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Original Article

Evaluation of hydrolytic degradation of bionanocomposites through fourier transform infrared spectroscopy

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Abstract: Studies about *in vitro* biodegradation of polymers have grown considerably due to the wide application of biodegradable polymers in biomedical areas. The objective of this study was to prepare bionanocomposites films of PHB, PEG, and organoclays by solution intercalation, and to evaluate the morphology, structure, hydrolytic degradation through FTIR and the calculation of carbonyl content. The results showed that bionanocomposites displayed intermediated dispersion of the filler, the polymer chains were intercalated into the organoclay layers and was observed some degree of exfoliation. There was an influence of PEG and of the clay on the degradation of the polymer, this fact was observed due to the decrease in the intensity of PHB carbonyl band in the region around 1275 cm^{-1}, affecting the amorphous and crystalline regions of the polymer. This reduction can be associated with the increase in hydrophilicity of the polymer caused by the presence of the PEG and clay, suggesting the possibility of increasing the biodegradability of the pure polymer. In future research, there will be made characterizations to know if these materials can be used in medical devices.

Keywords: biodegradation, bionanocomposites, hydrolytic degradation, polyhydroxybutyrate.

1. Introduction

The search for materials obtained from renewable sources has led to the growing interest in the use of biodegradable polymers, which can be used in several areas of society, i.e. the biomedical area. The most known and important biodegradable polymers are the aliphatic polyesters, poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(caprolactone) (PCL) and poly(hydroxybutyrate) (PHB)[1]. The main reasons for using these polymers in medical areas are their biocompatibility [2].

Among biodegradable polymers PHB can be highlighted, a polymer produced naturally by bacteria from renewable energy sources that can be biodegraded in nature[3]. However, PHB presents some disadvantages, for instance, narrow processability window and poor mechanical and barrier properties. In order to improve PHB properties, some modifications have been made, for example, blend and composite formation[4]. Fillers with dimensions on the range of nanometers have been widely investigated; since polymer's properties are greatly improved with just a low content of the filler. Clays are layered silicate minerals, such as montmorillonite that has high availability, versatility, low cost, which have minimal adverse effects on the environment and human health. The individual clay particle presents a platelet structure, with a thickness of approximately 1 nm and lateral dimensions up to 1 μm. In composites, the nanoclays reinforcing efficiency, good barrier properties, and improved dimensional and thermal stability are strongly related to their aspect ratio and large surface area[5,6].

Furthermore, the addition of a plasticizer can improve PHB properties, increasing its thermal stability and representing an effective way to develop a new material with desired properties [7,8]. In this sense, poly (ethylene) glycol (PEG) is a flexible and biocompatible polyester widely used to modify hydrophobic polymers and to form amphiphilic block copolymers[9]. PEG is non-toxic, soluble in water and inorganic solvents, chemically stable and inert in acidic and alkaline media. Additionally, it is widely used in different pharmaceutical, food, and cosmetic formulations[10,11].

The use of polymeric materials for diverse applications has increased since the synthetic polymers were discovered. In the case of biomedical applications, the use biodegradable polymers and bionanocomposites have been the great importance since they are widely used in the formation of implants, the manufacture of capsules for controlled drug delivery, and the develop of scaffolds for engineering tissue, among other applications. For biomedical application, polymers and bionanocomposites have to satisfy specific requirements such as compatibility and appropriate mechanical properties. Also, degradation products must be readily metabolized and excreted by the body without toxicity[12,13].

Thus, the present work had the objective of developing pure PHB and PHB/PEG/Organoclay bionanocomposite films in different compositions through the solution intercalation method. Subsequently, there were evaluated the systems morphology by optical microscopy, structure by X-ray diffraction analysis, hydrolytic degradation, and carbonyl content by Fourier Transform Infrared Spectroscopy, to evaluate the degradation state.

2. Materials and Methods

2.1 Materials

PHB as a yellowish powder with a high degree of purity of over 99.5% was supplied by PHB Industrial S/A, and it is biosynthesized by aerobic fermentation and extraction purification through a natural solvent. Mineração Pedra Lavrada (Paraiba) provided the expanded vermiculite clay for the development of this research. Poly (ethylene) glycol (PEG) and the chloroform solvent were purchased from Synth Ltda. The stearyl dimethyl ammonium chloride salt (Praepagen WB®) was purchased from Clariant do Brasil.

2.2 Chemical Modification Process of Vermiculite Clay (VMT)

The organofilization of the VMT clay was performed according to procedures followed by Barbosa et al.[14] and Mesquita et al.[15] which consisted in the preparation of a dispersion containing distilled water, natural clay, and ammonium salt.

