Original Article

Preparation and characterization of poly(hydroxybutyrate) and hollow glass microspheres composite films: morphological, thermal, and mechanical properties

Luis Miguel Araque\textsuperscript{a}, Ana Carolina Lemos de Morais\textsuperscript{b}, Tatianny Soares Alves\textsuperscript{a,b}, Joyce Batista Azevedo\textsuperscript{c}, Laura Hecker Carvalho\textsuperscript{d}, Renata Barbosa\textsuperscript{a,b,\textsuperscript{*}}

\textsuperscript{a} Graduate Program in Materials Science, Technology Center, Federal University of Piauí, Teresina, PI 64049-550, Brazil
\textsuperscript{b} Course of Materials Engineering, Technology Center, Federal University of Piauí, Teresina, PI 64049-550, Brazil
\textsuperscript{c} School of Technology SENAI CIMATEC, Salvador, BA 41650-010, Brazil
\textsuperscript{d} Graduate Program in Materials Science and Engineering, Science and Technology Center, Federal University of Campina Grande, Campina Grande, PB 58429-140, Brazil

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ABSTRACT

In this work, of poly(hydroxybutyrate) (PHB) and glass microspheres (HGM) in different compositions with polypropylene-grafted-maleic anhydride (PP-g-MA) composites were developed by melt intercalation, and then, films from the composites and the polymer matrix were obtained. Subsequently, the morphological, thermal, and mechanical properties were evaluated. A good distribution and intermediate dispersion of the filler throughout the matrix with the formation of some agglomerates was observed, while adhesion between the components was not achieved. The HGM did not affect significantly the thermal properties of the systems; there were discrete variations in the initial degradation temperature ($T_{\text{D}}$), peak temperature ($T_{\text{p}}$), and melting temperature ($T_{\text{m}}$). However, the degree of crystallinity decreased with the addition of the HGM, and the film with 3% HGM had a variation above 11%. Additionally, it was noticed that the composites (regardless of the presence of PP-g-MA) presented small values of elongation and ultimate stress compared with those of pure PHB.

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1. Introduction

Conventional polymers are one of the most used materials and their use has been growing over the years producing a vast volume of residues. The management of those residues is creating an environmental crisis since they present a high
resistance to degradation that increases the time to decompose them. Among the possible solutions to that problem are: to reuse, to recycle, and to create awareness on the discard and destination of those residues, but this demands time, human capital, and investment. However, biodegradable polymers offer an alternative which due to its economic and technical feasibility has a great expansion potential [1].

Biodegradable polymers are those polymers which undergo chains breakage by microorganism resulting in a decomposition of the material. There are necessary specific conditions of pH, moisture, oxygenation, and sometimes metals as a catalyst to assure their degradation. These polymers can be obtained from renewable sources such as starch and cellulose; they can be synthesized by bacteria from small molecules, i.e. butyric or valeric acid to obtain poly(hydroxybutyrate) (PHB) or poly(hydroxyvalerate) (PHV), and finally, they can be produced from fossil sources, such as poly(lactic acid) (PLA) or poly(butylene adipate-co-terephthalate) (PBAT). For being eco-friendly and having a positive CO₂ balance, biodegradable polymers from renewable sources have caught the attention of industry and scientists [2,3].

Among the biodegradable polymers, poly(hydroxybutyrate) (PHB) has been explored over the years because of its relevant thermal and mechanical properties; furthermore, it can be obtained from renewable resources, degrading enzymatically in different ecosystems (such as water, soil, and sludge, among others). PHB is part of the poly(hydroxyalkanoate) family, is an isotactic semicrystalline polyester, and has mechanical properties similar to those of the poly(lactic acid) (PLA), but with a narrow processing window, making it sensitive to thermal degradation [1].

