Biodegradability and plasticizing effect of *yerba mate* extract on cassava starch edible films

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ABSTRACT

Biodegradable and edible cassava starch-glycerol based films with different concentrations of *yerba mate* extract (0, 5 and 20 wt.%) were prepared by casting. The plasticizing effect of *yerba mate* extract when it was incorporated into the matrix as an antioxidant was investigated. Thermal degradation and biodegradability of the obtained biofilms were also studied. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR), X-ray diffraction analysis (XRD), water absorbance, stability in different solutions and biodegradability studies were performed. The clear correlation among the results obtained from the different analysis confirmed the plasticizing effect of *yerba mate* extract on the starch-glycerol matrix. Also, the extract led to a decrease in the degradation time of the films in soil ensuring their complete biodegradability before two weeks and to films stability in acidic and alkaline media. The plasticizing effect of *yerba mate* extract makes it an attractive additive for starch films which will be used as packaging or coating; and its contribution to an earlier biodegradability will contribute to waste reduction.

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1. Introduction

Packaging has a key role in containing and protecting food since it is highly manipulated by producers and consumers. However, packaging materials are one of the main solid wastes in major cities around the world (Elgaaïed-Gambier, 2014; Potter & Hotchkiss, 2012). A large portion of this waste is food containers. The reduction of the environmental impact by using biodegradable polymers in food industry is today an alternative for removing packaging from petroleum (Bonilla, Talón, Atarés, Vargas, & Chiralt, 2013; Chang-Bravo, López-Córdoba, & Martino, 2014; Seligra, Nuevo, Lamanna, & Famá, 2013). The term "biodegradable" materials is used to describe those materials which can be degraded by the enzymatic action of living organisms, such as bacteria, yeasts, fungi and the ultimate

end-products of the degradation process, these being CO_2, H_2O, and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions (Avella et al., 2005).

In this sense, starch edible films have been extensively studied in the last decades (Famá, Rojo, Bernal, & Goyanes, 2012; Gutiérrez, Morales, Pérez, Tapia, & Famá, 2015; Gutiérrez, Tapia, Pérez, & Famá, 2015b; López-de-Dicastillo, Gómez-Estaca, Catalá, Gavara, & Hernández-Muñoz, 2012; Machado, Nunes, Pereira, & Druzian, 2012; Souza et al., 2012).

Recently, it was demonstrated that starch-based products degradation time is shorter than other polymeric materials such as poly(lactic acid) (PLA) or poly(butylene adipate-*co*-terephthalate) (PBAT) (Weng et al., 2013). One of the advantages of a faster material degradation in landfill is that the volume of waste to be compacted would be also reduced. A decrease in the degradation time, even of a few days, represents a significant reduction of waste volume and hence, it leads to a very important benefit with regard to environmental care.

Several natural and synthetic additives are easily available for the development of starch based thermoplastics, such as process-

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a) Theobromine (Xanthin)   b) Caffeine (Xanthin)
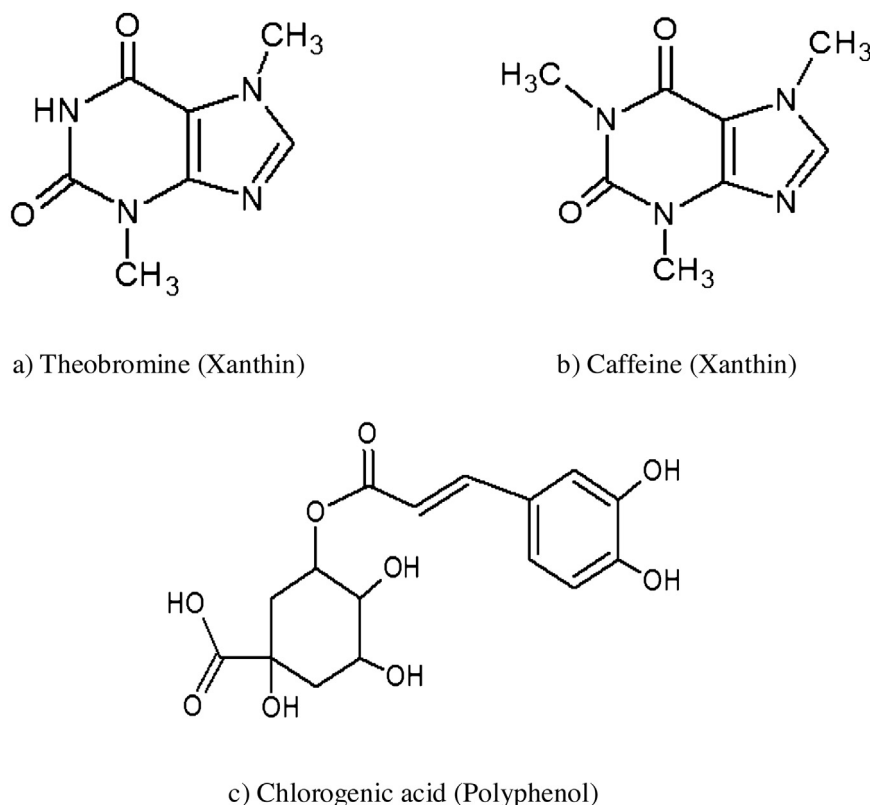
c) Chlorogenic acid (Polyphenol)

Fig. 1. Chemical structure of chlorogenic acid (a), caffeine (b) and theobromin (c).

ing aids, plasticizers, stabilizers, antimicrobial and antioxidants (Calatayud et al., 2013; López-de-Dicastillo et al., 2012; Mathew and Abraham, 2008; Soroka, 2002).

The primary role of the plasticizers is to improve the flexibility and processability of polymers. It is known that plasticizers are low molecular weight materials. This means they can occupy intermolecular spaces between the polymer chains, reducing secondary forces among them. These molecules change the three-dimensional molecular organization of polymers, reducing the energy required for molecular motion and the formation of hydrogen bonding between the chains (Vieira, da Silva, dos Santos, & Beppu, 2011). Thus, the degree of plasticity of polymers is largely dependent on the chemical structure of the plasticizer, including chemical composition, molecular weight and functional groups (Moreno, 1992).