2.3 Solution intercalation method

For the preparation of the films by the solution intercalation method, the PHB powder was previously sieved and oven dried at 70°C for 24 hours. Then 5g of PHB were dissolved in chloroform under mechanical stirring and heating at 80°C for 3 hours. To reduce solvent loss by vaporization, a condensation system was set up. For the formation of the pure PHB and bionanocomposite (BIO 95%, BIO 90%) films with 5 and 10% PEG, respectively, and with 3% organoclay vermiculite, the solutions were poured into marble plates, finally the films were removed from the plates. For the bionanocomposites, the ratio of parts per hundred of resin (PCR) was used, PHB + PEG were considered as resin.

2.4 Optical microscopy

Pure PHB and bionanocomposite films surface were observed using a Leica Microsystems MD500 optical microscope (OM), operating on transmission mode with ICC 50 E camera and magnificent of 40X (500 μm).

2.5 X-ray diffraction analysis

A Shimadzu XRD 6000 X-ray diffractometer system was used to perform XRD analyses. Scans were recorded in the range of 2Θ = 1.5° - 30°.

2.6 Hydrolytic degradation

The hydrolytic degradation tests of pure PHB and bionanocomposites films were performed according to ASTM F1635-11[16] controlling the pH and temperature of the system. The test was carried out for 12 weeks. The hydrolytic degradation of the samples was performed in saline phosphate buffer (pH 7.4 ± 0.2). The test was carried out in triplicate, and the films were packed in test tubes with 10 ml of PBS solution and kept in a water bath at 37°C (±2). At different time intervals (2nd, 4th, 6th, 8th, 12 th weeks), the films were removed from the controlled environment and then dried in an oven at 60°C.

Additionally, there were monitored the weight loss of the pure PHB and bionanocomposite films through gravimetric analysis along the degradation test. Time zero was set up as before initiating the test, and measures were made at the time of the film's withdrawals. The results of weight loss for the samples of the 12th withdrawal were not reported because the films were highly deteriorated due to the degradation. The results were obtained through:

Where #M is the weight loss, M_0 is the mass of the films before the degradation test and M_f is the mass of the films at the different removal times.

2.7 Fourier Transform Infrared Spectroscopy (FTIR)

The systems were characterized by FTIR, before and after the hydrolytic degradation test, FTIR analyses were performed on a SHIMADZU IRAffinity-1 model spectrometer with a scan of 4000 to 450 cm^{-1}. To the obtained spectra, it was applied a mathematical treatment known by deconvolution in the software Origin 8.0, in the Lorentzian function applied specifically to the bands of carbonyl (C = O) in (1722 and 1751cm^{-}1). Thus, the carbonyl content was obtained by the ratio between the peak area of the carbonyl and the peak area of the reference band (CH_3). The calculation was performed considering the samples before and after the withdrawals referring to the 2nd, 6th. The carbonyl indices for the samples of the 8th and 12th withdrawal were not reported because the films were highly deteriorated due to the degradation.

3. Results and Discussions

3.1 Optical microscopy

Optical microscopy was employed to evaluate the system's morphology. Figure 1 shows the optical micrographs of pure PHB and bionanocomposites films.

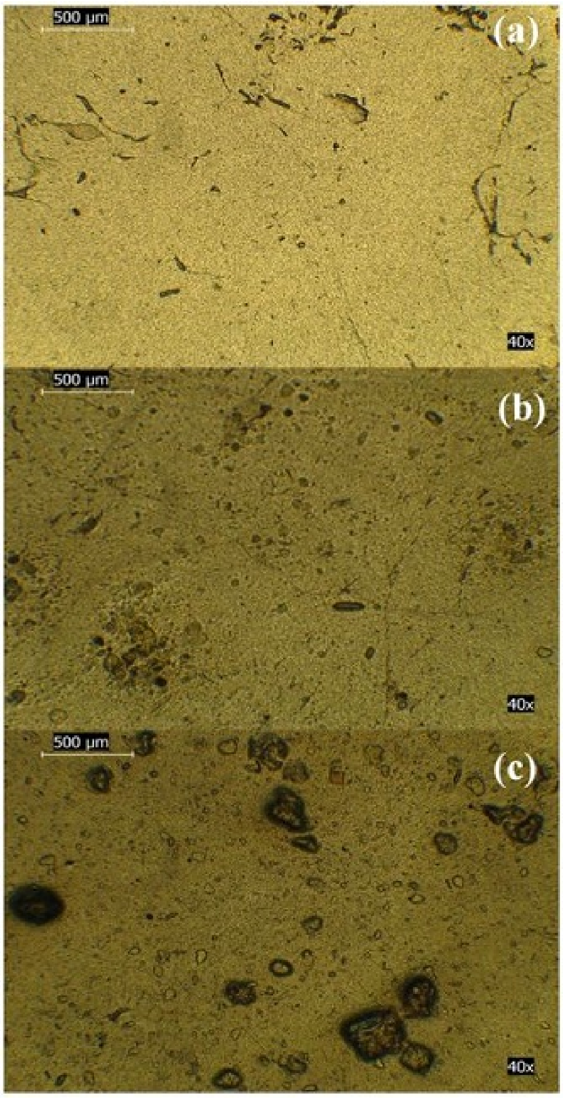


Figure 1.
Optical micrographs of the (a) pure PHB, (b) BIO 95% and (c) BIO 90% films.

