



Effect of potassium sorbate as an interface agent in biodegradable bi-layers polymers
Efecto de sorbato de potasio como agente de interfase en bicapas a base de polímeros biodegradables

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Abstract

Studies that are focused on the design and development of biodegradable materials with promising physicochemical properties for industrial use have been of great importance. In this research, bilayer materials were developed using thermoplastic starch (TPS) monolayers assembled with monolayers sheets of amorphous polylactic acid (PLA_a) and polycaprolactone (PCL). Potassium sorbate was evaluated as an interfacial adhesion material. Structural properties of the laminated materials (FTIR and SEM), behaviour with water (rate of water vapour transmission, solubility in water and moisture content) and biodegradation of the materials were evaluated. Potassium sorbate was found to act as a promising interface agent by increasing adhesion between polymer layers (SEM). The FTIR showed marked changes in the bands of the hydroxyl and carbonyl groups. Due to PLA_a and PCL's hydrophobic character, all bilayers showed excellent barrier properties against water vapor. Finally, the bilayers that degrade the fastest are PCL/TPS. These laminated materials are a great alternative to the decrease in the use of conventional plastics and are applicable as packaging in the food industry.

Keywords: Bilayer sheets, interfacial agent, physicochemical properties, biodegradation.

Resumen

Estudios enfocados en el diseño y desarrollo de materiales biodegradables con propiedades fisicoquímicas prometedoras para su uso industrial han sido de gran importancia. En esta investigación se desarrollaron materiales bicapa mediante monocapas de almidón termoplástico (TPS) ensambladas con monocapas de ácido poliláctico amorfo (PLA_a) y policaprolactona (PCL). El sorbato de potasio se evaluó como material de adherencia interfacial. Se evaluaron propiedades estructurales de los materiales laminados (FTIR y SEM), comportamientos con el agua (tasa de transmisión del vapor de agua, solubilidad en agua y contenido de humedad) y biodegradación del material. Se encontró que el sorbato de potasio actúa como un agente de interfaz prometedor al aumentar la adhesión entre las capas de polímero (SEM). El FTIR mostró cambios marcados en las bandas de los grupos hidroxilo y carbonilo. Debido al carácter hidrófobo de PLA_a y PCL, todas las bicapas mostraron excelentes propiedades de barrera contra el vapor de agua. Finalmente, las bicapas que se degradan más rápido son PCL/TPS. Estos materiales laminados presentan un gran potencial para el remplazo de plásticos de uso habitual y su aplicación como empaques en la industria de alimentos.

Palabras clave: Láminas bicapa, agente interfacial, propiedades fisicoquímicas, biodegradación.

1 Introduction

Currently, some of the existing environmental problems are strongly linked to the production of

non-biodegradable plastics. These problems have generated the necessity to study new alternatives to decrease the production of these contaminating plastics.

