Original Article

Thermal behavior of biodegradable bionanocomposites: influence of bentonite and vermiculite clays

Raimundo Miguel Silva Júnior\textsuperscript{a}, Thainá Araújo de Oliveira\textsuperscript{b}, Luis Miguel Araque\textsuperscript{a}, Tatianny Soares Alves\textsuperscript{a,c}, Laura Hecker de Carvalho\textsuperscript{d}, Renata Barbosa\textsuperscript{a,c,*}

\textsuperscript{a} Graduate Program in Materials Science and Engineering, Technology Center, Federal University of Piauí, Teresina, PI 64049-550, Brazil
\textsuperscript{b} Course in Chemistry, Sciences Center of Natural, Federal University of Piauí, Teresina, PI 64049-550, Brazil
\textsuperscript{c} Course of Materials Engineering, Technology Center, Federal University of Piauí, Teresina, PI 64049-550, Brazil
\textsuperscript{d} Federal University of Campina Grande – Center Science and Technology – Graduate Program in Materials Science and Engineering, UAEMa, Campina Grande, PB, Brazil

\textbf{A B S T R A C T}

The aim of this study was to manufacture and characterize bionanocomposites based on a poly(hydroxybutyrate)/polyethylene glycol blend (PHB/PEG) filled with an organobentonite (CLT1 and CLT3) or an organovermiculite (VMT1 and VMT3) in concentrations of 1 and 3 wt%. The systems were prepared by solution intercalation and further characterized by X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry. The use of these bionanocomposites aimed at improving the processing and compatibility of this blend in search of new properties and possible applications of these films in food disposable packaging. The thermal stability of the system varied according to the type of clay and, consequently, the chemical structure of the quaternary ammonium salt used. The VMT1, VMT3 and CLT3 systems showed increased degrees of crystallinity compared to neat PHB. Differences in bionanocomposites structure can be related to the type of clay used as two types of PHB/PEG blend.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. \textbf{Introduction}

Over the years, the consumption of plastic products has produced a large number of residues, which accumulates in landfills generating considerable environmental problems [1]. Non-biodegradable polymers greatly contribute to these problems due to their high degradation resistance, taking years to decompose. The awareness of proper disposal and appropriate destination are also fundamentally important. Recently the production and use of biopolymers and biodegradable polymers have emerged as an alternative with great potential for expansion due to their technical and economic viability [2]. Because they have similar properties to conventional polymers, biodegradable polymers can replace them in many applications such as packaging, medical devices, drugs capsules, personal hygiene products and agricultural applications, among others [1].

Poly(hydroxybutyrate) (PHB) and its copolymers are highlighted since they are naturally produced by renewable energy...
sources and are biodegradable over a wide range of bacteria and fungi. Among the various PHB characteristics, it can be emphasized: it has a glass transition temperature between 4 and −7 °C and melting temperature of approximately 175 °C, it presents biological compatibility, it is 100% biodegradable, it can be processed as conventonal thermoplastics, it is hydrophobic, and it has a high molar mass. In addition, it is highly crystalline (55–70%), has good chemical resistance, optical purity and good stability to ultraviolet radiation. Some barrier properties, however, limit its application [3].

The major drawback of PHB is its instability during processing as it starts to degrade near its melting temperature. A short exposure of PHB to temperatures near 180 °C could induce severe degradation accompanied by the production of olefinic and carboxylic acid compounds as products of its degradation. In fact, crotonic acid and various oligomers are generated during processing through the random chain scission reactions that involves a cis-elimination of β-CH and a six-member ring transition [4–6].

Another disadvantage of PHB is its brittleness, which is attributed to its high degree of crystallization and the post-crystallization experienced during storage that results in the formation of irregular pores on the surface and limits the flexibility of amorphous chains between the crystals. Molecular mechanics calculations also indicate that the secondary crystallization happening on storage can result in a narrow distribution of highly extended or overstressed chains, and subsequently lead to the brittleness of PHB samples [7]. Nonetheless, both shortcomings of PHB could be alleviated by various modification methods such as copolymerization with poly-(3-hydroxyvalerate) (HV) or poly-(3-hydroxyhexanoate) (HH); the use of polymeric additives such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN) and biocompatible polyvinylpyrrolidone (PVP); the use of compatibilizers and low molecular weight compounds to lower its processing temperature, etc. Among these methods, the easiest is the addition of compatible plasticizers into PHB.