Natural extracts are sources of antioxidants such as polyphenols and flavonoids, among others, whose activity is well known in pharmaceutical, cosmetic and food industries (Yilmaz and Toledo, 2006). They also are chemical analogues of synthetic stabilizers widely used in plastic industries (Cerruti, Malinconico, Rychly, Matisova-Rychla, & Carfagna, 2009). Additionally, the incorporation of natural extracts could improve the plasticizing properties of biomaterials (Mathew and Dufresne, 2002; Mathew and Abraham, 2008; Medina Jaramillo, González Seligra, Goyanes, Bernal, & Famá, 2015).

The composition of *yerba mate* has been partially characterized in the literature. It includes a variety of active phytochemicals, among them, the highest compounds are the polyphenols (chlorogenic acid) and xanthines (caffeine and theobromine) (Fig. 1), followed by purine alkaloids (caffeic acid, 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid), flavonoids (quercetin, kaempferol, and rutin), amino acids, minerals (P, Fe, and Ca) and vitamins (C, B1, and B2). These are the main constituents that are relevant for the antioxidant capacity of *yerba mate* (Bastos et al., 2007; Bravo, Goya, & Lecumberri, 2007; Filip, López, Giberti, Coussio, & Ferraro, 2001; Gosmann, Schenkel, & Selignmann, 1989; Pomilio, Trajtemberg, & Vitale, 2002).

The addition of *yerba mate* extract in biodegradable biopolymers could allow obtaining active films with antioxidant effects thus, having important benefits on the health of consumers (Bastos et al., 2007; Bravo et al., 2007; Filip et al., 2001; Gosmann et al., 1989; Pomilio et al., 2002). The effectiveness of yerba mate as an antioxidant when it was incorporated in a thermoplastic starch film (TPS) has been previously reported (Medina Jaramillo et al., 2015). Through DPPH• tests, the authors observed that the antioxidant activity of TPS containing 5wt.% and 20wt.% of extract of yerba mate was 3.0 ± 0.1 and 10.4 ± 0.1 mg/g of film, respectively.

Beyond that packaging can provide extra benefits to the food it must fulfill certain conditions to avoid adversely effects on the product or the environment. For this, some studies of thermal degradation reported that the temperature that can support a material, as well as its biodegradability in soil, should be fundamental in evaluating its ability to enter as packaging in market food industries. Biodegradation tests under composting conditions are important because they simulate the biodegradability under real life conditions and they are also treatment methods for municipal solid waste (Briassoulis, Dejean, & Picuno, 2010; Maiti, Ray, & Mitra, 2012).

In this context, some researchers studied the thermal degradation properties of starch-based films containing antioxidants (Moreno, Atarés, & Chiralt, 2015; Perazzo et al., 2014). In most investigations it has been shown that the addition of antioxidants leads to slight changes in thermal degradation parameters. Mainly, a beginning of material degradation at lower temperatures was reported. However, there are not researches that have investigated the effect of using an antioxidant in the degradation time in soil of functional packaging films with food oxidation inhibitors characteristics.

The aim of this study was to evaluate thermal degradation and biodegradability in compost as a function of time of cassava starch-glycerol-*yerba mate* extract films, as well as the plasticizing effect of different concentrations of the extract on starch-based materials. In particular, 5wt.% and 20wt.% of yerba mate extract were chosen for cover the largest and the smallest concentrations of additive (Calatayud et al., 2013; Siripatrawan & Harte, 2010). Degradation and thermal transitions processes of the films, as well as crystallinity, water absorption and swelling behaviour in different media, were evaluated. The selected assays were also used to analyze the plasticizing effect of yerba mate extract on the cassava starch matrix.

2. Experimental

2.1. Materials

Cassava starch (18wt.% amylose and 82wt.% amylopectin) was provided by *CODIPSA, Paraguay.* Glycerol was of analytical grade (Aldrich) and commercial *yerba mate* (*Ilex paraguariensis*) (*Taragüi* liviana) was from *Establecimiento Las Marías*, Corrientes, Argentina.

2.2. Preparation of yerba mate extract

The extract of *yerba mate* was obtained from an infusion as follows: 3 g of *yerba mate* were heated at 100 °C in 100 mL of distilled water for 40 min, using a magnetic stirrer. Immediately, the solution was filtered twice and stored in dark containers at ~5 °C (Deladino, Anbinder, Navarro, & Martino, 2008; López Córdoba, Deladino, & Martino, 2013). The resultant solids in the extract were around 1.2% (AOAC, 1995).

2.3. Films formation

Edible and biodegradable films were prepared by mixing 5wt.% of cassava starch, 1.5wt.% of glycerol as plasticizer, 93.5wt.% of distilled water and different concentrations of *yerba mate* extract (0, 5 and 20wt.%, namely TPS, TPS-Y5 and TPS-Y20, respectively). The solution was heated with constant stirring at 96 °C for 40 min to ensure starch gelatinization (Hernández, Emaldi, & Tovar, 2008). The gel was then degassed by applying vacuum for 7 min and poured on polypropylene plates, which were dried at 50 °C for 48 h at ambient relative humidity (RH). The thickness of the resultant films was ~0.25 mm.

Considering the cost of each of the components used for forming the materials, the estimated final price of the matrix film without production cost was USD 0.097 while the price of TPS-Y5 and TPS-Y20, was USD 0.1 and USD 0.13, respectively.

2.4. Characterization of the films

The developed films were conditioned at RH of 56.7% (NaBr) and ambient temperature, for 10 days before characterization.

2.4.1. Fourier transform infrared spectroscopy (ATR/FTIR)

The absorbance spectra of the starch-based films were recorded in an IR Affinity-1 Shimadzu Fourier Transform Infrared Spectrophotometer in transmission mode, using the single reflection horizontal attenuated total reflectance (ATR). The spectra were obtained with a resolution of 4 cm^{-1} as the average of 40 scans in the range of 4000–700 cm^{-1}.

2.4.2. Thermogravimetric analysis (TGA)

Thermogravimetric tests were performed using a Shimadzu DTG-60 equipment. Pieces of 3–4 mg of each film and ~ 9 mg of *yerba mate* extract were heated from room temperature to 00 °C

at a rate of 10 °C/min under nitrogen flow of 30 mL/min. From the plots of weight loss values *versus* temperature, the different degradation phases were obtained. The same analysis was performed on three replicates to ensure repeatability.

