Covalently γ -aminobutyric acid-functionalized carbon nanotubes: improved compatibility with PHBV matrix

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Abstract

The improvement of compatibility between carbon nanotubes (CNTs) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was achieved using CNT functionalized with γ -aminobutyric acid (GABA). The efficiency of the CNT functionalization with GABA was evaluated by X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FT-IR), Raman spectroscopy, and transmission electron microscopy (TEM). The PHBV/CNT nanocomposites were produced in the molten state with the addition of 0.5 wt% of CNT (pristine, oxidized and functionalized with GABA) and characterized concerning the Izod impact strength tests. The impact fracture morphologies were analyzed using scanning electron microscopy. The results showed that GABA was covalently attached to CNT, resulting in the detection of nitrogen in the XPS survey, the shift of carbonyl peak wavelength on FT-IR, and a higher degree of structural disorder, detected by Raman and observed in TEM images. The impact strength was not significantly affected by the introduction of CNT; however, the impact fracture mechanism was changed from fragile to ductile when CNT was functionalized with GABA. These results are promising for the production of environmentally friendly nanocomposites with superior properties.

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Graphic abstract

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1 Introduction

The increasing accumulation of waste in landfills linked to environmental pollution has been making researchers to seek alternatives to conventional plastics [1]. In this context, biodegradable matrices, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, have attracted the attention of the scientific community.

PHBV is biodegradable and biocompatible natural polyester from polyhydroxyalkanoates family (PHAs), which have properties that make them promising candidates to replace conventional thermoplastics [2]. However, PHBV has some shortcomings, such as brittleness, low mechanical properties and thermal stability, and a narrow processing window [3, 4]. To overcome the limitations of PHBV properties, the incorporation of nanoparticles has been a widely studied alternative [5–12]. Among nanoparticles, carbon nanotubes (CNTs) are specially investigated to improve properties of matrices, due to their outstanding electrical, optical, and mechanical properties [13].

The incorporation of CNT into PHBV has shown to change the mechanical properties, wettability, thermal stability, and crystallinity degree [10, 14, 15]. However, CNT has a great tendency to form bundles, making its dispersion into matrices difficult. Therefore, the process of CNT functionalization is extensively employed to enhance the dispersion and compatibility, producing nanocomposites

with improvements in their mechanical properties [16]. Usually, functionalization made with the same polymer used as the matrix results in better compatibility due to improved interfacial adhesion between the filler and the matrix [4, 8]. However, functionalizing CNT with polymers requires several steps and is much time-consuming process.

Some studies have shown that when CNT is functionalized with a molecule which interacts with the polymer repeating unit, the wettability of CNT by the polymer is improved, which provides enhanced interfacial compatibility between the polymer and the filler [17, 18]. In view of these assertions, in this work, CNT was functionalized with γ -aminobutyric acid (GABA), which has a molecular structure similar to that of hydroxybutyrate, the main monomer on PHBV chain. GABA is a four-carbon nonprotein amino acid which is involved in the transmissions in the mammalian central nervous system [19, 20].

In this study, γ -aminobutyric acid-functionalized multiwalled carbon nanotubes were prepared and characterized. To our knowledge, covalently GABA-functionalized CNTs were not reported yet and could be used to reinforce not only PHBV but also polyesters such as poly(ϵ -caprolactone), poly(lactic acid), among others. PHBV/CNT nanocomposites with pristine and oxidized CNTs were also prepared to compare the effectiveness of the functionalization process. The results demonstrated that when GABA

is attached to the CNT surface, the impact fracture of PHBV nanocomposite is modified, ranging from brittle to ductile. The findings suggest that increasing CNT-GABA concentration into PHBV matrix could lead to great improvements in the mechanical properties of this nanocomposite.

2 Experimental

2.1 Materials

PHBV was provided by NaturePlast, with 2 mol% of hydroxyvalerate units, molecular weight (M_w) from 400,000 to 500,000 g mol⁻¹, and was used as received. Multi-walled carbon nanotubes (MWCNTs) were supplied by Nanostructured & Amorphous Materials, Inc. (Houston, TX, USA) with specification #1229Y, with a minimum purity of 95%. They have a diameter in the range of 20–30 nm and length in the range of 10–30 μ m and were used as supplied. Gamma-aminobutyric acid (GABA) was obtained from Sigma-Aldrich with a minimum purity of 99%. Nitric acid (HNO₃) 65% and dimethyl sulfoxide (DMSO) P.A. ACS from Neon Comercial (Brazil) were used as received.