Several materials can be used as plasticizers to improve the toughness of PHB. Many chemicals, e.g., citrate ester, low molecular mass polyethylene-glycol (PEG), glycerol, acetyl tributyl citrate, soybean oil, triethyl citrate, acetyl tributyl citrate, triacetine and fatty alcohols, with or without glycerol fatty esters, have been investigated as the plasticizers for PHB. Many of them proved to have the capability of decreasing the glass transition temperature and increasing the flexibility (or elongation) as well as the toughness of PHB [8–17]. Even though plasticizer addition to PHB lowers both its processing and degradation temperatures, the thermal stability of plasticized PHB during processing can be enhanced compared to neat PHB. Indeed, plasticizers can increase the flexibility of the polymeric chain and decrease its melt viscosity.

One way to improve the physicochemical properties of PHB is the incorporation of additives such as the polyethylene glycol (PEG). This additive weakens the intermolecular forces between adjacent polymer chains, which provides a better adhesion between phases of the system, thus increasing its flexibility and its free volume, allowing a better interaction. In consequence, the incorporation of PEG leads to an increased segmental mobility of the PHB matrix [18–20].

Bentonite and vermiculite clays are among the most used silicates in bionanocomposites manufacturing. Indeed, mineral clays can modify the polymer characteristics and improve their processability. These silicates are composed of tetrahedral layers (silicon, tetracoordinate) and octahedral layer (aluminum, hexacoordinate) with lamellar crystallinity structure that is formed by the unit cell of mineral clay 2:1 [21].

As clays are naturally hydrophilic, in order to make the hydrophilic silicates more compatible with polymers, the cations between the layers can be changed by cationic surfactants like the alkyl ammonium (that has a range of 10–18 carbons atoms in the main chain) or alkyl phosphonium salts [22]. The modified clay becomes organophilic and its surface energy decreases and the interbasal distance increases. When the hydrophilic clay is rendered hydrophobic, the interfacial adhesion among the polymer/clay nanocomposites phases is enhanced. Furthermore, it makes possible the polymer molecules intercalate inside clays galleries [21,22].

Preparation of bionanocomposites, using low percentages of inorganic fillers, is one of the routes to improve some of the properties of biodegradable polymers such as thermal, mechanical and oxidative barrier. Among the traditional composites, bentonite is one of the lamellar silicates most used as an inorganic filler. This is because it is environmentally friendly and available in large quantities at relatively low cost [23–26].

The manufacture of bionanocomposites provides a potentially simple method to change and control the properties of polymeric materials, preserving its biodegradable characteristics [27].

The aim of this study was to develop and characterize a PHB/PEG blend and bionanocomposites based on this blend reinforced with organobentonite (CLT) or organic vermiculite (VMT) in concentrations of 1 and 3 wt%. The systems were prepared by casting (solvent evaporation technique) and characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In future work, these materials will be characterized for possible applications in packaging and medical devices.

2. Experimental

2.1. Materials

The materials used in this research were: poly(hydroxybutyrate) (PHB) – FE147 (lot number) as polymer matrix, provided by PHB Industrial S/A – São Paulo; vermiculite clay in the expanded condition (VMT(un)) provided by Mineração Pedra Lavrada, Santa Luzia – PB-mesh sieve N° 200 (D = 0.074 mm) and the quaternary ammonium salt used to modify it was Praepagen WB® (estearil dimethyl ammonium chloride salt) provided by Clariant, Recife – PE. The bentonite organoclay used was Cloisite 20A supplied by Southern Clay Products; The solvent used was chloroform produced by Dinâmica Química Contemporânea Ltda; and the plasticizer was polyethylene glycol (PEG) supplied by Dinâmica Produtos Químicos Ltda, number average molar mass of 1350 and 1650 g mol⁻¹.
2.2. Organophilization of the vermiculite clay

Organophilization of the vermiculite clay consisted in the preparation of dispersions containing distilled water, clay and ammonium salt, as described by Valenzuela-Diaz [28], Barbosa et al. [29] and Mesquita et al. [30].