In the optical micrograph of the pure PHB, Figure 1 a, there were observed superficial fissures that can be attributed to the solvent evaporation process, since the film adhered to the marble plates in which was poured. In the optical micrographs of the bionanocomposites films, Figures 1 1c there were perceived the same superficial fissures, and dark or dense zones along the films surface that can be ascribed to the formation of organoclay agglomerates. The BIO 90% film presented the greatest number of agglomerates, behavior that can be attributed to the poorer organoclay dispersion due to the higher PEG content, in comparison with the BIO 95% film. Similar results were reported by Mesquita et al.[17].

3.2 X-ray diffraction analysis

X-ray diffraction analyses were carried out to evaluated structural modifications of the PHB by the addition of the organoclay and

PEG. Figure 2 displayed the diffractograms of the pure PHB and bionanocomposites films.

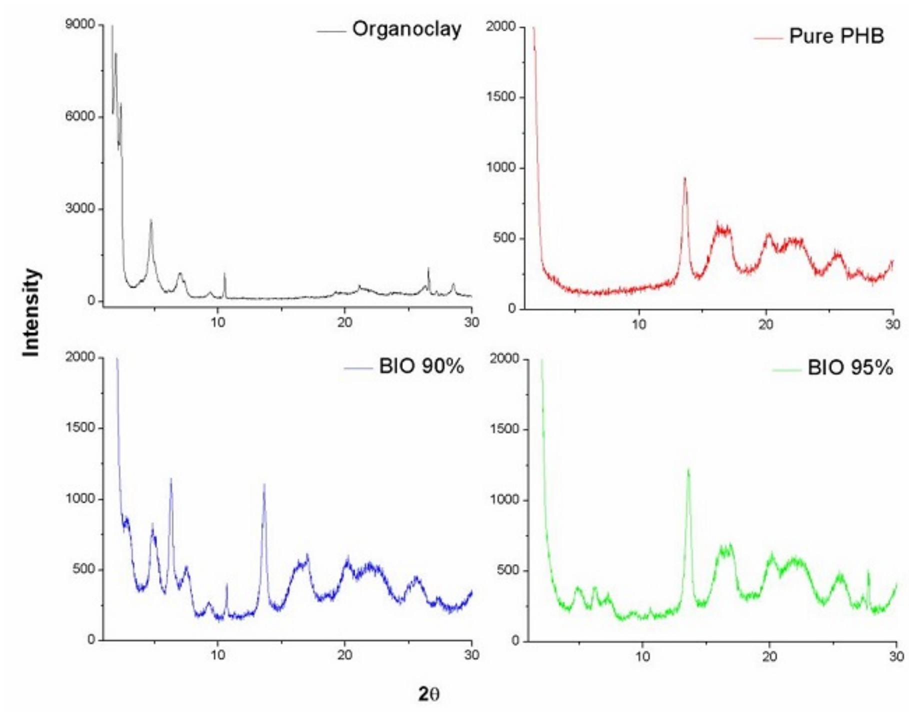


Figure 2.
Diffractograms of the organoclay and the pure PHB and bionanocomposites films.

