

Biodegradable Composites: Morphological, Chemical, Thermal, and Mechanical Properties of Composites of Poly(hydroxybutyrate-co-hydroxyvalerate) with Curaua Fibers After Exposure to Simulated Soil

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ABSTRACT: Composites produced from biodegradable polymeric matrixes reinforced with vegetable fibers have attractive mechanical properties and are environmentally friendly. This work is directed to the biodegradation of a composite made of a poly(hydroxybutyrate-co-hydroxyvalerate) matrix reinforced with curaua fibers (with and without alkaline treatment) in simulated soil. The composites were developed by extrusion and injection and were later buried in simulated soil according to the ASTM G160-03 method. Scanning electron microscopy showed evidence of microbial attack on the samples surfaces. Infrared spectra showed that the composites biodegradation was mainly caused by erosion of the surface layer resulting from microorganisms activity. Thermogravimetric analysis pointed out reduced thermal stability of the samples, and results of differential scanning calorimetry showed that the degree of crystallinity increases and then decreases progressively throughout the degradation period, indicating that enzymatic degradation primarily occurs in the amorphous phase material and thereafter in the crystalline phase. For curaua composite fibers, reductions in tensile strength and elastic modulus are more significant, indicating that the presence of fibers promotes biodegradation of the curaua fiber.

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INTRODUCTION

A growing global trend toward maximizing the use of natural resources through new products and processes has led to the study and exploration of materials derived from renewable natural sources.¹ Polyhydroxyalkanoate (PHA) biodegradable polymers are produced by microorganisms of various carbon substrates, and the variety of different substrates and microorganism metabolisms leads to different monomers, polymers, and copolymers.²

The poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) copolymer is one of the most important PHAs. It has a semi-crystalline structure and mechanical and thermal properties similar to those of polypropylene.^{3–5} These characteristics make it a potential replacement for conventional polymers derived from petroleum resins, with applications in the automotive, packaging, and biomedical industries.^{2,6–8}

Biodegradation of PHBV occurs by the action of PHB depolymerase enzymes, which are secreted by microorganisms present in the disposal environment. A common feature of depolymerase enzymes is a reaction mechanism that uses three amino acid residues—aspargate, histidine, and serine—which are referred to as the catalytic triad.⁹

The rate of biodegradation of these polymers depends on many factors, especially environmental factors (such as temperature, moisture, pH, and nutrients) and material characteristics (such as composition, crystallinity, surface area, and reactivity).¹⁰

Composites produced from biodegradable polymeric matrixes reinforced with natural fibers have interesting mechanical properties in addition to their environmental friendliness.¹¹ Studies have shown that natural fiber composites have mechanical properties superior to those of the neat polymers.^{12–14} Bledzki and Jaszkievicz³ reinforced PHBV with man-made cellulose,

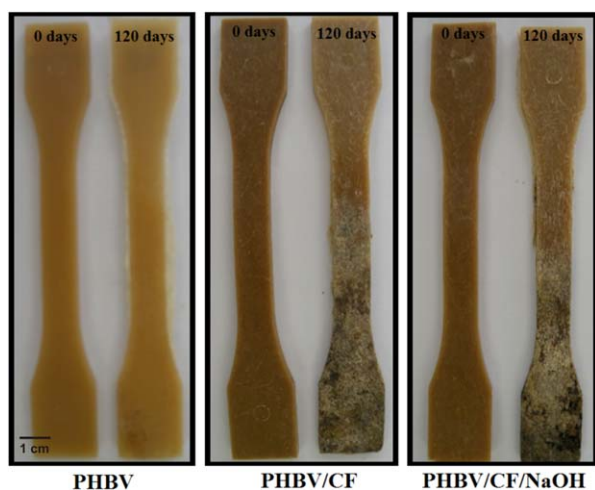


Figure 1. Visual appearance of the composites samples after degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

jute, and abaca fibers and found improvement in mechanical strength and elastic tension in all cases.

Curaua (*Ananas erectifolius* LB Smith) is a bromeliad characteristic of the Amazonian Pará State (Brazil), and fibers extracted from its leaves are widely used because of their strength, softness, lightness, and recyclability.¹⁵ The processes of selecting, washing, and drying the fibers are extremely important when these fibers are used as composites reinforcement, having significant influence on mechanical properties.¹⁶ The curaua fibers (CF) consist approximately of 73% cellulose, 10% hemicellulose, 8% lignin, 9% of moisture, the remaining being ash.¹⁷

CF are stronger than other fibers such as for example jute, sisal, and flax. Compared with glass fibers, CF have better mechanical properties such as hardness, impact resistance, and flexibility,^{16–18} and their use also leads to lower abrasion and lower energy consumption during processing.