2.2 Functionalization of MWCNT

The first step was the oxidation of MWCNT, based on our previously reported methodology [6]. In this step, pristine MWCNT (CNT) was oxidized in nitric acid 6 M at 120 °C for 5 h. After the oxidation period, the sample (CNT-Ox) was centrifuged (ROTINA 420R, Hettich) and washed thoroughly with distilled water until the removal of all remaining acid.

The functionalization with GABA was performed in DMSO at 120 °C. DMSO was firstly heated at 120 °C, then CNT-Ox was added, and lastly, GABA was slowly incorporated to the suspension (wGABA:wCNT-Ox = 1:1). The system was allowed to react at 120 °C for 10 h under stirring.

After the reaction period, CNT-GABA was filtered under vacuum and washed thoroughly with distilled water. This CNT was labeled as CNT-GB. Figure 1 shows a schematic representation of the functionalization process.

2.3 Production of PHBV/CNT nanocomposites

PHBV/CNT nanocomposites with 0.5 wt% of CNT were produced by melt mixing, followed by hot compression molding. Neat PHBV sample and PHBV/CNT, PHBV/CNT-Ox, and PHBV/CNT-GB samples were processed in a high-speed mixer (DRAIS mixer produced by MH Equipamentos Ltda, model MH50-H) rotating at 3000 rpm and mixing chamber with a capacity of 65 g of material. The mixing, melting, and homogenization of the composites occur due to the high friction generated between the rotor and the material. The polymer mass was previously oven-dried for 4 h at 40 °C. After 1 min of mixing, the homogenized composites were collected and pressed into 3.2-mm-thick plates with dimensions according to ASTM D256-06 for the mechanical impact tests in a hydropneumatic press (MH Equipamentos Ltda, model PR8HP) at 200 °C with a pressure of 5 bar for 3 min and then cooled for 2 min.

2.4 Characterization of CNT

X-ray photoelectron spectrometry (XPS) measurements were taken in an X-ray photoelectron spectrometer K-Alpha (Thermo Scientific) using the Al K α X-ray beam with a spot size of 400 μ m, pass energy of 200 eV, and energy step size of 1 eV. Fourier transform infrared (FT-IR) analysis was conducted in a Spectrum One PerkinElmer spectrometer in the 4000–400 cm⁻¹ range, using KBr pellet technique (0.5:300 mg). Raman spectra of the materials were collected with a LabRAM HR Evolution model Raman Spectrophotometer (Horiba) equipped with a camera and using an Ar laser (532 nm). The spectra were taken between 1100 and 1800 cm⁻¹ with an acquisition time of

Fig. 1 Schematic representation of the functionalization process

30 s, 3 cycles. The transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 instrument (JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 200 kV. Energy-dispersive spectrometer (EDS) from Oxford Instruments, model X-MaxN 80T was used.

2.5 Characterization of PHBV/CNT nanocomposites

Notched Izod impact strength test was performed according to ASTM D256-06 on PHBV/CNT, PHBV/CNT-Ox, and PHBV/CNT-GB samples. A CEA/Instron Impactor (model 905) was used with standard Izod-type hammers to perform the test following the Izod model. Impact loading was done with a 0.5 J hammer. Samples were notched using CEA/Instron equipment, V-notch impact test specimens with depth of 2.54 ± 0.1 mm. The test was carried out with a temperature of 25 °C and 50% humidity, and the samples were maintained under these conditions for 48 h before testing. Ten specimens were tested for each condition. Results were analyzed using one-way analysis of variance (ANOVA) and Tukey's multiple comparisons test on GraphPad Prism 6 (GraphPad Prism 6 Software Inc. USA). The results were presented as mean $\pm$ standard

deviation ($n = 10$). Mean values at $P < 0.05$ were considered significant.

The impact fracture surface morphology of the nanocomposites was observed by scanning electron microscopy (SEM) using an Inspect S50-FEI Company® (Oregon, USA) microscope, operating at 7.5 keV with detectors of secondary electrons. The samples were fixed on aluminum stubs and covered with gold. The roughness of the impact fracture surface was quantified ($n = 3$) through profilometry using a mechanical profilometer KLA Tencor P-7.

3 Results

3.1 X-ray photoelectron spectroscopy

XPS analysis was used to determine the elemental surface composition of the samples CNT, CNT-Ox, and CNT-GB. Layers of about 2–5 nm were analyzed through XPS, allowing to estimate the changes on the CNT surface after the functionalization process [18, 21]. Table 1 shows the atomic concentrations of carbon (C1s), oxygen (O1s), and nitrogen (N1s) based on the relative peak areas in the survey scans. Figure 2 shows the survey spectra for CNT, CNT-Ox, and CNT-GB.