Initially, mechanically stirred dispersions containing 768 ml of distilled water and 32 g of clay were prepared. The clay was slowly added to the water and the agitation was maintained for 20 min before a solution of distilled water and the quaternary ammonium salt was added to the dispersion and stirring was continued for another 20 min. Stirring was ceased and the containers were sealed and kept at room temperature for 24 h. Then, the obtained material was vacuum filtered to remove the excess salt and the product washed with 2000 ml of distilled water. The organoclay agglomerates were dried in an oven at 60 ± 5 °C for 48 h before being ground with the aid of mortar and pestle and sieved through 200 mesh (D = 0.074 mm) and to be added to the polymer matrix. The organo-vermiculite clay will be called VMT here.

2.3. Preparation of PHB films

In order to obtain films, PHB was added to chloroform and the solution (ratio 1:10) was stirred for 3 h at room temperature (23 °C) before being allowed to rest under the same temperature for 24 h in order to facilitate swelling and partial dissolution of the PHB grains. The solution was then heated to 80 °C and kept under stirring for 3 h under reflux. After homogenization, the solution was poured onto a marble plate and films were formed by the evaporation of the solvent at room temperature (23 °C). The films formed had an average thickness of 42 μm.

2.4. Preparation of the PHB/PEG films

For the preparation of the blends, the same procedure described earlier was used up to the swelling step. Thereafter, 5% PEG was added to the solution and it was stirred and heated at 80 °C for 3 h. The solution was then filtered to remove impurities. The solution was then cast on marble slabs, kept in an exhaust gas hood at room temperature, for 30 min to evaporate the solvent. The PHB/PEG (95/5) films were then removed from the marble slabs and placed in a vacuum oven at 30 °C for 24 h and subsequently stored in desiccators.

2.5. Preparation of bionanocomposite films

The bionanocomposites were prepared with organophilized bentonite and vermiculite clay with the respective percentages of 1% (CLT1 and VMT1) and 3% (CLT3 and VMT3) in the same procedure described above up to the swelling step. After swelling, the clay was added to the PHB/PEG solution and heated to 80 °C, under stirring, for 3 h before being cast on marble slabs. All subsequent steps were the same procedures described for the preparation of the PHB/PEG films.

2.6. X-ray diffraction

The films were characterized by X-ray diffraction on a Shimadzu XRD 6000 apparatus, using copper Kα radiation, voltage 40 kV, 30 mA, 2θ scan from 1.5° to 30° at a scan rate of 2° min⁻¹.

2.7. Thermal characterization (thermogravimetric analysis and differential scanning calorimetry)

TGA and DSC thermal analysis were performed under nitrogen atmosphere with a flow rate of 100 ml min⁻¹, heating rate of 10°C min⁻¹ and a temperature range of 32–600 °C in SDT Q600V 20.9 Build 20 equipment. Sample masses of about 10 mg were kept in alumina crucibles. Three scans were performed for each material.

DSC degree of crystallinity (%Xc) was calculated according to Eq. (1):

\[
%Xc = \left( \frac{\Delta Hf \times W_{PHB}}{\Delta Hf^0} \right) \times 100
\]

where \(\Delta Hf\) is the enthalpy of melting of the sample, \(\Delta Hf^0\) is the melting enthalpy of neat PHB and \(W_{PHB}\) is the weight fraction of PHB in the blend. The \(\Delta Hf^0\) value for neat PHB used was 146 J g⁻¹ [19,31,32].