2.4.3. Differential scanning calorimetry (DSC)

Melting temperature (T_m) of the films was determined by differential scanning calorimetry (DSC) (Mettler Toledo Schwerzenbach) from the peak temperature of the melting endotherm. Samples of approximately 5 mg of each system were contained in hermetically sealed aluminum pans and heated in the temperature range of 30 °C to 300 °C at 10 °C/min, under nitrogen atmosphere. Changes of phase or state and corresponding enthalpies were determined (Biliaderis, Lazaridou, & Arvanitoyannis, 1999; Chartoff, 1981).

2.4.4. X-ray diffraction (XRD)

X-ray diffraction analysis on the different films was performed using a vertical goniometer X-ray diffractometer (Siemens D 5000) (radiation Cu αK = 1.5406 Å, 40 kV and 30 mA). Scattered radiation was detected in an angular range of 6–33° (2θ), at a step size of 0.04 and a scan speed of 8 s. From the scattering spectrum, the effective percent crystallinity of films was determined according to Hermans and Weidinger (1961), as the ratio of the integrated crystalline intensity to the total intensity. Crystalline fraction was estimated by the area above the smooth curve drawn on the basis of the main peaks (main *d*-spacing) (Famá, Goyanes, & Gerschenson, 2007).

2.4.5. Water vapor absorption kinetics

Water vapor absorption of the films was determined by a gravimetric method at room temperature using the method proposed by Rhim, Koh, and Kim (2011). Pieces of each system (~0.5 g) were first placed in a desiccator containing CaCl$_2$ in order to dry them. Then, they were deposited in a desiccator with relative humidity (RH) of 56.7%. The samples weight during the water vapor absorption process was measured every 24 h until reaching constant value (Rhim et al., 2011).

2.4.6. Stability in acidic and alkaline solutions

In order to evaluate the stability of the films in acidic and alkaline solutions, pieces of 16 mm of diameter were immersed in containers with 10 mL of standard solutions of hydrochloric acid (pH = 3), distilled water and sodium hydroxide (pH = 12). The containers were sealed and kept at 25 °C for 12 days. Changes in the appearance of the samples were recorded with a Samsung camera model ST70 having 14.2 mega pixels.

2.4.7. Biodegradability in vegetable compost

Vegetable compost (soil) was poured into a plastic tray (10 × 20 × 5 cm) up to a height of about 40 mm. Samples of each system (20 mm × 20 mm) were weighed and then buried in the soil to a depth of approximately 10 mm. Plastic trays were kept at ambient temperature. Water was sprayed twice a day to sustain the moisture. At different times (first, sixth, ninth and twelfth day), samples were carefully taken out and dried in a vacuum oven at 50 °C. After that they were weighed according to the method described by Dalev, Patil, Mark, Vassileva, and Fakirov (2000) with some modifications (Dalev et al., 2000).

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (ATR/FTIR)

Fig. 2 shows ATR/FTIR spectra of the different films. An important absorption peak around 3300 cm^{-1} (stretching of OH group belonging to starch, glycerol and water), which can be associated to
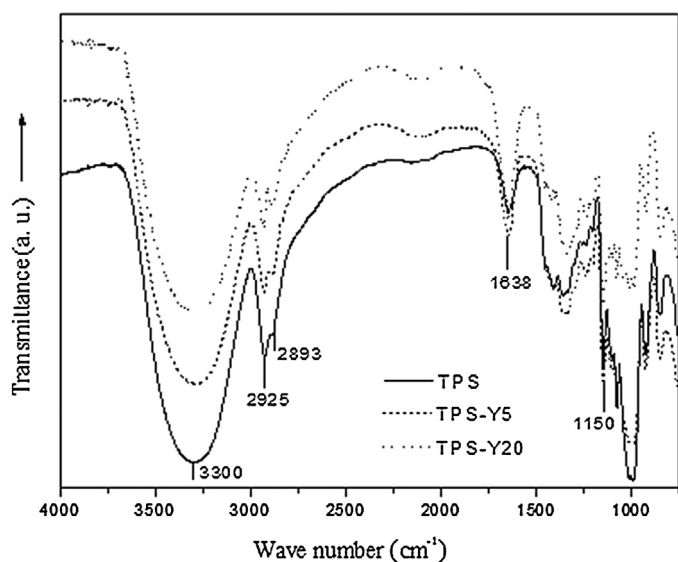
Fig. 2. ATR/FTIR of the different developed films: TPS (a), TPS-Y5 (b) and TPS-Y20 (c).

Fig. 3. (A) TGA of TPS (a), TPS-Y5 (b), TPS-Y20 (c) and yerba mate extract(d); and (B) First derivate of TPS (a), TPS-Y5 (b) and TPS-Y20 (c).

the stretching vibration of C—O groups (Pereira et al., 2015; Xu, Kim, Hanna, & Nag, 2005) was observed. As it can be seen, the intensity of this band was similar in all systems. This band is strongly related to OH groups. A material with OH that more easily vibrate and/or form more hydrogen bonds is prone to present a wider and less intense band (Seligra, Medina Jaramillo, Famá, & Goyanes, 2016). In a previous work, Medina Jaramillo et al. (2015) reported that water content of the films with the extract was lower than that of the matrix. Taking this into account, another phenomenon that did not change the band around 3300 cm^{-1} could be expected: the appearance of primary amines that are part of the Xanthin compounds, specifically Theobromine and Caffeine of *yerba mate* extract. This band is also around 3400–3250 cm^{-1} (Silverstein, Webster, Kiemle, & Bryce, 2014). Then, while the reduction in the moisture content of TPS-Y5 and TPS-Y20 led to a decrease in the intensity of this peak, the emergence of the amines in these films counteracted this effect.

The peaks at 2893 and 2925 cm^{-1} are associated to C—H stretch vibrations (Mathew, Brahmakumar, & Abraham, 2006) and they are characteristic of polymer matrix materials. With the increase in the extract concentration, the band at around 2893 cm^{-1} also increased. This fact could be attributed to the appearance of methyl groups which were present in *yerba mate* extract.

At around 1638 cm^{-1} there is an absorbance band which is sensitive to both H-bonding and the amount of hydroxyl interactions (Fama, Bittante, Sobral, Goyanes, & Gerschenson, 2010). This band seemed to be not affected by the incorporation of the extract.

Likewise, the characteristic absorption peak assigned to C—O—C in glycosidic linkage at approximately 1150 cm^{-1} was similar in all systems, indicating that the glycosidic chain length was not modified by the extract (Silva-Weiss, Bifani, Ihl, Sobral, & Gómez-Guillén, 2013).