The surfaces of CNT and CNT-Ox consist of C and O, with C1s and O1s peaks, near 533 eV and 285 eV, respectively, however, with different ratios. For CNT, a small amount of 2.0% of oxygen was detected, which is attributed to functional groups on the tube's edges [22]. After oxidation, the oxygen content increased from 2.0 to 4.7%, indicating that oxygen-containing functional groups were introduced

Table 1 Elemental surface composition of CNT, CNT-Ox, and CNT-GB

Samples	Atomic concentration (%)		
	C1s	O1s	N1s
CNT	98.0	2.0	–
CNT-Ox	95.3	4.7	–
CNT-GB	94.1	4.8	1.1

Fig. 2 Survey spectra of CNT, CNT-Ox, and CNT-GB (left) and zoom on CNT-GB spectrum (right)

onto the CNT surface. In the spectrum of CNT-GB, an additional peak near 400 eV is observed, corresponding to N1s, indicating the presence of nitrogenated functional group on the CNT-GB surface [17], confirming the CNT functionalization with GABA.

3.2 Infrared spectroscopy

FT-IR was used to evaluate the functional groups attached to the CNT surface after both functionalizations. Figure 3 shows the spectra of neat KBr, CNT, CNT-Ox, CNT-GB, and neat GABA in the range of 2000–500 cm^{-1} , to facilitate the observation of some absorption bands. Neat KBr disk spectrum is showed to avoid improper peak attribution.

Pristine CNT shows a band at 1575 cm^{-1} , which is attributed to the vibration of carbon skeleton [23]. After acid oxidation, CNT-Ox presented a new peak at 1720 cm^{-1} , related to the (O=C–OH) stretching vibrations of the carboxylic acid group [18, 24, 25]. After GABA-functionalization, the peak at 1720 cm^{-1} was shifted to lower wavenumber (1706 cm^{-1}) and had its shape changed. This is due to the presence of amide groups on the CNT-GABA surface, resulting from the covalent attachment of GABA. This covalent bond is changing the behavior of carbonyl groups, once amide carbonyl groups appear at lower wavenumbers compared to the carbonyl from

Fig. 3 FT-IR spectra of KBr, CNT, CNT-Ox, CNT-GB, and GABA

the carboxylic acid group [18, 23, 25]. Another evidence of GABA grafting to CNT-GABA surface is the disappearance of the band at 1261 cm^{-1} , which is attributed to C–O stretching of aromatic groups of the nanotube structure [25]. The intensity of this band was reduced for CNT-Ox and completely disappeared for CNT-GABA, reflecting the consumption of these C–O groups for the GABA attachment. This result confirms that GABA is not adsorbed, but covalently attached to the CNT surface. Another evidence is the increase in the intensity of the peak at 1575 cm^{-1} , which is characteristic and very intense peak of GABA, as can be seen in Fig. 3.

3.3 Raman spectroscopy

Raman spectroscopy is an essential technique for the characterization of carbon-based materials because it provides information regarding the microstructure without destructing the sample [6, 18]. Raman spectra of pristine, oxidized and GABA-functionalized CNT are shown in Fig. 4, where it is possible to recognize the main D and G bands, characteristics of carbon nanotubes. D band concerns of sp^2 carbons comprising impurities or other symmetry-breaking defects and G is the first-order tangential band, assigned to the stretching mode of sp^2 carbon atoms of graphitic materials. A small shoulder on G band is labeled as D' and is associated with out-of-plane defects [18, 26–28].

The ratio between the integrated areas of the D and G bands (I_D/I_G), and D' and G bands ($I_{D'}/I_G$) is useful to provide an approach regarding the extent of functional groups

Fig. 4 Raman spectra of CNT, CNT-Ox, and CNT-GB

introduced on the CNT surface, by measuring the sp^3 atoms in the structure [29]. Increased values of I_D/I_G and $I_{D'}/I_G$ were obtained for oxidized and GABA-functionalized CNT. CNT-P exhibited an I_D/I_G ratio of 0.89 and $I_{D'}/I_G$ ratio of 0.07, while for CNT-Ox and CNT-GB, the ratio I_D/I_G was 1.01 and 1.25, respectively; and the $I_{D'}/I_G$ ratio was 0.08 and 0.11, respectively. These values indicate that the surface structure of the nanotubes was modified, with the

introduction of defects and an increased number of sp^3 -hybridized carbons [21]. In this particular case, the increase in the I_D/I_G and $I_{D'}/I_G$ ratio values is due to covalent binding of carboxylic and hydroxyl groups emerging from oxidation for CNT-Ox, and covalent binding of GABA groups on CNT-GB.

