



**Bi-layer materials based on thermoplastic corn starch, polylactic acid and modified polypropylene**

**Materiales bicapas a base de almidón de maíz termoplástico, ácido poliláctico y polipropileno modificado**

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**Abstract**

Currently, the development of environmentally friendly materials with suitable properties for industrial use has become of great importance. In this work, bilayer materials were developed by assembling thermoplastic- corn starch monolayers (TPS) combined with semi-crystalline polylactic acid (PLA<sub>s</sub>) monolayers and maleic anhydride grafted polypropylene (PP<sub>MA</sub>). The presence of a potassium sorbate solution was evaluated as interface material. Structural properties (FTIR and SEM), interactions with water (water vapor transmission rate, solubility in water and moisture content) and biodegradation of the materials were evaluated. FTIR spectra showed that potassium sorbate promotes chemical interactions between TPS monolayers (-OH group) and PLA monolayers (C = O group) or PP<sub>MA</sub> (C-O-C, C-O, C-H groups). For their part, SEM micrographs reveal that when adding potassium sorbate, higher interfacial adhesion develops between TPS and PP<sub>MA</sub> than between TPS and PLA<sub>s</sub>. As for the interactions with water, when using a PLA or PP<sub>MA</sub> monolayer, due to its hydrophobic characteristics, the high permeability to water vapour and the sensitivity to liquid water that starch-based materials present would be avoided. Finally, the biodegradation test showed that TPS biodegrades faster than other materials, followed by PLA. The results obtained are interesting since the addition of an adhesive material to assemble the low chemical affinity monolayers would be avoided. The developed materials exhibit great potential for application as packaging in the food industry.

*Keywords:* Bilayer films, interfacial agent, physicochemical properties, biodegradation.

**Resumen**

En la actualidad ha cobrado gran importancia el desarrollo de materiales amigables con el medio ambiente y que tengan propiedades fisicoquímicas adecuadas para su uso industrial. En este trabajo se desarrollaron materiales bicapa mediante el ensamblaje de monocapas de almidón de maíz termoplástico (TPS) combinadas con monocapas de ácido poliláctico semicristalino (PLA<sub>s</sub>) y polipropileno agrafado con anhídrido maleico (PP<sub>MA</sub>). Como material de interfase se evaluó la presencia de una disolución de sorbato de potasio. Se evaluaron propiedades estructurales (FTIR y SEM), interacciones con el agua (tasa de transmisión del vapor de agua, solubilidad en agua y contenido de humedad) y biodegradación de los materiales. Los espectros FTIR mostraron que el sorbato potasio promueve interacciones químicas entre los monocapas de TPS (grupo -OH) y los monocapas de PLA<sub>s</sub> (grupo C=O) o PP<sub>MA</sub> (grupos C-O-C, C-O, C-H). Por su parte, las micrografías SEM revelan que, al adicionar sorbato de potasio, se desarrolla mayor adhesión interfacial entre TPS y PP<sub>MA</sub> que entre el TPS y PLA<sub>s</sub>. En cuanto a la interacciones con el agua, al usar un monocapa de PLA<sub>s</sub> o PP<sub>MA</sub>, por sus características hidrofóbicas, se evitaría la alta permeabilidad al vapor de agua y sensibilidad al agua líquida que presentan los materiales a base de almidón. Finalmente, la prueba de biodegradación mostró que el TPS se biodegrada a mayor velocidad que los demás materiales, seguido por el PLA<sub>s</sub>. Los resultados obtenidos son interesantes puesto que se evitaría la adición de un material adhesivo para ensamblar los monocapas de baja afinidad química. Los materiales desarrollados presentan gran potencial de aplicación como empaques en la industria de alimentos.

*Palabras clave:* Películas bicapa, agente interfacial, propiedades fisicoquímicas, biodegradación.