According to Chen et al. [4] and Jing and Qiu [5] with the formation of blends or polymeric composites, improvements are obtained in the thermal stability of PHB. PHB composites employing a wide range of fillers, such as cellulose nanocrystals [4], agave fiber [6], chitosan and catechin [7], graphene [5], eggshell of the American Rhea [8] and vermiculite clay [9] have been developed over the last few years. However, in the literature there are no studies with PHB polymer composites as the matrix and glass microspheres (HGM) as the filler, making this research novel.

The HGM is an inorganic filler that consists of an external rigid shell filled with an inert gas, which have diameters in the range of 10–100 μm. HGM have received great attention due to their properties such as well-defined morphology, uniform size, low density, high surface area and high resistance to fracture [10].

In the literature, a low compatibility between the HGM and different polymer matrices has been reported. However, the use of compatibilizing agents such as poly(propylene-grafted-maleic anhydride) (PP-g-MA), poly(ethylene-grafted-maleic anhydride) (PE-g-MA) [11] and coupling agents such as Markoni® Silane HK-560 based on 3-glycidoxypropyltrimethoxysilane [12], as well as the surface modification of HGM with silver particles [13] and carbon nanofibers [14], offer alternatives to increase the compatibility between polymer matrices and HGM.

Radio frequency identification (RFID) technology consists in a reader which capture information stored in a tag. To overcome the limitations of RFID in terms of cost, chipless RFID tags have been introduced as a low cost and reliable solution. In fact, the chip removal has enable the diffusion of new circuit fabrication techniques, which have paved the fabrication of circuit on unconventional substrates, such as polymers, textiles, and plenty of materials never adopted for electronics before. The signal-conveying efficiency is an important parameter when proposing a material as a RFID tag substrate. Materials with low dielectric constant and dielectric loss are required to increase the velocity of signal propagation and decrease the loss of signal intensity. Both materials, PHB and HGM, have low dielectric constant and dielectric loss [15,16].

In this work, PHB and HGM composite films were developed by melt intercalation with different percentages of inorganic filler. Subsequently, the morphological, thermal, and mechanical properties were evaluated. The mechanical and morphological properties of the PHB/PP-g-MA/HGM composites were also evaluated to verify the influence of a polar compatibilizer. In further work, the dielectric properties of the developed materials will be evaluated as well as its applicability as substrate for RFID tags.

2. Materials and methods

2.1. Materials

PHB was used as the polymer matrix in powder form, supplied by PHB industrial S/A (Serrana, SP), molecular weight (600,000 g mol⁻¹) having been synthesized by aerobic fermentation and previously sifted with a kitchen sieve to remove any impurities. Glass Bubbles IM16k manufactured by 3M (Minnesota, USA) and donated by SENAI-CIMATEC, BA, were used as the filler (HGM). According to the manufacturer’s data sheet, the mean diameter of the HGM was 20 μm, and they were composed of common glass and borosilicate glass. The polar compatibilizing agent, poly(propylene-grafted-maleic anhydride) (PP-g-MA; Polybond 3200), was supplied by Cromton-Additives Olefin and Styrenics (Sao Paulo, SP) with a flow index of 115 g 10 min⁻¹ at 230 °C/2.16 kg.

2.2. Methods

2.2.1. Melt-compounding process

The polymer matrix of PHB and HGM were oven dried at 60 °C for 12 h. The compositions containing 1% and 3% HGM by weight were mixed by manual barrel finishing and then processed in an AX Plastic brand model Lab16 mono-screw extruder at a screw speed of 50 RPM with a temperature profile of 160, 165 and 175 °C (for the 1st, 2nd, and 3rd zones, respectively). The systems were continuously extruded, cooled and granulated. For comparison purposes, pure PHB was prepared under the same conditions. In addition, composites with 1% or 3% HGM and 5% PP-g-MA were prepared under the same conditions. The percentages of the filler were defined according to Silva Junior et al. [17].