It is very important to note that in both TPS-Y5 and TPS-Y20, interactions occurred between starch-glycerol and *yerba mate* extract and these interactions were large enough to alter infrared spectra.

3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out in order to analyze the thermal stability of the different systems (Fig. 3A a–c) and *yerb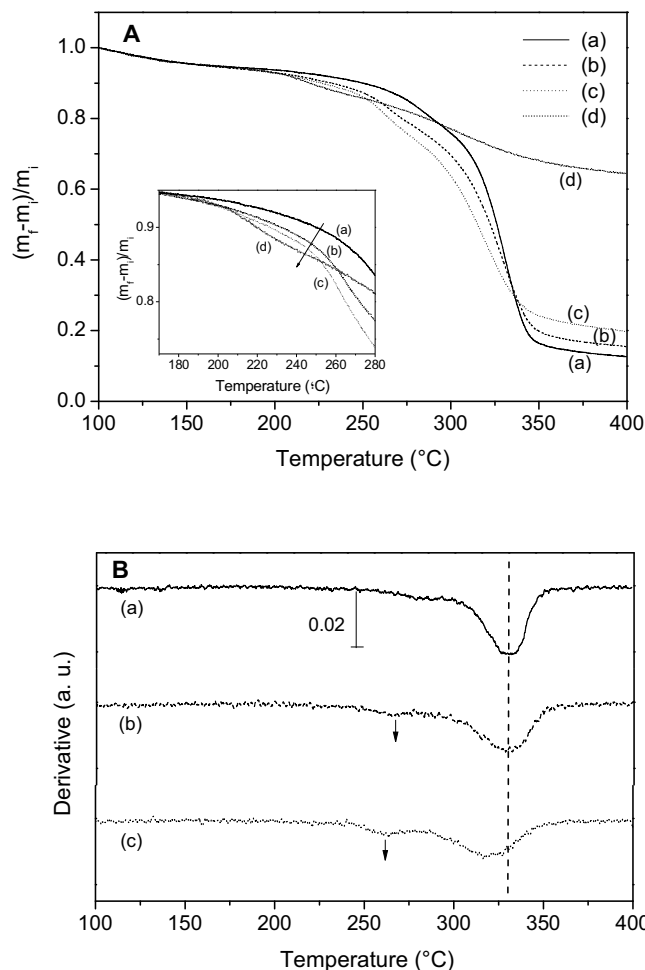a mate* extract (Fig. 3A d). Besides, in order to determine the thermal decomposition temperatures of all developed films, the first derivative function to the TGA curves were performed (Fig. 3B).

As it can be seen in Fig. 3A a–c, the thermal decomposition of the developed biofilms occurred in three main stages, which agree with those reported in the literature for films based on starch-glycerol (Ayala, Agudelo, & Vargas, 2012; García, Famá, Dufresne, Aranguren, & Goyanes, 2009; Gutiérrez, Morales et al., 2015; Marques et al., 2006; Pelissari, Andrade-Mahecha, & Menegalli, 2013). The first stage corresponds to water and/or volatiles evaporation (100–150 °C). The second is associated to the decomposition of the glycerol-rich phase which also contains starch and to the degradation of some low molecular weight components of the extract (180–260 °C); and the third stage is related to the degradation of the components of the starch, that happens between 250 °C and 350 °C (García et al., 2009; Liu, Xie, Yu, Chen, & Li, 2009; Wilhelm, Sierakowski, Souza, & Wypych, 2003).

The mass loss associated with the evaporation of water stage was found to be around 5% for all studied systems. In the first derivative of the curves (Fig. 3B) the corresponding decomposition peak was not found, probably due to the low weight loss values observed. The typical mass loss related to the decomposition of the glycerol-rich phase observed in the matrix was also presented, but more evidently, by the films containing *yerba mate* extract. Along that process, the mass loss was higher for the systems with the extract than for the matrix, being more noticeable in the case of the film with the highest concentration of the aggregate (the difference between TPS and TPS-Y20 was about 7% at 260 °C). This

behavior was also observed in the derivative curves (Fig. 3B) with the appearance of a very small peak at around 268 °C and 263 °C in both TPS-Y5 and TPS-Y20, respectively, which was more evident in the case of the film with 20 wt.% of the extract. This fact can be explained considering the sharp drop of the curve of *yerba mate* extract (Fig. 3A d). As it can be seen, the extract mass loss began at ∼ 180 °C. This step was the result of the degradation of some low-molecular-weight compounds from the extract (Zeppa, Gouanvé, & Espuche, 2009).

The step related to the decomposition of the starch-rich phase began at slightly lower temperature in the films containing the extract of *yerba mate*. TPS resulted thermally stable up to a temperature of about 260 °C, whereas starch-extract films were thermally stable up to ∼240 °C. The onset of this degradation at lower temperature suggests that the incorporation of the extract allows decreasing the molecular interactions between the starch–starch chains, and strengthens the hydrogen bonding interactions between the hydroxyl groups of the starch and the polar compounds (polyphenols) of the *yerba mate* extract (Cyras, Tolosa Zenklusen, & Vazquez, 2006; García et al., 2009; Gutiérrez, Morales et al., 2015; Gutiérrez, Tapia et al., 2015; Mathew and Abraham, 2008; Pelissari et al., 2013). A slight decrease in the decomposition temperature related to the starch-rich phase with the incorporation of the highest concentration of the extract was observed: while in TPS and TPS-Y5 the material degraded at ∼330 °C, in TPS-Y20 degradation temperature was around 320 °C (Fig. 3B). A decrease in the thermal degradation temperature of this step in thermoplastics from the incorporation of different antioxidants has been previously reported (Cerruti et al., 2011; Hwang et al., 2013; Mathew and Abraham, 2008). This behavior was also observed in polymer-based films with the increase in plasticization (Curvelo, de Carvalho, & Agnelli, 2001; García et al., 2009; Sanyang, Sapuan, Jawaid, Ishak, & Sahari, 2015). Therefore, the extract of *yerba mate* not only acts as an antioxidant on a starch-glycerol polymer, but also would function as a plasticizer. This possible behavior of the extract is consistent with previous results of our group (Medina Jaramillo et al., 2015) on the mechanical response and surface properties of the same films.