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## 1 Introduction

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In recent years, the development of studies focused on the design of materials that come from renewable sources has been a very active field due to the problems derived from the high environmental impact of plastics from oil (Rodríguez-Soto *et al.*, 2019; Piñeros-Guerrero *et al.*, 2020). As a result, an alternative to minimize this environmental problem is the study of biodegradable polymers. Starch is the most important polysaccharide that is used to develop biodegradable films because it can form a continuous matrix, and it is also an abundant renewable resource (Tampau *et al.*, 2020). However, starch has several disadvantages, one of them is its strong hydrophilicity and poor mechanical properties compared to conventional synthetic polymers, which make it insufficient for some applications such as packaging (Chen *et al.*, 2020). Mixing starch with more hydrophobic polymers is a widely studied strategy to improve starch film properties. Some aliphatic polyesters are biodegradable synthetic materials of a more hydrophobic nature that can be combined with starch in different ways to modulate the properties of films to improve their functionality (Collazo-Bigliardi *et al.*, 2019).

Incompatible biopolymer blends (hydrophilic and hydrophobic) generally do not lead to improvement of their individual properties. Therefore, the design of multilayer materials is convenient, where each layer retains its properties and complements the rest of the material. Currently, non-biodegradable multilayer films are already used in many food packages (Youssef and El-Sayed, 2018). These laminated films combine the properties of their starting materials into a single multilayer structure (Ortega-Toro *et al.*, 2015). Taking advantage of these premises, TPS multilayer films could be obtained in combination with hydrophobic polymers that would complement the excellent oxygen barrier properties of starch, the water vapor barrier properties, and structural properties of other polymers. Some examples of starch/ PCL multilayers, obtained by coextrusion, can already be found in bibliography (Takala *et al.*, 2013). Bilayer films are a type of film that consists in three parts, two layers and an adhesive to join these two layers. This is done in order to improve the mechanical, optical and barrier properties of the specific material or materials. Muller *et al.*, 2017 developed bilayer materials between TPS and PLA<sub>s</sub> in which starch exhibited a good oxygen barrier capacity

and PLA<sub>s</sub> a barrier against water vapor. Likewise, the study affirms that, although the mechanical resistance of PLA<sub>s</sub> is superior to that of starch, its combination could improve the mechanical behaviour of the film.

Biodegradable films and edible coatings that include antioxidant and antimicrobial agents in their formulation have also been extensively studied (Sivakanthan *et al.*, 2020). In most cases, these bioactive compounds are added using “wet methods”, such as casting (Cian *et al.*, 2014). Casting has the advantage that it is carried out at room temperature, so that bioactive compounds do not suffer any type of thermal degradation. However, “dry methods” should also be considered as a promising option, due to their greater efficiency and practicality. Among these processes are extrusion, injection moulding (injection compression moulding, lost-core process, gas-assisted injection moulding, coinjection moulding, two-shot injection moulding, thermoforming, blow moulding, rotational moulding (centrifugal casting) and foaming (Ortega-Toro *et al.*, 2018). One of the most interesting aspects of these dry methods is that they allow the processing of both conventional and biodegradable plastics. Furthermore, many researchers have evaluated substances such as potassium sorbate, ascorbic acid, chitosan and cinnamaldehyde, as important adhesive agents, since their components are compatible with thermoplastic starch and with different biopolymers (Ortega-Toro *et al.*, 2015). There are also studies which affirm that these components provide great benefits due to the particularity, these substances have antimicrobial and antioxidant properties, improving the material. It also can be used in applications such as food packaging, in the pharmaceutical area, among others. The objective of this work was to improve the properties of thermoplastic starch through the development of bilayer materials. Monolayers of corn thermoplastic starch were combined with monolayers of semi-crystalline polylactic acid (PLA<sub>s</sub>) and maleic anhydride grafted polypropylene (PP<sub>MA</sub>). Potassium sorbate (PS) was used as the interface material, which in turn confers antimicrobial properties.

## 2 Materials and methods

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### 2.1 Development of bilayer materials

Firstly, the corn starch monolayers were obtained by adding 25% glycerol and 50% water in relation to

the corn starch. Then, it was homogenized manually in a beaker and mixed in a double roller mixer at 160 °C and 8 rpm for 15 min. This mixture was conditioned for 3 days at a relative humidity of 53% using supersaturated magnesium chloride solutions. Subsequently, the thermoplastic starch films (TPS) were obtained in a hydraulic press where 4g of sample per film was used and moulded at 135 °C and 200 kg/cm<sup>2</sup> for 5 min and a cooling cycle of 2 min. The pure PLA<sub>s</sub> and PP<sub>MA</sub> monolayer films were obtained in the hydraulic press at 160 °C and 200 kg/cm<sup>2</sup> for 5 min and a cooling cycle of 2 min.