However, good interaction between the components of a composite is very important since adhesion problems between the

fiber and polymer matrix may decrease the shear transfer, compromising the mechanical properties of the composite.¹⁹

Various approaches can be used to improve adhesion between the fiber and the matrix,^{20,21} including alkali treatment and the use of coupling agents. These procedures could improve fiber/matrix adhesion by contributing to decreased fiber pull-out and leading the fiber to break closer to the matrix.²² An alkali treatment leads to disruption of the hydroxyl groups (OH), hydrogen bonds present in the fiber structure, thereby increasing surface roughness.^{23,24} This treatment removes a certain amount of lignin, wax, and oils that cover the outer surface of the fiber wall, resulting in cellulose depolymerization.

The aim of this work is to investigate the biodegradation of PHBV composites reinforced with CF (with and without alkali treatment) by examining the morphological, chemical, thermal, and mechanical properties.

EXPERIMENTAL

Materials

Biocycle PHBV polymer (containing 18.25% (wt/wt) hydroxyvalerate (HV), molecular weight 514.778 Da, crystallinity 36.5%, melting point temperature 160.7°C) was supplied by PHB Industrial, Brazil. CF were supplied by CEAPAC (Support Center for Community Action Projects) of Santarém (PA), Brazil, and sodium hydroxide was obtained from Sigma-Aldrich (USA).

Preparation of the Curaua Fibers

The CF were selected, combed, and cut into 2.5 cm long strands and then immersed in distilled water for 1.0 h to remove any debris. The fibers were then dried in an oven with air circulation at 60°C for 24 h.

The alkali treatment solution was prepared with 5% (m/vol) sodium hydroxide in distilled water. A portion of the CF were immersed in the alkali solution at a proportion of 10:1 (solution : fibers) for 2 h at a temperature of 50°C. Subsequently, the fibers were washed with distilled water (until the pH of the remaining wash solution was 7.0), and then the fibers were dried at 60°C for 12 h.

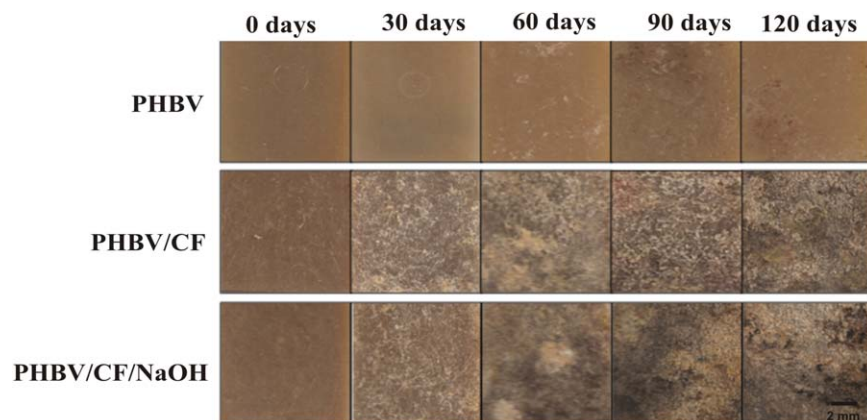


Figure 2. Images of the composites sample surfaces after different degradation periods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

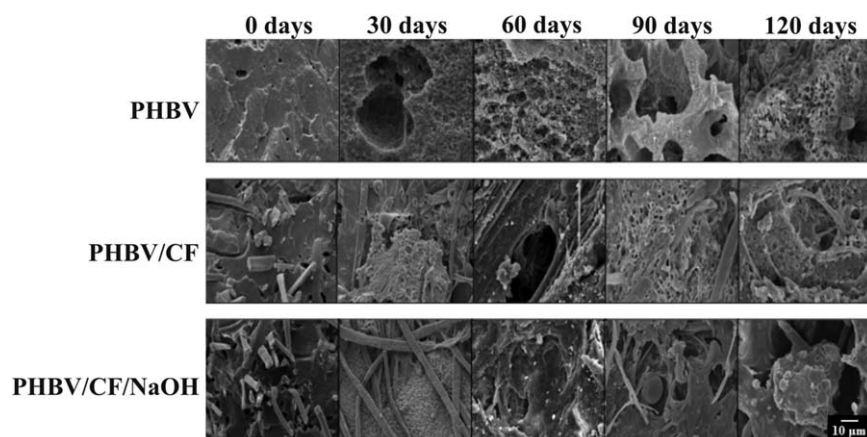


Figure 3. SEM micrographs of the polymer and composites after different degradation periods.

