



Material properties

Fully bio-based and biodegradable polylactic acid/poly(3-hydroxybutyrate) blends: Use of a common plasticizer as performance improvement strategy



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ABSTRACT

Biodegradable polymeric blends based on poly(3-hydroxybutyrate) (PHB) and polylactic acid (PLA) were prepared by melt mixing. Trybutyrin, a bio-based plasticizer, was added at a fixed proportion in all blends. Crystal structure, percent crystallinity, miscibility, mechanical properties and permeation of fully biodegradable PHB/PLA blends were investigated in detail by Differential Scanning Calorimetry (DSC), Fourier Transformed Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), tensile tests and water vapor permeation tests. From the thermal test, two glass transition temperatures were found for the whole range of compositions, which reveals the immiscibility between PHB and PLA. Moreover, the biphasic melt further confirms this fact. Tensile tests showed an increase in the elongation at break with the PLA content. SEM images reveal debonding between the interfacial surfaces, which justifies the increase in the elongation at break. Water vapor permeation values for blends were slightly higher than that of the plasticized pristine polymer. The plasticized polymer blends showed valuable properties to extend the applications of PHB and PLA.

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1. Introduction

In recent years, there has been an expansion of biopolymer research activities in order to overcome the environmental impact produced by petroleum-based plastic residue. Among the vast number of biopolymers studied, two of the most promising are poly(3-hydroxybutyrate) (PHB) and polylactic acid (PLA), both biodegradable and biocompatible polyesters that can be produced from renewable resources.

PHB is a natural polymer synthesized by different species of bacteria as an intracellular storage material with a remarkable stereo-regularity of the perfectly isotactic chain configuration, which gives it unusually high crystallinity. It is a crystalline thermoplastic polyester with similar properties to those of synthetic polypropylene; it presents a high melting point (173–180 °C) and a glass transition temperature around 5 °C. The main drawbacks of PHB are that it is mechanically fragile and shows a narrow window for the processing conditions due to the proximity of the melting

and degradation temperatures [1,2]. Different strategies have been studied with the aim of improving its mechanical and thermal properties, such as the preparation of nanocomposites with nanofillers [3,4] or the addition of another polymer to obtain blends [5]. Polymer blends represent an interesting strategy to adjust certain properties of the polymers. However, it is generally very difficult to improve a property without detriment of others. PLA appears as a good alternative for blending with PHB.

PLA is a semi-crystalline polyester derived from lactic acid, obtained entirely from renewable resources such as corn, sugar beet and wheat. The glass transition temperature of PLA is in the range of 50 °C–80 °C while the melt temperature is in the range of 130 °C–180 °C. It has greater mechanical strength and easier processability than PHB. Although PLA is compatible with many current processing techniques, the fact that it has a high glass transition temperature leads to brittleness in the final products [6]. From this viewpoint, a good balance of amorphous and crystalline domains (45–50%) along with low T_g (–10 °C) is an ideal target to aim for. Therefore, a lowering of T_g and crystallization temperature (T_c) as well as an increase in crystallinity are goals for improved in PLA based materials. Changes in PLA packing structure to shift T_c have been reported [6]. Conventionally, addition of a nucleating

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agent is the simplest way to induce crystallization [7]. In addition, the use of PLA is limited by its low heat resistance [8] and poor barrier properties [9].

In order to overcome the aforementioned difficulties, several authors have formulated blends of PHB/PLA by using limonene [5], polyethylene glycol (PEG) [10] as plasticizers and also by blending PLA with atactic PHB [11] and other PHB copolymers [12,13]. While some improvement has been obtained, parameters such as the elongation at break have not shown significant improvements, and the influence on the barriers properties when a hydrophilic plasticizers is added, such as PEG, has not been extensively studied.

In this work, different PHB/PLA blend compositions were processed. A natural hydrophobic plasticizer, tributyrin (TBL), was used to facilitate the polymer processability. TBL is a natural triglyceride present in fats and oils that has shown to be a good candidate as plasticizer for bio-based polymers [14].

The aim of this work is to obtain and characterize PHB/PLA blends with improved mechanical properties, through the addition of a natural mutual hydrophobic plasticizer, without altering considerably the good properties of the pristine polymers. This should be important to modify the properties and extend the practical application of these biodegradable polymers. Finally, concern was given to understand the relationship between structure, composition and properties of the blends.