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Among these alternatives, the development of biodegradable materials based on natural renewable sources has been of great importance (Chotiprayon *et al.*, 2020; W. Liu *et al.*, 2020; Piñeros-Guerrero *et al.*, 2020; Xia *et al.*, 2016). Regarding biodegradable polymers, starch is considered one of the most promising raw materials in the production of biodegradable plastics, due to its high availability, low cost and excellent degradability (Chotiprayon *et al.*, 2020; Ortega-Toro *et al.*, 2015). However, the intermolecular and intramolecular hydrogen bonds in the starch macromolecules create difficulties in the processing of the starch, since it degrades before reaching the melting temperature (W. Liu *et al.*, 2020). This event is commonly solved by using plasticizers, which promotes the gelatinization of the starch, releasing the content of amylose and amylopectin (Collazo-Bigliardi *et al.*, 2019). Among the most widely used plasticizers are polyhydric alcohols, such as glycerol, sorbitol, xylitol and ethylene (Kahvand & Fasihi, 2019; Masina *et al.*, 2017). Glycerol is one of the most commonly used plasticizers in the development of starch-based materials, due to its colourless, odourless, non-toxic properties and its low cost (Ivanič *et al.*, 2019). However, the addition of plasticizers in high proportions generates TPS with significantly reduced mechanical properties and increased sensitivity to humidity and ageing (Dang *et al.*, 2015; C. Liu *et al.*, 2016). To improve these weak properties, blending with second-generation polymers has been studied, as it is an effective alternative to obtain materials with better characteristics. Polymers such as polycaprolactone (PCL), polyvinyl alcohol (PVA), aliphatic polyesters (poly(tetramethylene succinate) and poly(ethylene succinate)), polylactic acid (PLA), polyhydroxyalkanoates (PHAs) and cellulose are used to improve the properties of the starch-based plastics (Zhong *et al.*, 2020). In particular, PLA is a bio-based, biodegradable thermoplastic obtained from renewable agricultural sources to produce lactic acid. PLA is also known to have attractive and comparable mechanical properties with commodity polymers such as polyethylene (PE) and polypropylene (PP). It has Young's modulus of approx. 3-GPa, tensile strength 50-70 MPa, elongation at the breakpoint is about 4% (Tobi Adesina *et al.*, 2020). On the other hand, PCL is a semi-crystalline biodegradable polymer commonly used in many applications such as tissue engineering, drug delivery systems, food packaging, and shape memory biomaterials. This polymer generally comes from fossil sources and is characterized by a high

deformation capacity (greater than 100%) (Emre Bulbul *et al.*, 2020). Blending thermoplastic starch with other hydrophobic degradable polymers (i.e. PLA or PCL) can reduce the water's affinity and significantly improve other film properties (Wei *et al.*, 2015; Zhong *et al.*, 2020).

The combination of thermoplastic starch and aliphatic polyesters is of great interest, as it could lead to the development of a new range of biodegradable polymer matrices. To improve the individual properties of each polymer, the design of multilayer laminated materials is convenient, where each sheet retains its properties and integrates the other polymer into an interface. Multilayer materials are defined as those made up of two or more layers of different material; generally, they are assembled with adhesives between the layers. Industrially they are produced by co-extrusion or compression moulding. These laminated materials associate the starting properties of each polymer in a single multilayer structure. Some researchers have developed multilayers of TPS / PLA containing cinnamaldehyde at the interface (Muller *et al.*, 2017), TPS / polypropylene with potassium sorbate at the interface (Díaz-Pedraza *et al.*, 2020) and TPS / chitosan with essential oils as interface material (Valencia-Sullca *et al.*, 2018). However, aliphatic polyesters and natural hydrophilic polymers are immiscible, leading to poor adhesion between polymer components. The use of different compatibilizers and additives to improve interfacial adhesion has been extensively studied (Diani *et al.*, 2006; Fabra *et al.*, 2013). The key to obtaining a quality multilayer laminated material is to get sufficient adhesion at the interface to avoid the detachment of the layers. Adhesion materials such as potassium sorbate, ascorbic acid, chitosan and cinnamaldehyde have been used in different studies to improve the affinity between layers. These bonding materials can enhance and create bonds between the two layers, improving bonding at the interface. Furthermore, they can provide antimicrobial and antioxidant properties (Ortega-Toro *et al.*, 2015; Valencia-Sullca *et al.*, 2018). In different studies, it has been observed that potassium sorbate improves the processability of polymer blends, confers antimicrobial properties, acts as a plasticizer, and can promote the decrease of the water vapour permeability. It is recommended to use potassium sorbate in concentrations less than 3% concerning the weight of the polymer since it could recrystallize (Sousa *et al.*, 2013; 2016; Kowalczyk *et al.*, 2020). This study aims to obtain multilayer

laminated materials based on TPS assembled with PLA_a sheets or PCL sheets and to evaluate the effect of potassium sorbate (PS) as an interfacial agent.

2 Materials and methods

2.1 Materials

Corn starch (amylose 18.2% and amylopectin 81.8%) was purchased from the local market in Bogotá D.C. (Colombia); PLA (LL700, with a density of 1.25 g/cm³) was supplied by NatureWorks (U.S.A). Sigma-Aldrich supplied PCL (average Mn 80.000). Glycerol, used as plasticizer of TPS, and other reagents were provided by Sigma-Aldrich and Panreac (Bogotá-Colombia).