Preparation of the Composites

The PHBV polymer, in the form of small granules, was dried in a stove under the same conditions used for the fibers. The composites were prepared by conveying PHBV and 20% wt CF to a single screw extruder (Seibt brand, model ES 35FR) at temperatures of 150°C, 155°C, and 160°C and a screw speed of 50 rpm, followed by milling in a knife mill (Primotécnica, model 1001). The resulting material was then processed by a twin-screw extruder (MH Equipamentos, model COR 20-32-LAB), with a minimum temperature of 150°C and a maximum temperature of 170°C at a screw speed of 200 rpm, followed by milling in a knife mill and injection (Himaco Hidráulicos e Máquinas, model LH150-80) at temperatures of 145°C, 150°C, and 155°C and a screw speed of 100 rpm.

Preparation of the Simulated Soil

Biodegradation tests were carried out in simulated soil according to ASTM G160-03, with three equal parts of soil, sand, and horse manure. After the soil maturation period, the composites were placed in soil (five replicates) and removed at regular intervals of 30, 60, 90, and 120 days, when the samples were

washed with distilled water and placed in a desiccator for 96 h for characterization.

As required by ASTM G160-03, some soil parameters were monitored during the maturation period and during the period of biodegradation test. Soil moisture remained around 30–32%, pH was between 6.55 and 7.50, and the temperature was between 15 and 30°C. All tests were performed according to standard requirements and the results are within the recommended range.

Characterization

The surface morphology of the degraded samples was observed by scanning electron microscopy (SEM), performed on a Shimadzu SSX-550 Superscan microscope with an accelerating voltage of 10 kV.

Fourier transform infrared spectroscopy (FTIR) analysis was performed using the attenuated total reflectance (ATR) technique on a Nicolet IS10 ThermoScientific instrument with a measurement range of 4000 cm^{-1} to 400 cm^{-1} .

The thermal properties of the degraded samples were determined by thermogravimetric analysis (TGA) and differential

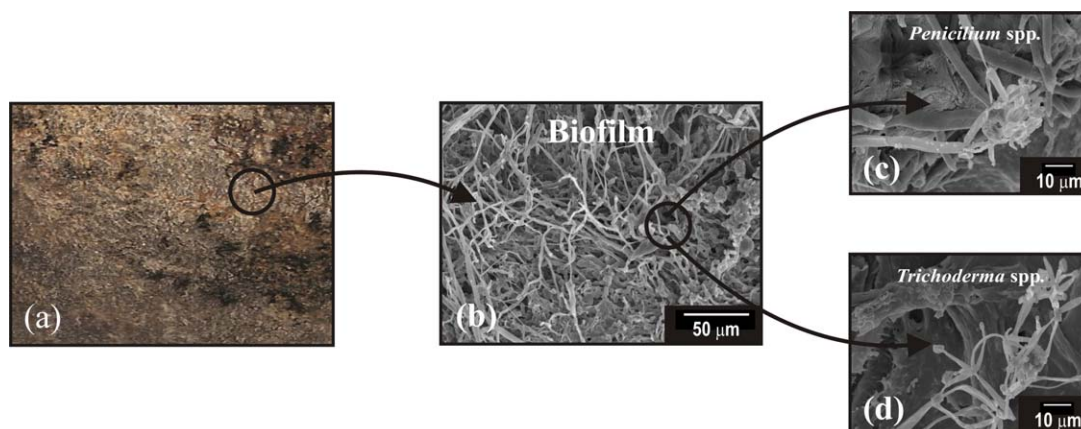


Figure 4. PHBV/CF sample after 120 days of biodegradation: (a) biodegraded surface (5 \times), (b) biofilm attached to the surface (400 \times); fungi identified on the surface: (c) *Penicillium* spp. and (d) *Trichoderma* spp. (1000 \times). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