2. Materials and methods

2.1. Materials

PHB (kindly supplied by PHB Industrial S. A., Brazil) (Mw = 2,46,000) and PLA, with a molecular weight Mn = 88,500, (NatureWorks®) were used as polymeric hosts. TBL was purchased from Fluka and was employed as plasticizer for both polymers.

2.2. Preparation of the blends

In order to obtain the blends, the raw PHB and PLA pellets were mechanically mixed with the TBL prior to melting in a Haake mixer at 185 °C and a screw rotation speed of 50 rpm for 3 min. Blends were then molded into films (thickness: 100 μm) at 190 °C in a hot press. The materials were kept between the plates at atmospheric pressure for 1 min until melting and then for 2 min at 5 MPa. The PLA and PHB pellets were previously dried in a vacuum oven at 80 °C overnight. The proportion polymer blend/plasticizer was remained at 80/20wt.% in the different blends of PHB/PLA ratios: 100/0, 70/30, 60/40, 50/50, 40/60, 30/70 and 0/100. The samples were designated as listed in Table 1. In the same way, in order to determine the miscibility between the plasticizer and each polymer, blends of polymer/TBL in 90/10, 85/15, 80/20 and 75/25 wt. ratio, were prepared. The pure polymers without TBL were also processed in order to be used as reference materials.

Table 1
Name and description of the composition of the materials studied.

Name	PHB/PLA/TBL (wt.%)
PHB-TBL20	80/0/20
PHB/PLA (70/30)	56/24/20
PHB/PLA (60/40)	48/32/20
PHB/PLA (50/50)	40/40/20
PHB/PLA (40/60)	32/48/20
PHB/PLA (30/70)	24/56/20
PLA-TBL20	0/80/20

2.3. Characterization techniques

X-ray diffraction (XRD) analysis was performed on the blend films using an X-Pert pro diffractometer, operating at 40 kV and 40 mA, with CuKα radiation ($\lambda = 1.54 \text{ \AA}$), at a scanning speed of 1.5°/min. The crystallinity index was calculated by dividing the crystalline area by the total area (crystalline + amorphous) [15].

Scanning differential calorimetry (DSC) was carried out on a Pyris 1, Perkin Elmer. The mass of each sample was 10–12 mg and the carrier gas was nitrogen at a flow rate of 20 mL/min. The scanning process comprised initial heating from –50 °C to 190 °C at 10 °C.min⁻¹ followed by cooling from 190 °C to –50 °C at 80 °C.min⁻¹ and, finally, a second temperature scanning from –50 °C to 190 °C at 10 °C min⁻¹. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting temperature (T_m) of both polymers were determined. The degree of crystallinity (X_c) was calculated using the following Equation (Eq. (1)):

$$X_{c_i} = \frac{\Delta H_{m,i} - \Delta H_{cc,i}}{\Delta H_{m,i}^0 \cdot \phi_i} \quad (1)$$

where i subscript indicates the polymer in the blend, ϕ is the mass fraction of the polymer in the blend, $\Delta H_{m,i}$ is the melting enthalpy, $\Delta H_{cc,i}$ is the enthalpy of cold crystallization, ΔH_m^0 is the melting enthalpy of PHB or PLA 100% crystalline (146 J/g and 93 J/g, respectively) [16]. Reported values were the average of at least 3 scans.

Fourier Transform Infrared spectroscopy analysis in attenuated total reflectance (FTIR-ATR) was performed using a Thermo Scientific Nicolet Instrument 6700 in the range 400–4000 cm⁻¹ by performing overlapping 32 scans at a resolution 4 cm⁻¹, at room temperature.

Mechanical properties of the samples were determined using a universal testing machine, INSTRON 4467. Uniaxial tensile tests were performed at a traverse rate of 1 mm/min, using dumbbell specimens (ASTM D1708-93). Reported values were the average of at least 5 valid tests.

Scanning electron microscopy (SEM) was employed using a microscope JSM 6460. In order to observe the morphology of the samples, fracture surface from films broken in liquid nitrogen were analyzed. All the samples were coated with a thin gold foil.