3. Results and discussion

3.1. X-ray diffraction

The properties of the blends depend on the miscibility of its components, its morphology and crystalline structure of the polymer. PHB is a semicrystalline polymer of organized structure, in which the crystals are present in an orthorhombic structure with network parameters of the unit cell a = 0.56 nm, b = 1.32 nm and c = 0.59 nm [33].

Fig. 1 illustrates the XRD patterns of PHB films, of the PHB/PEG blend, the unmodified vermiculite clay (VMT_un), the modified vermiculite clay (VMT) and bionanocomposites with vermiculite clay (VMT1 and VMT3).

For the unmodified vermiculite clay three characteristic peaks in 2θ equal to 3.96, 6.28 and 7.18° were observed with basal distances of 23.92; 14.04 and 12.30 Å respectively. This result corroborated the one found in the diffractograms of natural vermiculite conducted by Reis et al. [34] when studying the same type of clay. Similar results were reported by Turianicová et al. [35], Udoudo et al. [36] that stated that peaks at 6.22° (14.21 Å) and 7.19° (12.29 Å) are associated to the different water layer hydration states and the presence of interstratified phases. The literature indicates that the characteristic peak of this type of magnesium mineral clay occurs in 2θ = 6.28° (14.06 Å) Grim [37], Moore and Reynolds [38] and Muiaamo et al. [39]. The broad reflection at 2θ = 3.96° (23.92 Å) is indicative of the presence of interstratified phases [39].

The XRD pattern of the organophilic clay (VMT) displays four different peaks at 2θ = 1.94, 2.34, 4.74 and 7.06°, which correspond to basal spacings of 45.48, 37.71, 18.62 and 12.51 Å.
respecively. These distances are larger for the modified vermiculite than the natural clay. The increase in basal spacing suggests that the alkyl ammonium cations were well intercalated between layers of silicate, and agree with the results reported by Fernández and Aranburu [33] and Gomes et al. [40].

The diffraction profiles of PHB films and of the PHB/PEG blend show the following values of 2θ: 13.00° (0 2 0 reflection), 17.00° (1 1 0 reflection), 20.05° (0 2 1 reflection), 22.00 (1 0 1 reflection) and 27.00 (0 7 0 reflection) were observed. The same diffraction planes and angles were observed by Blazek [41]. Although the addition of PEG caused minimum shift in 2θ, differences could be noted in the relative intensity of the diffraction peaks. This result was also observed by Zhijiang et al. [42] on films obtained by intercalation solution of PHB/PEG at concentrations of 85 and 80% PHB. Roa et al. [43] reported that plasticizers in polymeric matrices act as good compatibilizers, reducing the interfacial tension and thereby promoting improvements in mechanical and morphological properties.

In order to observe possible changes that occurred in PHB with the insertion of the clay, X-ray diffraction analyses were also performed on the bionanocomposites. In general, the crystallization behavior of the nanocomposites is greatly influenced by the degree of dispersion of the clay nanolayers in the polymer matrix [44].

The reflection peaks of the clay for 2θ greater than 26° are related to the mineralogical phases of vermiculite and they disappear in the bionanocomposites [45]. This behavior can also be associated with the dissolution of the salt ions in the structure or exfoliation of the lamellar clay mineral during solution intercalation, which induces changes in the crystal structure of aluminosilicate minerals [46]. As for the VMT1 and VMT3 bionanocomposites, the PHB molecules were effectively inserted between the clay lamellae, suggesting that an exfoliated/intercalated system was obtained, as it can be verified by the disappearance or displacement of the peak of the d_{001} plane of the clay to 2θ angles in the range of 2°–5°, as shown in Fig. 1. According to Araújo et al. [46], a contraction of the basal reflection to a constant value will occur up to a certain number of carbon atoms present in the quaternary ammonium salt, which would probably be the C16 carbon present in the composition of the ammonium salt, and from a value greater than the number of carbons, the basal reflection increases to a constant value, possibly related to the C18 carbon. Therefore, the chemical composition and the size of the chain determine the basal interplanar distance of the organoclay and control a wide range of properties, especially the colloidal and adsorptive ones [27].

