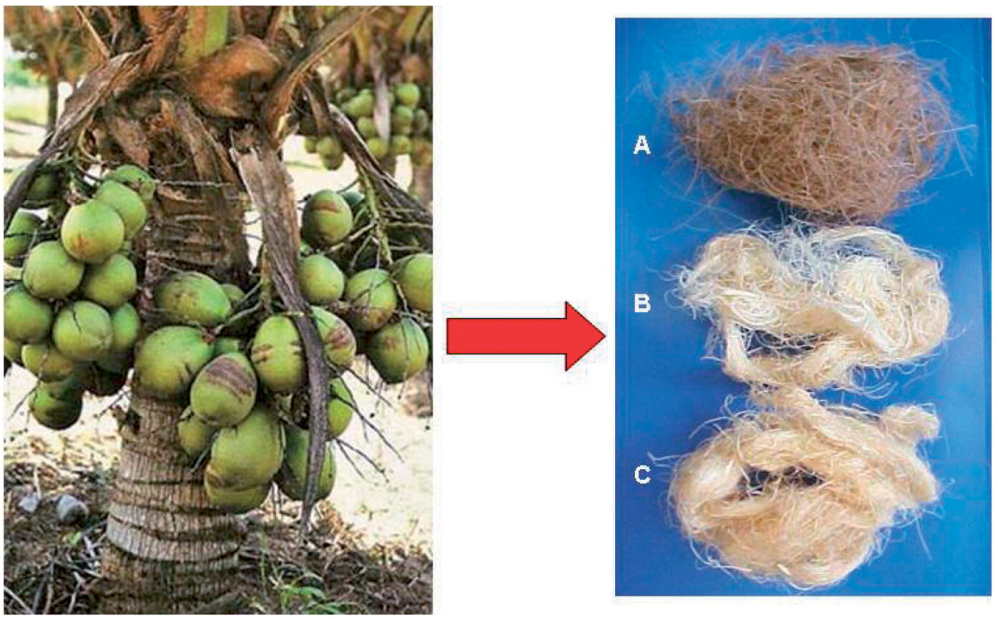


Figure 1. (a) Raw dwarf-green coir fibers, (b) dwarf-green coir fibers treated with sodium hydroxide (NaOH) 5% and (c) dwarf-green coir fibers treated with NaOH 10%.

Considering that the –OH groups present in the fibers correspond mostly to the alcoholic hydroxyls (weak acids), one can propose that the interaction is similar to the one represented in equation (4)[15,19–21]

$$Fiber - OH + NaOH \rightarrow Fiber - O^-Na^+ + H_2O \quad (4)$$

Synthesis of resol resin

The resin synthesis was carried out in a laboratory glass reactor equipped with a stirrer, thermometer and reflux condenser. Resol was synthesized by mixing cardanol (phenol from CNSL) and formaldehyde aqueous solution in the presence of a basic catalyst (NH_4OH). The mixture was heated to 80°C during 24 h. Formaldehyde/phenol (F/P) with a molar ratio of 1 : 2 was prepared in the synthesis. The resol obtained was characterized as containing about 5% unreacted cardanol. The resol resin obtained was cured by thermal treatment with a resin epoxy in the presence of 2-(dimethylamino) ethyl benzoate (99%) as catalyst in the proportion 0.93 : 1 : 0.03, respectively.

Preparation of biocomposites

Cardanol-based resin was used as a building block for the development of a thermosetting matrix. Biocomposites based on natural components were prepared by open molding and hand layup impregnation of the fibers with the thermally polymerizable cardanol-based resin, and cured at a moderately high temperature. The resin was applied to make reinforced composites with the untreated and treated fibers.

The fibers used to prepare the composites (20% by volume) were of uniform length. The biocomposites were obtained by a vacuum infusion technique,[22] in which resin enters through two injection points located at the corners of the mold and then flows to the center. Biocomposite sheets (150 × 160 × 3 mm) were prepared by hot-press molding at 10,000 Kgf, at 120°C for 6 h.