On the other hand, a potassium sorbate solution was prepared as the interface material. It was prepared in such a way that 1 mL of solution contains 0.1 g of compound/g of starch in the film. The bioactive compound concentration was 10% in relation to the starch contained in the films, based on previous studies (Ortega-Toro *et al.*, 2015).

Finally, the bilayer films were obtained by means of a second compression moulding process. To achieve greater adhesion and plasticization at the interface, 1 mL of potassium sorbate solution was sprayed on the starch-containing films, and then the pure PLA<sub>s</sub> and PP<sub>MA</sub> films were placed on the previous monolayer. Different temperature conditions were considered for each formulation (PP<sub>MA</sub> at 175 °C and PLAS at 160 °C). For all bilayer films, compression moulding at 150 °C and 150 kg/cm<sup>2</sup> for 4 min and a cooling cycle of 2 min were used. The formation of the bilayers was evaluated with the addition of potassium sorbate and with the addition of distilled water.

## 2.2 Material characterisation

### 2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy was used to analyse the interactions of the components in the films. These measurements were made using a Tensor 27 mid-FTIR Bruker spectrometer (Bruker, Karlsruhe, Germany) attached to a platinum ATR optical cell and RT-D1a TGS detector (Bruker, Karlsruhe, Germany). The diaphragm was adjusted to 4 mm for analysis, and the spectra were obtained between 4000 cm<sup>-1</sup> and 800 cm<sup>-1</sup> using a resolution of 4 cm<sup>-1</sup>. The analysis was carried out on both sides of the bilayer film. The data was analysed using the OPUS software (Bruker, Karlsruhe, Germany).

### 2.2.2 Scanning Electron Microscopy (SEM)

Images of the cross section of the bilayer films were obtained by means of a scanning microscope (JEOL, JSM-5410, Japan). The samples were conditioned in a desiccator with phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) one week before analysis. Subsequently, the samples were cryo-fractured with liquid nitrogen, coated with gold, and observed using an acceleration voltage of 10 kV.

### 2.2.3 Water vapour transmission rate (WVTR)

The water vapor transmission rate (WVTR) of the films was determined by means of a modification of the gravimetric method E96-95 (ASTM, 1995) proposed by McHugh *et al.*, 1993. Airtight containers of 5 cm height were used, in which 20 mL of distilled water were introduced, in order to expose the study face of the film to 100% RH. The containers were placed in a desiccator with a saturated solution of magnesium nitrate (53% RH) and this, in turn, was taken to a natural convection oven at 25 °C. The WVTR study was performed by weighing each container with an electronic scale at 2-hour intervals over a 24-hour period. In a first approach, the face of each of the pure polyesters and polyolefin was studied separately, followed by the thermoplastic starch monolayer films. Considering the above, WVTR values (g·h<sup>-1</sup>·ft<sup>-2</sup>) were obtained and studied for the bilayer films exposing only the most unfavourable face to 100% RH, carrying out each test in triplicate. The rate of water vapor transmission with the slopes of the period in the steady state of the weight loss curves as a function of time was calculated.

### 2.2.4 Water absorption

Water absorption of the films was determined according to the D570-98 standard (ASTM, 2010) and the methodology described in previous studies by Ortega-Toro *et al.*, 2015. Samples with dimensions of 76.2 mm long and 25.4 mm wide were cut according to the standard, then, they were dried in an oven at 50 °C for 24 hours to remove the water contained in the films, after this time they were weighed immediately. The fragments of each of the samples were placed in crystalline containers, distilled water was added in a film: water ratio of 1:10 (w/w) and they were subsequently stored in an oven at a temperature of 23 °C for 24h and weighed again. The water solubility of the film was estimated from the initial and final weight difference related to the weight of the dry film. The test was done in triplicate.