After degradation, the films underwent a significant mass loss, being about 87% respect to its original mass in the case of TPS, and approximately 83% and 80% in TPS-Y5 and TPS-Y20, respectively. Generally, components with aromatic rings tend to yield some char residues, which are stable up to 600 °C under nitrogen atmosphere. The larger is the amount of aromatic rings, the greater are the char residues (Patel et al., 2010).

3.3. Differential scanning calorimetry (DSC)

Fig. 4 shows the DSC thermograms of the studied films and *yerba mate* extract. As it can be seen, the heat flow curves of all materials presented an endothermic peak in the range of 40 °C and 180 °C. In the case of the films, an endothermic peak around 280 °C was also observed.

In starch films (Fig. 4a–c), the first endotherm around 90 °C has been attributed to the melting of the starch crystallites formed during retrogradation (Chang, Cheah, & Seow, 2000; Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011b; Rindlav-Westling, Stading, & Gatenholm, 2002). This phenomenon has been already observed several times (Avilés, 2006; Bergo et al., 2008; López-de-Dicastillo et al., 2012). It has been reported in the literature that the melting endotherm in starch films could be originated from the cocrystallized amylose and amylopectin during the film-forming process, which would allow continuous crystallization of amylopectin (Chang et al., 2000; Miles, Morris, & Ring, 1985; Rindlav-Westling et al., 2002; Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). *Yerba mate* extract curve only showed an endothermic transition around 85 °C (Fig. 4b), which
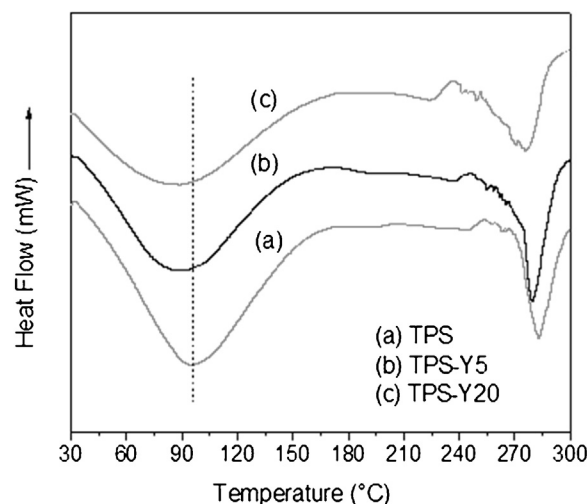

Fig. 4. DSC of the different developed films: TPS (a), TPS-Y5 (b) and TPS-Y20 (c).

was very broad probably due to the great diversity of compounds which were present in the extract.

As it can be observed, the melting temperature (T_m) of the first process decreased with the increase in *yerba mate* extract content. T_m of cassava starch film was de 96 ± 1 °C, and for TPS-Y5 and TPS-Y20 was 89 ± 1 °C and 86 ± 1 °C, respectively. This behavior indicates that the incorporation of *yerba mate* extract limited crystal growth and recrystallization because they interacted with the polymeric chains hindering their alignment and, thus, crystal formation.

According to the literature, some additives or components can lead to a decrease in the melting temperature of thermoplastic materials. In our case, the decrease in T_m of starch films containing the extract could be due to two factors. On one hand, it is well known that the melting temperature of films with antioxidants is greatly affected by the T_m of the extract (Mathew and Abraham, 2008; Rachtanapun and Tongdeesoontorn, 2009). Taking into account that yerba mate extract had its T_m around 85 °C (López Córdoba et al., 2013), it was expectable that the melting temperature of TPS-Y5 and TPS-Y20 shifted to lower temperatures. Films containing low polar antioxidant, which had a T_m lower than matrix, would have caused a decrease in T_m of the films. This is due to the low polar group of antioxidants decreased the intermolecular binding in the polymer chain (Hernandez, 2000; Mathew & Abraham, 2008; Rachtanapun and Tongdeesoontorn, 2009). In this case, *yerba mate* extract would have decreased the molecular interactions between the starch–starch chains and the strength of the hydrogen bonding interactions between the hydroxyl groups of the starch chains and the polar compounds (polyphenols) of *yerba mate* extract (in agreement with ATR/FTIR studies), enhancing the mobility of the starch chains. In recent years, several authors have reported a similar effect on T_m in edible films from the addition of any antioxidant containing polyphenols (Hwang et al., 2012, 2013; Soto-Valdez, Auras, & Peralta, 2011; Wu, Chen, Li, & Li, 2009). In particular, Wu et al. (2009) investigated the effect of tea polyphenols on thermal properties of rice starch and demonstrated that T_m decreased as tea polyphenols level increased, suggesting that the antioxidant interacted with side chains of amylopectin and bound to the amorphous region of starch granules changing the coupling forces between the crystallites and the amorphous matrix.

On the other hand, several authors reported a decrease in T_m of starch films from the incorporation of a plasticizer (Garcia, Martino, & Zaritzky, 2000; Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011a; Jouki, Mortazavi, Yazdi, & Koocheki, 2014; Maria, de Carvalho, Sobral, Habitante, & Solorza-Feria, 2008), and
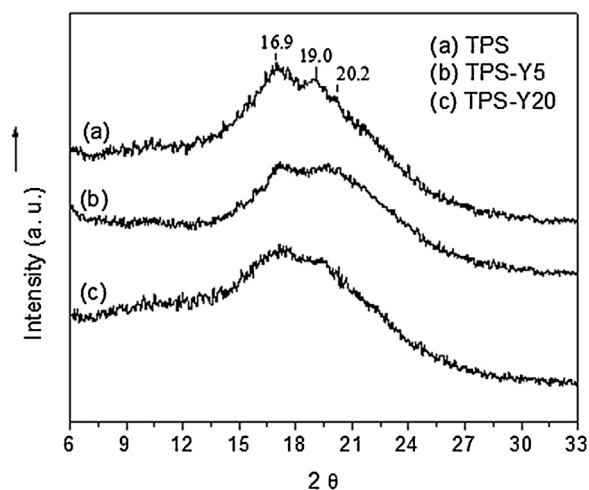
Fig. 5. DRX of the different developed films: TPS (a), TPS-Y5 (b) and TPS-Y20 (c).

attributed this shift to the plasticizing effect that weakens the inter-molecular forces between polymer chains (Hulleman, Janssen, & Feil, 1998; Talja, Helén, Roos, & Jouppila, 2007), thereby increasing the free volume (by its low molecular weight) and thus, limiting the crystals formation and growth. The interaction of the plasticizer with the polymeric chains can hinder their alignment and recrystallization (García, Martino, & Zaritzky, 2000). This effect could also be due to the addition of any additive with lower molecular weight compared to the starch, such as polyphenols (Quiñones, Miguel, & Aleixandre, 2012), which leads to an increase in the free volume, modifying the structure of the material, as when a plasticizer is incorporated.