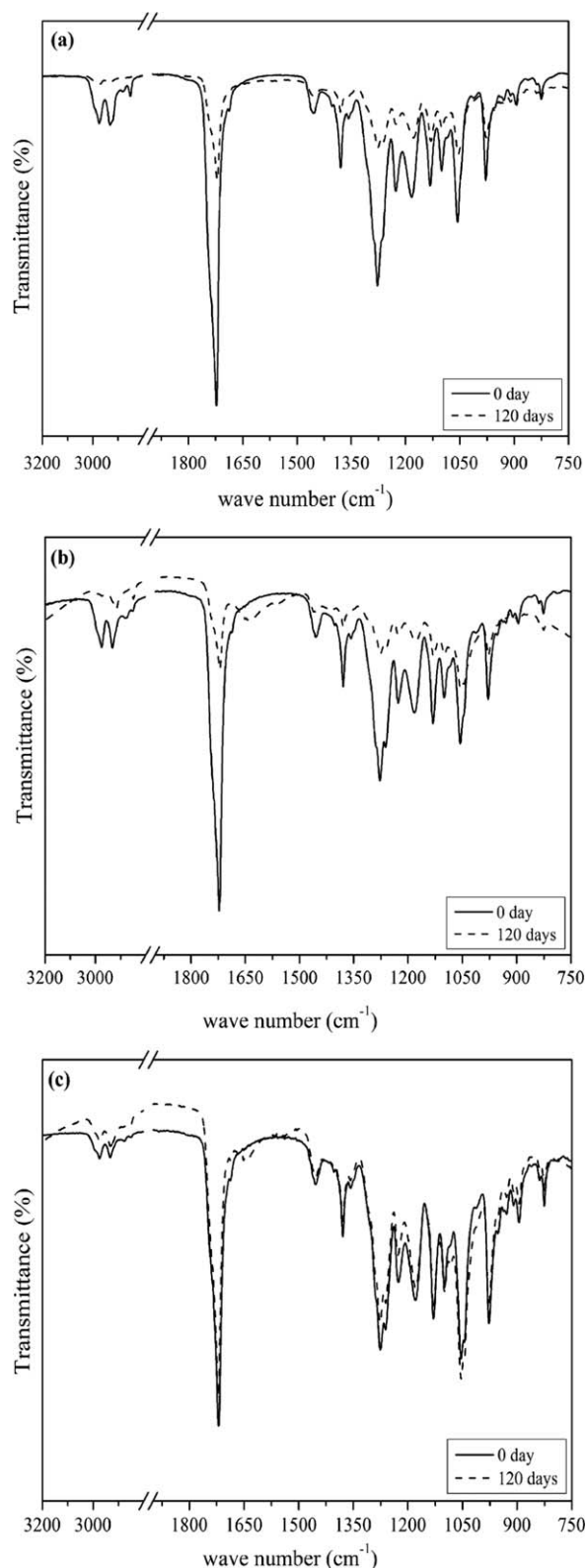


Figure 5. ATR-FTIR spectra for the composites: (a) PHBV, (b) PBHV/CF, and (c) PHBV/CF/NaOH, before and after biodegradation.

scanning calorimetry (DSC). The TGA and DTG (derivative) were performed with a 50-Shimadzu TGA instrument over a temperature range of 23 to 700°C with a heating rate of

10°C·min⁻¹ under nitrogen (N₂) flow rate of 50 mL·min⁻¹. The DSC test was performed on a Shimadzu DSC-60 device according to ASTM D3418:08 with a heating and cooling rate of 10°C·min⁻¹ and nitrogen (N₂) flow of 50 mL min⁻¹.

The degree of crystallinity (X_c) was calculated by eq. (1), where ΔH_m is the variation in enthalpy of melting (J g⁻¹), $\Delta H_{m100\%}$ is the variation in enthalpy of melting for a hypothetical 100% crystalline polymer (J g⁻¹), and W is the PHBV fraction (wt) in the composite.²⁵