### 2.2.5 Moisture content ( $X_p$ )

The films were conditioned at 25 °C and 53% RH for 2 weeks, placed in an oven at 50 °C for 24h, and then stored in a desiccator with phosphorous pentoxide ( $P_2O_5$ ) for 16 days at 25 °C. The initial and final weight of the sample was recorded, being the difference, the amount of water absorbed during the storage period, the results were expressed on a dry basis and three repetitions per formulation were considered.

### 2.2.6 Biodegradation tests

The biodegradability of bilayer films was studied using the respirometry technique employing HANDHELD GAS ANALYSE (PBI Dansensor) which is designed to detect extremely low levels of oxygen consumption and  $CO_2$  production. It was studied at a temperature of 25 °C according to standard D5338-98 (ASTM, 2003) and D5988 (ASTM, 1999). The water content of the soil was around 60% by weight and a pH of 9.38. Each material was placed in a bottle with dimensions of 2 cm in diameter and 4.5 cm in height. Subsequently, 1 g of compost per bottle was placed, the analysis was carried out for 45 days in an aerobic and controlled composting environment. The sample dimensions were approximately  $1 \times 1 \text{ cm}^2$ . After this time, the samples were recovered from the compost, later washed with distilled water, and dried in an oven at 50 °C, and finally they were weighed to know the percentage of weight loss for each material (Mathew *et al.*, 2005).

### 2.2.7 Statistical analysis

Statgraphics Centurion XVI software was used to perform the statistical analyses of the results by means

of analysis of variance (ANOVA). Fisher's Least Significant Difference (LSD) procedure was used at the 95% confidence level.

## 3 Results and discussion

### 3.1 Structural properties

Table 1 shows the wavelengths of the most characteristic FTIR peaks for the monolayers and bilayers studied. The FTIR of the bilayers were made on both sides and remarkable differences were found only when the  $PLA_s$  or  $PPMA$  face reading was taken. Therefore, the FTIR of these faces is reported. The dominant peak that identifies  $PLA_s$  is the carbonyl group at  $1747.2 \text{ cm}^{-1}$  and for  $PPMA$  the most important peaks occur in the  $CH_3$  o  $CH_2$  methyl groups at  $2917.8 \text{ cm}^{-1}$  (Muller *et al.*, 2017). In the  $PLA_s/TPS$  bilayers it is observed that there are changes in the wavelengths of the carbonyl group ( $C=O$ ) and the hydroxyl group ( $-OH$ ) with respect to the monolayers. These changes are more visible when potassium sorbate is added as a coupling agent, especially for the hydroxyl group. This would indicate interaction at the interface of the two layers promoted by potassium sorbate. In the case of  $PPMA/TPS$  bilayers, significant changes in the wavelengths of the  $C-O-C$ ,  $C-O$ ,  $C-H$  and  $-OH$  groups are observed, indicating strong interactions at the interface of the polymers. The peak at  $1651.9 \text{ cm}^{-1}$  corresponding to  $C=O$  would be present in the bilayers when SP is added, which was to be expected since it is characteristic of the material. Similar interactions have been reported in previous studies for TPS and polycaprolactone bilayers with potassium sorbate at the interface (Ortega-Toro *et al.*, 2015).

Table 1. Wavelengths ( $\text{cm}^{-1}$ ) of the most relevant peaks obtained by FTIR-ATR of the monolayer and bilayer films studied.

Formulations	C-O-C	C-O	C=O	C-H	-OH
	(1090-900)	(1330-1090)	(1790-1650)	(2960-2850)	(3650-3200)
$PLA_s$	1078.9	1180.7	1747.2	2944.9	3507.7
$PPMA$	973.1	1166.6	---	2917.8	---
TPS	994.4	1240.6	---	2924.2	3274.6
$PLA_s/TPS$ with PS	1080.1	1181.1	1748.1	2947.5	3503
$PLA_s/TPS$ without PS	1080.6	1181.3	1747.4	2947.6	3488.7
$PPMA/TPS$ with PS	1044.6	1260.4	1651.9	2917.9	3376.7
$PPMA/TPS$ without PS	1045.16	1255.6	---	2951.8	3371.6