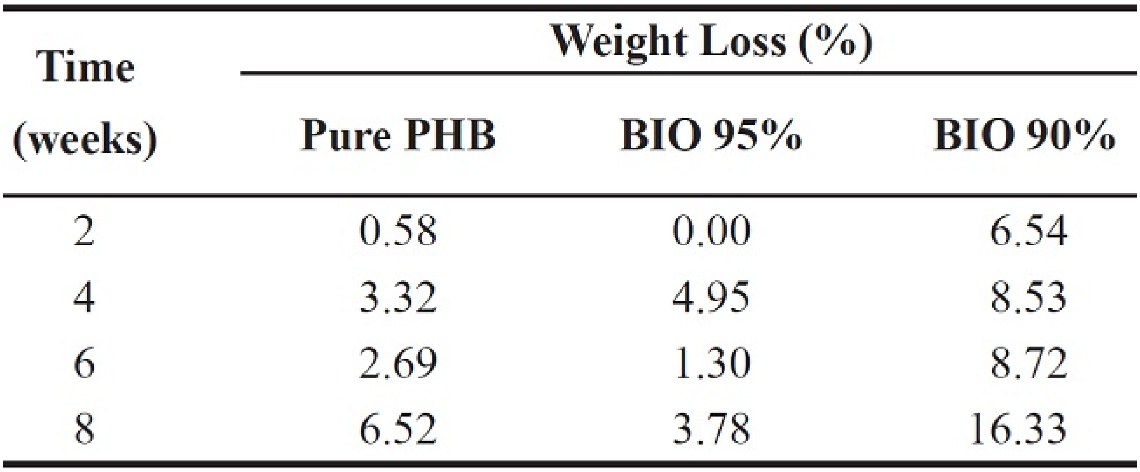
As it was expected, the diffractograms of the pure PHB showed the characteristic peaks. For the organoclay, there were perceived six peaks between 2θ angles of 2 and 10.55° indicating the ammonium salt intercalation between the clay layers. In the diffractogram of the BIO 90%, there were noted 5 new peaks different to the displayed in the diffractogram of the pure PHB due to the organoclay presence. Those peaks were shifted to smaller 2θ angles in comparison with the organoclay peaks. Similarly, in the diffractogram of the bionanocomposite BIO 95%, there were noted 4 new peaks shifted to smaller 2θ angles and with lower intensities than the organoclay peaks and the BIO 90% peaks. The decrease of the 2θ angles indicated an increase in the interlayer spaces of the clays because the polymer chains entered between the clay layers. Besides, the difference in peaks intensity revealed the destruction of the clays crystalline order as a consequence of the intercalation of polymer chains in the clays layers, and the disappearance of peaks revealed some degree of exfoliation. Finally, it was noted that high PEG content decreased the intercalation and exfoliation degree since the PHB chains were impeded to enter the organoclay layers. Similar results were reported by Crétois et al.[18] and Silva et al.[19].

3.3 Hydrolytic degradation

3.3.1 Weight loss

In Table 1 are listed the results of weight loss of the pure PHB and bionanocomposite films while the hydrolytic degradation test.

Table 1.
Weight loss of the pure PHB and the bionanocomposites (BIO 95%, BIO 90%) films during the hydrolytic degradation test.



Time (weeks)	Weight Loss (%)		
	Pure PHB	BIO 95%	BIO 90%
2	0.58	0.00	6.54
4	3.32	4.95	8.53
6	2.69	1.30	8.72
8	6.52	3.78	16.33

It was observed different trends in the weight loss behaviors of the three systems. The pure PHB film lost weight linearly in the first two weeks and it decreased in the sixth week. For the bionanocomposites, there were observed oscillation, BIO 95% did not lose weight at the beginning of the test, on the other hand, BIO 90% lost 6.50% of its weight on the second week, and 16.33% on the eighth week, being the biggest loss in comparison with the other systems. It may be suggested that the degradation was affected by the addition of the organoclay and PEG, which promoted the water penetration into the systems, caused the diminution of the polymer chains, and increased the disintegration of the systems. Similar results were reported by Kmita et al.[20] and Zhao et al.[21].

3.3.2 Carbonyl content

Figure 3 shows the FTIR spectra, and Table 2 shows the carbonyl content obtained from the amorphous and crystalline regions, before and after the hydrolytic degradation of the pure PHB. Based on these values, it is possible to observe a significant increase of the crystalline phase content, and a discrete increase in the amorphous phase content of the polymer, after it has been submitted to the degradation test. The degradation of the pure polymer occurred preferentially in the amorphous regions as a consequence of the increase in crystallinity, also taking into account that there was a reduction in the peak intensity of the region at 1750 cm^{-1}.

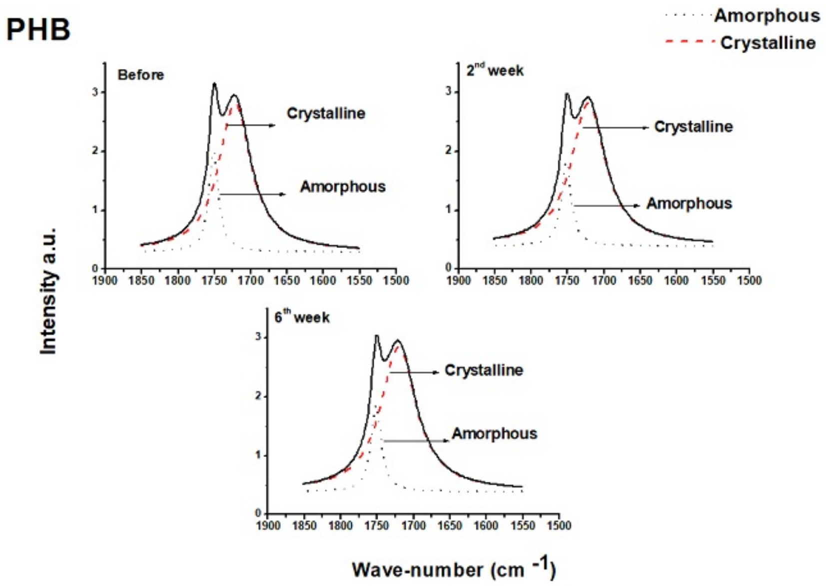


Figure 3.
PHB spectra after deconvolution (C=O carbonyl band) before and after degradation.