2.2 Development of bilayer materials

Dry corn starch was mixed in 25% w/w of glycerol concerning the starch and 50% w/w of water about the starch. Subsequently, the mixture was homogenized manually and mixed in a double roller mixer at 160 °C and 8 rpm for 15 min. The resulting paste was ground and conditioned at 53% R.H. for three days in a desiccator. Consecutively, the TPS sheets were moulded in a hydraulic press (Marshal, Darteno Industries, Gujarat, India), 4 g of sample per film were used at moulding conditions of 135 °C and 200kg/cm² for 5 minutes and a cooling cycle of 2 minutes. Potassium sorbate was prepared in such a way that 1 mL of solution contained 0.1 g of the compound for each g of starch (Ortega-Toro *et al.*, 2015).

At last, the multilayer sheets were obtained in a second compression moulding. Subsequently, TPS sheets were wetted with 1 mL of potassium sorbate solution to achieve higher adhesion and at the interface. Afterwards, the PCL or PLA sheets were located on the surface of the wet TPS sheet. The multilayer sheets were moulded at 150 kg/cm² for 4 minutes and a cooling cycle of 2 minutes. The properties of the bilayer materials were evaluated with the addition of potassium sorbate and with the addition of distilled water as interfacial agents.

2.3 Material characterisation

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy was used to assess the presence of existing functional groups in each of the sheets. These measurements were made using a spectrometer Bruker Tensor 27 mid-FTIR (Bruker, Karlsruhe, Germany) connected to an ATR platinum optical cell and an RT-D1a TGS detector (Bruker, Karlsruhe, Germany). The diaphragm was adjusted to 4 mm for analysis, and the spectra were obtained between 4000 cm⁻¹ and 800 cm⁻¹ using a resolution of 4 cm⁻¹. The study was carried out on both sides of the bilayer sheet. The data was analysed using OPUS software (Bruker, Karlsruhe, Germany).

2.3.2 Scanning Electron Microscopy (SEM)

Cross-sectional images of the bilayer sheets were analysed using a scanning electron microscope (JEOL, JSM-5410, Japan). Phosphorous pentoxide (P₂O₅) was used to condition the samples at 0% R.H. The bilayer sheets were fractured with liquid nitrogen, gold-coated and observed using an acceleration voltage of 10 kV.

2.3.3 Water Vapor Transmission Rate (WVTR)

The water vapour transmission rate (WVTR) is one of the most critical parameters for laminated polymeric materials and is often measured in quality control and to identify its suitability for use as packaging materials (Sängerlaub *et al.*, 2018). The water vapour transmission rate (WVTR) of the laminated materials was analysed by modifying the gravimetric method E96-95 (ASTM, 1995) proposed by McHugh *et al.*, 1993. Airtight containers were used, 20 mL of distilled water was added to expose 100% RH to one side of the material studied. The containers were placed in a desiccator with a saturated solution of magnesium nitrate (53% RH) and this, in turn, was conditioned at 25°C in a forced convection oven. The containers were weighed separately in 2-hour intervals over 24 hours. The analysis was performed independently, the face pure PLA or PCL and followed by the sheets of the thermoplastic starch (monolayer). According to the WVTR (g·h⁻¹·ft⁻²) values of the individual sheets, the most unfavourable bilayer side of the sheets was exposed to 100% RH, carrying out tests in triplicate. The water vapour transmission rate (WVTR) was

calculated with the slopes of the period in the steady-state of the weight loss crows as a function of time.

2.3.4 Water absorption

The laminated materials were cut with dimensions of 76.2 mm long and 25.4 mm wide. Subsequently, they were dried in an oven at 50 °C for 24 hours to remove the water contained in each sheet, after which time they were weighed immediately. The specimens of each laminated material were placed in Petri dishes, distilled water was added in a water ratio 1/10 (w/w). Finally, they were stored in an oven at 23°C for 24 hours, after which time had elapsed again, they weighed. The water absorption of the sheets was determined according to the D570-98 standard (ASTM, 2010) and the methodology described in previous studies by Ortega-Toro *et al.*, 2015. The water solubility of the sheets was estimated at from the initial and final weight difference related to the weight of the dry material.