Structural characterization of the dwarf-green coir fibers and biocomposites

Crystallinity fraction

X-ray diffraction (XRD) patterns were obtained from dwarf-green coir disks at room temperature (300 K), using a Rigaku powder diffractometer model DMAXB. The samples were pulverized and their particles were compacted in a cylindrical mold into disc format (Ø 1.7 cm) and submitted to the pressure of 111 MPa. Cu-Kα tube was operated at 40 kV and 25 mA, and the measurements were performed using the Bragg–Bretano geometry in continuous mode with scan speed of 0.5/min and step size of 0.02° (2θ) in the angular range of 5–40°(2θ). The dwarf-green coir crystalline fraction (F) was obtained through separation and integration of crystalline and amorphous peak areas under the XRD plot.[15,19,23,24]

Thermal analysis

The thermal stability of the biocomposites was evaluated by thermogravimetric analysis (TGA), using a Shimadzu thermogravimetric analyser TGA 50 H. The decomposition analysis was performed under nitrogen atmosphere in a constant flow of 50 cm^3/min, with heating range of 10.0°C/min, sample mass of 10 mg and temperature programs from 30 to 800°C. In the case of biocomposites, it was necessary to use the samples fragmented into small pieces.

Scanning electron microscopy

The morphological characterization of the biocomposites was done by scanning electron microscopy (SEM). This technique was used to observe the surface morphology and make an analysis of the microstructure in both natural and chemically treated forms. The micrographs were obtained by the electron microscope model DSM 960/Zeiss, with 20 kV electron beam. The samples were coated with gold (Au) and 'sputter counted' with argon plasma model BALZERS 5CD50.Mechanical analysis

Tensile testing was carried out in an Emic DL10000 testing machine at a crosshead speed of 8.0 mm/min. Test specimens were cut from composite sheets and the tensile testing was carried out in an FIE Emic DL10000 universal tensile testing machine, according to ASTM D638 and D3039. The load–displacement curves were obtained and flexural strength and modulus were calculated. A minimum of four samples were tested in each case and the average value was calculated.

Biodegradability analysis of fibers

The measurements were obtained by the mass retention technique. The specimens were weighed and buried in simulated soil at room temperature. The simulated soil consisted of 23% loamy silt, 23% organic matter (cow manure), 23% sand and 31% distilled water (all wt/wt). Biodegradation was monitored for 150 days by measuring the mass retention. The buried specimens were then recovered, washed with distilled water and dried at room temperature until there was no further variation in weight. After that, the specimens were buried again in their respective trays. The experiments were performed in triplicate.

Results and discussion

Figure 2 shows the XRD patterns of the raw dwarf-green coir, treated with NaOH 5 and 10%. The main peaks representing the planes 002 and 101 at $2\theta = 22.46°$ and $2\theta = 16.7°$, respectively, are characteristic of the cellulose crystalline phase.[23] They assign the cellulose standard profile from International Centre for Diffraction Data (ICDD) data bank (00-050-2241). It was observed that when the dwarf-green coir received alkali solution treatments, the cellulose relative peaks intensity and crystalline fraction increased due to the lignin being partial removed in alkali solution.[19] Lignin is associated to cellular wall,

conferring mechanical strength to the natural composite, and when its concentration increases, the crystalline fraction decreases.[19] The crystallinity fraction was 33.74% for untreated fibers, 40.94% and 41.41% after treatment with 5 and 10% NaOH, respectively.[23]