In Fig. 4 it can also be seen the widening and reduction in the intensity of the peaks of TPS-Y5 and TPS-Y20, leading to a decrease in the melting enthalpy (ΔH_m). Lower ΔH_m was previously observed in plasticized films compared with unplasticized ones (García et al., 2000), as well in starch containing polyphenols (Wu et al., 2009). In this sense, the extract led to a similar effect than a plasticizer, limiting crystal growth and recrystallization because they interacted with the polymeric chains hindering their alignment and, thus, impeding the formation of crystals. In TPS-Y20 the decrease in ΔH_m was more evident due to the chances of the extract to interact with polymeric chains were higher.

The decrease in both, melting temperature and enthalpy in starch-yerba mate extract films, probably indicates a less stable crystalline structure, requiring less energy to melt (Kaur, Singh, & Singh, 2004), leading to better quality for using in the manufacture of packaging.

The second endotherm could be ascribed to the polymer decomposition, in this case to the thermal degradation of the starch-rich phase (Liu et al., 2009). TPS presented a strong and broad peak at ~283 °C with an onset degradation temperature (T_o) of ~245 °C. As it can be seen, T_o decreased as the extract of *yerba mate* content increased (approximately 4 °C for TPS-Y5 and ~6 °C for TPS-Y20). It is important to note that, in accordance with TGA assays, all materials analyzed by DSC confirmed be thermally stable up to a temperature of about ~240 °C.

3.4. X-ray diffraction (XRD) analysis

Fig. 5 shows the X-ray diffraction patterns for the developed films. All systems showed typical behavior of tuber starches films with B-V type crystal structure, (Morales, Candal, Famá, Goyanes, & Rubiolo, 2015; Seligra et al., 2016; Shi et al., 2007), composed of an important contribution of an amorphous phase with small diffrac-

Table 1
Crystallinity values of the developed films.

Film	Crystallinity (%)
TPS	4.0 ± 0.3
TPS-Y5	3.3 ± 0.3
TPS-Y20	<1

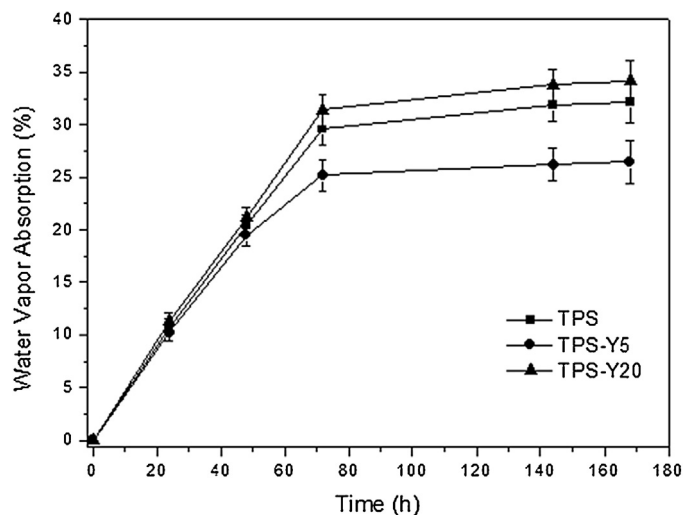**Fig. 6.** Water vapor absorption curves of TPS (a), TPS-Y5 (b) and TPS-Y20 (c).

tion peaks at: $2\theta \sim 17$ (5.2 Å), 19.1 (4.6 Å) and 20.2 (4.4 Å) which can be attributed to the retrogradation during storage (Morales et al., 2015)

DRX patterns of films containing *yerba mate* extract presented lower crystallinity fraction compared with the matrix. The greater the concentration of extract, the lower the crystallinity was, leading to a more amorphous pattern and suggesting that the extract hindered the retrogradation phenomenon. Crystallinity values for the different films are shown in Table 1.

Taking into account the above comments and according to trends observed in DRX patterns, the decrease in crystallinity of TPS-Y5 and TPS-Y20 would indicate that the incorporation of *yerba mate* extract provoked a plasticizing action on starch-glycerol films, probably due to the extract interference affecting the starch chains attraction.

The above behavior agrees with the results of DSC (Fig. 4), where the systems with *yerba mate* extract showed a decrease in the endotherm around 8 °C associated with the melting of the starch crystalline fraction. These results are very important because they confirm that the incorporation of the *yerba mate* extract was able to retard recrystallization or retrogradation of the thermoplastic films.

Starch retrogradation not only involves changes in the amylopectin crystalline fraction but also in the amylose crystalline fraction. Amylose recrystallization is faster and occurs about 1 day after cooling, while amylopectin recrystallization is slower and mainly responsible for deterioration of starch for packaging.

