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Research paper

Active and smart biodegradable packaging based on starch and natural extracts

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ABSTRACT

Active and smart biodegradable films from cassava starch and glycerol with 5 wt.% of different natural extracts such as green tea and basil were obtained by casting. Their functional capacity as antioxidants and their physicochemical properties achieved from the incorporation of these types of extracts were evaluated. The content of phenolic compounds in the extracts led to films with significant antioxidant activity, being greater in the case of the system containing green tea extract. Color changes in both materials after immersion in different media (acid and basic) due to the presence of chlorophyll and carotenoids in the extracts were observed, but the film with basil extract reacted most notably to the different pH. These films degraded in soil under two weeks and were thermal stable up to 240 °C. Finally, the incorporation of extracts of green tea and basil led to thermoplastic starch films with lower water vapor permeability retaining their flexibility.

1. Introduction

Contaminations associated with synthetic food packaging and current increasing concerns related to the negative environmental impact of plastic packaging materials derived from petroleum, have driven significant interest from both academia and industry in natural and biodegradable materials (Bonilla, Talón, Atarés, Vargas, & Chiralt, 2013; Chang-Bravo, López-Córdoba & Martino, 2014; Fama, Bittante, Sobral, Goyanes, & Gerschenson, 2010; Gonzalez Seligra, Medina Jaramillo, Famá, & Goyanes, 2016). Different authors studied the feasibility of using starch films as packaging of food products due to their easy manipulation and optimal properties for that application (Bonilla et al., 2013; Campos, Gerschenson, & Flores, 2011; Mali, Grossmann, García, Martino, & Zaritzky, 2004; Versino, Lopez, Garcia, & Zaritzky, 2016). However, the current demand of consumers for more durable food products makes necessary the development of eco-friendly materials that are also functional, such as packaging with active compounds that can improve the quality of the products they cover, further contributing to the nutritional value of food. In this sense, several researchers investigated the use of antioxidants (Cerruti et al., 2011; Moreno et al., 2015), or antimicrobial agents in polymer matrices (Pelissari, Grossmann, Yamashita, & Pineda, 2009), obtaining the so-called "functional packaging". Although today packaging are composed of multiple layers, the possibility of developing edible films with these capabilities as "primary packaging" (i.e. the layer in direct contact with food) is under investigation (Van Herpen, Immink, & Van den Puttelaar, 2016; Wu & Dunn, 1995).

On the other hand, there are also defined intelligent packaging; a packaging system that is capable of carrying out intelligent functions (such as detecting, sensing, recording, tracing, communicating, and applying scientific logic) to facilitate the decision to extend shelf life, enhance safety, improve quality, provide information and warn about possible problems (Kerry, O'Grady, & Hogan, 2006; Yam, Takhistov, & Miltz, 2005).

Changes in pH are one of the indicators of the state and the quality of a food product (Dainelli, Gontard, Spyropoulos, Zondervan-van den Beuken, & Tobback, 2008). In most cases, when deterioration occurs in a food product, a change in pH is observed. In this sense, pH evaluation is essential in a product before buying or consuming it (Bamore, Luthra, Mueller, Pressley, & Beckwith, 2003; Veiga-Santos, Ditchfield, & Tadini, 2011).

There are components such as chlorophyll and carotenoids, which possess the property of giving yellow-green pigmentation. These kinds of components can be found in green tea and basil, in particular in their extract form, and they undergo color changes when they are exposed to different pH conditions (Lee, 2012).

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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 & Toledo, 2006). Additionally, they could improve the plasticizing properties of biomaterials (Mathew, Brahmakumar, & Abraham, 2006; Medina Jaramillo, González Seligra, Goyanes, Bernal, & Famá, 2015).

The extract of green tea (*Camellia sinensis*), contains polyphenols that mainly include catechins, epicatechins, epigallocatechins, epicatechin gallate, epigallocatechin gallate, chlorogenic acid and gallic acid. The epigallocatechin gallate is the most abundant catechin that has major health benefits and prevents various diseases (Jiang, Engelhardt, Thräne, Maiwald, & Stark, 2015; Pasrija, Ezhilarasi, Indrani, & Anandharamakrishnan, 2015; Yang & Koo, 1997). "Perazzo et al. (2014) incorporated green tea extract into a starch matrix and reported significant improvements in the films mechanical properties, water vapor barrier properties and antioxidant activity. However, the ability of green tea extract as an active component in starch films to generate an intelligent coating has not been already investigated.

Basil (Ocimum basilicum L.) is an aromatic herb that has been traditionally used as a medicinal herb for the treatment of headaches, coughs, diarrhea, constipation, warts, worms and kidney malfunctions (Politeo, Jukic, & Milos, 2007; Simon, Morales, Phippen, Vieira, Hao, & Janick, 1999). It contains active compounds with antioxidant qualities such as linalool, chlorogenic acid and methyl chavicol, and it is stable at relatively high temperatures, being able to resist starch casting process to be used in packaging applications (Suppakul, Sonneveld, Bigger, & Miltz, 2008). These attractive characteristics of basil along with its ability to detect changes in the quality of a product and to impart pleasing sensorial characteristics to the consumer make this component very promising for using in the food packaging industry. However, to date, no studies have been found in the literature regarding the effect of basil on thermoplastic starch films, neither on its potential use as a component of active and intelligent packaging.