2.3.5 Biodegradation tests

The laminated materials with dimensions of 1 cm² were placed in an airtight container with dimensions of 2 cm in diameter and 4.5 cm in height. Subsequently, 1 g of compost was used in each vessel; the analysis was carried out for 45 days in a controlled aerobic composting environment. The compost presented 60% by weight of water content and a pH of 9.38. After, the sheets were extracted from the compost, washed with distilled water, and dried in an oven at 50°C. Finally, they were weighed to know the percentage of weight loss of each laminated material (Mathew *et al.*, 2005). The biodegradability was analysed according to the respirometry technique, for this was used a Handheld Gas Analyse (PBI Dansensor), designed to

detect insufficient levels of O₂ consumption and CO₂ generation. During this procedure, a temperature of 25 °C was used according to the D5338-98 (ASTM, 2003) and D5988 (ASTM, 1999) standard. The films were conditioned at 53% relative humidity and 25 °C for one week before each determination.

2.4 Statistical analysis

The statistical analysis was carried out through analysis of variance (ANOVA) using the Statgraphics Centurion XVI software. Fisher's Least Significant Difference (LSD) procedure was used at the 95% confidence level.

3 Results and discussion

3.1 Structural properties

The wavelengths of the characteristic FTIR peaks for the sheets can be seen in Table 1. The typical peak for the pure polymers (PLA_a and PCL) is the carbonyl group at 1747.2 cm⁻¹ (Muller *et al.*, 2017). The FTIR wavelength for the bilayer sheets was analysed on both sides; significant differences were found when reading the PLA_a and PCL. The PLA_a/TPS and PCL/TPS bilayer sheets had changes in the wavelengths of the carbonyl group (C=O) (for PLA and PCL) and the hydroxyl group (-OH) (for TPS) due to the addition of potassium sorbate. In this case, potassium sorbate acts as an agent that improves adhesion between polymer layers. Possibly potassium sorbate promotes the breaking of the PLA and PCL chains, generating terminations with -OH groups, which would interact with the -OH of TPS.

Table 1. Wavelengths (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 _a	1042.3	1181.4	1745.8	2945.5	- - -
PCL	961.3	1160.8	1720.6	2943.3	3444.3
TPS	994.4	1240.6	- - -	2924.2	3274.6
PLA _a /TPS with PS	1039.9	1261.3	1746	2945.3	3317.6
PLA _a /TPS without PS	1077.5	1266.9	1745.9	2944.9	3488.2
PCL/TPS with PS	1045.4	1240.3	1721.6	2943.4	3384.6
PCL/TPS without PS	1045.1	1240.1	1721.9	2943.6	3453.2

