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Development of PLA / PHB blown films with improved performance for food packaging applications

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In the present work, the suitability of Polylactic acid (PLA) / Poly-² -hydroxybutyrate (PHB) blends for blown film extrusion was evaluated in a broad range of compositions, obtaining films with improved performance for food packaging applications. Blending PHB with PLA enhanced the processability of the systems for the film blowing process than neat PLA. Moreover, even though the polymers were found to be immiscible, the addition of PHB improved the crystallization of PLA, with a consequent increase in the stiffness, barrier properties and light-screening ability of the final developed systems. An increase in the ductility of the films was also achieved with a PHB content up to 30 wt.%. Correlations between the transparency and the crystallinity degree, and between the oxygen permeability and the elastic modulus of the films were also evaluated.

1. Introduction

The use of biodegradable and biobased materials for food packaging applications has the potential to reduce the environmental impacts generated by plastics. In this perspective, the so-called bioplastics are attracting growing interest (Apicella et al., 2019). PLA and PHB are among the most common polymers belonging to this class.

PLA is a biodegradable polymer that derives from renewable sources, it has a good processability with conventional techniques and it has desirable properties in the food packaging field such as resistance to oils, high transparency and good sealability (Pietrosanto et al., 2020a). However, it has some drawbacks, like high brittleness and high oxygen and water vapor permeability (Bassani et al., 2019). PHB, belonging to the family of polyhydroxyalkanoates (PHA), is also a bio-based and biodegradable thermoplastic polymer. It is a highly crystalline material and has good barrier properties. However, it has a melting temperature very close to the degradation ones, which makes it difficult to process with conventional techniques for thermoplastic polymers (Arrieta et al., 2017).

The melt blending of PLA and PHB proved to be an easy way to overcome these drawbacks: it allows the processing of PHB with conventional equipment and, at the same time it improves PLA properties. In fact, the addition of PHB to PLA proved to improve the stiffness (Arrieta et al., 2014), the ductility (Zhang et al., 2011) and the barrier properties (Burgos, 2017) of the final system, which are considered as key properties for food packaging materials. There are different examples of PLA-PHB films for food packaging applications produced with several techniques, such as compression molding (Arrieta et al., 2014), cast extrusion (Armentano et al., 2015), solvent casting (El-Hadi, 2017).

In this work, the suitability of PLA/PHB blends for blown film extrusion was evaluated in a wide range of compositions obtaining films with improved performance for food packaging applications. The blown film extrusion is one of the most common methods to make plastic films, especially for the packaging industry and very few data are reported in the literature on PLA /PHB blown films (Jandas et al., 2013; Mosná•ková et al., 2019).

1.1 Experimental

1.2 Materials

PLA 4032D, purchased from NatureWorks^{TM} (U.S.A.), has a content of D-isomer equal to 1.5 wt %, a specific gravity of 1.24 g/cm^3 and a melting temperature between 155 - 170 °C. An experimental grade of PHB was used with a melting temperature between 170 - 180 °C and a complex viscosity (190 °C, 0.1 rad/s, 5 % strain) of 4700 Pa·s.

1.3 Preparation of the films

PLA and PHB pellets were dried under vacuum at 70 °C for 16 h prior to processing. PLA and PHB at different PLA/PHB concentrations (100/0, 80/20, 70/30, 60/40 by weight) were melt-blended in a Collin ZK25 co-rotating twin extruder (D = 25 mm, L/D = 42) with a screw speed of 100 rpm and a temperature profile of 135 – 180 – 180 – 185 – 175 – 185 – 180 – 175 °C from the hopper to the die. Then, pure PLA and each blend were dried under vacuum at 70 °C for 16 h before processing. The blown films were prepared in a single screw extruder GIMAC (D = 12mm, L/D = 24), and, for each system, the process conditions were optimized, in order to produce blown films with a constant thickness of 45 µm. The temperature profile ranged from 190 to 185 °C. The take-up speed was set to 3 m/min and the screw speed from 25 rpm for pure PLA to 18 rpm for PLA/PHB 70/30 and 60/40 blends.