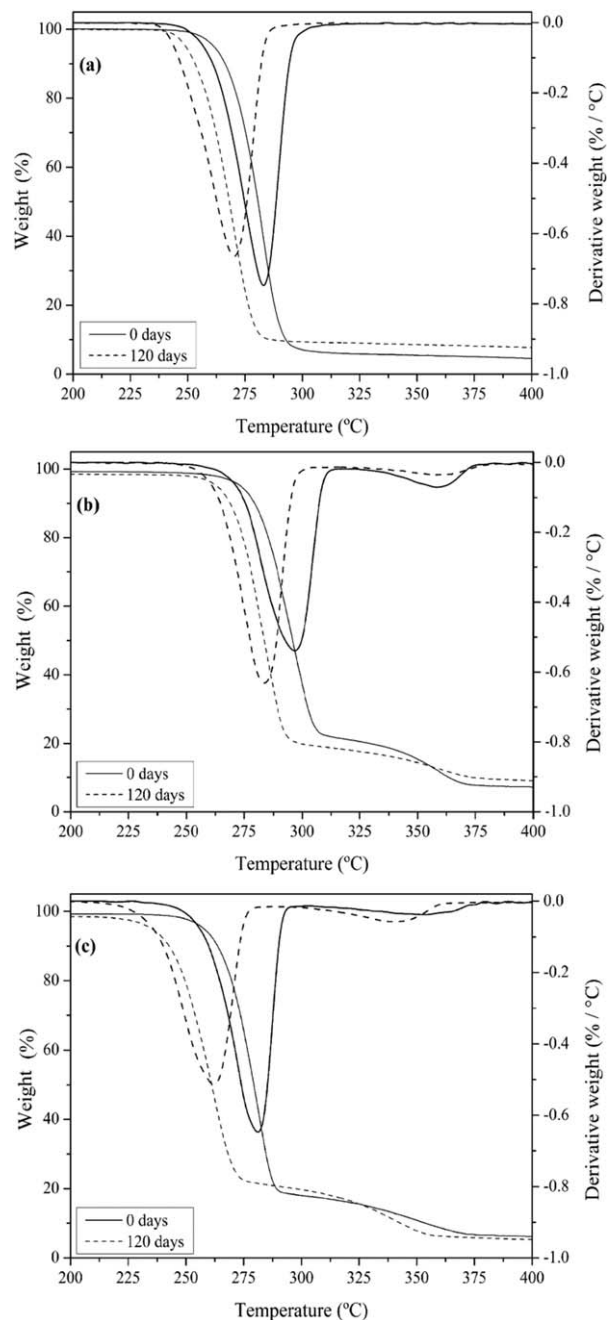


Figure 6. TGA and DTG curves for the composites: (a) PHBV, (b) PBHV/CF, and (c) PHBV/CF/NaOH, before and after biodegradation.

Table I. TGA Thermal Characteristics for the Samples Before and After Biodegradation

Sample	Degradation (days)	Decomposition stage	T_{onset} (°C)	T_{max} (°C)	T_{endset} (°C)
PHBV	0	1st	260	280	310
		2nd	-	-	-
	120	1st	250	270	286
		2nd	-	-	-
PHBV/CF	0	1st	276	296	303
		2nd	320	358	367
	120	1st	266	283	292
		2nd	310	256	360
PHBV/CF/NaOH	0	1st	262	280	287
		2nd	298	355	364
	120	1st	242	262	271
		2nd	283	338	350

$$X_c = [(\Delta H_m / \Delta H_{m100\%}) \times W] \times 100 \quad (1)$$

The enthalpy of 100% crystalline PHBV is $109 \text{ J} \cdot \text{g}^{-1}$, according to Qiu et al.,²⁶ Buzarovska et al.,²⁷ and Singh et al.²⁸ for a PHBV polymer containing approximately 20% HV.

The mechanical properties of the degraded samples were determined by tensile tests carried out in accordance with ASTM 638:10, at a rate of $5 \text{ mm} \cdot \text{min}^{-1}$, using a universal testing machine (EMIC DL 2000).

The mass loss (ML) after the biodegradation process was evaluated by comparing the sample weight before and after exposure to simulated soil (the samples were washed with distilled water and placed in a desiccator for 5 days). Equation (2) was used to calculate the percentage ML, where M_i is the initial mass (g) and M_f is the final mass of the sample (g).

$$\text{ML} = [(M_i - M_f) / M_i] \times 100 \quad (2)$$

The neat processed polymer (PHBV), the PHBV composite with CF (PHBV/CF), and the PHBV composite with CF treated with a sodium hydroxide (PHBV/CF/NaOH) alkali solution were subjected to biodegradation and characterization. All characterization tests were performed on five specimens of each sample evaluated.

RESULTS AND DISCUSSION

Figure 1 visually illustrates the degradation of the composites, and Figure 2 presents images of the composites surface after different degradation periods. The surface of the PHBV sample exhibited whitish spots beginning from the 60th day of biodegradation. The images of samples on days 90 and 120 exhibited increase in whiteness and decrease in the sample dimensions.

After 30 days of biodegradation, the PHBV/CF and PHBV/CF/NaOH composites exhibited browning and formation of grooves on the surface. After 60 days of exposure, major spots, large cracks, and fungal mycelium (white spots) adhered to the sample surface were observed. At 90 days of exposure, the samples exhibited reduction in size and significant surface darkening. At the end of the test period (120 days of exposure) the sample

surface had significantly degraded, with large dark spots, deep cracks, and significantly smaller dimensions.

Figure 3 presents sample's SEM micrographs after different periods of biodegradation.

The degradation began at discrete locations on the surface and then expanded over the sample surface with degradation time. Similar behavior was reported in the study by Hermida et al.,²⁹ where PHBV biodegradation was observed to start with small erosions in specific areas. As exposure time was increased, the quantity of holes scattered across the surface drastically increased while the sample size decreased. According to these authors, at the beginning of the degradation, the microbial colonies are small and poorly distributed. Over time, the microbial population multiplies and extends over almost the entire sample, increasing the surface area of microorganism attack.

The micrographs show that the PHBV sample surfaces have spherical cavities, whereas PHBV/CF and PHBV/CF/NaOH samples exhibit longitudinal surface erosion. According to Sang et al.,³⁰ surface erosion of composites with natural fibers is caused by fungi. The fungal biodegradation process begins around the hyphal segments with excretion of depolymerase enzymes, forming long and narrow cavities. This behavior indicates that the concentration of fungal colonies was higher on the surface of the composite with CF, while pure polymer samples were primarily subjected to bacterial attack, which forms deeper, spherical cavities.