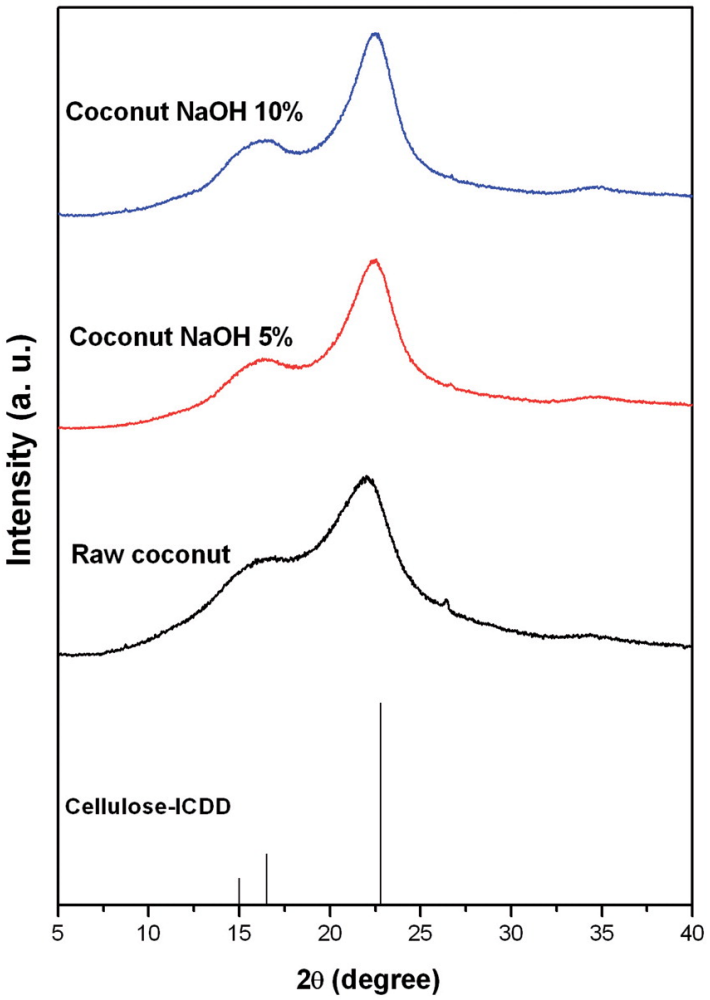
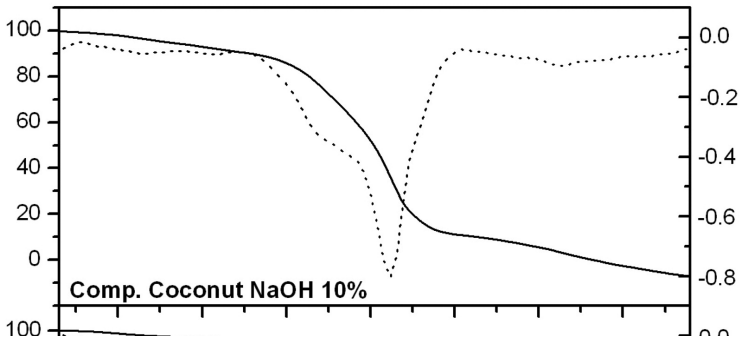


Figure 2. X-ray diffraction (XRD) of dwarf-green coir fibers after and before alkali treatment.

The small peak observed at ~26.2° is not from dwarf-green coir fiber and can be attributed to inorganic impurities such as SiO_2 and $CaCO_3$,[19] whose intensities decreased after alkaline treatment; that is, the alkali solution processes improved the purity of the fiber.

The thermogravimetric (TG) and differential thermogravimetry (DTG) curves of the biocomposites, in inert atmosphere (N_2), are shown in Figure 3. In all samples, it was found that a small weight loss occurs from room temperature to 130°C. This process corresponds to loss of water in the biocomposites. It is possible to see that the materials maintain the thermal stability even at approximately 300°C, when DTG curve shows a shoulder in the range 280–380°C due to decomposition of hemicellulose.[25]



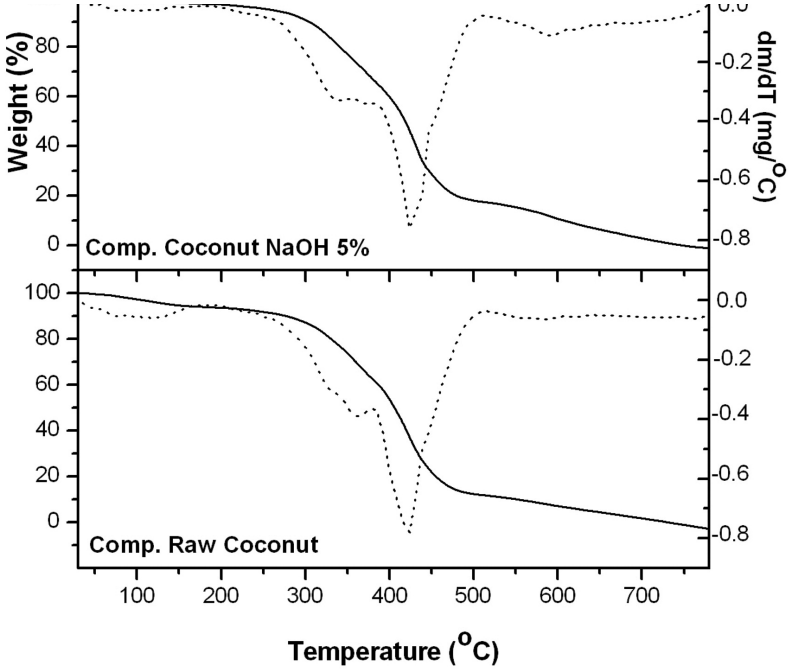


Figure 3. Thermogravimetric (TG)/differential thermogravimetry (DTG) of the composites reinforced with raw and dwarf-green coir chemical treated.