1.4 Characterization

A rheological analysis in oscillatory mode was carried out on pellets of PLA, and PLA/PHB blends using an oscillatory shear strain-controlled rheometer ARES. Pellets were dried under vacuum at 70 °C for 16 h prior to testing. Frequency sweep tests were performed with a parallel-plate geometry (d = 25 mm) with a gap of 1 mm at 190 °C under a nitrogen atmosphere, to minimize thermo-oxidative degradation at a strain equal to 5%. First, a strain sweep test was performed to ensure the linear viscoelastic regime for each composition.

For the morphological analysis, film samples were cryo-fractured in their transverse direction (TD) and then coated with a thin gold layer (Agar Auto Sputter Coater mod. 108 A, Stansted, UK) at 30 mA for 160 s to increase their conductivity. After, their cross sections were scanned by field emission scanning electron microscope (FESEM) (LEO 1525 model, Carl Zeiss SMT AG, Oberkochen, Germany).

Thermal characterization of the films was performed through a Differential Scanning Calorimeter (DSC mod. 822, Mettler Toledo) under a nitrogen gas flow (100 mL/min). First, samples were heated from 25 °C to 200 °C with a speed of 10 °C/min and held at 200 °C for 5 min. They were then cooled at 25 °C at 10 °C/min and heated again to 200 °C at 10 °C/min. The crystallinity degrees, Xc, were calculated according to Eq(1):

$$Xc = \frac{\Delta Hm - \Delta Hcc}{\Delta Hm^0} \times 100 \qquad (1)$$

Where • H_m and • H_{cc} (J/g) are the heat of melting and the heat of cold crystallization of the samples respectively. The • H_m^0 is calculated according to the additive mixing rule (Gerard, 2012).

Mechanical characterization of the blown films was carried out through a SANS dynamometer equipped with a 100N load cell. Films were cut into rectangular samples (width = 12.7 mm and length = 50 mm) and the crosshead speed was set in accordance with ASTM D822 standard. Tensile properties were evaluated in the machine direction (MD). All the data are the average of ten measurements.

Films' transparency was determined according to ASTM D1746. A rectangular sample of each film was positioned on the internal side of the spectrophotometer cell. The transmittance was evaluated using a UV-VIS spectrophotometer (Lambda 800, USA) in the 800-200 nm region. After, the transparency of the films was measured at 560 nm and 280 nm. Three replicates of each film were tested.

The percent transparency (TR) was calculated as reported in Eq(2):

$$TR = {}^{T_R}/_{T_0} * 100 \qquad (2)$$

Where T_r is the transmittance with the specimen in the beam and T_0 is the transmittance with no specimen in the beam.

Oxygen transmission rate (OTR) measurements were carried out through a permeability meter (GDP - C 165 of Brugger), with a manometric operation, connected to a thermo-controlled bath (ThermoHaake). An evacuation of the upper and the bottom half-cells was carried out before testing, to remove humidity and residual gases. The test temperature was set at 23 ° C and the oxygen flow to 80 ml/min, according to ISO 15105-1. The area of the tested films was 6.25 cm^2. The values of the permeability coefficients, P O_2, were obtained by multiplying the measured value of OTR by the respectively thickness (mm) of the films.

Water vapor permeability tests were performed through a Water Vapor Permeation Analyzer (Model 7002 - Systech Illinois), which provides a modular system for the determination of water vapor permeability using a sensor based on P_2O_5. Tests were carried out according to ASTM F 1249-90 standard (with the only exception of sensor technology) at 23 °C and 65 % of relative humidity. The area of the tested films was 5 cm^2. The values of the permeability coefficients, P H_2O, were obtained by multiplying the measured value of WVTR by the respectively thickness (mm) of the films.

2. Results and Discussion

2.1 Processability of PLA/PHB blends

Rheological analysis of PLA/PHB blends was carried out to investigate the flow behavior and the processability of these blends for the film blowing process and the results are reported in Figure 1. Neat PLA exhibits a low-frequency Newtonian plateau and a shear thinning behavior at higher frequency values (Figure 1a). The increase of PHB content in the blended system leads to an increase in the zero-shear viscosity and to an enhancement of the shear-thinning behavior that can be related to an increase of chain branching and molecular weight distribution (Pietrosanto, 2020b). Moreover, blended systems show also a higher elastic response for low frequency value than neat PLA (Figure 1b). Both these behaviors suggest that the addition of an increasing amount of PHB in the blends led to an improvement of the processability of the systems for the film blowing process compared to neat PLA.