Water vapor permeation (WVP) of the materials was determined according to ASTM E 96-9500e1. CaCl₂ was used as a drying agent, previously dried in an oven as detailed in the standard. Teflon capsules of 5 cm of diameter were used. The capsules were placed in a chamber at 65% relative humidity at an average temperature of 18 °C. Until steady state was reached, weight measurements were performed at regular time intervals. The WVP of the films was calculated according to Equation (2):

$$WVP = \frac{WVTR \cdot d}{\Delta P} \quad (2)$$

where $WVTR$ is water vapor transmission rate through the film (g/m².s), d is the average film thickness (m) and ΔP is the difference in partial vapor pressure (Pa) between both sides of the film. Reported values were the average of at least 3 tests.

3. Results and discussions

In order to investigate the crystalline structure and to calculate the degree of crystallinity of PHB/PLA blends, XRD tests were performed. The diffractograms of PHB/PLA blends in the whole range of compositions are shown in Fig. 1a. PHB is a highly ordered

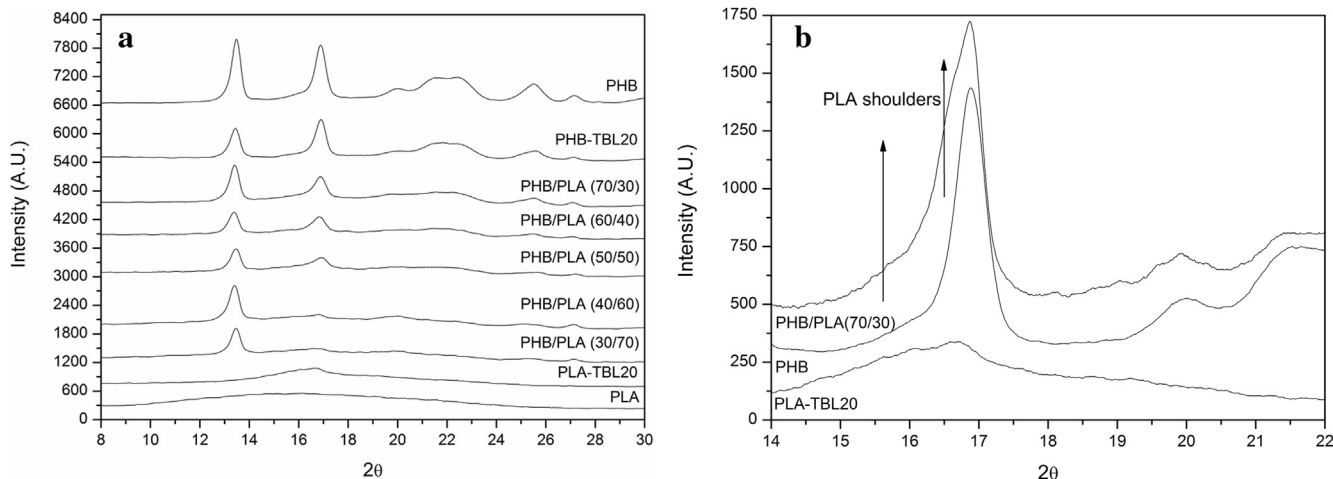


Fig. 1. a) DRX diffractograms for PHB, PLA and theirs blends. b) Shoulder in PHB/PLA (70/30) blend.

polymer and crystallizes in an orthorhombic cell form. Characteristic PHB diffraction peaks appear at 13.5° , 16.9° and three weak at 19.9° , 22.3° (typical structure of orthorhombic form) and 25.5° [16], which almost coincides with the PLA diffraction peaks. In this case, for pure processed PLA no diffraction peaks were observed, which indicates that the PLA displays amorphous structure. However, when 20wt.% of TBL was added to PLA, a diffraction peak at around 16.6° appears. That peak also appeared in all blends, like a shoulder on the highly intense diffraction peak at 16.9° of the PHB, which becomes broader than in the pure PHB diffraction pattern. The presence of that shoulder was more clearly shown in the diffractogram of PHB/PLA (70/30) blend (Fig. 1b) in the range from 14 to 22° . Also, the pattern of the blends showed that the intensity of the diffraction peaks at 16.9 and 16.6° , representative of PHB and PLA, respectively, varied in the same way than the composition of each polymer, revealing that PHB and PLA crystallize separately in the blends. Therefore, blending two plasticized semicrystalline polymers, PHB and PLA, the crystal structure of the each polymer was not modified but the intensity of the XRD diffraction peaks were reduced in the blends [17].