Fig. 2 shows the diffractograms of the PHB films, the PHB/PEG blends, the unmodified bentonite clay (CL T_m), the modified bentonite clay (CL T) and the bionanocomposites with its clay (CL T1 and CL T3).

Results indicate that, in the modified clay, the peak is displaced to smaller angles. In other words, the basal distance, d_{001} increased, which shows the effective intercalation of the quaternary ammonium cations in the interlayers of clay.

For the CL T3 bionanocomposite, a high intensity peak was observed around 2θ near 4.76°; and for CL T1 a peak of lower intensity was also observed in the same region, indicating the presence of intercalated structures. The explanation for this behavior is associated with replacement of the Na⁺ cations present in the clay for the quaternary ammonium salt (NH₄⁺) cations increasing the basal interplanar distance.

XRD results indicate that there are differences in the formation of the structure of bionanocomposites [47], and transmission electron microscopy (TEM) is needed for the type of structure to be determined. Even though, the differences in structure can be associated with the type of clay since two types, vermiculite and bentonite, were used in the formation of the bionanocomposites. Although these clays possess crystal- line structures and identical geometries (2:1), they can differ with respect to their surface charge, miscibility, polarity and the type of interaction or intermolecular forces. These differences, added to the kind of surfactant used in the organic modification of each clay, suggest different interlayer structures for the he bionanocomposites.

3.2. Thermogravimetric analysis (TGA and DTG)

Fig. 3a and b, respectively, illustrates the TGA and DTG of neat PHB films, of the PHB/PEG blend, the organo vermiculite clay (VMT) and of vermiculite clay bionanocomposites (VMT1 and VMT3).
corresponding to PEG degradation. Rodrigues et al. [48] prepared, by casting, a PHB/PEG blend with similar composition and observed that its degradation started around 256 and 257°C.

The same behavior observed for the PHB and for PHB/PEG blend was displayed by the bionanocomposites. The VMT1 composition had an initial degradation temperature at 230°C and its final one was at 301°C, while the VMT3 composition had its initial degradation temperature around 200°C ending at 295°C. TGA results indicate that the thermal stability of the PHB/PEG blend decreases with increasing clay content, which is taken as an indication that the clay can catalyze the degradation of the polymer. As for the VMT1 system, there was an improvement in bionanocomposite barrier properties compared to the neat polymer, which was attributed to the increased path tortuosity imposed by the clay on gas diffusion [49].

Table 1 shows the temperatures \( T_1 \) – initial temperature and \( T_2 \) – end temperature of the event with greater weight loss) and the peak temperature \( (T_p) \) obtained by TGA measurements.

![Fig. 2 – Diffractograms of the (a) PHB films, the PHB/PEG blends, the unmodified the bentonite clay (CLT_un), the modified bentonite clay (CLT) and of the bionanocomposites (CLT1 and CLT3).](image)

The data indicate that PHB has a single degradation stage starting at 215°C and ending at 283°C [41].

The PHB/PEG blend shows an increase in the initial degradation temperature; it was displaced from 231 to 294°C. It could be observed by TGA, and confirmed by DTG, as shown in Table 1.

![Table 1 – Mass versus loss temperatures for PHB, PHB/PEG, VMT1 and VMT3.](image)

![Fig. 3 – Curves (a) TGA and (b) DTG for PHB, PHB/PEG, (VMT), VMT1 and VMT3.](image)
compared to the PHB, which can be explained by the degradation behavior of clay that may have occurred in several stages by slowing or speeding the degradation process [50]. There were events between 300 and 400 °C that pointed out to the existence of two polymer fractions with different crystalline structures competing between the lamellae of clays and presenting different behaviors in the second degradation event. Also, some interference possibly happened in the components used in the modification of clays [27].