Table 2.
Carbonyl PHB indices of amorphous and crystalline phase calculated before and after degradation.

	IC		
PHB	**Before degradation**	**2nd week**	**6th week**
Crystalline$_{(1722/1380)}$	1.61	3.90	4.02
Amorphous$_{(1751/1380)}$	0.32	0.65	0.68

According to Faria and Franchetti[22], the degradation of the polymer can occur due to the increase of the crystalline phase, and consequently, the consumption of the amorphous phase at the ends of the chain. The amorphous phase consumption induces the reorganization of the remaining chains and, as a result, the increase in crystallinity[21].

The data analyzed showed degradation in the amorphous region of the polymer, followed by an increase in crystallinity for the pure PHB. Such behavior is due to the time and hydrolysis conditions used. Spyros et al.[23] observed that the degradation of the pure PHB can occur in both phases, depending on the time of biotreatment of the polymer. Bonartseva et al.[24] obtained similar results, in which the degradation of the PHB film is followed by the increase of the crystallinity.

Figure 4 shows the FTIR spectra obtained in the carbonyl region for the composite BIO 95%. The band referring to the carbonyl of the crystalline region was larger and less intense. The carbonyl contents presented in Table 3 showed that the insertion of the clay next to the PEG in the pure polymer altered the crystallinity of the material.

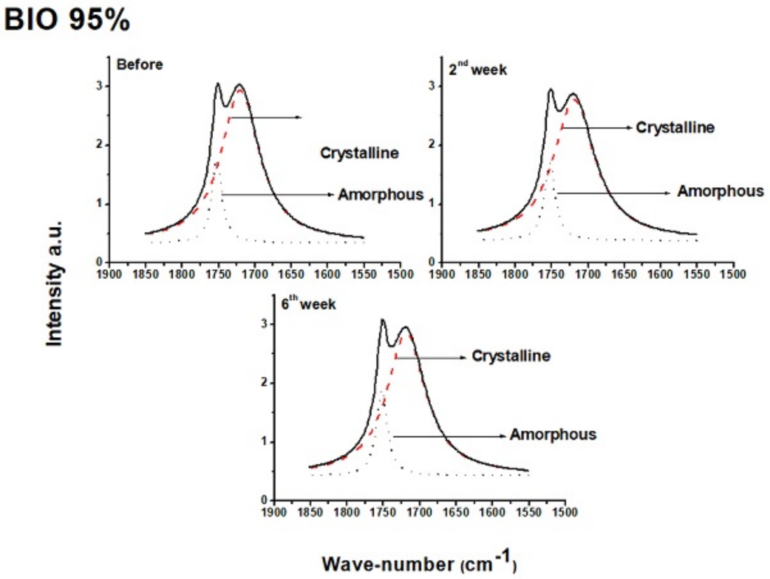


Figure 4.
BIO 95% spectra after deconvolution (C=O carbonyl band) before and after degradation.

Table 3.
Carbonyl BIO 95% indices of amorphous and crystalline phase calculated before and after degradation.

	IC		
BIO 95%	**Before degradation**	**2nd week**	**6th week**
Crystalline$_{(1720/1380)}$	3.49	3.04	3.29
Amorphous$_{(1752/1380)}$	0.07	0.006	0.53

In the work developed by Branciforti et al.[25], the authors verified the alteration in crystallinity by adding montmorillonite to the pure PHBV. The carbonyl content for BIO 95% showed that there was a reduction of the amorphous and crystalline phase content of the polymer during the degradation time. Kmita et al.[20] studied the hydrolytic degradation in PLA and clay nanocomposites and observed that the addition of the clay promotes the penetration of the water into the polymeric structure, which causes consequently a greater degradation of the materials.

Figure 5 shows the deoxygenated spectra for BIO 90% and the C = O carbonyl indices are presented in Table 4 . With the increase of 10% PEG and the insertion of the organoclay, it was observed a proportional change in the content of amorphous and crystalline phases of PHB, verifying that the composition obtained results that corroborate with the loss of mass in the continuation of this work, and that the degradation can have been caused by the increase of the addition of PEG and the presence of the clay.