3.5. Water vapor absorption kinetics

The curves of water vapor absorption kinetics for the films tested at room temperature and 56.7% RH can be observed in Fig. 6. The water vapor absorption behavior of all studied materials exhibited similar characteristics to those of biopolymer films (Rhim et al., 2011). At the initial moisture sorption, the typical progress with high rate of absorption taking place at short times occurred, with similar values for the different samples. As the water vapor sorption
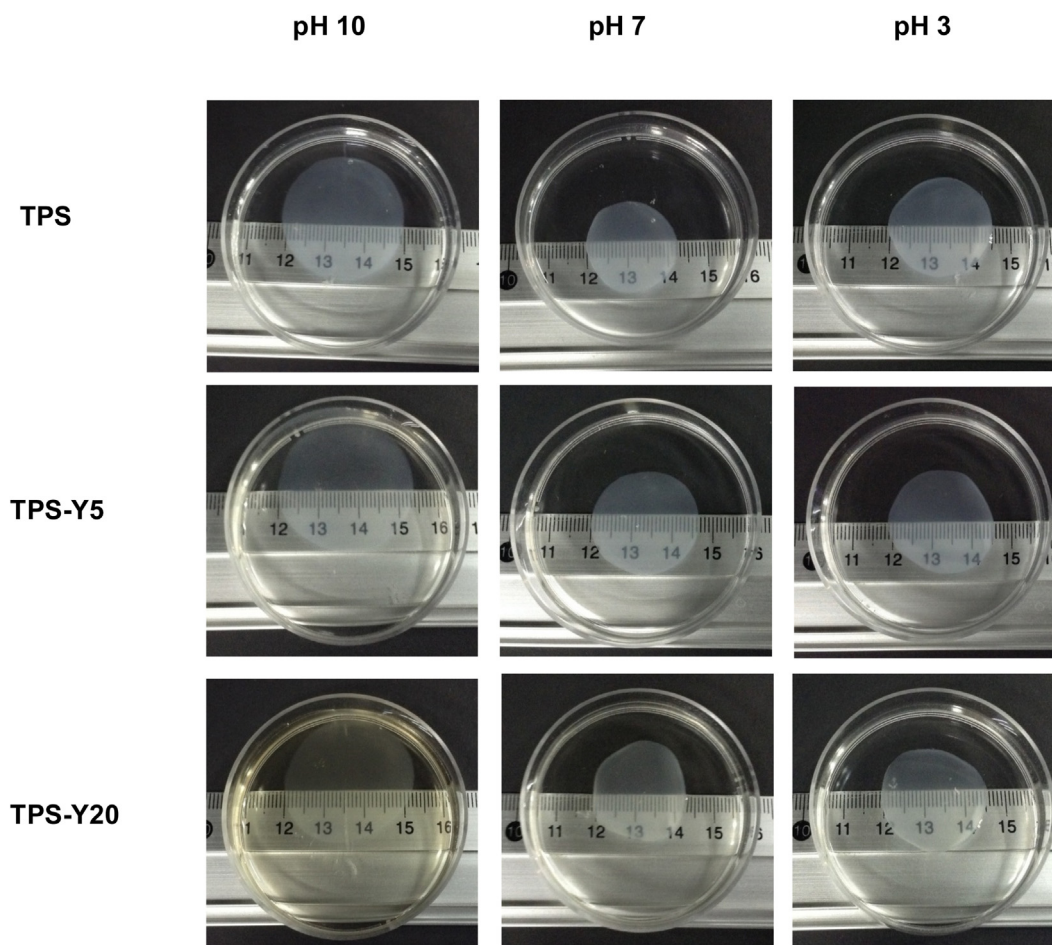
Fig. 7. Digital photographs of the thermoplastic starch films immersed in alkaline, neutral and acid medium after 12 days.

proceeded, the sorption rate decreased until reaching the equilibrium condition, at which the maximum water vapor sorption of the film was attained. In all studied films, the equilibrium state was reached at around 72 h, resulting water vapor absorption values of: $32 \pm 2\%$, $26 \pm 2\%$ and $34 \pm 2\%$ for TPS, TPS-Y5 and TPS-Y20, respectively.

While the use of 20wt.% of extract had the same capacity to absorb water than the matrix, the addition of the lowest concentration of *yerba mate* extract (5wt.%) led to a slight decrease in this parameter. The incorporation of additives into hydrocolloid films usually changes their hydrophobicity due to the presence of more hydrophobic tails and the interactions among components that affect some active points for water sorption (Fabra, Talens, & Chiralt, 2009; Fabra, Talens, & Chiralt, 2010; Pereda, Marcovich, & Mosiewicki, 2015). In a recent work, Medina Jaramillo et al. (2015) demonstrated that the addition of *yerba mate* extract led to more hydrophobic cassava starch films and also to a decrease in their humidity content. This behavior resulted more pronounced in the films with 5wt.% of the extract than in TPS-Y20. Thus, the slight decrease in water absorption of TPS-Y5 observed here was the result of the more hydrophobic nature of this material and the strong hydrogen bonding interactions between the hydroxyl groups of the starch and the polar compounds of the *yerba mate* extract, as revealed from TGA, DSC and ATR/FTIR analysis. The greater interaction would have reduced the availability of hydrophilic free groups to interact with water, hindering the course of water through the film.

In TPS-Y20 two opposite effects might have been causing moisture sorption remained similar to that of the matrix. On one hand, the hydrophobic character of TPS-Y20 with respect to the matrix and the strong hydrogen bonding interactions between the OH groups of its compounds would have led to a decrease in water sorption. On the other hand, the great concentration of the extract would have led to a material with free hydroxyl groups that would have interacted with the OH of water, increasing the moisture sorption.

3.6. Stability in acidic or alkaline solutions

Taking into account that the potential use of these new materials is to replace synthetic packaging in the food industry to coat products with a wide range of pH (fruits, meat, and cheese among others), the stability of the films subjected to different pH conditions is a benchmark property.

Fig. 7 shows images of the different films after immersion in an acid, neutral or alkaline medium for 12 days. Note that all the samples had the same dimensions at the beginning of the test: 16 mm in diameter.

When all the systems were subjected to the acidic medium, they swelled ~1.6 times, showing significant stability in this medium until the end of the measurements. This behavior is very important considering the possible use of the films on acidic foods like most of fruits and meats in the market.

In neutral pH, TPS and TPS-Y20 showed a very similar increment in diameter (~1.4 and 1.5 times, respectively); while the film containing 5wt.% of *yerba mate* extract swelled about 1.7 times respect to their initial dimension.
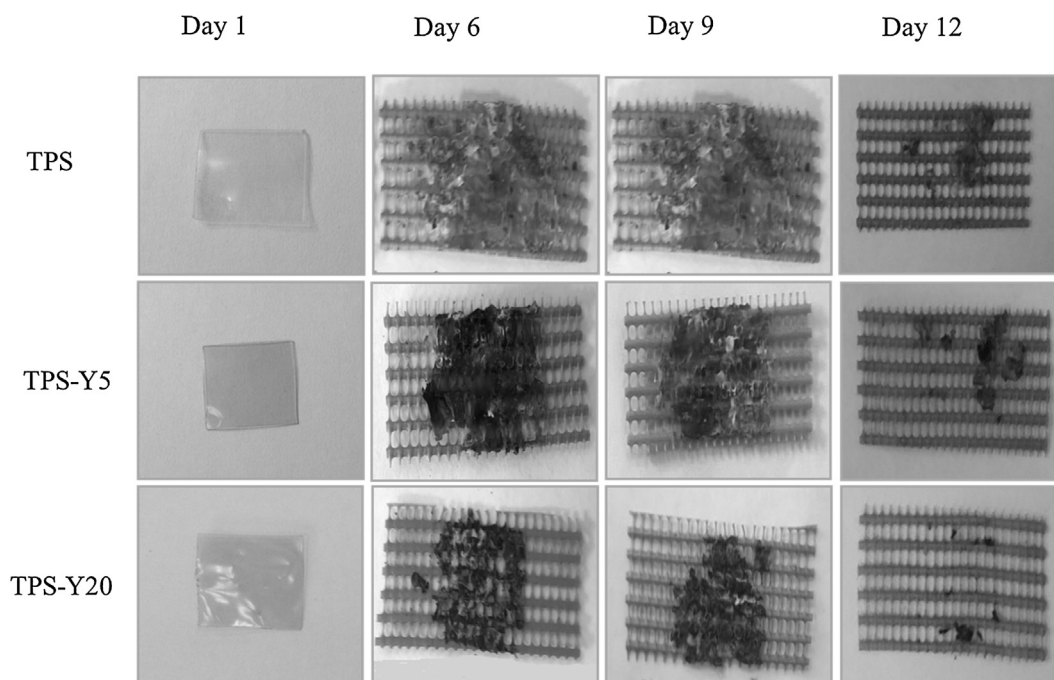
Fig. 8. Biodegradability in vegetal compost.