The bionanocomposites degradation can correspond to surfactant degradation inside nanoclays [27], as the results reveal that the two different ammonium salts were intercalated in the layers in the silicates of vermiculite and bentonite clay. For vermiculite, the modifier was diestheryl dimethyl ammonium chloride salt (Praepagen), which has two methyl groups and two alkyl chains 18C long attached to a nitrogen atom in its structure while the organic modifier of the bentonite clay has two methyl groups and two saturated alkyl chains composed of a mixture of 65% C18, 35% C16 and 5% C chains bonded to a nitrogen atom. The vermiculite (VMT) modified bionanocomposites have a better thermal stability when compared with that of CLT bionanocomposites. Araújo et al. [46] reported an improvement in the thermal stability of bentonite nanocomposites, using the organic modifier Praepagen. It is believed that the Praepagen salt used to modify the vermiculite clay has a higher thermal stability than the dimethyl tallow salt used to modify the bentonite clay and this would be the reason for the higher thermal stability of the VMT bionanocomposites.

Table 2 presents temperatures $T_1$ and $T_2$ ($T_1$ – initial temperature and $T_2$ – temperature end of the event with greater weight loss) and the peak temperature ($T_p$).

Table 2 – Mass versus temperature for PHB, PHB/PEG, CLT1 and CLT3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_1 \rightarrow T_2 / ^\circ C$</th>
<th>$T_p / ^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>215–283</td>
<td>276</td>
</tr>
<tr>
<td>PHB/PEG</td>
<td>231–294369–414</td>
<td>280399</td>
</tr>
<tr>
<td>CLT1</td>
<td>199–284358–408</td>
<td>270393</td>
</tr>
<tr>
<td>CLT3</td>
<td>221–293330–370</td>
<td>276358</td>
</tr>
</tbody>
</table>

The data indicate that, for the bionanocomposites produced with 1% of organophilized vermiculite clay, an increase of almost 7% in the initial degradation temperature, with respect to the neat PHB was obtained. Whereas for the bionanocomposite with 3% of VMT there was a decrease of almost 7% of the initial degradation temperature, relative to the pure PHB. This behavior probably occurs because the clay acts as accelerator of degradation with the increase of content of clay. It is believed that the alkylammonium cations of the modified organoclays are thermodemically decomposed, following Hofmann elimination. It should be noted that the reaction products, as well the clay itself, can catalyze the degradation of the polymer. As pointed out by Ray et al. and Zhao et al. [51,52], it is hence very important to analyze the thermal stability of the bionanocomposites.

On the other hand the bionanocomposites produced with 1% bentonite clay showed a 7.4% decrease in the initial degradation temperature, compared to neat PHB, while bionanocomposites produced with 3% bentonite clay showed a slight increased (2.8%) in initial mass loss. It is possible that the organoclay thermal degradation occurs in several stages and that it affects the thermal behavior the bionanocomposites.

3.3. Differential scanning calorimetry (DSC)

Fig. 5 and Table 3 show the curves and parameters obtained by DSC of neat PHB, PHB/PEG blend and vermiculite clay (VMT1 and VMT3) bionanocomposite films.

Results indicate that there was no variation in melting temperature ($T_m$) of the systems with both PEG or VMT
addition. However, variations were observed corresponding to the degree of crystallinity of the systems, as the degree of crystallinity of the blend (PHB/PEG) increased by 3.83% compared to the pure PHB. This increase is related to the fact that PEG does not act on the PHB matrix as a plasticizer, interfering with intermolecular interactions of the PHB. These results were also observed by Parra et al. [53].

Blazek [41] obtained similar results, showing that the degree of crystallinity of PHB/PEG blends varied with PEG content. Blazek produced 70/30, 80/20, 90/10 and 95/5 PHB/PEG blends and their respective degrees of crystallinity were 55.4%, 47.2%, 48.6% and 50.1%, while that of neat PHB was 54.7%.