Crystallinity plays a very important role in the physical properties of biodegradable polymers, such as thermal and mechanical, and also affects biodegradability. The degree of crystallinity was calculated only for pure and plasticized polymers (Table 2) because the diffraction peaks of PHB and PLA overlapped each other (Fig. 1b). As expected from the diffractograms, the index of crystallinity of plasticized PLA was three times higher than the pure polymer, while the crystallinity of PHB, a highly crystalline polymer, does not change with the addition of plasticizer.

Due to the difficulty in accurately estimating the crystallinity values of each component with XRD tests, DSC experiments were used because they represent an excellent alternative to assess this parameter. From these experiments, important thermal properties of each blend, such as glass transition temperature, cold crystallization temperature and melting temperature can be obtained. Additionally, the miscibility between both polymers can be evaluated.

Table 2
Index of crystallinity for pure and plasticizer polymers.

Material	Index of crystallinity (%)
PHB	74.9
PHB-TBL20	75.9
PLA-TBL20	12.9
PLA	4.0

Fig. 2 shows the first heating scan for all the materials processed. The glass transition temperature is one of the most important miscibility criteria in polymer blends [18]. When each polymer was mixed with TBL, a single T_g was observed, which was reduced by 30°C and 25°C for PHB and PLA, respectively. Therefore, in both cases, it can be inferred that the plasticizer chosen was miscible [19].

To further deepen the study of the compatibility PHB/TBL and PLA/TBL, the Nishi and Wang model was used [20], which is based on the Flory-Huggins Theory. According to Flory-Huggins theory, the melting point depression is related to the interaction parameters, $\chi_{1,2}$, through the following relation:

$$\frac{1}{T_{mi}} - \frac{1}{T_{mi}^0} = -\frac{RV_2}{\Delta H_{mi} \cdot V_1} \cdot \chi_{12} \phi_1^2 \quad (3)$$

where subscripts 1 and 2 represent the pure and the plasticized polymer, respectively, and subscripts i represent each polymer; T_{mi} and T_{mi}^0 are the equilibrium melting point of the crystallizable component in the pure state and the blend, respectively; R is the universal gas constant; V_i is the molar volume of the respective component ($V_{PHB} = 75 \text{ cm}^3 \text{ mol}^{-1}$, $V_{PLA} = 57.7 \text{ cm}^3 \text{ mol}^{-1}$,

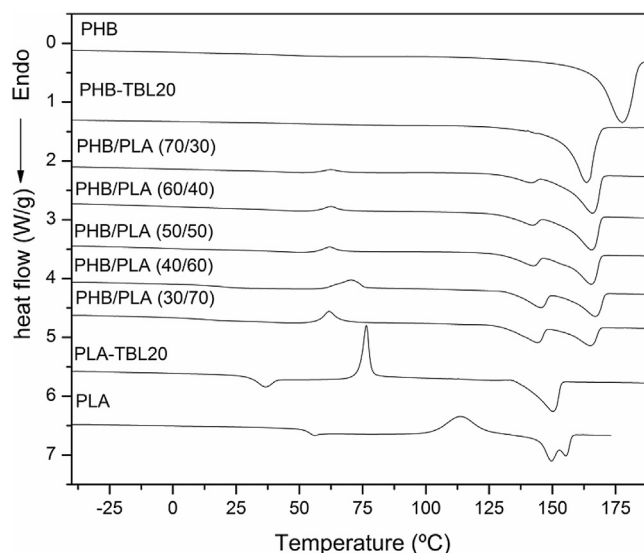


Fig. 2. First DSC scans for PHB, PLA and theirs blends.

Table 3
Thermal properties of PLA, PHB and their blends.