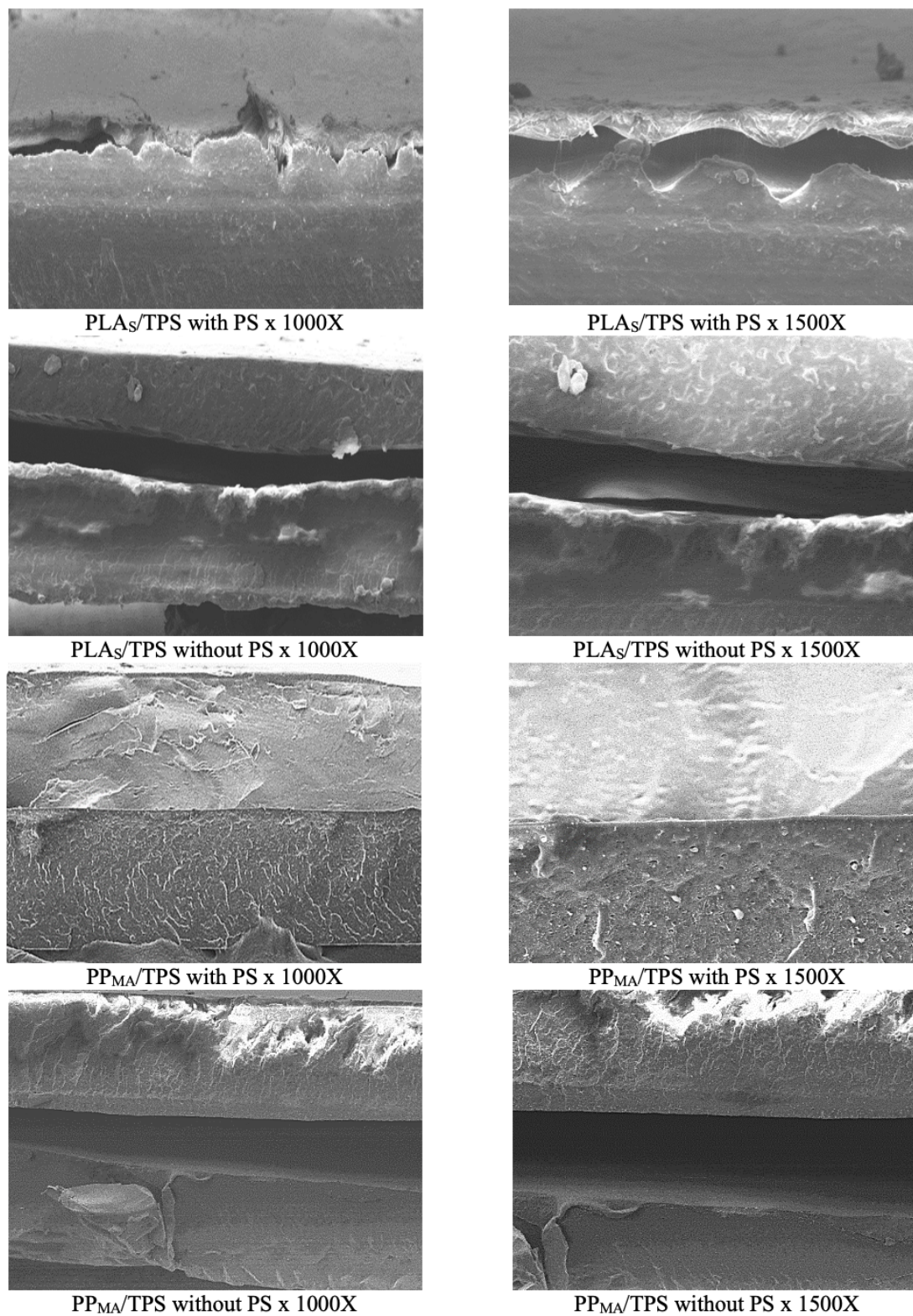


Fig. 1. Cross-section SEM micrographs of the bilayer films studied with and without potassium sorbate.