Our data indicate that VMT clay addition to the 95/5 PHB/PEG blend studied here, led to increases in the system’s degree of crystallinity of about 1.17% for VMT1 and of 3.19% for VMT3 compared to neat PHB. The addition of VMT clay and its interaction with the PEG provided an increase in the number of crystals, which can be related to the ability of both to act as reinforcement in a polymer matrix, increasing the packing of the polymer segments, and thereby the crystallinity of the bionanocomposite. In studies by D’Amico et al. [44] about PHB nanocomposites containing 4% of sodium bentonite clay (CNa+) as well as organobentonite clays C15A and C93A, an increase in the degree of crystallinity of 40, 60 and 80% with the clays present in the nanocomposite was observed. Silva et al. [45], on studies of PHB nanocomposites containing 1–10% of Viscogel B8 and Viscogel S7 clays, observed a reduction in the degree of crystallinity of PHB with the addition of both clays, which was attributed to the type of organic modifier used in their organophilization.

Fig. 6 and Table 4 show, respectively, the curves and parameters obtained by DSC for neat PHB, PHB/PEG blend and for the bentonite clay bionanocomposites (CLT1 and CLT3) films.

The data indicate that the degree of crystallinity of CLT1 bionanocomposites decreased approximately 5.87% compared to that of neat PHB. As for the CLT3 composition, there was a slight increase of 0.61% in the degree of crystallinity. It is believed that for the CLT1 system, the polymer chains have a lower mobility, resulting in a decrease of the crystallinity.

It should be taken into account that the analysis was performed in a single thermal cycle, where the samples were heated to temperatures above their melting temperature. However, the results obtained in the systems with bentonite clay refer to a probable secondary crystallization event. This behavior is usually observed in semi-crystalline polymers through DSC, and it was also observed in PHB by Pearce and Marchessault [54]. The values found can be explained by the presence of more than one group of crystals with different network parameters or crystallites with varied lamellar thickness, or even by a recrystallization process that occurred during the DSC test, in which a thinner lamellar crystallite is melted at a lower temperature, recrystallized in a thicker lamella and is remelted for a second time. The same researchers also noted that this recrystallization process is common when the samples are prepared by dissolving in chloroform, probably by the ion present in the halogenated compound.

According to the results of the VMT1, VMT3 and CLT3 systems, in which there was an increase of crystallinity, these values can be related to the presence and reinforcement affinity of the polymeric matrix. During the preparation of bionanocomposites, as in the case of loading materials, these have the ability to act as nucleating agent facilitating the crystallization process [55]. In the case of the CLT1 composition, this behavior can be associated with a better homogenization, influencing the effect of the plasticizer of the (PEG) clay.
4. Summary and conclusions

This study evaluated the thermal behavior of poly(hydroxybutyrate)/polyethylene glycol (PHB/PEG) blend and PHB/PEG/clay bionanocomposites. For the PHB/PEG blend, it was observed an increase in the initial decomposition temperature compared to neat PHB, corresponding to a greater thermal stability. Besides that, it was observed that the initial temperature of degradation of bionanocomposites showed different behavior for the two types of organobentonite (CLT) and organovermiculite (VMT) clays. Increasing VMT clay content led to lower thermal stability of the blend while the thermal stability of CLT bionanocomposites increased with organobentonite content. Best overall thermal stabilities were obtained with VMT1 and CLT3 bionanocomposites. The degree of crystallinity of the blend (PHB/PEG) was higher than of neat PHB. This increase probably occurred because the PEG did not act on the PHB matrix as a plasticizer, interfering with intermolecular interactions PHB. It was also verified that clay addition to most of the systems led to an increase of crystallinity compared to the PHB matrix which was attributed to clay nucleating effect. Differences in bionanocomposite structure can be associated with the type of clay and organic modifier used. Indeed, the two types of clays were organophilized with different salts (diesthearil dimethyl ammonium chloride salt for the vermiculite clay and dimethyl dihydrogenated tallow for bentonite) in manufacturing the bionanocomposites. These differences, added to the type of surfactant used in the organic modification of each clay, suggest different interlayer structures for the bionanocomposites.

Conflicts of interest

The authors declare no conflicts of interest..

Acknowledgments

The authors thank the Graduate Program in Materials Science (UFPI) by the physical structure, by the partnership Federal University of Campina Grande (UFCG), PHB Industrial for donating the resin and CNPq for financial support (Process: 306501/2012-0, 446530/2014-0 and 446655/2014-7).

References