2.2.2. Compressing molding

The granulated systems of both the pure PHB polymer matrix and the PHB/HGM composites with 1% or 3% filler (with and without the compatibilizer PP-g-MA) were oven dried at
60 °C for 12 h and then formed into films with the aid of a SOLAB brand hydraulic press, model SL-11. The conditions used in the preparation of the films were a pre-pressing of 1 t for 60 s at 180 °C; a pressing of 6 t for 90 s for pure PHB, 75 s for systems with 1% HGM (with and without compatibilizer) and 60 s for systems with 3% HGM (with and without compatibilizer) at the same temperature. The compressing molding times decreased with the increase of HGM content in order to maintain standardized thicknesses of the films. The films obtained were approximately of 0.150 mm in thickness.

2.3. Characterization

2.3.1. Morphology
The morphological evaluation of the surface of the films was performed by capturing images using an optical microscope (Leica Microsystems model MD500) operating in the transmission mode with an ICC 50E capture camera and a magnification of 40× (500 μm).

In addition, the morphology of the fracture surface of the films was evaluated, as the HGM are below the surface of the films, by means of scanning electron microscopy (FEI model Quanta FEG 250, with an acceleration voltage of 5 kV: Ametek HX-1001 (Apollo X silicon drift detector (SDD)). The samples were coated with Au in a Quorum Q150R model metallizer for 30 s, at 20 mA, and plasma generated in an argon atmosphere.

2.3.2. Thermal characterization
Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of the pure PHB and PHB/HGM composites. Also, the thermal behavior of the samples was studied via differential scanning calorimetry (DSC). Both tests were performed on a Q600SDT TA instrument. Each sample (5 mg) was heated at 10 °C/min from 20 °C to 600 °C, under argon atmosphere. The crystallinity (Xc) was determined from the DSC curves. These values were calculated according to Eq. (1):

\[ X_c = \frac{\Delta H_m}{\Delta H_{m}^0} \times 100 \tag{1} \]

where \( \Delta H_m \) is the experimental heat of fusion, \( \Delta H_{m}^0 \) is the theoretical heat of fusion of fully crystalline PHB (146 J g⁻¹) [18] and \( \phi \) is the weight fraction of the polymer matrix in the composites.

2.3.3. Mechanical characterization
Tensile strength tests of the pure PHB and PHB/HGM composites were performed using a DL 1000 tensile machine by EMIC, equipped with a 20 N local cell in accordance with ASTM D882-02 for polymeric films. Five specimens were used for each test with dimensions of 100 mm in length, 10 mm in width, and approximately 0.150 mm in thickness. Tests were conducted at room temperature, crosshead speed of 50 mm min⁻¹, and initial grip separation of 50 mm.

3. Results and discussion

3.1. Morphology
Optical micrographs and scanning electron micrographs of the pure PHB and PHB/HGM composites are shown in Fig. 1.

In the optical micrograph of the pure PHB film (Fig. 1A), the following was observed: denser points where the melting was probably not complete; black areas from the presence of impurities; and parallel lines and differences in relief due to the marks of the aluminum plates that were used in the compression process. In the images of the composite films (Fig. 1B and C), it was observed that even at low HGM content (1–3%), there was a uniform filler distribution along the PHB matrix with the formation of some agglomerates, and the composite with 3% HGM presented a larger amount of agglomerates. This result evidences adequate distribution and intermediate dispersion of HGM in the PHB matrix because of the use of a mono-screw extruder.

As expected, the scanning electron micrograph of the fracture surface of the pure PHB (Fig. 1D) shows only one phase. Flow patterns similar to wave fronts (white arrows) were observed, suggesting that the fracture was plastic. By means of the scanning electron micrographs of the fracture surface of composites with 1% and 3% HGM (Fig. 1E and F) it was observed that most of the HGM remained intact after the extrusion and fracture processes. It was also observed that the lack of flow indicated that the fracture mechanism was modified with the addition of HGM to a more brittle fracture. Finally, the HGM that were adhered to the fracture surface of the other fragment of the film generated circular cavities (white arrows), indicating a deficiency in the adhesion between the PHB and the HGM.