Figure 1 shows the cross-section SEM micrographs of the bilayer films studied. In all micrographs, the TPS monolayer can be differentiated from the other polymers because it presents deformations in the cryofracture, PLA<sub>s</sub> and PP<sub>MA</sub> are fractured in a cleaner way and exhibit smoother-looking cross sections. Significant differences between the different treatments are observed. Firstly, the chemical compatibility between TSP and PLA<sub>s</sub> and TPS and PP<sub>MA</sub> is low, this can be observed in the micrographs of the materials that do not contain potassium sorbate. Secondly, the addition of potassium sorbate at the interface improves the adhesion between both polymers, especially in the case of the bilayer formed between TPS and PP<sub>MA</sub>. The above, is in line with the strong interactions of some chemical groups observed by FTIR. It is possible that potassium sorbate acts as a destructuring agent for PLA<sub>s</sub> and PP<sub>MA</sub>, generating partial depolymerization of these polymers, thus increasing the number of chain terminations and therefore the possibilities of interacting with TPS (Ortega *et al.*, 2015). On the other hand, it is necessary to consider that polypropylene, when grafted with maleic anhydride, would have polar groups in its structure capable of interacting with the hydroxyl groups of starch (Ortega-Toro *et al.*, 2016).

### 3.2 Interaction with water

Table 2 shows the rate of transmission to water vapor, water solubility and moisture content of the monolayers and bilayers studied. The water vapor barrier properties show significant differences between

the TPS monolayers and those of the PLA<sub>s</sub> and PP<sub>MA</sub> monolayers, this due to the hydrophilic nature of the carbohydrate, unlike the hydrophobic nature of polyester and polyolefin. There are no significant differences between the PLA<sub>s</sub> and PP<sub>MA</sub> bilayers and monolayers, although slightly lower values are observed in the materials with PP<sub>MA</sub>. This result was expected since in the bilayers the barrier properties are defined by the least permeable material. On the other hand, the addition of potassium sorbate to the interface did not affect this parameter. Regarding the solubility in water, it is observed that the TPS monolayer has the highest solubility, while the solubility of PLA<sub>s</sub> and PP<sub>MA</sub> tend to be nil. Regarding bilayers, low solubility values are recorded, with the TPS monolayer being the most affected. Furthermore, it is observed that the addition of potassium sorbate significantly increases the solubility (in the case of PLA<sub>s</sub>). This may be due to a depolymerizing effect of sorbate on the polylactic acid molecule, as observed in previous studies (Ortega-Toro *et al.*, 2015). In relation to the moisture content, it is observed that the TPS monolayers have higher values compared to the other monolayers. The moisture content of the bilayers presented great similarity, although a significant effect is observed between treatments with and without potassium sorbate at the interface. When potassium sorbate is added, lower values are obtained, this because the interfacial agent promotes adhesion between the layers, generating more compact matrices and with less free space where moisture can be absorbed. Agreeing with that observed in SEM cross-section micrographs.

Table 2. Average values and standard deviation of water vapour transmission rate (WVTR, (g·h<sup>-1</sup>·ft<sup>-2</sup>)), water solubility (g dissolved film / g dry film) and moisture content (g water / g dry film) of the studied films conditioned at 53% humidity.

Formulations	WVTR	Water solubility	Moisture content
PLA <sub>s</sub>	0.19 ± 0.09 <sup>b</sup>	0.0008 ± 0.0002 <sup>d</sup>	0.0024 ± 0.0008 <sup>c</sup>
PP <sub>MA</sub>	0.13 ± 0.05 <sup>b</sup>	0.0000 ± 0.0000 <sup>d</sup>	0.0016 ± 0.0006 <sup>c</sup>
TPS	1.8 ± 0.3 <sup>a</sup>	0.228 ± 0.004 <sup>a</sup>	0.062 ± 0.003 <sup>a</sup>
PLA <sub>s</sub> /TPS with PS	0.19 ± 0.07 <sup>b</sup>	0.147 ± 0.019 <sup>b</sup>	0.052 ± 0.006 <sup>b</sup>
PLA <sub>s</sub> /TPS without PS	0.19 ± 0.09 <sup>b</sup>	0.107 ± 0.008 <sup>c</sup>	0.0560 ± 0.0012 <sup>ab</sup>
PP <sub>MA</sub> /TPS with PS	0.14 ± 0.09 <sup>b</sup>	0.100 ± 0.010 <sup>c</sup>	0.0445 ± 0.00 <sup>b</sup>
PP <sub>MA</sub> /TPS without PS	0.13 ± 0.05 <sup>b</sup>	0.095 ± 0.003 <sup>c</sup>	0.0558 ± 0.0017 <sup>ab</sup>