A second stage occurred at intervals between 400 and 460°C, characteristic of the degradation of soft segment of the matrix, while the last stage occurred at intervals between 450 and 650°C, attributed the degradation of the carbonaceous residues that are justified by intrinsic need of nutrients for the fiber's growth and development.[15] During these last stages, a significant difference in the maximum temperature of degradation for the sample reinforced with raw coconut (563°C), coconut treated with NaOH 5% (586°C) and coconut treated with NaOH 10% (617°C) was observed. In other words, there was a variation of 54°C comparing the composite reinforced by raw coconut with the composite reinforced with coconut treated with NaOH 10%. These results reflect a better diffusion of the resin inside the fibers treated with alkali solution.

The resistance and rigidity of biocomposites are closely linked to the reinforcing agents, while their mechanical behavior is regulated by the synergy between the reinforcing agent and the matrix.[26] The contact surface, homogeneity of distribution and orientation of the fibers in the matrix are fundamental to define the properties of the composites. Alkali treatment favorably affects the mechanical properties of the fibers and composites. Based on these considerations and with previous knowledge of the mechanical behavior of dwarf-green coir,[23] it is possible to predict the properties of the biocomposites generated. Table 1 shows the mechanical results obtained for the dwarf-green coir biocomposites. From these results, it was concluded that those prepared with coir fibers treated with NaOH 10% presented the best overall results.

Fiber	Yield strenght (MPa)	Breaking load (N)	Deformation (%)	Tensile strength (MPa)
Biocomposites with raw dwarf-green	6.42	403.2	8.8	10.5
Biocomposites with dwarf-green treated with NaOH 5%	13.45	675	6.8	16.9
Biocomposites with dwarf-green treated with NaOH 10%	18.21	676.3	5.1	20.4

NaOH: sodium hydroxide.

The biocomposites were also examined to determine the effects of the treatment on their mechanical

characteristics. Important changes were observed in all the parameters. The strength and breaking of the composites are closely related to their building agents, while the mechanical behavior is governed by synergy between the reinforcing agent and the matrix. Knowing the mechanical behavior of the fibers, it is possible to predict the mechanical properties of the composites. In the case of the composite containing dwarf-green coir fibers, it was observed that those treated with NaOH 10% had the largest stretch modulus.[23] There was an increase of around 61% and 94% in the value of the tensile strength for composites where the dwarf-green coir fibers were treated with NaOH 5% and 10% respectively, when compared with the composites reinforced with raw dwarf-green coir.

The biocomposite morphology was also studied by SEM at ×500 amplification, where it was possible to identify the fibers in the polymer matrix. The biocomposites reinforced with raw fiber and fiber chemically treated with NaOH 5% and 10% are presented in Figure 4(a)–(c), respectively.

