Polyhydroxyalkanoates-based cast film as marine biodegradable packaging for fresh fruit and vegetables: manufacturing and characterization

Annalisa Genovesi (✉ annalisa.genovesi@uniroma3.it)
Università degli Studi Roma Tre

Clizia Aversa
Università degli Studi Roma Tre

Massimiliano Barletta
Università degli Studi Roma Tre

Research Article

Keywords: biopolymers, packaging, cast extrusion, Polyhydroxyalkanoates

Posted Date: February 7th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2542224/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

The packaging sector is one of the main responsible of post-consumer plastic waste in the European Union. The increasing consumer pressure and the banning or limitation of some materials are pushing producers towards new solutions. Polyhydroxyalkanoates (PHA) are a class of compostable bioplastics, easily degraded in composting facilities as well as on soil and aquatic environment. Three different blends of P(3HB)(3HH), poly-3-hydroxybutyrate-co-3-hydroxyhexanoate, and of P(3HB)(4HB), poly-3-hydroxybutyrate-co-4-hydroxybutyrate are studied to achieve a thin film suitable for the manufacturing of films for food packaging. The compounds were produced by twin-screw extrusion and then processed by cast film extrusion. The properties of the films depend on the percentage of P(3HB)(4HB) of the blend, and confirmed the possibility of employing PHA-based films as packaging with low environmental footprint.

Introduction

The packaging sector uses about 40% of the produced plastics and it is responsible for around 60% of post-consumer plastic waste in the European Union. Most of it is only used once and then discarded. Many producers are moving away from traditional plastic packaging and are switching to other materials, due to the increasing consumer pressure and to the adoption of policy measures addressing plastic pollution, banning or limiting the use of certain plastic products. Among the alternative materials, bioplastics are gaining a lot of attention as substitutes of conventional fossil fuel-based plastics [1].

New market opportunities are appearing in the sector of fresh fruit and vegetables, as their demand is increasing. Prolonging the shelf-life of these products is fundamental to reach new customers and to reduce food waste. This can be achieved by combining various technologies, like refrigerating the products or using a controlled atmosphere inside the packaging [2]. The preservation of fresh fruit and vegetables is challenging, since they possess the ability to respire [3]. The process of degradation of food depends on the surrounding environment, thus packaging plays a fundamental role by controlling the mass transfer. Moisture barrier is essential in order to preserve texture and to control the development of aerobic spoilage and pathogen micro-organism. Bioplastic film present a higher gas transfer rate than most commercial plastic film, allowing the respiration of fresh products. In fact, most fossil-based films lead to a sharp drop in oxygen concentration after the sealing of the packaging, creating damaging anaerobic conditions. Some films are perforated in order to avoid this phenomenon, but this strategy does not allow to create a modified atmosphere inside the packaging. The perforations lead to a similar diffusion rate for Oxygen and Carbon Dioxide, creating non-desirable conditions for $\text{CO}_2$ – sensitive products, such as mushrooms and asparagus. This problem may be overcome by using biopolymer-based plastics [4]. In particular, blends of Polyhydroxyalkanoates (PHAs) are studied.