The interfacial adhesion of the polymer matrix to the filler was also studied via SEM of the fracture surface of the composites at a magnification of 20,000× (Fig. 1G and H). For both composites, matrix-filler interfacial adhesion was not achieved because spaces between the HGM and the matrix were observed, that is, there was no bond formation between the OH groups of the HGM borosilicate and the PHB groups. As a consequence, during the breaking process, the fracture propagated along the discontinuous interface of PHB–HGM. Fig. 11 shows a schematic of the discontinuous filler–matrix interface for spherical fillers when good adhesion was not achieved. Finally, further evidence of the low adhesion between the components of the system was the absence of matrix residues on the HGM surface, as was best observed in Fig. 1G and H.

Fig. 2 shows SEM images of the fracture surface of the composites in the presence of the compatibilizer.

In all micrographs, it was observed that PP-g-MA did not act as a compatibilizer between PHB and HGM because it formed a new phase in the form of small disks of irregular geometry (white arrows), indicating immiscibility with the PHB. A lack of flow was again noticed; therefore, the addition of the compatibilizer did not change the mechanism of the fracture of the composites, which continued to display brittle fractures.
In the micrographs with a magnification of 20,000× (Fig. 2B and D), it was observed that the composites showed the formation of a discontinuous PHB–GM interface, indicative of the lack of adhesion between the components.

Similar results were reported by Malinowski et al. [19] for PLA and HGM composites, Dombia et al. [20] for high impact polypropylene (HIPP) and HGM composites, Patankar and Krano [21] for high density poly(ethylene) (HDPE) and HGM, Herrera-Ramírez et al. [14] for polyurethane acrylic resin and HGM or HGM coated with carbon nanofibers.

### 3.2. Thermogravimetric analysis (TGA)

The effect of HGM on the thermal properties of the PHB films was investigated by thermogravimetric analysis. Fig. 3A and B display the TGA and DTGA curves respectively, and the main thermal parameters obtained from the curves are summarized in Table 1.

The thermal properties of the PHB did a significant change with the addition of HGM. The degradation process of the PHB film began at 266 °C, and for the composite films with 1 and 3 wt% the initial degradation temperature ($T_{\text{onset}}$) decreased by 0.38% and 1.13%, respectively. This behavior can be attributed to the thermal nature of the inert gas inside of HGM. In spite of the low thermal diffusivity of the glass, gases present higher values of diffusivity, hence, it can be assumed that the inner gas of HGM allowed a higher amount of energy flow through the thin film accelerating the degradation. Furthermore, the final decomposition temperature ($T_{\text{end}}$) for the three systems was the same at 282 °C, and the decomposition profile was not altered with the addition of HGM, it remained in just one stage.

Despite displaying lower values of $T_{\text{onset}}$, the composites presented a slight increase in the peak temperature ($T_p$), which increased by 0.63% and 1.04% for the composite films with 1 and 3 wt% of HGM respectively. The slight increase in the thermal stability can be ascribed to the barrier effect of HGM, which restricted the mobility of polymer chains, and prevented the liberation of decomposition products, thus the thermal decomposition of the systems was delayed.

Herrera-Ramírez et al. [14] reported similar results, the $T_{\text{onset}}$ of polyurethane acrylic resin was not affected by the addition of HGM and HGM coated with carbon nanofibers. On the other hand, Li et al. [22] studied the effect of HGM on the thermal properties of poly(butylene succinate) (PBS) and found that the $T_{\text{onset}}$ increased with the addition of the filler.
Furthermore, Liu et al. [23] developed ethylene-vinyl acetate, magnesium hydroxide, and HGM composites, and studied the synergetic effect of both fillers in the properties of the polymer. Besides, the two-stage decomposition profile of the polymer was modified, increasing the first one and decreasing the second one.