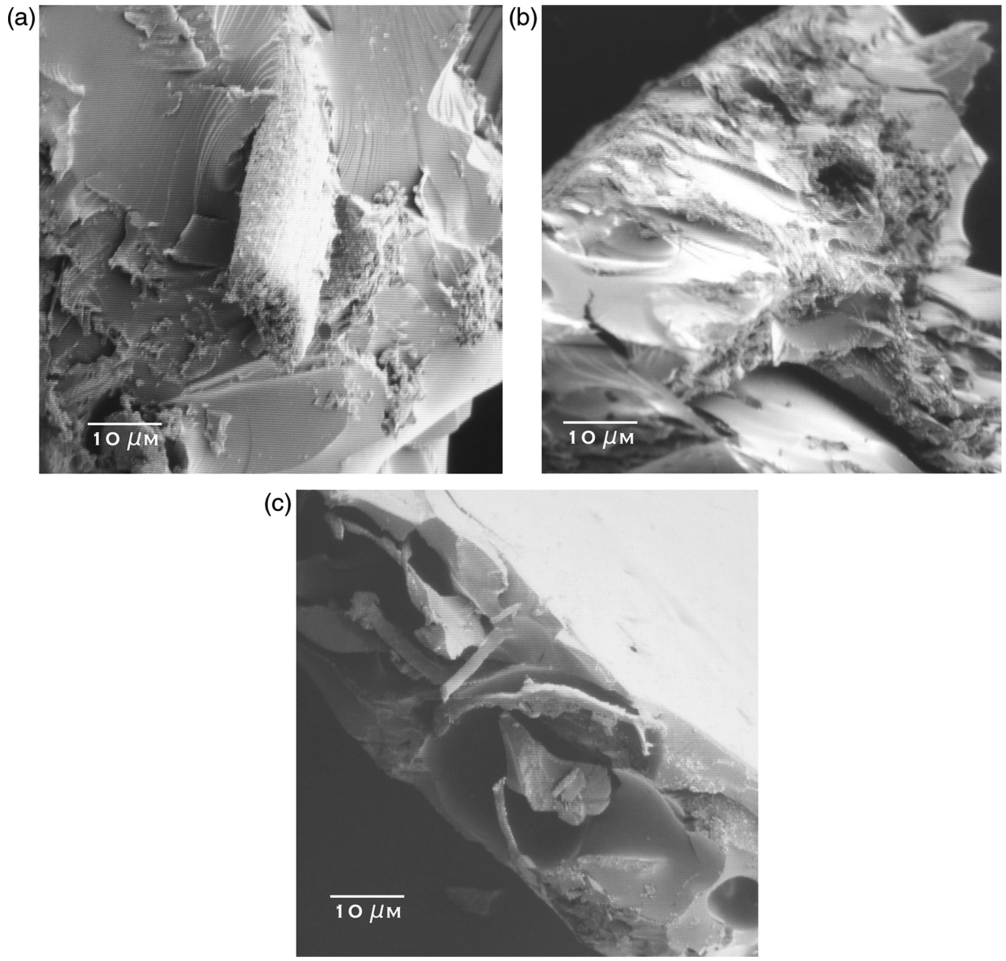


Figure 4. Micrographs of the biocomposites containing dwarf-green coir fibers: (a) untreated, (b) and (c) after treatment with sodium hydroxide (NaOH) 5% and 10%, respectively.

There was low interaction in biocomposites with untreated fibers (Figure 4(a)), while those biocomposites reinforced with fibers treated with NaOH 10% (Figure 4(c)) presented a strong adhesion between polymer matrix and fibers. The adequate treatment allowed the resin to penetrate the cavities, making the biocomposites more homogeneous. These results corroborated the observations from the mechanical tests, that is, the treatment with NaOH 10% reduced the fibers' exposure and improved their distribution in the matrix because of the better adhesion provided by the chemical treatment under these experimental conditions. The same behavior was observed in the morphological characteristics of dwarf-green coir fibers.[23] It was verified that concentrations lower than 5% did not lead to significant

alterations on the surface of the fibers, while solutions containing NaOH concentration higher than 10% and temperatures above 90°C cause defibrillation and significant damage to the fibers.[23]

The removal of compounds containing heteroatom changed the biodegradation. It is well known that the biodegradation rate depends strongly on the polymer's composition. The linkages in the polymer's backbone, end-groups and their chemical activity are important factors which affect the biodegradation.[15,27] Linkages involving heteroatom, such as cellulose and hemicellulose, are considered susceptible to enzymatic degradations. Hemicellulose can be considered as the fiber's most vulnerable component to biodegradation, because it is located in the noncrystalline domains. Next in line are noncrystalline and crystalline celluloses; whereas, protolignin is less prone to biodegradation, due to its cross-linked and aromatic character.[15,28] In general, the number of microbial cells or the biomass of the species acting on the chemical of interest increases, as the degradation proceeds. Pure polymers are not usually degraded because of their hydrophobic character, which inhibits the enzymatic activity of the microorganisms.[15,29]

Figure 5 shows the biodegradation results of the dwarf-green coir fibers after 150 days exposure to microorganisms in simulated soil. The biodegradability of the fiber depended on the applied treatment. Dwarf-green coir fibers untreated and submitted to treatment with solutions of 5% and 10% NaOH showed different degree of degradation with 5.08%, 26.14% and 13.3% of weight loss, respectively, after 30 days. It was observed that the natural fibers were more resistant to the action of the microorganisms due to the presence of more lignin and hemicellulose, which provide additional protection to the fiber. After 150 days of experiment, it was observed that for raw dwarf-green coir, the microorganism adsorption which occurred on the surface must also be responsible for increase in the mass. This same behavior was observed by Barreto et al.,[19] in the study of sisal fibers.