PHAs are one of the largest families of thermoplastics, presenting over 125 polymers and 150 monomers variations. The range of achievable properties is extremely wide but only a few of these PHAs were produced in sufficient amounts to be characterized and to be effectively applied. [5]–[7] These polymers...
are often proposed to replace non-biodegradable plastic, like polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET), for both their flexible properties and for their relatively sustainable production process compared to synthetic plastics [8]–[10]. These polymers are produced by at least 75 different types of bacteria under condition of nutrient stress and act as a carbon and energy reserve. [11] One of the most remarkable properties of these materials is that they are at the same time biodegradable with zero toxic waste, renewable and recyclable into organic waste [12], [13]. In nature, a vast range of microorganism is able to degrade PHAs and the degradation rate strongly depends on the conditions of the environment [14], be it soil, compost or marine sediment. In fact, micro-organism in soil, sea, lake water and sewage can completely degrade PHAs to water and carbon dioxide under aerobic conditions and to methane under anaerobic conditions. The dynamic of degradation for PHAs is caused by bacteria catalysed erosion from the surface to the interior, whereas other bioplastics undergo the process of hydrolytic degradation [15]. The biodegradation of PHAs proceeds fast if compared to other bioplastics, such as polyactic acid (PLA) [16]. Furthermore, PHAs are non-toxic and biocompatible. [11] Thanks to their properties and their numerous fields of application, these materials have been studied by engineers, polymer scientists and medical experts, becoming an example of multidisciplinary research [17]. The substitution of polyolefins, such as polypropylene, with PHAs, such as polyhydroxy-β-butyrate PHB, presents advantages from an environmental point of view, evaluated through Life Cycle Assessment (LCA) analysis [18]. Further great improvements in sustainability can be made by transferring all the laboratory developments in this field to industrial-scale production [19]. PHAs present appealing properties for their application in the packaging sector. Polyhydroxybutyrate (PHB) can be used as packaging material also in the food industry, as substitute of polypropylene for the storage of fat rich products, also in freezers and microwave ovens [20]. Furthermore, it presents a lower Oxygen Permeability compared to fossil-based plastics, slightly higher Water Vapour Permeability [21] and lower values of Carbon Dioxide ($CO_2$) permeability compared to non-polar polymers like LDPE or polyesters like PLA [22]. In this study, two different co-polymers of Polyhydroxybutyrate are used. The possibility of tailoring barrier and mechanical properties by changing the percentage of the two polymer phases is studied.

Poly(3−hydroxybutyrate−co−3−hydroxyhexanoate) PHBH is a promising polyhydroxyalkanoate, since it presents both flexibility and room temperature compostability [23]. It is a random copolymer, formed by medium-long chains of 3-HH units and short-chain 3-HB units, which guarantee some degree of hardness and toughness [24]. 3-HH units are highly crystalline whereas 3-HB units present an elastomeric behaviour [25], so the properties of this polymer can be tailored depending on the application. The presence of aleatory 3-HH chains broadens the fusion peak [26], increases the processing window of the material with minimized thermal degradation [25] and has an influence on the crystallinity and on the crystallization rate [27].

Poly(3-hydroxybutyrate-4-hydroxybutyrate) P(3HB)(4HB) is a copolymer consisting of 3-HB and 4-HB units. By changing the ratio of 3-HB and 4-HB, it is possible to adjust the properties of the material according to the required application. Consequently, the behaviour of this polymer can range from highly crystalline to elastomeric [28]–[30]. This polymer presents a degree of biodegradation even higher than PHB [31].
In literature, there are various examples of successfully extruded PHAs-based films. Blends of PHB/PHBV [32], [33], of starch/PHAs [34], PHBV/P(3HB)(4HB) and wood flour [35], PHBH/PHBV with wine lees wastes [36], PHBH/PBAT [37] were processed and evaluated. The appealing properties of blends of PHBH and P(3HB)(4HB) were evaluated by Luo, Wei, e Chen 2009 [28], who produced films by solution cast. This is therefore the context in which the present paper moves to investigate the processability and to evaluate the properties of PHA-based blends for their application as food packaging materials. In particular, different combinations of Poly(3−hydroxybutyrate−co−3−hydroxyhexanoate) PHBH and Poly(3-hydroxybutyrate-4-hydroxybutyrate) P(3HB)(4HB) are studied. Three different PHBH/P(3HB)(4HB) blends were manufactured by melt processing. First, the pellets of each blend were produced via reactive extrusion and cut using a strand pelletizer. The films were then produced by cast extrusion process and their mechanical and thermal properties were evaluated.

Materials And Methods

3.1 Materials

PHBH was purchased from Kaneka (Kaneka Belgium NV, Westerlo-Oevel, Belgium). Kaneka Biodegradable Polymer Green Planet X131N was the used grade. It presents an average molecular weight of 440.000 and contains 6 mol% of 3-HH monomers [39]. The P(3HB)(4HB) was purchased from CJ Cheiljedang (Seoul, South Korea) and presents a percentage of 4HB monomer superior to 30% [40]. The composition of each blend is reported in Table 1. EBS (ethylene-bis-stearamide) (Eviwax C140, Eigenmann & Veronelli, Italy) and silica (SiO₂) (Gasil 114, PQ Corporation, Malvern PA) were used as process aids.