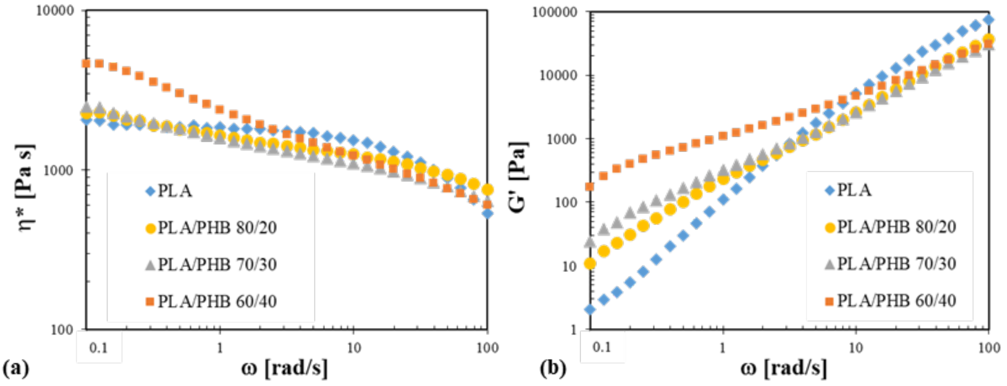

Figure 1: (a) Complex viscosity and (b) Storage Modulus of neat PLA and PLA/PHB pellets.

2.2 Morphological analysis of the films

The morphology of the developed film was investigated, and the images of their fracture surfaces are reported in Figure 2.

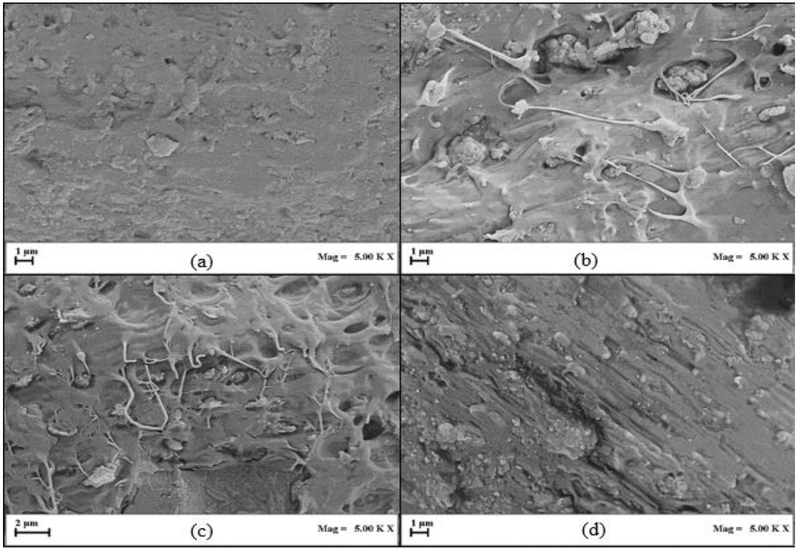

Figure 2: FESEM images of: (a) neat PLA; (b) PLA/PHB 80/20; (c) PLA/PHB 70/30; (d) PLA/PHB 60/40.

From Fig.2 it can be seen that PLA shows an inhomogeneous and brittle fracture surface and all the blends exhibit the typical two-phase structure with voids and inclusions of variable shape and dimensions, a sign of the immiscibility between PLA and PHB. Most of the PLA/PHB blends reported in literature, were found to be immiscible, except for low PHB molecular weight (9400 g/mol) (Ohkoshi et al., 2000). Moreover, the fracture surfaces of the PLA/PHB 80/20 and 70/30 blends show signs of a plastic deformation that preceded the break, while the fracture surface of the PLA/PHB 60/40 sample shows signs of brittle deformation and look more like PLA than the other blends.