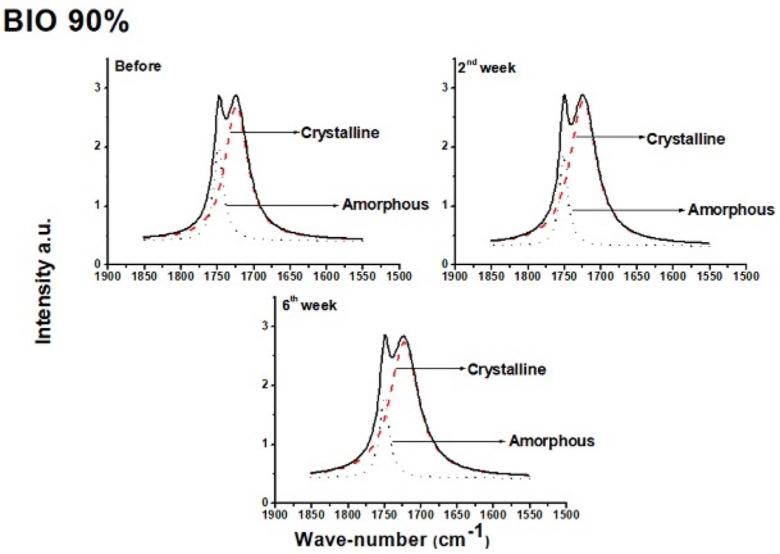


Figure 5.
BIO 90% spectra after deconvolution (C=O carbonyl band) before and after degradation.

Table 4.
Carbonyl BIO 90% indices of amorphous and crystalline phase calculated before and after degradation.

	IC		
BIO 90%	**Before degradation**	**2nd week**	**6th week**
Crystalline$_{(1723/1380)}$	5.12	4.63	4.07
Amorphous$_{(1752/1380)}$	1.52	0.88	0.85

The determination of the carbonyl content for the BIO 90% showed a reduction of more than 50% of the carbonyl content in the amorphous phase in relation to the start of the test and a proportional reduction of the crystalline phase content. The incorporation of PEG and clay resulted in an increase in hydrolysis, thereby facilitating water penetration and ester bond cleavage[26].

This fact can be related to the value of the basal interlamellar distance of the bionanocomposite, which too depends on the length of the PEG chain and of the quaternary ammonium salt. These factors affect the dispersion of organoclay in the pure polymer[27]. The degradation of the bionanocomposites can be directly related to the degradation of the surfactant (quaternary ammonium salt) present in the organoclay, in which an intercalation of the ammonium ions within the silicate layers of the vermiculite clay can occur.

For the bionanocomposites, the degradation occurred in the amorphous and crystalline regions of the polymer, evidenced by the decrease of both phases. For the BIO 90%, the results were more expressive since there was a bigger consumption of crystalline and amorphous fraction over the weeks, and the amorphous region was the most degraded. This behavior can be related to a better homogenization, influenced by the effect of plasticizer and clay.

The presence of 3% clay and 10% PEG possibly affected the crystallinity of the polymer, facilitating the hydrolysis of the ester bonds, making it difficult to reorganize the chain and thereby increase the degradation process. Chandra and Rustgi[28] stated that degradation in the PHB occurs with the increase in crystallinity of the polymer. The clay content used in this work was constant (3%), and the variation of the carbonyl content for the compositions of the bionanocomposites is probably related to the interaction between the plasticizer and the organoclay.

In the literature, there have not been reported studies that correlate the evaluation of the calculation of the carbonyl content through FTIR and the degradation behavior of these materials. Therefore, this work is of fundamental importance that can help in future research.

4. Conclusions

PHB, PEG and organoclay bionanocomposites were developed by the solution intercalation method. Bionanocomposites displayed intermediated dispersion of the filler along the matrix, the polymer chains were intercalated into the organoclay layers, and was observed some degree of exfoliation. It was observed in the FTIR analysis that the insertion of the clay and the PEG did not change the chemical structure of the polymer. After the test, the calculation of the carbonyl content indicated that, for the pure PHB, the degradation in the amorphous regions occurred. This fact was evidenced by the increase of the carbonyl content of the crystalline polymer region. The BIO 90% composition showed a proportional reduction for the amorphous and crystalline phases of the polymer over the 12 test weeks, showing that the introduction of PEG and organoclay facilitated the penetration of water in the chain, and that the degradation of bionanocomposites can be directly linked to the degradation of the surfactant present in organoclay. It was noticed, in this study, that the addition of PEG and of the organoclay vermiculite affected the chain regularity and increased the hydrolytic degradation of the PHB polymer, acquiring desirable degradation characteristics for the possible application in biomaterials. For future researches, we recommend to make further characterizations of these materials, which permit to evaluate their use as medical devices.

5. Acknowledgements

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6. References

1 Rhim, J. W., Park, H. M., & Ha, C. S. (2013). Bio-nanocomposites for food packaging applications. *Progress in Polymer Science*, *38*(10), 1629-1652. http://dx.doi.org/10.1016/j.progpolymsci.2013.05.008.

2 De Paula, E. L., Mano, V., & Pereira, F. V. (2011). Influence of cellulose nanowhiskers on the hydrolytic degradation behavior of poly (d, l-lactide). *Polymer Degradation & Stability*, *96*(9), 1631-1638. http://dx.doi.org/10.1016/j.polymdegradstab.2011.06.006.