<table>
<thead>
<tr>
<th></th>
<th>CH10</th>
<th>CH20</th>
<th>CH30</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHBH</td>
<td>89%</td>
<td>79%</td>
<td>69%</td>
</tr>
<tr>
<td>P(3HB)(4HB)</td>
<td>10%</td>
<td>20%</td>
<td>30%</td>
</tr>
<tr>
<td>EBS</td>
<td>0.8%</td>
<td>0.8%</td>
<td>0.8%</td>
</tr>
<tr>
<td>Silica</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

3.2 Production of the pellets

All the materials were premixed by hand and then fed into a Leistritz twin screw extruder (Leistritz ZSE MAXX 27 I (Nuremberg, Germany), screw diameter D = 27 mm and length L = 40D). The length of the extruder allows an effective compounding process. The extruder allows to control 10 temperature zones independently. The tenth zone corresponds to the extrusion die. In this case, a parabolic temperature profile was adopted. The maximum temperature was reached in zones 3 and 4. The temperature of the last zone was increased to avoid head-blocking phenomena. The screw speed was set at 180 rpm. The
pellets were produced by means of a strand pelletizer system. All the pellets were then dried at 25°C for 5 hours before further processing.

<table>
<thead>
<tr>
<th>Temperature profile adopted in reactive extrusion of pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
</tr>
<tr>
<td>Zone 2</td>
</tr>
<tr>
<td>Zone 3</td>
</tr>
<tr>
<td>Zone 4</td>
</tr>
<tr>
<td>Zone 5</td>
</tr>
<tr>
<td>Zone 6</td>
</tr>
<tr>
<td>Zone 7</td>
</tr>
<tr>
<td>Zone 8</td>
</tr>
<tr>
<td>Zone 9</td>
</tr>
<tr>
<td>Zone 10</td>
</tr>
</tbody>
</table>

3.3 Production of the films by cast extrusion

The films were cast extruded using an Eurexma MicroCast Extruder («Eurotech Extrusion Machinery - Eurexma», Tradate (VA), Italy). The system is equipped with a single screw (diameter D = 17.5 mm, ratio length to diameter L/D = 25). It is also equipped with a 120 mm wide die and one chilled roll. This extruder allows to control four temperature zones: the first two zones correspond to the cylinder, the third zone corresponds to the extrusion head, the fourth zone corresponds to the die lip. The materials tested boasted a good range of processability, and it was possible to produce a wide range of films with different thicknesses. Some preliminary adjustments on the temperature profile were required to avoid degradation. At first, the temperature profile adopted produced films which presented visible defects and a lack of clarity. By progressively reducing the temperature, the optimal conditions were achieved and the films presented a smooth surface. The final adopted temperature profiles are presented in Fig. 3.
Table 3

Temperature profiles adopted for cast extrusion of the three blends

<table>
<thead>
<tr>
<th>(°C)</th>
<th>CH10</th>
<th>CH20</th>
<th>CH30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>155</td>
<td>145</td>
<td>155</td>
</tr>
<tr>
<td>Zone 2</td>
<td>158</td>
<td>150</td>
<td>158</td>
</tr>
<tr>
<td>Zone 3</td>
<td>157</td>
<td>152</td>
<td>157</td>
</tr>
<tr>
<td>Zone 4</td>
<td>160</td>
<td>155</td>
<td>155</td>
</tr>
</tbody>
</table>

Characterization

4.1 Mechanical characterization

Mechanical properties were evaluated according to ISO 527-3 using a Shimadzu AGS-X tensile tester (Shimadzu Corporation, Kyoto, Japan). The tensile properties were tested both in machine direction (MD) and in transverse direction (TD). The tensile specimens in machine direction present a width of 20 mm, an average thickness of 60 µm and a gauge length of 60mm. The tensile specimens in transverse direction present a width of 20mm, an average thickness of 60 µm and a gauge length of 50mm. The tests were performed using a strain rate of 50mm/s and of 100 mm/s.