The surface of the composite with curaua fiber exhibits biofilm formation. Biofilms are surface-attached complex microbiological ecosystems formed by populations that develop from a single or multiple species such as bacteria and fungi, in isolation or in combination with their extracellular products, constituting an organic polymer matrix. Figure 4 depicts the identification of some fungi of the *Penicillium* spp. and *Trichoderma* spp genera on the biofilm.

Studies by Luo and Netravali [32] showed that for PHBV samples biodegraded by composting, the weighted molar mass of the surface was reduced while the interior of the sample remained unchanged. Thus, knowing that the biodegradation

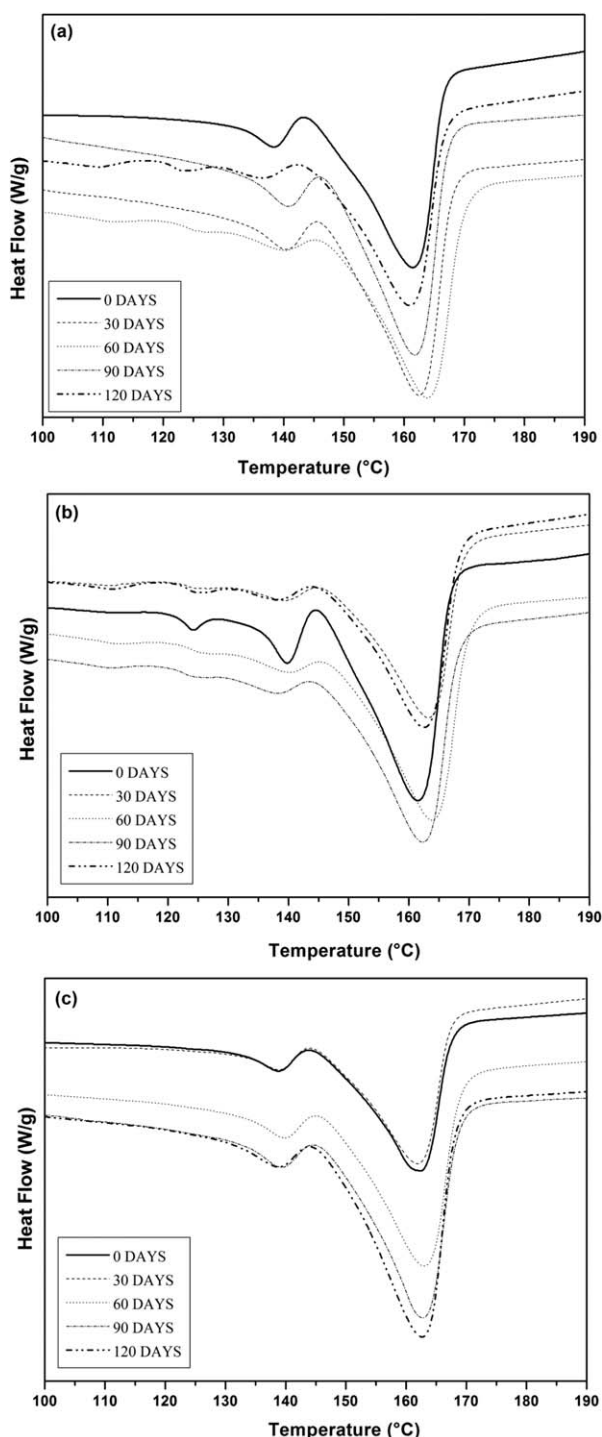


Figure 7. DSC curves for the composites: (a) PHBV, (b) PBHV/CF, and (c) PBHV/CF/NaOH, during biodegradation test.

process involves the cleavage of the polymer chain, which results in reduction in polymer molecular weight, these authors stated that the biodegradation only occurred on the sample surface.

Figure 5 presents the FTIR spectra for the samples before and after biodegradation. The PHBV sample spectrum [Figure 5(a)] after biodegradation demonstrates a marked decrease in the 1725 cm^{-1} ($\text{C}=\text{O}$) band intensity, indicating that microbial attack promoted the breakage of ester bonds. The band at 2745 cm^{-1} disappeared

and the band at 979 cm^{-1} was reduced, indicating the breakage of the polymer $\text{C}-\text{H}$ bonds. A decrease in the 1050 cm^{-1} band representing the $\text{C}-\text{O}$ bond was also observed.

The carbonyl index was not quantified due to the lack of a reference band for PHBV. A qualitative analysis was then carried out by observing the intensity of the carbonyl band, which became smaller after biodegradation.