2.3 Thermal analysis (DSC) of the films

The thermal properties of the films were also investigated since they influence the performance of the final manufacture and are reported in Table 2.

Table 2: Thermal parameters of PLA/PHB films.

Sample	T_g [°C]	T_{cc} [°C]	” H_{cc} [J/g]	T_m [°C]	” H_m [J/g]	X_c [%]
PLA	65.33	102.45	30.85	168.53	38.26	7.92
PLA/PHB 80/20	61.01	95.45	22.02	167.34	45.48	22.54
PLA/PHB 70/30	59.67	97.78	24.21	167.31	49.65	23.27
PLA/PHB 60/40	58.66	97.45	20.73	167.46	52.91	28.09

Neat PLA shows a glass transition temperature (T_g) at 65 °C, a melting temperature (T_m) around 168 °C and a crystallinity degree (X_c) around 8 %. The blends show a glass transition temperature of the PLA component, which became lower as the content of PHB increased, indicating good compatibility between the polymers. The recrystallization peak of PLA is observed in all the samples, with the cold crystallization temperature (T_{cc}) of the blends lower than the one of pure PLA indicating that PHB improves the crystallization of PLA, in accordance with other authors (Zhang, 2011). The endothermic peak is related to the melting of both PLA and PHB crystals since according to the literature, PHB has a melting temperature of around 170 - 180 °C (Arrieta et al., 2017) which is very close to the melting temperature of the kind of PLA used in this study. Furthermore, the addition of PHB caused an increase in the melting enthalpy (” H_m) and consequently in the crystallinity degree, which increased as the content of PHB in the blend increased.

2.4 Tensile properties of the films

Tensile properties of the films are reported in Table 3. The addition of PHB to PLA causes an increase in the elastic modulus. The increased stiffness of blends films can be attributed to the morphology of the blends characterized by a crystallinity degree greater than that of pure PLA., as reported in Table 2. However, the blending with PHB caused a slight decrease of the yield stress compared to neat PLA. The addition of PHB up to 30%, caused an increase in elongation at break compared to neat PLA, in accordance with previous studies (Zhang, 2011; Jimenez et al., 2015).

Table 3: Tensile and barrier properties of PLA/PHB films: Elastic Modulus (E), Yield stress ($Ã_y$), elongation at break (• $_b$), Oxygen permeability coefficient (PO_2) and water vapor permeability coefficient (P H_2O).

Sample	E [MPa]	$Ã_y$ [MPa]	• $_b$ [%]	PO_2 [cm^3*mm/m^2*d*bar]	P H_2O [mm*g/m^2*d]
PLA	2140 ± 55	45 ± 2	13 ± 3	24.3	1.5
PLA/PHB 80/20	2264 ± 68	38 ± 2	20 ± 6	18.5	1.1
PLA/PHB 70/30	2341 ± 89	39 ± 3	26 ± 7	12.2	0.9
PLA/PHB 60/40	2466 ± 62	37 ± 5	8 ± 2	10.9	0.8

In particular, the elongation at break gradually increases with the PHB content and then it reaches a maximum at a 30 wt. % PHB content to which corresponded an increase in the ductility of 100% compared to neat PLA. As the content of PHB further increases up to 40 wt.%, the elongation at break drastically decreases and became lower than pure PLA, according to the fracture surfaces of the films which revealed a brittle deformation for this blend, as observed in the morphological analysis.

2.5 Barrier properties of films

Oxygen and water vapor barrier are among the most important issues to be considered for materials intended to be used in food packaging. Permeability coefficients to oxygen and water vapor of the films analyzed are reported in Table 3. In general, PHB has significantly higher barrier properties than neat PLA (Arrieta et al.,

2014). Indeed, an increase in the barrier properties to both oxygen and water vapor, increasing the PHB amount to PLA based blends can be observed. This behavior is related to the increased crystallinity content of blends compared to neat PLA and, in the case of water vapor, an increase in the hydrophobicity of the material.
As both elastic modulus and oxygen permeability are related to the crystallinity degree and to the mobility of the amorphous chain segments, it is possible to correlate these values (Russo et al., 2006). Thus, Figure 4 shows the experimental values of permeability as a function of the experimental values of the elastic modulus.