4.2 X-ray diffraction

X-ray diffraction was performed to evaluate the possible effects of the processing on the crystallinity of the various blends. The test was performed on 60 µm-thick cast films. The XRD was performed at different temperatures ranges, to assess the evolution and the stability of the crystalline phases. The measurements were carried out using a Rigaku Smartlab machine (Rigaku Corporation, Austin, TX).

4.3 Differential scanning calorimetry

A Differential Scanning Calorimetry (DSC) analysis was performed to assess the thermal properties of the pellets and the crystallinity derived from the production process of the pellets. A DSC3 (Mettler Toledo, Columbus, Ohio) was used to perform the measurement. Each sample was put into an aluminium crucible. Nitrogen with a flow rate of 50 ml/min is used as purge gas, according to ISO11357. Three thermic ramps were applied to the samples: a first heating ramp from −70°C to 190°C with a heating rate of 10°C/min, a cooling ramp from −190°C to -70°C with a cooling rate of -10°C/min and a second heating ramp from −70°C to 190°C with a heating rate of 10°C/min. The degree of crystallinity $X_c$ of PHBH was calculated using the following expression.

$$X_c (%) = \frac{\Delta H_m}{\Delta H_{0m} \cdot \Phi} \cdot 100\%$$
The melt enthalpy of each sample $\Delta H_m$ was obtained from the second heating curve. $\Delta H_{0m}$ is the enthalpy of 100% crystalline PHBH, which was assumed to be equal to 146 J/g [42]. $\Phi$ is the percentage of PHBH present in each blend.

### 4.4 Gas permeability

Oxygen Transmission Rate and Water Vapour Transmission Rate was evaluated using a MultiPerm Extrasolution Machine (Extrasolution made by PermTech, Pieve Fosciana (LU), Italy). An aluminium surface reducer purchased from Extrasolution was used to perform the measurement, since the produced film was not wide enough to cover the whole surface of the machine. Using the surface reducer, the surface of the tested film is 2.01 cm$^2$. The Oxygen Transmission Rate was measured at 23°C and 50% relative humidity (RH). The Water Vapour Transmission Rate was measured at 23°C and 85% RH.

### Results And Discussion

#### 5.1 Mechanical properties

The results of the mechanical characterization are summarized in Table 2. The Stress-Strain curves in machine direction are presented in Fig. 1. With increasing P(3HB)(4HB), the maximum stress and the Young’s Module are reduced whereas the maximum deformation increases. The tensile strength decreased from 27.5 MPa of CH10 to 13.5 MPa of CH30. The elongation at break in Machine Direction increased sensibly, from 10.5% of CH10 to 483% of CH30. In transverse direction, CH10 and CH20 broke with a deformation inferior to 10% while CH30 presented a deformation at break higher than 30%. Blends of PHBH and P(3HB)(4HB) present higher flexibility and elongation and break compared to PHBH even when films are produced by solution cast [28].

<table>
<thead>
<tr>
<th>Max Stress MD (MPa)</th>
<th>Max deformation MD (%)</th>
<th>Young's Module MD (MPa)</th>
<th>Max Stress TD (MPa)</th>
<th>Max deformation TD (%)</th>
<th>Young's Module TD (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>50 mm/min</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH10 27,5</td>
<td>10,5%</td>
<td>1237</td>
<td>15,6</td>
<td>5,3%</td>
<td>938</td>
</tr>
<tr>
<td>CH20 18,0</td>
<td>422%</td>
<td>685</td>
<td>8,7</td>
<td>9,3%</td>
<td>501</td>
</tr>
<tr>
<td>CH30 13,5</td>
<td>483%</td>
<td>529</td>
<td>8,4</td>
<td>59,2%</td>
<td>458</td>
</tr>
<tr>
<td><strong>100 mm/min</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH10 29,6</td>
<td>10,4%</td>
<td>1296</td>
<td>15,7</td>
<td>4,2%</td>
<td>852</td>
</tr>
<tr>
<td>CH20 16,5</td>
<td>432%</td>
<td>537</td>
<td>8,7</td>
<td>7,6%</td>
<td>458</td>
</tr>
<tr>
<td>CH30 14,5</td>
<td>445%</td>
<td>540</td>
<td>8,7</td>
<td>34,8%</td>
<td>464</td>
</tr>
</tbody>
</table>
5.2 XRD analysis

The XRD spectra of the three films are reported in Fig. 2 and correspond to those of semi-crystalline materials. The crystalline lattice of medium-chain-length PHAs is typically orthorhombic and it is formed by helix-conformed molecules. The lattice usually presents two molecules per unit cell. [43]. In particular, PHB can assume a helix conformation, the α form, or a planar zig-zag conformation, the β form. The α form results in crystals formed of lamellae and it is the most common [5]. In this case, the orthorhombic structure of poly(3-hydroxybutirate) (PHB) in α-form can be identified [42].