The PHBV/CF composite [Figure 5(b)] exhibited a new band at 1642 cm^{-1} related to $\text{C}=\text{C}$ bond formation. This band was also observed by Shah et al.³¹ in their study of PHBV degradation in soil. According to those authors, $\text{C}=\text{C}$ bond formation indicates PHBV cleavage by depolymerase enzymes.

The spectra of the PHBV/CF/NaOH sample [Figure 5(c)] exhibit decreasing intensity of the 1050 cm^{-1} band, related to the $\text{C}-\text{O}$ bond, and the formation of a band at 1642 cm^{-1} , representing $\text{C}=\text{C}$ bond formation.

Similar results were observed by Weng et al.³² in studies of biodegradation of PHBV films through composting. These authors state that biodegradation of the polymer matrix is caused by erosion of the surface layer due to the action of microorganisms, and that the chemical structure of the polymer was not significantly altered during the degradation process.

The TGA and DTG thermograms for the samples before and after biodegradation are shown in Figure 6, and the degradation temperatures are reported in Table I.

The thermal stability decreased for all samples, indicating that exposure to simulated soil promoted the degradation of these materials. However, the PHBV/CF/NaOH composite exhibited major reduction in thermal stability.

According to Meschede et al.,³³ lignin is a heterogeneous polymer mainly composed of phenylpropane subunits, which

Table II. DSC Thermal Characteristics of the Composite Samples After Different Degradation Times

Sample	Degradation (days)	T_m (°C)	ΔH_m ($\text{J}\cdot\text{g}^{-1}$)	X_c (%)
PHBV	0	160.9	30.1	27.6
	30	162.3	47.5	43.6
	60	161.8	31.4	28.8
	90	161.7	30.9	28.3
	120	161.1	30.1	27.6
PHBV/CF	0	161.5	24.2	27.8
	30	163.4	32.9	37.7
	60	164.1	40.2	46.1
	90	162.6	39.9	45.8
	120	161.8	37.6	43.1
PHBV/CF/NaOH	0	161.9	25.1	28.8
	30	162.9	33.5	38.4
	60	163.3	43.8	50.2
	90	163.0	42.9	49.2
	120	162.8	42.3	48.5

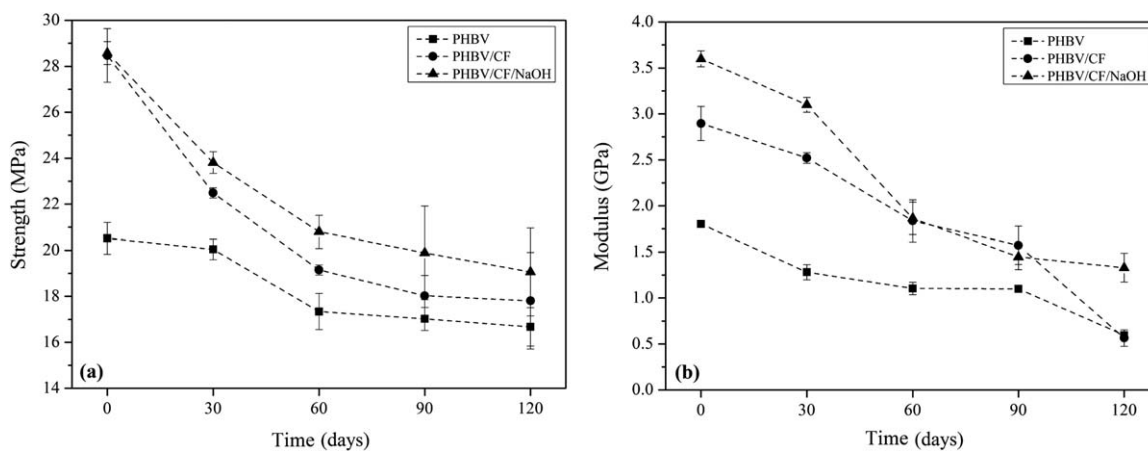


Figure 8. Tensile strength (a) and elastic modulus (b) of the samples before and after biodegradation.

protects the natural fibers from microorganisms attack. Therefore, the removal of lignin promoted by alkali treatment stimulated microorganism action, making easier the biodegradation process.

According to the study of Weng et al.,³² PHBV biodegradation led to reduction in molecular weight, which lowered the thermal stability of the material; however, no change was observed in the chemical structure of the polymer. These authors assert that this is because the biodegradation by erosion only occurs on the surface of the material, while the interior remains unchanged.

Figure 7 shows the DSC curves and Table II shows that the degree of crystallinity gradually increases until 30 or 60 days of exposure and then decreases. Changes in the crystallinity of the composites are consequent to the early biodegradation of the amorphous region of the polymer.