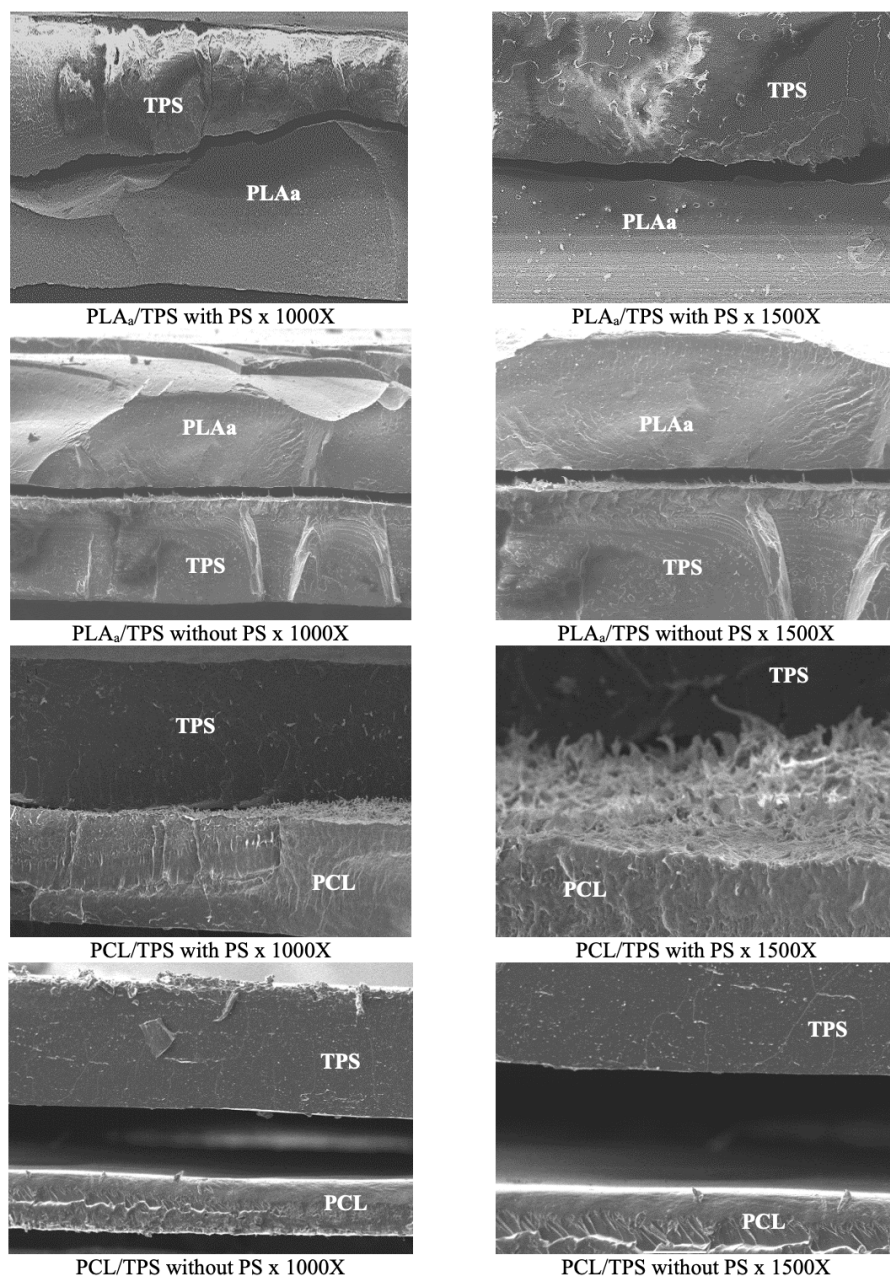


Fig. 1. Cross-section SEM micrographs of the bilayer films studied with and without potassium sorbate.

In general, for bilayer sheets, characteristic changes in wavelengths are observed in the C–O–C, C–O, C–H and –OH groups, promoted by the interactions between the two monolayer sheets. Similar interactions have been reported in previous studies for TPS and polycaprolactone bilayers with potassium sorbate at the interface (Ortega-Toro *et al.*, 2015; Díaz-Pedraza *et al.*, 2020).

Figure 1 shows the SEM micrographs of the cross-section of the bilayer sheets in the study. In micrographs of PCL sheets, they fracture more cleanly and exhibit smoother cross-sections compared to PLA sheets. In the two treatments, significant differences are observed in the interface. The compatibility and miscibility of PLA_a and TPS are low. This fact can be seen in the micrographs that do not

contain potassium sorbate. The immiscibility can be attributed to the low interfacial tension between the hydrophilic surface of TPS and the hydrophobic surface of PLA. The PCL/TPS bilayer sheets show junction points at the interface of both polymers, constituted by the interpenetration of “fibrils” of the PCL towards the starch layer. Probably, the addition of potassium sorbate favoured the adhesion between the two sheets. Previous studies (Ortega-Toro *et al.*, 2015) showed a small degree of PCL miscibility in TPS by decreasing the glass transition temperature of starch when PCL is added. Also, the interactions of some functional groups observed by FTIR may be associated. Potassium sorbate may have acted as a destructuring agent for PLA_a and PCL, generating partial depolymerization of these polymers, thus increasing the number of chain terminations and, therefore, increasing the possibilities of interacting with TPS (Ortega-Toro *et al.*, 2015). Other researchers have used potassium sorbate to improve blends between rice flour/ poly (butylene adipate co-terephthalate) (Sousa *et al.*, 2013; 2016), and pullulan/gelatine (Kowalczyk *et al.*, 2020).