Similar behavior, although more noticeable, was observed after immersion in the alkaline medium. In this case, TPS and TPS-Y20 swelled approximately 1.9 and 2 times, respectively, while the diameter of TPS-Y5 increased almost 2.2 times. In the alkaline medium, all films presented the highest swelling. It is important to note that all the systems studied here, showed greater stability in an alkaline medium than other TPS films reported in the literature (Hu, Chen, & Gao, 2009; Medina, Pardo & Ortiz, 2012).

Probably, the less stability in neutral and alkaline media observed in the films with the extract, especially in the film with 5% *yerba mate*, was due to the plasticizing effect caused by this extract, which would have allowed greater mobility of the starch chains. Thereby, the starch chains would have been exposed to disintegration and dissolution in the alkaline medium because the sodium hydroxide could have reacted with the hydroxyl groups of the starch molecules. This would have destroyed the hydrogen-bonding and the molecular interactions between the starch macromolecules thus, enhancing the swelling and starch gelatinization (Gutiérrez, Morales et al., 2015; Hu et al., 2009).

3.7. Biodegradability in vegetal compost

In order to evaluate the biodegradability of the films, a qualitative study of the materials degradation as a function of time burying samples in a compost of vegetables was performed. Weight values could not be accurately obtained as residual soil affected weight measurements. Images of the films are shown in Fig. 8. It can be seen, that after 6 days of storage all the films experienced changes in their tonality and breakdowns, indicating the beginning of degradation. Decomposition of the films occurred almost entirely on day 12 of the study. There are some works in the literature that showed the degradation of starch in time in compost (Torres, Troncoso, Torres, Díaz, & Amaya, 2011; Xiong et al., 2008). For example, Xiong et al. (2008) observed that the biodegradation rates of starch films occurred in 100 days. Torres et al. (2011) noted that the weight of starch films decreased leading to a total mass loss of 99.35% after 31 days.

TPS-Y5 and TPS-Y20 showed further deterioration from the 9 day until the end of the test, and practically degraded on day 12. Taking into account the preparation methodology used and that the extract of *yerba mate* was natural; then, an increase in the microorganisms attack in both TPS-Y5 and TPS-Y20 was expectable. Furthermore, some of the compounds of *yerba mate* had low molecular weight and, therefore, they degraded before starch. While the yerba mate extract was incorporated into the starch in a dilute water solution (1.2%), it would be impossible to perform any degradation study in such solution.

The important result of the biodegradability study developed in this work was that the incorporation of the extract improved the biodegradability of starch-glycerol films, leading to new polymeric materials which degraded in 12 days. The faster degradation in soil of the starch-glycerol-*yerba mate* extract films makes them very promising to continue with new trends to preserve the environment.

Considering the short time of degradation of the materials studied in this work, and its decrease due to the addition of yerba mate extract, as it has recently promoted by FAO (2016), the waste of these materials could be disposed in urban gardens without industrial intervention. In addition, this fact also may help to reduce government spending in processing materials.

4. Conclusions

Biodegradable and edible starch-glycerol based films containing different concentrations of a natural antioxidant as *yerba mate* extract (0, 5 and 20wt.%) were evaluated with the aim to obtain promising biodegradable edible films to be used as packaging.

Throughout different studies such as TGA, DSC, ATR/FTIR and X-ray diffraction, it was possible to demonstrate that *yerba mate* extract acted as a plasticizer when it was incorporated as an antioxidant into starch-glycerol based films. Besides, the use of the extract improved the biodegradability of the films in compost and preserved their stability in acidic and alkaline media.

Both TGA and DSC results demonstrated that thermal stability of all films existed up to 240 °C. Thermogravimetric assays showed

that the weight loss of the extract was in the range of plasticizers due to the degradation of some of its low-molecular-weight compounds. This led to a shift of the temperature of the most important degradation of starch films; however, the change was only 3–5 °C to lower temperature. Melting temperature and enthalpy of crystallization derived from starch retrogradation decreased with the increase in *yerba mate* extract content as revealed by DSC analysis. Thus, similar to what happens with plasticizers, the extract limited crystal growth and recrystallization, as well as retarded starch retrogradation. This behavior was also observed by DRX, in which a decrease in crystalline-amorphous ratio was produced by the incorporation of the additive, trending to a typical plasticized starch structure pattern.

The low molecular weight of most of *yerba mate* extract compounds were probably responsible to thermal properties and crystallinity results, because a reduction in the molecular interactions between the starch–starch chains and a strengthening of the hydrogen bonding interactions between the hydroxyl groups of the starch and the polar compounds of the extract occurred when the extract was present.

Finally, the extract led to a faster degradation of the films in vegetal compost, practically ensuring their complete biodegradability before two weeks, and preserved the stability of the films in both acidic and neutral media, showing also greater stability in an alkaline medium.

Beyond the antioxidant characteristics of *yerba mate* extract, its plasticizing effect and contribution to a faster biodegradability in compost, as well as the higher films stability it promotes, make it an attractive additive for using in starch films to be applied as packaging or coating, helping waste growth and therefore, following the current trends to environmental care.

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