Material	T _g (°C)		T _{cc} (°C)		T _m (°C)		ΔH _{cc} (J/g)		ΔH _m (J/g)		X _c (%)	
	1 ^a	2	1 ^a	2	1	2	1 ^a	2 ^a	1	2	1	2
PHB	2.2	–	53	–	176	–	35	–	91	–	62	–
PHB-TBL20	–27	–	19	–	165	–	18.5	–	73	–	60.3	–
PHB/PLA(70/30)	–27	3.6	–	62.4	166	142	–	–2.1	50	10	60.9	35.2
PHB/PLA(60/40)	–27	3.2	–	62.2	166	142	–	–3.3	42	13	60	31.7
PHB/PLA(50/50)	–30	2.5	17.5	62.1	165	142	4	–3.1	36	14	61.2	29.5
PHB/PLA(40/60)	–23	19	23.7	70.3	167	146	5.5	–7.7	28.5	16	61	18.4
PHB/PLA(30/70)	–28	12	21	62.1	165	144	2	–7	22	18	62.8	21.7
PLA-TBL20	–	28	–	75.8	–	150	–	–18	–	28	–	13.7
PLA	–	53	–	114	–	155	–	–25	–	27.4	–	2.7

1: PHB, 2: PLA.

^a Second scan.

$V_{TBL} = 292 \text{ cm}^3 \text{ mol}^{-1}$ [21,22]); ΔH_{mi} is the heat of fusion per mole of repeat unit and ϕ_i is the volume fraction of each polymer component in the blend obtained as the ratio between the mass fraction and the density of the amorphous phase of each polymer ($\delta_{PHB} = 1.15$, $\delta_{PLA} = 1.25$, $\delta_{TBL} = 1.032 \text{ g/cm}^3$ [21,22]). A plot of the left-hand side of Equation (3) versus the square of the PHB or PLA volume fraction ϕ_i in the blend can be used to estimate the PHB/TBL and PLA/TBL interaction parameters χ_{12} . This should give a straight line passing through the origin if χ_{12} is independent of the composition and the melting point depression is not influenced by morphological effects.

The χ_{12} values found to PHB/TBL and PLA/TBL were -8.6 and -2.2 , respectively, which indicates miscibility between both polymers and TBL.

The miscibility between PHB and PLA has been studied. PLA and PHB were reported immiscible unless the molecular weight of PLA and/or PHB is very low [23,24,25]. DSC experiments reveal two T_g for blends PHB/PLA/TBL (Table 3), one for each biopolymer, indicating the immiscibility between them. However, the T_g values of the PLA in the blends were lower than that of PLA-TBL20 (Table 3). This could be due to the partial miscibility between PHB and PLA, which would be evident in the further reduction in the T_g of each polymer [13]. A reduction of 10°C was found in the melting temperature of each plasticized polymer matrix, which is further evidence of miscibility between the polymer and the plasticizer.

Moreover, regardless of the composition of the blends, two T_m , corresponding to each polymer were found. T_m values in the mixtures did not vary significantly compared to plasticized polymers.

The two endothermic peaks corresponding to the melting of each polymer, and the exothermic peak of cold crystallization of PLA, were considered to calculate the degree of crystallinity in the blends (Table 3).

PLA crystallinity increased with the PHB content, as was shown in the XRD test, probably due to the PHB crystals that may act as nucleating agents [26]. This is evidenced by reductions of 14°C and 50°C in the cold crystallization temperatures of PLA in the blends in relation to those of the plasticized and pure polymer, respectively [27]. Also, the increment in the polymer chain mobility, displayed by a reduction in T_g , favored the crystallization process, as shown by the higher degree of crystallinity of the plasticized PLA compared to the pure PLA (Table 3) [7,28].

PHB crystallinity remained nearly constant. The same behavior was found in our previous work, where the crystallinity does not change despite the addition of another phase, even if that phase can act as a nucleating agent [3,29].

In order to analyze the polymer structure in the blends FTIR spectra of PHB/PLA/TBL samples were done and are shown in Fig. 3 in the $1650\text{--}1800 \text{ cm}^{-1}$ range. The characteristic peak

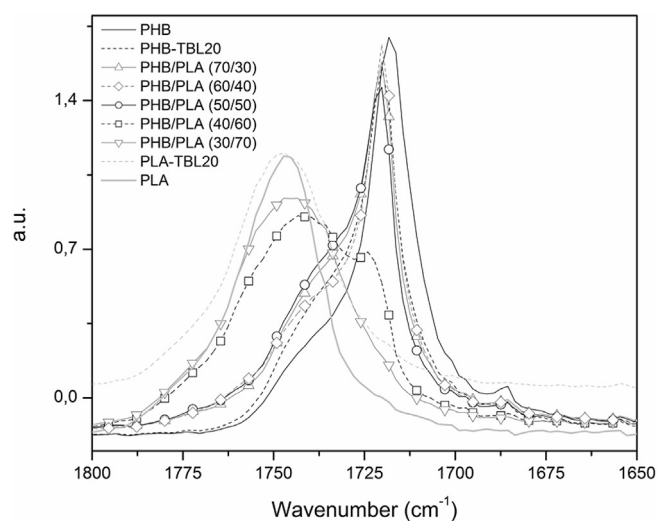


Fig. 3. FTIR spectra of PHB/PLA/TBL blends.