PHBH presents only the crystalline form of PHB lattice, since 3HH does not participate to crystalline phase. This phenomenon was observed, in particular, for PHBH films with a composition up to 25% of 3HH monomers [44]. For CH10, the following peaks can be identified, which correspond to the following families of (hkl) planes: (020) at 13.5°, (110) at 16.9° and (021) at 20.1°. For CH20, only two families of planes appear: (020) at 13.6° and (110) at 17.0°. For CH30, the following families of planes appear: (020) at 13.6°, (110) at 17.1° and (021) at 20.2° [42].

The position and the intensity of the peaks remains almost unchanged among the three blends, meaning that the crystal planes of PHBH are not significantly changed [45]. A small expansion of (110) spacing can be observed as temperature increases [46], as the correspondent peak slightly moves to lower angles. The same phenomenon can be observed for (021) spacing in CH10 and CH30. For CH10, the crystalline family (021) appears only during fusion, above 110°C. At 150°C, no diffraction peak can be identified.

5.3 Thermal analysis

The results of the DSC scans are displayed in Fig. 3. The main parameters are evaluated from the second heating scan and are presented in Table 3. All the blends presented a double endothermic peak of fusion, that is caused by the recrystallization process of PHBH [45]. The two melting temperatures are defined as \( T_{m1} \) and \( T_{m2} \). In the second heating, the double melting peak becomes neater. This is due to the formation of imperfect crystals during the first heating ramp and the following cooling. These imperfect crystals undergo a process of melting and rearrangement at \( T_{m1} \), resulting in more stable structures, that then melt at \( T_{m2} \) [24]. This behaviour can be also due to the polymorphism of PHBH crystals during crystallization process. The same phenomenon occurs to many other polyhydroxyalkanoates (PHAs) [47].

During the first heating scan, beside the glass transition temperature, several other endothermic peaks are visible at temperatures lower than \( T_{m1} \). These peaks are associated with the melting of the solid crystalline phase [48]. The process of cooling of these blends can determine the formation of different crystalline structures. Secondary lamellae can also be formed at room temperature during the storage of the materials [49]. The fusion of these structures determines the small endothermic peaks which appear in the first heating curves by the temperature of about 50°C.

The increasing percentage of P(3HB)(4HB) also leads to a slight decrease in both \( T_{m1} \) and \( T_{m2} \). This could be due to the fact that amorphous P(3HB)(4HB) makes the crystals of PHBH less complete,
requiring lower temperature to melt [50]. Lower melting temperature indicates a decreased thermal stability [51].

From the cooling curves, it is evident that the increase of the percentage of Poly(3-hydroxybutyrate-4-hydroxybutyrate) leads to lower temperatures of crystallization ($T_c$) and to lower enthalpies of crystallization ($\Delta H_c$). In general, a high melt-crystallization temperature can be considered as an indicator of fast crystallization [52]. All the blends present a second crystallization peak during the cooling curve at 134.1°C. PHBH can present a cold crystallization peak at 60–70°C during the heating scans [48], [53], [54]. In this case, none of the materials presented it, meaning that PHBH could crystallize [55] during the cooling process after the pellet production or during the cooling scan of DSC. The crystallinity of the PHBH present in the blends slightly increases in function of the amount of amorphous P(3HB)(4HB) present in the blend, going from 35% of CH10 and 37% of CH20 to 39% of CH30.

The Glass Transition Temperatures $T_g$ of CH10 ad CH20 can be attributed to PHBH, whose glass transition temperature is close to 0°C [47]. The $T_g$ of CH30 is closer to the glass transition temperature of P(3HB)(4HB).