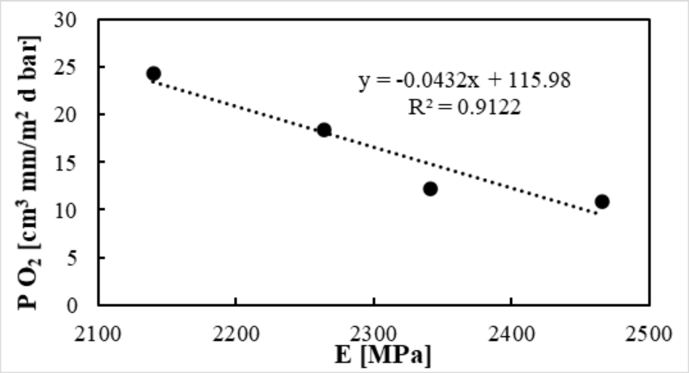

Figure 4: Relation between the experimental values of O_2 Permeability coefficient and the Elastic modulus.

These data follow a linear trend except from PLA/PHB 70/30 samples, which has a lower permeability coefficient compared to the trend line. This could be related to the morphology of this blend; in fact, the small finely dispersed aggregates, as reported in the morphological analysis, could enhance the path tortuosity for the oxygen molecules.

2.6 Optical properties

Transparency is an important physical property of packaging films, which provides see through property or prevents light transmission. PLA exhibited higher transmittance values at visible region (TR 560 nm = 89.7 %) compared to UV region (TR 280 nm = 82.3 %) and the light transmission of the blended systems decreased with the increase of PHB content in the blend (TR at 560 nm and 280 nm varied from 42.7 and 4.1 for PLA/PHB 80/20 to 24.1 and 1.0 for PLA/PHB 60/40). This is attributable to the crystallinity degree of the blends, which increased with the PHB content, therefore reducing the transparency of the films. The plot of the transparency at 560 nm versus the crystallinity degree of the films, calculated in the first heating scan, shows a linear trend with the transparency that decreases as the crystallinity degree of the films increases (Figure 5).

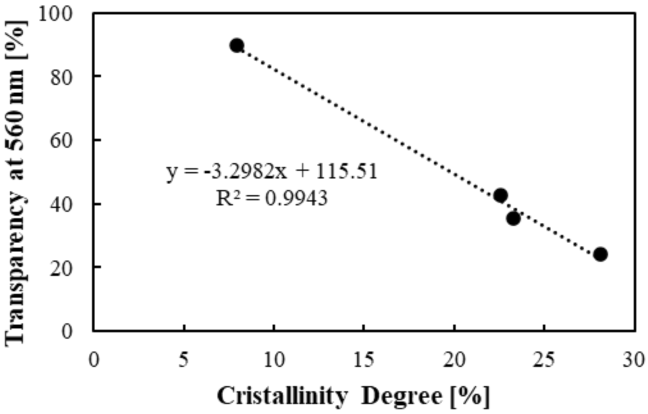

Figure 5: Transparency at 560 nm versus crystallinity degree of PLA/PHB films.

Moreover, the presence of PHB into the films reduced the transmission of UV light greater than the visible ones, and the UV screening ability of the films is a desirable property since it allows to prevent UV light-driven lipid oxidation and discoloration of the packed food stuff. Therefore, even though the addition of PHB led to a reduction of the transparency of the films in the visible light region, it provided protection against UV-light.

3. Conclusions

In this work, blown films for food packaging applications with improved performance based on PLA/PHB blends were developed and characterized. PLA/PHB blends, with content of PHB equal to 20, 30 and 40 wt.%, proved to be suitable for the film blowing process with improved processability compared to neat PLA. The blending with PHB enhanced the crystallization of PLA, increasing the elastic modulus of the blended systems and, up to a content of 30 wt. %, it also led to a significant increase in the elongation at break compared to neat PLA. Moreover, the addition of PHB improved the barrier properties to oxygen and water vapor of the films and reduced the transmission of UV light greater than the visible one, providing protection against UV-light. Linear correlation between the elastic modulus and the oxygen permeability and between the transparency and the crystallinity degree of the developed films were also found.

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