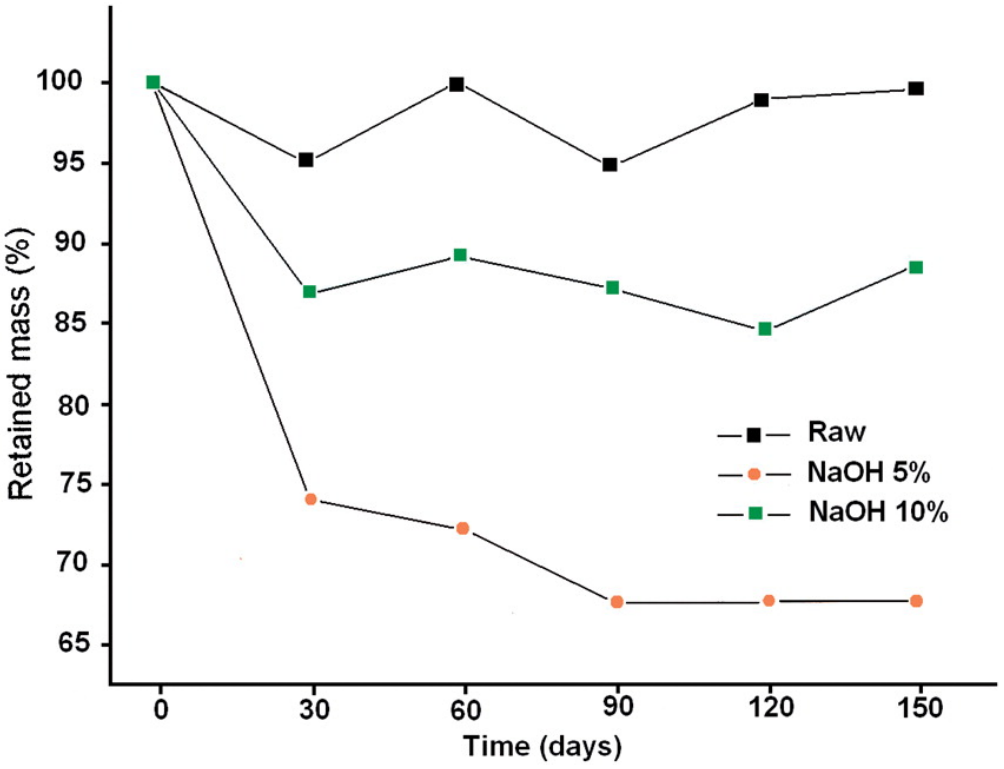


Figure 5. The biodegradation of the dwarf-green coir fibers.

Dwarf-green coir fibers submitted to treatment with solutions of 5% and 10% NaOH showed degradation (33% and 12% of weight loss, respectively), under the conditions studied after 150 days. For the dwarf-green coir fibers treated with NaOH 10%, the action of the microbial population could be

justified by: (a) the larger concentration of the alkali applied, which promoted partial degradation of the fiber's constituents such as hemicellulose, pectin, fat and lignin and (b) the change of the composition, which altered the organization of the chains and, consequently, led to a better packing of the cellulose chains, resulting in an increase of the crystalline fraction and maintenance of an excess of hydroxyl groups.[23]

Conclusions

The chemical treatment depends upon several variables (reagent concentration, temperature and time), and the results directly affect the thermal and mechanical properties, the biodegradability and, consequently, the adhesion between matrix and fiber. The XRD showed that the chemical treatment increased the crystalline fraction due to partial removal of amorphous components (hemicellulose, lignin and wax). The morphology of the biocomposites was analyzed by SEM, where an improvement of the adhesion of the fiber matrix in the biocomposites due to the exposure of the cellulose structures after chemical treatment was observed. The better adhesion of the fiber leads to materials which are more homogeneous and resistant to thermal decomposition. The biodegradation experiments were carried out in a period of 150 days, when there was exposure to microorganisms in simulated soil. Some differences between raw fibers and chemically treated ones were observed, with NaOH 5%-treated fibers showing higher weight loss. The biodegradability test was useful to evaluate the possible use of dwarf-green coir fibers as a renewable material, when its behavior is changed by chemical treatment.

Overall, this work showed the first experimental results involving the preparation of biocomposites using the dwarf-green coir fibers from Brazil, a renewable and recyclable material, in combination with a polymeric resin of CNSL, a by-product of food consumption, without aggregated value. The results are very promising for its use as reinforcement in biocomposite materials, especially when the fibers are previously treated with alkali solution of NaOH 10%.

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Conflict of interest

None declared.

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