Microorganisms have preference for the amorphous regions of the polymer structure due higher mobility of oxygen in these regions. Therefore these regions are prone to enzymatic hydrolysis followed by consumption by the microorganisms.³⁴

Similar results were reported by Luo and Netravali³⁵ in their study of the properties of PHBV following composting. The rate of the enzymatic degradation of the amorphous region was higher than that of the crystalline region. Based on these results, these authors concluded that the PHB depolymerase enzyme predominantly hydrolyzes the amorphous region of the PHBV polymer.

This behavior suggests that enzymatic degradation initially occurs in the amorphous phase of the material,³⁶ which promotes a percentage increase in the degree of crystallinity, until most of the amorphous region is depleted. After that stage the degradation of the crystalline phase is initiated, which promotes a percentage decrease in the degree of crystallinity. However it is indicated to perform a statistical analysis to get real information on the effect of degradation on PHBV crystallinity.

Figure 8 shows the tensile strength and elastic modulus results. Higher decreases in tensile strength and elastic modulus occurred for the PHBV/CF and PHBV/CF/NaOH composites, indicating that the presence of CF favors biodegradation, with a particularly large effect observed after 60 days of exposure.

It is observed that the tensile strength decreased 19% for the PHBV sample, 37% for the PHBV/CF sample, and 33% for the PHBV/CF/NaOH sample, when comparing values at 0 days and until 120 days. A decrease of 66% was observed in the elastic modulus for the PHBV sample, 80% for the PHBV/CF sample, and 63% for the PHBV/CF/NaOH sample by comparing values at 0 day and after 120 days.

Luo and Netravali³⁵ investigated changes in mechanical properties of PHBV after composting and reported that the tensile strength and modulus of elasticity decreased significantly with composting time due to surface defects promoted by biodegradation.

According to Hermida et al.,²⁹ during surface degradation, the sizes of pores and microcracks increase up to a critical size, resulting in faults. When samples are subjected to mechanical stress, tension is concentrated around these faults, promoting catastrophic failure in response to small plastic deformation.

Figure 9 reports the samples ML after biodegradation. All samples exhibited gradual ML, and the rate of ML increased after the 60th day. Luo and Netravali³⁵ stated that these variations are due to changes in microbial activity in which the consortium of microorganisms increases over time until reaching a maximum and then decreasing.

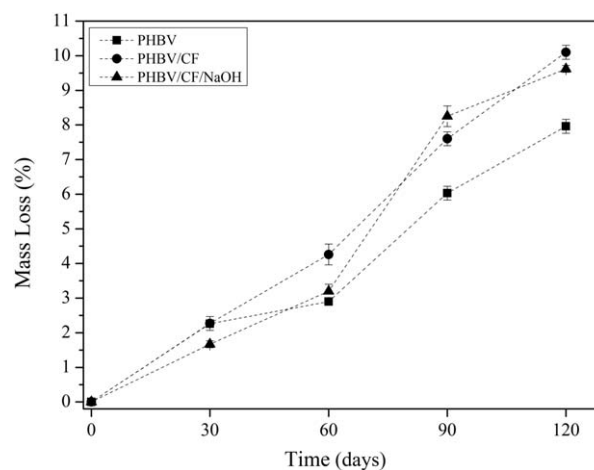


Figure 9. Weight loss after degradation for the composites samples.

CONCLUSIONS

Natural fibers have long been used as reinforcement in polymer matrices of composite materials. In addition to improving the mechanical properties of composites, these fibers also make the composite more environmentally friendly due to their overall biodegradability.

SEM images showed that PHBV was the most susceptible to bacterial attack, while for the PHBV/CF and PHBV/CF/NaOH samples biodegradation was primarily accomplished by fungal action. Sample biodegradation was confirmed by FTIR analysis, where we observed changes in the main bands, indicating that the degradation is caused by surface erosion due to the action of microorganisms. TGA analysis demonstrated decreased thermal stability of all the samples, and DSC analysis showed that enzymatic degradation acts initially on the amorphous phase of the composite, leading to increase in the degree of crystallinity.

The tensile strength and ML results showed that after exposure to simulated soil the mechanical properties of all samples decreased, and all samples lost a significant percentage of mass. However, samples with CF exhibited more pronounced losses. This is due to the presence of fibers, which promote the entry of water and microorganisms into the composite, thus facilitating biodegradation.

These results demonstrate that the addition of CF as reinforcement for PHBV produces a composite with a completely biodegradable character, more biodegradable than the neat polymer, namely, the presence of fiber assists and promotes the PHBV degradation process.

Additionally, alkali treatment of the fibers did not significantly alter their performance in the composite, in view of the fact that biodegradation results of composites with alkali-treated fibers were similar to those of composites with untreated fibers.

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