Table 4
Mechanical properties for the materials.

Material	E (GPa)	σ_b (MPa)	ϵ_b (%)
PHB	2.23 ± 0.20	34.6 ± 2.6	4.1 ± 1.5
PHB-TBL20	0.82 ± 0.07	11.2 ± 0.8	2.2 ± 0.2
PHB/PLA(70/30)	0.5 ± 0.07	11.0 ± 0.6	12.5 ± 5.2
PHB/PLA(60/40)	0.35 ± 0.02	9.5 ± 0.8	30.7 ± 9.7
PHB/PLA(50/50)	0.33 ± 0.04	9.0 ± 1.7	45.1 ± 34.7
PHB/PLA(40/60)	0.53 ± 0.15	13.7 ± 0.9	148.8 ± 19.4
PHB/PLA(30/70)	0.07 ± 0.01	14.4 ± 1.8	193.2 ± 51.0
PLA-TBL20	1.85 ± 0.20	27.4 ± 3.3	5.2 ± 1.7
PLA	2.80 ± 0.20	55.9 ± 2.9	4.8 ± 2.2

corresponding to the asymmetric stretching of the carbonyl group $\text{C}=\text{O}$ near 1720 cm^{-1} was observed for all compositions [5]. It was found at 1747 cm^{-1} and 1718 cm^{-1} for pure PLA and PHB, respectively. As expected, that peak shifted from 1747 cm^{-1} to 1718 cm^{-1} as PLA content decreased in the blends. It can be seen that the intensity of these peaks increases with the composition of each polymer, which suggests that the material is macroscopically homogeneous.

From the uniaxial tensile tests, mechanical properties of the different materials were obtained (Table 4). Both pure polymers are rather hard and brittle materials and not very useful for many applications. The pure PLA had higher values of ultimate stress and elastic modulus compared to PHB. The addition of TBL reduced in both polymers the maximum stress value (σ_b) and the tensile

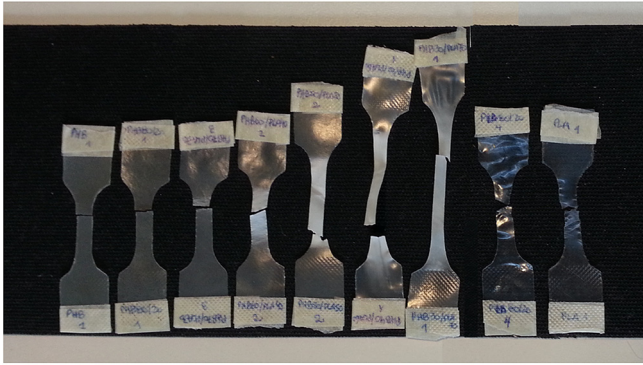


Fig. 4. Specimens from tensile test: PHB, PHB-TBL20, blends PHB/PLA: 70/30,60/40,50/50,40/60,30/70, PLA-TBL20 and PLA.

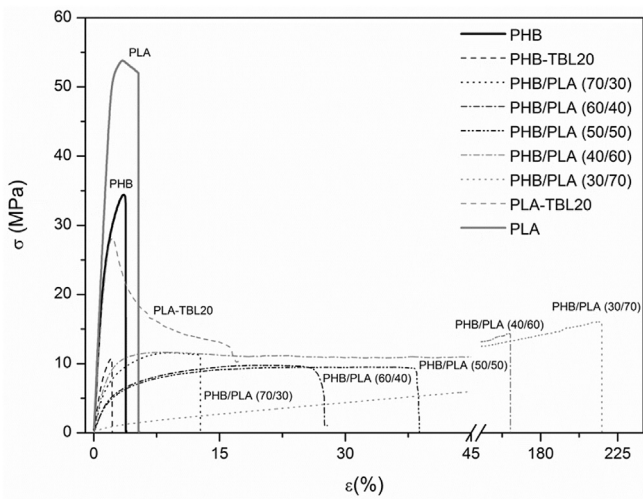


Fig. 5. Curves strain-stress for PHB, PLA and their blends.

modulus (E); the same behavior was observed for all blends. No significant changes were observed in the elongation at break (ϵ_b) for plasticized pure polymers, finding values of 2% and 5% for PHB-TBL20 and PLA-TBL20, respectively.