Different superscripts within the same column indicate significant differences between formulations (p < 0.05)

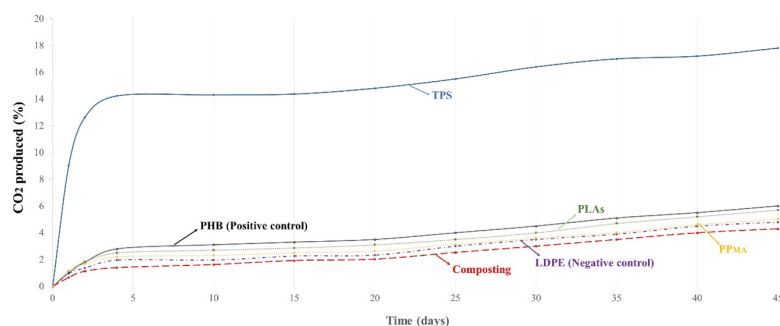


Fig. 2. Biodegradation of the polymers studied, polyhydroxy butyrate (PHB), low density polyethylene (LDPE) and composting material.

### 3.3 Biodegradation assays

Figure 2 shows the production of CO<sub>2</sub> by aerobic biodegradation during 45 days in composting at 25 °C, pH of 9.39 and humidity percentage of 56%. Low density polyethylene (LDPE) was used as a negative control and polyhydroxy butyrate (PHB) as a positive control. As expected, corn starch TPS produces a greater amount of CO<sub>2</sub> than the rest of the studied materials due to its natural origin and because its bonds are hydrolysed more easily. The next polymers to degrade are PHB, followed by PLA<sub>s</sub>. CO<sub>2</sub> production is attributed to the high carbon content of these polymers and to the hydrolysable bonds under composting conditions, allowing microorganisms in the environment to degrade them more easily (Mahendraker and Viraraghavan, 1995; Emadian *et al.*, 2017). On the other hand, it is observed that PP<sub>MA</sub> and LDPE present little significant changes in terms of CO<sub>2</sub> production, because these polymers do not degrade under composting conditions, being similar to composting curves without adding materials. Regarding the loss of weight of the materials, it was found that, at the end of the 45 days of the test, the TPS lost 100% of its weight since no fraction of the material could be recovered, the PHB and PLA<sub>s</sub> lost nearly 90% and 85% of its weight. And finally, PP<sub>MA</sub> and LDPE did not register significant weight loss.

## Conclusions

Bilayer materials were obtained by assembling thermoplastic corn starch monolayers combined with PLA<sub>s</sub> and PP<sub>MA</sub> monolayers. As interface material for bonding the layers, the presence of a potassium sorbate

solution was evaluated. Remarkable changes in the hydroxyl groups of TPS and carbonyl of PLA<sub>s</sub> were observed in the FTIR test, especially when potassium sorbate is added at the interface. Indicating that potassium sorbate promotes the molecular interactions between TPS and PLA<sub>s</sub> as it similarly occurs in the case of PP<sub>MA</sub>. The improvement in the interface of the materials is reflected in the SEM micrographs, where it is evident that the presence of potassium sorbate promotes adhesion between the layers. This result is interesting since the addition of an adhesive material to assemble the monolayers would be avoided. Regarding the permeability to water vapor, it is observed that the PLA<sub>s</sub> or PP<sub>MA</sub> layer limits the transport between the material. The solubility in water showed that when adding potassium sorbate, a two-layer weight loss was generated with PLA<sub>s</sub>, showing a destructuring effect of potassium sorbate on this material. Finally, in the biodegradation test, the ease of degradation of TPS was verified in comparison with the other evaluated materials. The materials studied in this work have high application in the food industry since when combining a TPS layer with layers of hydrophobic materials, the barrier properties are complemented. This material could be useful for products with low moisture content such as flour, cereal grains, and cookies. Also, inorganic adhesives would be avoided because of the potassium sorbate was used as an agent of the interface.

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