3 Quental, A. C., Carvalho, F. P. D., Tada, E. D. S., & Felisberti, M. I. (2010). Blendas de PHB e seus copolimeros: miscibilidade e compatibilidade. *Quimica Nova* , *33*(2), 438-446. http://dx.doi.org/10.1590/S0100-40422010000200035.

4 Brito, G. F., Agrawal, P., Araujo, E. M., & Melo, T. J. A. (2011). Biopolimeros, polimeros biodegradaveis e polimeros verdes. *Revista Eletrônica de Materiais e Processos* , *6*(2), 127-139. Retrieved in 2017, February 20, from http://www2.ufcg.edu.br/revistaremap/index.php/REMAP/article/view/222/204.

5 Reis, D. C. C., Oliveira, T. A., Carvalho, L. H., Alves, T. S., & Barbosa, R. (2016). The influence of natural Clay and organoclay vermiculite on the formation processo of bionanocomposites with poly(3-hydroxybutyrate-co-3-hydroxyvalerate). *Revista Materia* , *22*(4), e-11886. http://dx.doi.org/10.1590/s1517-707620170004.0220.

6 Reis, D. C. C., Oliveira, T. A., Carvalho, L. H., Alves, T. S., Barbosa, R. Biodegradability of and interaction in the packaging of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-vermiculite bionanocomposites. *Applied Polymer Science*, *134*(15), 1-9. http://dx.doi.org/10.1002/app.44700.

7 Machado, M. L., Pereira, N. C., Miranda, L. F. D., Terence, M. C., & Pradella, J. G. (2010). Estudo das propriedades mecanicas e termicas do polimero poli-3-hidroxibutirato (PHB) e de compositos PHB/po de madeira. *Polímeros: Ciência e Tecnologia* , *20*(1), 65-71. http://dx.doi.org/10.1590/S0104-14282010005000011.

8 Puglia, D., Fortunati, E., D'amico, D. A., Manfredi, L. B., Cyras, V. P., & Kenny, J. M. (2014). Influence of organically modified clays on the properties and disintegrability in compost of solution cast poly (3-hydroxybutyrate) films. *Polymer Degradation & Stability*, *99*, 127-135. http://dx.doi.org/10.1016/j.polymdegradstab.2013.11.013.

9 Cao, Z., & Jiang, S. (2012). Super-hydrophilic zwitterionic poly (carboxybetaine) and amphiphilic non-ionic poly (ethylene glycol) for stealth nanoparticles. *Nano Today*, *7*(5), 404-413. http://dx.doi.org/10.1016/j.nantod.2012.08.001.

10 Ko, P. T., Lee, I. C., Chen, M. C., & Tsai, S. W. (2015). Polymer microneedles fabricated from PCL and PCL/PEG blends for transdermal delivery of hydrophilic compounds. *Journal of the Taiwan Institute of Chemical Engineers*, *51*, 1-8. http://dx.doi.org/10.1016/j.jtice.2015.01.003.

11 Parra, D. F., Fusaro, J., Gaboardi, F., & Rosa, D. S. (2006). Influence of poly(ethylene glycol) on the thermal, mechanical, morphological, physical–chemical and biodegradation properties of

poly (3-hydroxybutyrate). *Polymer Degradation & Stability* , *91*(9), 1954-1959. http://dx.doi.org/10.1016/j.polymdegradstab.2006.02.008.

12 Laycock, B., Nikolic, M., Colwell, J. M., Gauthier, E., Halley, P., Bottle, S., & George, G. (2017). Lifetime prediction of biodegradable polymers. *Progress in Polymer Science*, *71*, 144-189. http://dx.doi.org/10.1016/j.progpolymsci.2017.02.004.

13 Ginjupalli, K., Shavi, G. V., Averineni, R. K., Bhat, M., Udupa, N., & Nagaraja Upadhya, P. (2017). Poly(-hydroxy acid) based polymers: A review on material and degradation aspects. *Polymer Degradation & Stability*, *144*, 520-535. http://dx.doi.org/10.1016/j.polymdegradstab.2017.08.024.

14 Barbosa, R., Araújo, E. M., Oliveira, A. D., & Melo, T. J. A. (2006). Efeito de sais quaternários de amônio na organofilizacao de uma argila bentonita nacional. *Cerâmica*, *52*(324), 264-268. http://dx.doi.org/10.1590/S0366-69132006000400009.

15 Mesquita, P. J. P., Araujo, R. D. J., Carvalho, L. H., Alves, T. S., & Barbosa, R. (2016). Thermal evaluation of PHB/PP#g#MA blends and PHB/PP#g#MA/vermiculite bionanocomposites after biodegradation test. *Polymer Engineering and Science* , *56*(5), 555-560. http://dx.doi.org/10.1002/pen.24279.