Regarding the polymer blends, it was found that the elongation at break increased from 6 to 70 times up to 60% PLA content with respect to PHB-TBL20. Moreover, the PHB/PLA (30/70) blend

showed elastomeric behavior, stretching 85 times more than plasticized PHB, as shown in Fig. 4.

In general, as the elongation at break increased, both the maximum tension and the elastic modulus decreased (Fig. 5). However, this was not the case for PHB/PLA (40/60), that not only showed an elastic modulus and a maximum stress similar to those of the blends with less PLA content, but also a larger elongation at break. Probably, from 50/50 to 30/70 blend, the continuous matrix is PLA, with PHB plasticized as the dispersed phase. The plasticized PHB dispersed phase would induce deformation mechanisms that the PLA and the PLA-TBL20 cannot generate at room temperature, resulting in improvement in ductility of blends [12].

In order to analyze the effect of the PHB dispersed phase, SEM microscopy for pure PLA and the PHB/PLA (50/50) blends was done. Fig. 6a shows that the pure PLA has a smooth and uniform fracture surface characteristic of a brittle polymer, while the PHB/PLA (50/50) blend (Fig. 6b) reveals an irregular fracture surface with two types of microstructure. The elongated fibrils were clearly seen (inset), indicating that fibrillation and interfacial debonding are mainly responsible of the improved ductility [12,18].

As it was mentioned previously, another important property that deserves being evaluated in materials with potential

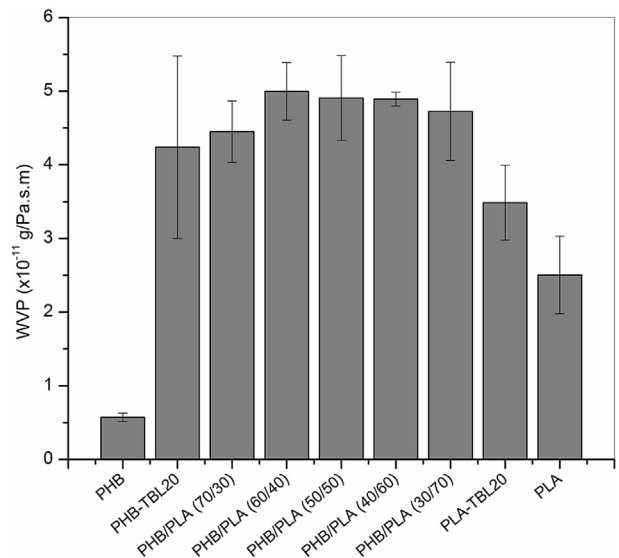


Fig. 7. WVP of PHB, PLA and their blends with TBL.

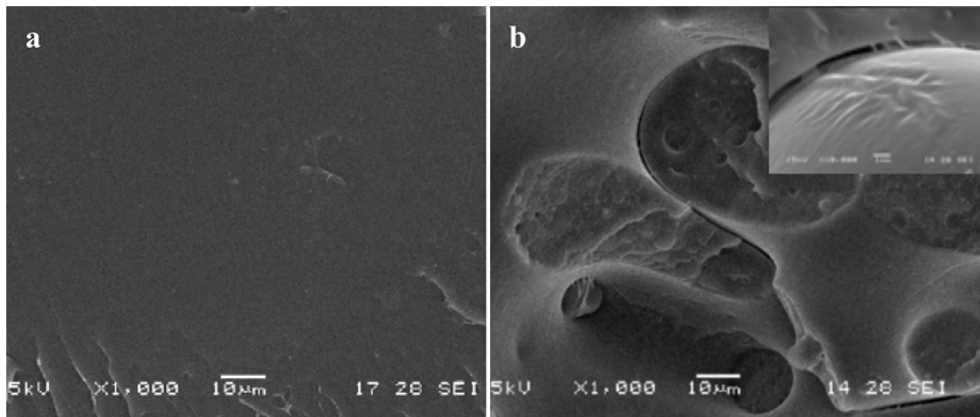


Fig. 6. SEM micrograph of fracture surface: a) PLAx1000 b) PHB/PLA(50/50)x1000 and inset PHB/PLA(50/50)x10,000.