3.3. Differential scanning calorimetry (DSC)

The behavior of the melting temperature (\(T_m\)) and of the crystallinity (\(X_c\)) of the pure PHB and composites with HGM are displayed in Fig. 4a and b respectively, and parameters obtained are summarized in Table 2.

It was observed that the HGM did not have a significant effect on the melting temperature of the PHB film. For the pure PHB film, \(T_m\) was recorded at 155.16 °C; with the addition of 1% HGM, \(T_m\) decreased 1.44%; and with the addition of 3% HGM, \(T_m\) increased 0.48%. For the crystallinity values (\(X_c\)), decreases of 9.25% and 11.11% were observed for the films of composites with 1% and 3% HGM, respectively. This result could be attributed to the presence of the HGM, which, despite being a nucleating agent, restricted the mobility of the polymer chains and decelerated the crystallization because of the formation of agglomerates, as observed in the morphological analysis, negatively affecting the formation and growth processes of crystallites by decreasing the interface between the polymer chains and the HGM.

Similar results were reported by Malinowski et al. [19] for PLA and HGM composites, through DSC analysis it was observed that HGM had no effect in PLA melting temperature, behavior attributed to the slow nucleation, which formed few crystallites with large size. Likewise, Li et al. [22] observed that the \(T_m\) and crystallinity of PBS did not change with the addition of HGM. Authors attributed that result to agglomerates formation that decreases the nucleation agent effect of the filler, and to the barrier effect of HGM that restrict the mobility of polymeric chains impeding crystallites growth.

3.4. Tensile strength testing

The effect of the HGM and compatibilizer on the mechanical properties of PHB was investigated through the tensile strength test, and the main parameters obtained from the stress–strain graph are presented in Fig. 5: elongation (\(\varepsilon\)) (Fig. 5A) and ultimate strength (\(\sigma_m\)) (Fig. 5B). The results are summarized in Table 3.

It was observed that the addition of the HGM did not result in an increase in the mechanical properties of the pure PHB film. This behavior was expected, as PHB is brittle in nature, and the HGM is a rigid-type filler, which acts as a stress concentrator.

The elongation for the pure PHB film was 7.24 ± 0.81%, a value that was decreased by nearly an exponential drop with the addition of the HGM and compatibilizer. For the composites without the compatibilizer (PHB/HGM), it was observed that the elongation values decreased with increasing filler content, being 49% and 69% lower for the composites with 1%

| Table 1 – Thermal stability parameters for the pure PHB and PHB/HGM composites. |
|--------------------------------------|-----------------|-----------------|-----------------|
| Composite                            | \(T_{\text{onset}}\) (°C) | \(T_{\text{endset}}\) (°C) | \(T_p\) (°C)   |
| Pure PHB                             | 266             | 282             | 275.86         |
| PHB/HGM 1%                           | 265             | 282             | 277.60         |
| PHB/HGM 3%                           | 263             | 282             | 278.72         |

\(T_{\text{onset}}\) - initial degradation temperature; \(T_{\text{endset}}\) - final decomposition temperature; \(T_p\) - peak temperature.
Fig. 3 – (A) TGA and (B) DTGA curves of the pure PHB and PHB/HGM composites.

Fig. 4 – (a) DSC and (b) crystallinity of the pure PHB and PHB/HGM composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>T_m (°C)</th>
<th>X_c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PHB</td>
<td>155.16</td>
<td>31.55</td>
</tr>
<tr>
<td>PHB/HGM 1%</td>
<td>152.96</td>
<td>22.30</td>
</tr>
<tr>
<td>PHB/HGM 3%</td>
<td>156.43</td>
<td>20.44</td>
</tr>
</tbody>
</table>

and 3% HGM, respectively, than that for pure PHB. In addition, the elongation values or both composites with the compatibilizer (PHB/PP-g-MA/HGM) did not show significant differences between them.