16 American Society for Testing and Materials – ASTM. (2010). *ASTM F1635-11: standard test method for in vitro degradation testing of hydrolytically degradable polymer resins and fabricated forms for surgical implants*. West Conshohocken: ASTM.

17 Mesquita, P. J. P., Araujo, R. D. J., Andrade, D. L. A. C. S., Carvalho, L. H., Alves, T. S., & Barbosa, R. (2016). Evaluation of biodegradation of PHB/PP-g-MA/vermiculite bionanocomposites. *Materials Science Forum*, *869*, 289-302. https://doi.org/10.4028/www.scientific.net/MSF.869.298.

18 Crétois, R., Follain, N., Dargent, E., Soulestin, J., Bourbigot, S., Marais, S., & Lebrun, L. (2014). Microstructure and barrier properties of PHBV/organoclays bionanocomposites. *Journal of Membrane Science*, *467*, 56-66. http://dx.doi.org/10.1016/j.memsci.2014.05.015.

19 Silva, R. M., Conceicao, I. D., & Silva, J. E., Alves, T. S., & Barbosa, R. (2016). Characterization of bionanocomposites PHB, PEG and organophilic clay. *Materials Science Forum* , *869*, 303-307. http://dx.doi.org/10.4028/www.scientific.net/MSF.869.303.

20 Rapacz-Kmita, A., Stodolak-Zych, E., Szaraniec, B., Gajek, M., & Dudek, P. (2015). Effect of clay mineral on the accelerated hydrolytic degradation of polylactide in the polymer/clay nanocomposites. *Materials Letters*, *146*, 73-76. http://dx.doi.org/10.1016/j.matlet.2015.01.135.

21 Zhao, Q., Cheng, G., Li, H., Ma, X., & Zhang, L. (2005). Synthesis and characterization of biodegradable poly (3-hydroxybutyrate) and poly (ethylene glycol) multiblock copolymers. *Polymer*, *46*(23), 10561-10567. http://dx.doi.org/10.1016/j.polymer.2005.08.014.

22 Faria, A. U. D., & Martins-Franchetti, S. M. (2010). Biodegradacao de filmes de polipropileno (PP), poli (3-hidroxibutirato)(PHB) e blenda de PP/PHB por microrganismos das aguas do Rio Atibaia. *Polímeros: Ciência e Tecnologia*, *20*(2), 141-147. http://dx.doi.org/10.1590/S0104-14282010005000024.

23 Spyros, A., Kimmich, R., Briese, B. H., & Jendrossek, D. (1997). 1 H NMR imaging study of enzymatic degradation in poly (3-hydroxybutyrate) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate). Evidence for preferential degradation of the amorphous phase by PHB depolymerase B from pseudomonaslemoignei. *Macromolecules*, *30*(26), 8218-8225. http://dx.doi.org/10.1021/ma971193m.

24 Bonartseva, G. A., Myshkina, V. L., Nikolaeva, D. A., Rebrov, A. V., Gerasin, V. A., & Makhina, T. K. (2002). The biodegradation of poly-β-hydroxybutyrate (PHB) by a model soil community: the effect of cultivation conditions on the degradation rate and the physicochemical characteristics of PHB. *Microbiology*, *71*(2), 221-226. http://dx.doi.org/10.1023/A:1015162608031. PMid:12024829.

25 Branciforti, M. C., Corrêa, M. C. S., Pollet, E., Agnelli, J. A. M., Nascente, P. A. P., & Avérous, L. (2013). Crystallinity study of nano-biocomposites based on plasticized poly (hydroxybutyrate-co-hydroxyvalerate) with organo-modified montmorillonite. *Polymer Testing*, *32*(7), 1253-1260. http://dx.doi.org/10.1016/j.polymertesting.2013.08.001.

26 Liao, L., Dong, J., Shi, L., Fan, Z., Li, S., & Lu, Z. (2015). In vitro degradation behavior of l-lactide/trimethylene carbonate/glycolide terpolymers and a composite with poly (l-lactide-co-glycolide) fibers. *Polymer Degradation & Stability*, *111*, 203-210. http://dx.doi.org/10.1016/j.polymdegradstab.2014.11.013.

27 Bordes, P., Hablot, E., Pollet, E., & Averous, L. (2009). Effect of clay organomodifiers on degradation of polyhydroxyalkanoates. *Polymer Degradation & Stability* , *94*(5), 789-796. http://dx.doi.org/10.1016/j.polymdegradstab.2009.01.027.

28 Chandra, R., & Rustgi, R. (1998). Biodegradable polymers. *Progress in Polymer Science*, *23*(7), 1273-1335. http://dx.doi.org/10.1016/S0079-6700(97)00039-7.

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