application in packaging is WVP. In semicrystalline polymers such as PHB and PLA, the crystalline regions are commonly considered impenetrable for small molecules such as H₂O, CO₂, with a low number of exceptions [30]. For this reason, it is assumed that semicrystalline polymers are predisposed to exhibit better barrier properties than amorphous polymers. In the most extensively accepted view of the diffusion process in semicrystalline polymers, the diffusivity is considered to be reduced with respect to the fully amorphous polymer by a geometric impedance factor and a chain immobilisation factor. The former is related to the more tortuous path that the penetrant molecules must follow in order to bypass the impermeable crystals, and the latter is connected to the crosslinking effect of the crystallites of the amorphous chains that restricts their mobility [31].

The calculated values of WVP for all materials studied are summarized in Fig. 7.

The WVP value of PHB-TBL20 was found to be an order of magnitude higher than that of pure PHB. Miguel et al. (2001) [32] studied the barrier properties of PHB blends with amorphous polymers; they found a lineal increase in the diffusion coefficient with the amorphous polymer content. It is shown in Table 2 that the crystallinity of PHB and PHB-TBL20 remains almost unchanged; however, the *T_g* decreased almost 30 °C due to the incorporation of TBL, which leads to an increase on the free volume and mobility of the polymer chains of the matrix. This effect would produce a less dense structure allowing the water and other molecules to diffuse through the matrix [33]. In the case of PLA and PLA-TBL20, the increase in WVP was lower than for PHB-TBL20 with respect to the pure polymer. While *T_g* also decreased almost 30 °C, the crystallinity of PLA increased, creating a tortuous path for H₂O molecules.

The WVP values obtained for all blends are around 4.8×10^{-11} g/Pa s m, which is close to that of some commodity polymeric packaging [34]. Again, this behavior may be interpreted as a result of the compromise between the increase in the degree of crystallinity of PLA in blends as well as in the permeability of the amorphous phase exerted by the TBL. In addition, the materials obtained were highly transparent, as it can be seen from the visual appearance of films observed in Fig. 4. It is noticeable that this characteristic is an important requirement for a material to be used as food packaging.

4. Conclusions

Fully biodegradable PHB/PLA blends have been prepared and characterized using TBL as a common natural plasticizer.

An increase in the degree of crystallinity of PLA due to the addition of the plasticizer was observed. Both polymers crystallize separately in the blends. It was found that all compositions of the blends presented two glass transition and melting temperatures, indicating the immiscibility between PHB and PLA. The *T_g* of the pure polymers was reduced in the blends due to the presence of the other polymer in the material. Furthermore, the crystallinity of PLA increased significantly with the PHB content in the blends.

Regarding the mechanical performance, some blends possess synergistic properties not achievable by individual components. For PLA-rich blends, a certain amount of plasticized PHB can significantly improve the elongation at break without loss in tensile strength and Young's modulus with respect to PLA-TBL20. Therefore, it was possible to obtain ductile materials blending two plasticized fragile polymers. The SEM images showed fibrillation and debonding between the interfacial surfaces, which justifies the increase in the ductility observed in the tensile test.

Water vapor permeation values for blends were slightly higher than that of the plasticized pristine polymer. However, they were an order of magnitude higher compared to pure PHB due to the

incorporation of the plasticizer, which increases the free volume and mobility of the polymer chains of the matrix causing a less dense structure, allowing water to diffuse through the matrix.

The obtained results are advantageous because it was possible to modify the polymer performance in order to extend the practical application of these biodegradable polymers. Therefore, it could be concluded that plasticized PHB/PLA (30/70) and PHB/PLA (40/60) blends, may be considered a sustainable alternative to current non-natural and non-biodegradable materials for food packaging films considering their flexibility, transparency, possibilities for processing at the industrial level and compostable in terms of their final disposition.

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