3.2 Interaction with water

Table 2 shows the water vapour transmission rate, the solubility in water and the moisture content of each sheet. The water vapour transmission rate shows significant differences between the TPS, PLA_a and PCL monolayer sheets, due to the hydrophilic nature of the starch and the hydrophobic nature of the polymers. Significant differences between the monolayer and bilayer sheets of PLA_a and PCL are evident (Ortega-Toro *et al.*, 2015; Díaz-Pedraza *et al.*, 2020). The two-layer PCL/TPS sheets had

a lower transmission rate to water vapour. There are no significant differences between the bilayer sheets of PLA_a and PCL, although slightly low values are present in materials with PLA_a. These results are as expected since the permeability of the hydrophobic polymer defines the barrier properties of the bilayer material. Similar results was reported by TPS/PLA bilayers (Muller, González-Martínez, & Chiralt, 2017), TPS/ grafted polypropylene (Díaz-Pedraza *et al.*, 2020) and TPS/chitosan bilayers (Valencia-Sullca *et al.*, 2018). On the other hand, the added potassium sorbate does not seem to affect this parameter.

The water solubility of each of the sheets was studied. It is observed that the TPS monolayer presented a higher solubility, for the PLA_a and PCL polymers the solubility is low. The PCL/TPS bilayer sheets had lower solubility compared to the PLA_a/TPS bilayer materials. Furthermore, it is observed that the addition of potassium sorbate significantly increases the solubility of PLA_a/TPS.

This fact may be related to the depolymerizing effect of potassium sorbate on the polylactic acid molecule, as observed in previous research (Ortega-Toro *et al.*, 2015). This result can also be explained by a possible increase in the plasticization of the material due to potassium sorbate (Souza *et al.*, 2013; 2016). The moisture content for monolayer sheets increases with the addition of polymer in its polymer matrix, compared to TPS. No significant differences were observed between the bilayer sheets, although it is evident that the values for the PLA_a/TPS sheets have a lower moisture content. The addition of potassium sorbate increases the moisture content in the bilayer sheets.

Table 2. Average values and standard deviation of water vapour transmission rate (WVTR, (g·h⁻¹·ft⁻²)), 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 _a	0.3 ± 0.9 ^b	0.0006 ± 0.0002 ^c	0.0035 ± 0.0011 ^c
PCL	0.2 ± 0.1 ^b	0.0018 ± 0.0002 ^c	0.0019 ± 0.0012 ^b
TPS	1.8 ± 0.3 ^a	0.228 ± 0.004 ^a	0.062 ± 0.003 ^a
PLA _a /TPS with PS	0.13 ± 0.01 ^c	0.263 ± 0.008 ^a	0.0573 ± 0.0009 ^a
PLA _a /TPS without PS	0.14 ± 0.06 ^c	0.252 ± 0.012 ^a	0.0462 ± 0.0021 ^a
PCL/TPS with PS	0.15 ± 0.09 ^c	0.128 ± 0.024 ^b	0.0592 ± 0.0024 ^a
PCL/TPS without PS	0.15 ± 0.03 ^c	0.127 ± 0.008 ^b	0.0552 ± 0.0002 ^a