Also, a shift in the wavelength for D and G bands (Table 2) was observed after both functionalizations,

Table 2 Raman position and FWHM of CNT, CNT-Ox, and CNT-GB

Samples	D band		G band		I_D/I_G	$I_{D'}/I_G$
	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})		
CNT	1340	53.6	1573	46.9	0.89	0.07
CNT-Ox	1343	52.8	1578	49.3	1.01	0.08
CNT-GB	1341	53.2	1575	51.6	1.25	0.11

Fig. 5 TEM images of **a, b** CNT, **c, d** CNT-Ox, **e, f** CNT-GB

Fig. 6 Notched Izod impact resistance obtained for PHBV, PHBV/CNT, PHBV/CNT-Ox, and PHBV/CNT-GB

indicating a meaningful impact on the graphitic wall structure [26, 30]. This result suggests that the electrochemical structure was modified due to distinct chemical groups attached to the walls of the nanotubes [21, 31, 32].

The broadening of the FWHM on G band also confirms that the structural order of CNT was diminished after both functionalizations [33], providing another evidence that the attachment of functional groups could be successfully performed.

3.4 Transmission electron microscopy

Figure 5 shows TEM images of CNT, CNT-Ox, and CNT-GB. CNT micrograph showed, in its majority, black dots along the tubes, which are catalyst metallic particles used in the production step of CNT [10, 13, 34]. The black spots are easily observed in Fig. 5a (identified by arrows) and were detected as nickel particles by EDS technique. Figure 5b shows CNT with a higher magnification, where it is possible to confirm the multi-walled characteristic of the tubes, as well as to identify a small layer of amorphous carbon, with relatively smooth and regular surface [18, 35]. CNT has an average of 30 walls, with a distance of about 3.4 Å between walls. After oxidation, CNT-Ox suffered a great reduction in the amount of metallic particles, once the liquid phase oxidation with nitric acid is widely used for purification of CNT, in addition to generating numerous oxygenated groups in the surface of the tubes [27]. CNT-Ox suffered some end opening due to acid treatment, as well as the tubes surface became rougher and relatively thicker. Figure 5c shows an open edge of CNT-Ox and allows the observation of rougher surface. Figure 5d shows

damages in the side wall, with evidence of wall openings. The functionalization of CNT with GABA did not change the overall morphology of the tubes, as can be seen in Fig. 5e, f. However, some surface regions present an additional outer layer that may be attributed to GABA, especially on the tube's edges, which are the most reactive regions of CNT due to pentagonal defects, curvature, and strain [36]. These results are in accordance with Raman, which showed higher structural disorder on the CNT surface with the functionalizations.

3.5 Notched Izod impact strength

Izod impact strength of neat PHBV, PHBV/CNT, PHBV/CNT-Ox, and PHBV/CNT-GB was performed to verify the effectiveness of the functionalization of CNT in the mechanical properties. Figure 6 shows the average results and standard deviation obtained for ten notched specimens of Izod impact strength.

The impact strength of neat PHBV, which was 38.6 J/m, was significantly reduced to 34.0 J/m after the addition of CNT. According to the Tukey's test, both samples are statistically different, displaying a reduction of about 12% in the impact resistance value. This reduction was expected since the addition of CNTs increases the stiffness of the polymer matrix and consequently reduces the impact strength, and similar results were found in the literature [37]. Moreover, PHBV/CNT nanocomposite suffered a reduction in the impact strength because the dispersion of CNTs into PHBV matrix was not good enough, changing the tenacity mechanism and consequently reducing the energy absorption [38, 39]. After functionalization, the impact resistance was slightly increased if compared to PHBV/CNT. Samples produced with CNT-Ox and CNT-GB presented average values of impact resistance lower than that observed for neat PHBV; however, statistical analysis showed that the three samples PHBV, PHBV/CNT-Ox, and PHBV/CNT-GB have similar impact strength.

Agglomerate particles act reducing the impact strength of polymer matrices [40]. In the case of PHBV/CNT-Ox and PHBV/CNT-GB, the functionalization acted positively, leading the impact strength value similar to that of neat PHBV. In this case, the improvement in impact strength may be related to good dispersion of CNT and increased compatibility between the filler and the polymer matrix.

Improved interfacial compatibility is essential for obtaining nanocomposites with superior mechanical properties due to a continuous interface formed between the polymer and the matrix [4, 8] and better dispersion of the nanotubes [41, 42]. Improvements in mechanical and thermal properties are observed when good compatibility is obtained between CNTs and the matrix [17].