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH10</td>
<td>2,6</td>
<td>132,5</td>
<td>147,3</td>
<td>45,9</td>
<td>82,4</td>
<td>40,8</td>
</tr>
<tr>
<td>CH20</td>
<td>4,9</td>
<td>129,7</td>
<td>146,7</td>
<td>42,9</td>
<td>65,4</td>
<td>36,7</td>
</tr>
<tr>
<td>CH30</td>
<td>-17,7</td>
<td>127,0</td>
<td>144,5</td>
<td>40,1</td>
<td>62,3</td>
<td>29,7</td>
</tr>
</tbody>
</table>

### 5.4 Oxygen Transmission rate and Water Vapour Transmission Rate

The barrier properties of the blends are evaluated by measuring the Oxygen Transmission Rate (OTR) and the Water Vapour Transmission Rate (WVTR). The increasing percentage of amorphous P(3HB)(4HB) leads to a substantial increase in OTR, which duplicates from CH20 to CH30. The increase in WVTR is not as remarkable passing from CH20 to CH30.

The increasing OTR can be explained by considering the process of permeation of a gas through a polymeric matrix. It can be substantially divided into four steps: the sorption of the gas molecule on the film surface, the following dissolution of the gas into the polymer and its diffusion through it and finally the desorption of the gas from the other surface of the polymeric film [56]. The permeation can proceed only into the amorphous regions of the polymer [57]. Any modification of the crystallinity, of the morphology or of the extent of free volume can lead to a variation on the permeability, as it changes the diffusion path [58]. Therefore, the increased percentage of amorphous Poly(3-hydroxybutyrate-4-...
hydroxybutyrate) and the small variation in crystalline percentage of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) explain the trend of OTR values.

The variation in composition leads also to a modification of WVTR. In fact, crystalline regions have the effect of reducing the permeability to water vapour of the polymeric matrix. This is mainly due to their low permeability and to their small cross section [56].

**Conclusions**

Marine biodegradable blends of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and Poly(3-hydroxybutyrate-4-hydroxybutyrate) P(3HB)(4HB) were prepared by reactive extrusion. The pellets were then cast-extruded and thin films were produced and characterized. The increasing percentage of P(3HB)(4HB) improves the deformation at break of the films whereas it reduces the tensile strength and the elastic modulus. The data derived from the DSC graphs were used to evaluate the crystallinity of PHBH, which does not change sensibly in function of the percentage of Poly(3-hydroxybutyrate-4-hydroxybutyrate). The types of crystalline structures were identified through XRD analysis. The gas permeabilities of the films were evaluated by measuring the Oxygen Transmission Rate OTR and the Water Vapour Transmission Rate WVTR, which both increases with the increasing percentage of P(3HB)(4HB) of the blend. The interesting mechanical, thermic and gas barrier properties of these materials confirm the possibility of using them as packaging materials for fresh fruit and vegetables with low environmental footprint.

**Declarations**

**Acknowledgements**

The authors wish to thank Giulia Cappiello, Alessandra Piselli and Nazan Koca for their kind contribution.

**Funding**

No funding

**Author contribution**

Prof. Barletta contributed in conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, and writing – review and editing. Dr. Aversa contributed in writing – review and editing. Ing. Genovesi contributed in data curation, formal analysis, investigation, validation, visualization, and writing – original draft.

**Conflict of interest**

I declare that the authors have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author, AG, upon reasonable request.

References


37. M. Zhang, X. Diao, Y. Jin, e Y. Weng, «Preparation and characterization of biodegradable blends of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) and poly(butylene adipate-co-terephthalate)»,


**Figures**
Figure 1

Figure 3 Stress - Strain curves of specimens in Machine Direction

Figure 2
Figure 4 XRD spectra of CH10 (a), CH20 (b) and CH30 (c) evaluated at different temperatures.

Figure 3

Figure 5 DSC scans CH10, CH20 and CH30. (a) First heating, (b) Second heating and (c) Cooling.
Figure 4

Figure 6 Oxygen Transmission Rate (OTR) and Water Vapour Transmission Rate (WVTR) of PHBH/P(3HB)(4HB) blends