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

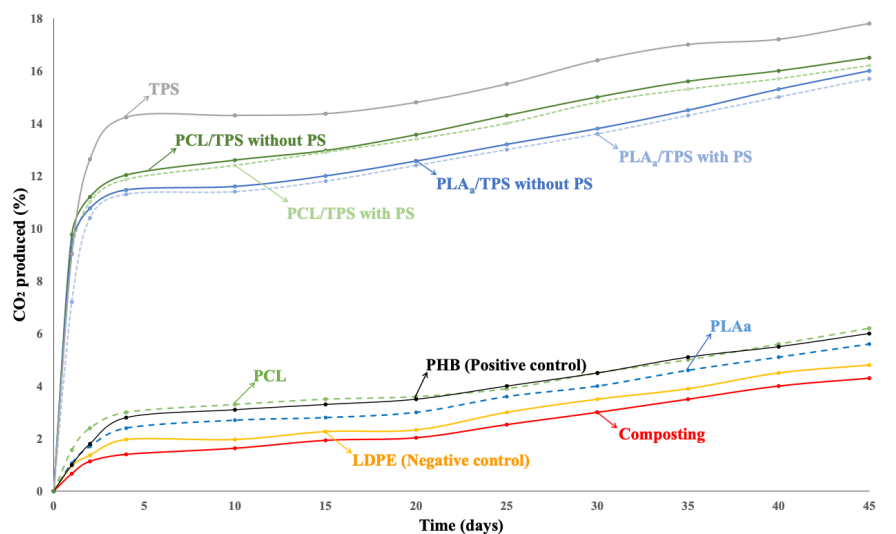


Fig. 2. Biodegradation of the polymers studied, polyhydroxy butyrate (PHB), low density polyethylene (LDPE) and composting material.

3.3 Biodegradation assays

Figure 2 shows the generation of CO₂ 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. The TPS produces a higher amount of CO₂ compared to the different sheets under study since its bonds are easily hydrolysed. The generation of CO₂ is attributed to the carbon content of these polymers and the hydrolysable bonds in composting conditions. This situation allows the degradation of the material by microorganisms in the environment (Mahendrakar y Viraraghavan, 1995; Emadian *et al.*, 2017). There are no significant differences in the degradation of the monolayer laminated material concerning the bilayers since it exhibits the same behaviour. It is observed that the PCL and PHB do not present significant changes in terms of CO₂ production. Significant differences in the production of PLA_a concerning PCL and PHB are evidenced. This fact demonstrates that the degradation of the material depends on its synthesis and characteristics. LDPE exhibits low degradation compared to degradable materials under composting conditions. The bilayer sheets reduce CO₂ generation by aerobic biodegradation compared to TPS, where significant differences are evident. The PCL/TPS bilayers have a higher CO₂ generation, obtaining a higher degradation rate than the PLA_a/TPS bilayers. There is no significant effect of potassium sorbate on

the evaluation of this parameter. After 45 days, the weight loss for the monolayer materials was 100% of their weight since the fraction of the material studied was degraded. The bilayer sheets of PLA_a/TPS and PCL/TPS presented a weight loss of 64% and 60%; this is mainly due to the degradation of the material on the TPS side. PHB and PLA_a lost almost 90% and 85% of their weight. Furthermore, LDPE did not record significant weight loss.

Conclusions

The bilayer sheet materials exhibited interlayer adhesion promoted by the addition of potassium sorbate. The presence of potassium sorbate promoted adhesion between the PLA_a/TPS sheets. The bilayer PLA_a/TPS and PCL/TPS material had notable changes in the wavelengths of the carbonyl group (C=O), and the hydroxyl group (-OH) due to the addition of the coupling agent. The bilayer sheets had excellent water vapour transmission properties exposing only the TPS face. PCL/TPS bilayer sheets were found to have a lower water vapour transmission rate compared to PLA_a/TPS. The solubility in water showed that when adding potassium sorbate, a weight loss is generated in the bilayer sheet of PLA_a. Furthermore, it shows a destructuring effect of potassium sorbate on the material. Finally, the PCL/TPS bilayer

laminates have a higher CO₂ generation, obtaining a higher degradation rate than the PLA_a/TPS bilayers. Furthermore, the PLA_a/TPS and PCL/TPS sheets had a higher degradation compared to the other polymers. The materials developed in this work generate an alternative for application in the food industry due to the combination of TPS and polymers such as PLA_a and PCL, where significant changes in the physical properties of WVT, water-solubility, water absorption and biodegradation were evident. The application of potassium sorbate as an interface agent would avoid the use of inorganic adhesives.

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