Fig. 7 SEM notched Izod impact surface fractures of neat PHBV (**a**), PHBV/CNT (**b**), PHBV/CNT-Ox (**c**), and PHBV/CNT-GB (**d, e**)

Fig. 8 Impact surface fracture roughness of PHBV, PHBV/CNT, PHBV/CNT-Ox, and PHBV/CNT-GB. Results are given as mean $\pm$ SD ($n=3$), significance levels: ** $p < 0.01$; *** $p < 0.001$

3.6 Scanning electron microscopy (impact surface)

SEM images from Fig. 7 show the notched Izod impact fracture surfaces of the neat PHBV (Fig. 7a) and the nanocomposites with CNT (Fig. 7b), CNT-Ox (Fig. 7c), and CNT-GB (Fig. 7d, e). Figure 7a–c shows similar fracture mechanisms, with relatively smooth surfaces, reflecting a fragile (brittle) fracture mode. Figure 7d fracture surface is clearly different from the others, displaying regions which suffered plastic deformation, represented by the regions of shear flow, characteristics of typically ductile fractures [43–45].

Figure 7e shows a greater magnification from Fig. 7d and allows to identify some ears on the fracture surface of PHBV/CNT-GB, which are an indication of local plastic deformation [46]. Such localized plastic deformation shown in Fig. 7d consists of the formation of fibrils and microvoids, since in thermoplastic polymers, the primary deformation mechanism is called crazing, which is a localized plastic deformation. This region of plastic deformation fracture consists of a highly misaligned and stretched region, involving tearing of materials [47].

Although the impact resistance values were not significantly changed with the addition of CNT-GB, the fracture surface morphology shows that the functionalization with GABA changes the fracture mode from relatively fragile to ductile, evidenced by the regions with plastic deformation. This behavior may be justified because GABA has a similar structure to the hydroxybutyrate monomer from PHBV. Better compatibility with improved interfacial adhesion

will be achieved when a nanoparticle is functionalized with the same polymer used as matrix [4, 8]. Moreover, the mechanical properties of nanocomposites are directly affected by the dispersion of CNT in the matrix, the presence of effective functional groups, and strong interfacial adhesion between nanoparticle and polymer matrix [48].

The nanocomposites reported in this work were produced with 0.5 wt% of CNT; however, the results obtained are promising for producing nanocomposites with higher concentrations of CNT-GB, which could result in much improvement in the mechanical properties of PHBV.

3.7 Impact surface roughness

Roughness measurement was taken to evaluate and quantify the changes in the impact surface. Figure 8 shows the average roughness (R_a) and the standard deviation of the measurements. The average roughness for neat PHBV was the smallest from all samples, 1.9 μm , designating a fragile fracture mode. PHBV/CNT sample showed an average roughness of 2.3 μm , and as can be seen, with no significant difference from neat PHBV, and therefore, also indicating a fragile fracture mode. PHBV/CNT-Ox and PHBV/CNT-GB presented the highest surface roughness, 6.0 and 7.7 μm , respectively. Although not presenting a significant difference between them, PHBV/CNT-GB surface roughness was 28% higher than PHBV/CNT-Ox, exhibiting a trend to present higher roughness values for higher CNT-GB concentrations. Rougher surfaces are attributed to the sliding of the polymer chains, meaning greater deformation during fracture [6]. The higher roughness obtained for PHBV/CNT-GB is in accordance with the SEM images observed in Fig. 7 and supports the assertion that this sample suffered ductile fracture mode.

The compatibility of CNT-GB with PHBV matrix was significantly improved, once GABA has a similar structure to PHBV, leading to better polymer–filler interactions [49], which was responsible for changing the fracture mode of this sample.

4 Conclusions

The unprecedented functionalization of multi-walled carbon nanotubes with GABA was successfully reported. The presence of nitrogen from GABA was detected by XPS, and FT-IR confirmed its covalent attachment on the CNT surface. Raman and TEM contributed to evidence the functionalizations, showing higher structural disorders for functionalized samples, as expected. Nanocomposites

with 0.5 wt% of CNT, CNT-Ox and CNT-GB and PHBV were produced to evaluate the effectiveness of CNT functionalization in the compatibility between the filler and the matrix. The addition of CNT-GB showed changes in the impact fracture mode of PHBV from fragile to ductile, evaluated through SEM images and average roughness of the impact fracture surface, which was increased by about 300% for PHBV/CNT-GB compared to neat PHBV. This result suggests that the compatibility between CNT-GB and PHBV was greatly improved, being a promising result for the production of biodegradable thermoplastic nanocomposites.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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