These results were expected and attributed to the discontinuous matrix–filler interface presented by the composites (with and without the compatibilizer), as was observed in the morphological analysis, because of the ineffective adhesion between PHB and the HGM. As shown in Fig. 6A, the interface between the polymer matrix and spherical fillers was perpendicular to the direction of the tensile stress, so when the material was pulled, displacements were produced, and the HGM acted as a point of failure and not as a reinforcement. PHB is a material with a low elongation capacity, and when the HGM were added to the composites, the material became even more brittle.

The tensile strength for the pure PHB film was 32.31 ± 0.86 MPa, a value that decreased with the addition of the HGM and the compatibilizer. The values of the tensile strength of the composite films with 1% and 3% HGM presented a significant difference and were 41.19% and 22.22% smaller, respectively, than that of PHB. Additionally, the composites with PP-g-MA and 1% and 3% HGM presented reductions of 19.09% and 66.59%, respectively, compared with that of the PHB film.

This behavior could be attributed to several factors. (i) Because they concentrate stress when subjected to tensile
stress, the HGM restrict and decrease the mobility of the polymer chains producing a more brittle material than that of the pure polymer. (ii) As determined by the DSC analysis, the PHB crystallinity was reduced with the addition of the HGM, resulting in a decrease in the tensile strength of the films of the composites compared with that of the pure PHB film; the ineffective interfacial adhesion between the HGM and PHB and the formation of filler agglomerates, as observed in the morphological analysis, also reduced the tensile strength of the composites. (iii) Through the morphological analysis, the formation of some clusters was observed, and adhesion between the matrix and the filler was not achieved, compromising the mechanical properties of the films because tension was not transferred and propagated by the filler but by the discontinuous PHB–HGM interface.

The compatibility between components has great influence on the mechanical properties of polymer composites, and in the case of spherical loads, the interface filler–matrix is perpendicular to the direction of the stress, as shown in Fig. 6A. Therefore, when adhesion cannot be achieved, the stress is transferred through the discontinuous matrix–filler interface, promoting displacements and deforming the matrix without affecting the filler (Fig. 6B.2), thus compromising the mechanical performance of the material. However, when the material is pulled and proper interfacial adhesion is achieved, the stress is transferred between the matrix and the filler, and a fracture is produced and propagated in the two phases, as shown in Fig. 6B.1, increasing the strength and improving the mechanical performance of the material [24–26].

Similar results were reported for polymeric composites with HGM as the filler, Doumbia et al. [20] developed HIPP and HGM composites and observed that the tensile strength, elongation, and other mechanical properties decreased with the content increase of the filler. Besides, Li et al. [22] found that the tensile strength of PBS and HGM composites decreased with the increase of HGM content, because of the low affinity between components that formed weak bonds, which are not appropriate for the stress transfer.

4. Conclusion

In this study, composite films of PHB, HGM and PP-g-MA were developed through the melt intercalation technique to evaluate the properties of the materials by means of morphological, thermal, and mechanical properties. The melt intercalation technique has the advantage of causing little impact to the environment because it does not require solvents. The morphology of the systems was evaluated by OM and SEM, and in the composites, it was observed that the dispersed phase showed good distribution within the polymer matrix and intermediate dispersion with the formation of some agglomerates. It was also observed that PHB and PP-g-MA were not miscible, and interfacial matrix–filler adhesion was not achieved. The HGM did not significantly affect the $T_m$, $T_p$ and $T_{endset}$ of the PHB. Additionally, it was observed that the degradation profile was not modified with the addition of the HGM. The HGM did not significantly affect the PHB melting temperature; however, they decreased the crystallinity of the polymer film. The addition of the HGM and PP-g-MA negatively affected the mechanical properties of the PHB film; the values of the ultimate stress and the elongation of the composite HGM films, with or without PP-g-MA, were lower than those for the pure PHB.

Conflicts of interest

The authors declare no conflicts of interest.

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Fig. 6 – Schematic of stress transfer in composites with spherical fillers with low adhesion (A). Mechanisms of fracture of composites with spherical fillers depending on the adhesion state (B). Image adapted from [24–26].
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