Migration evaluation of polymer based films is explained from the physical principle of diffusion and according to Article 2 of the European Economic Community (EEC) Directive 85/572/EEC, and it uses accelerated tests to estimate the real conditions avoiding the long analysis times (Baner, Bieber, Figge, Franz, & Piringer, 1992). According to the literature, water is a typical simulant of foods that have high water content and ethanol as a fatty food simulant, in migration tests (Busolo & Lagaron, 2015; Paseiro-Cerrato et al., 2017; Rodríguez-Martínez et al., 2016). In particular, Talón et al. (2017) developed starch-quitosan based films that presented water solubility of around 23% and investigated the kinetics of release of polyphenols from thyme extract in the films using different solvents as food simulants, including water (Talón, Trifkovic, Vargas, Chiralt & González-Martínez, 2017).

The aim of this work was to determine the ability of green tea and basil extracts to generate active and intelligent primary packaging from their antioxidant components and their pH-related color changes when incorporated into a biodegradable and edible starch based film.

2. Experimental

2.1. Materials

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

2.2. Preparation of green tea and basil extracts

Green tea and *basil* extracts were obtained using the infusion methodology previously described by Medina Jaramillo et al. (2015). Commercial green tea or basil leaves (~3 g) were immersed in 100 mL of distilled water and heated at 100 °C for 40 min. After that, the system were cooled, filtered through a mesh of approximately 20 μm, and stored in dark flasks until use.

2.3. Films formation

Three different thermoplastic starch films were prepared by casting according the methodology described by Medina Jaramillo et al. (2015). The thermoplastic starch (TPS) matrix consisted on cassava starch (5 wt.%), glycerol as plasticizer (1.5 wt.%) and distilled water (93.5 wt.%). The films with natural extracts (green tea, *TPS-T*, and basil, *TPS-B*) had the same concentration of starch and glycerol than the matrix but 5 wt.% of the distilled water was replaced by each extract. All components were mixed and homogenized for 45 min at ambient temperature (25 °C) with controlled stirring. Then, the mix was heated at 96 °C for 40 min to ensure starch gelatinization (Hernández, Emaldi, & Tovar, 2008; Medina Jaramillo et al., 2015). The gel was degassed by applying vacuum for 7 min and it was deposited 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.

2.4. Films characterization

All films were conditioned at RH of 56.7% and ambient temperature for 10 days before characterization.

2.4.1. Total polyphenols content (TPC)

Total polyphenols content (TPC) was determined by the Folin–Ciocalteu methodology (Singleton, Orthofer, & Lamuela-Raventós, 1999), as follow: 160 μL of Na_2CO_3 (7% w/v) (Anedra, Argentina) were mixed with 400 μL of the sample and 200 μL of Folin–Ciocalteau reagent (Anedra, Argentina, 1:10 diluted). After 30 min, sample absorbance was measured at 760 nm in a spectrophotometer (Shimadzu, UV-1800, Japan). Chlorogenic acid (Fluka, USA) was used as standard. Determination was performed in triplicate.

2.4.2. Migration tests of green tea and basil extract from active films to food simulants

Migration tests were performed following the methodology reported by Busolo and Lagaron (2015), Baner et al. (1992), and Article 2 of the EEC (European Economic Community Directive 85/572/EEC), which indicate that water can be used as aqueous simulant of foods. Samples (film pieces of ~ 200 mm^2) were deposited in 5 mL of water and placed in an orbital shaker at 25 °C at 100 rpm for 24 h. After that, migration of both green tea and basil polyphenols was evaluated by the Folin-ciocalteu method.

2.4.3. Scanning electron microscopy (SEM)

Cryo-fractured surfaces were examined using a scanning electron microscope with a Field Emission Gun (FEG) Zeiss DSM982 GEMINI, in order to investigate the morphology of the films.

Samples were cooled in liquid nitrogen, broken and coated with a thin sputtered gold layer before the analysis.

2.4.4. Water vapor permeability (WVP)

Water vapor permeability (WVP) tests were carried out following ASTM-E96-00, (1996) standard recommendations, and using the correction method described previously by (Gennadios, Weller, & Gooding, 1994). WVP (g Pa^{-1} s^{-1} m^{-1}) values were calculated as follows:

$$WVP = \left(\frac{G}{P \times RH \times A}\right) \times d \quad (1)$$

where G is the weight gain in time (g s^{-1}), A the cell area (m^2), P the saturation vapor pressure of water (Pa), RH the relative humidity, and d the film thickness (m).

2.4.5. Differential scanning calorimetry (DSC)

Thermal analysis of the films was performed by differential scanning calorimetry (DSC) (Mettler Toledo Schwerzenbach) using ~5 mg of each system, a range of temperature between 30 °C–320 °C and a rate of 10 °C/min, under nitrogen atmosphere. Changes of phase or state and corresponding enthalpies were determined (Biliaderis, Lazaridou, & Arvanitoyannis, 1999). Melting and degradation temperatures (Tm and T_d, respectively) were obtained from the peak temperature of each endotherm.

2.4.6. Moisture content (MC)

Moisture content (MC) of the different films was determined using the standard method of the International Association of Official Analytical Chemistry (AOAC, 1995). Pieces of ~ 0.6 g of each system were dried in an oven at 100 °C for 24 h. Water content was calculated as:

$$MC = \left(\frac{m_i - m_f}{m_i}\right) \times 100 \quad (2)$$

Where m_i is the initial weight and m_f is the dry weight of the samples. Five measurements for each system were performed and the main and statistic error were reported.

2.4.7. Water solubility (S)

Water solubility values were obtained following the method described by Romero-Bastida et al. (2005) and the correction method described by Hu, Chen, and Gao (2009). Solubility values were determined as:

$$Solubility \quad (\%) = \frac{(m_{si} - m_{sf})}{m_{si}} \times 100 \quad (3)$$

where, m_{si} is the initial dry weight and m_{sf} is the final dry weight.

Initial dry weight (m_{si}) was determined by subjecting disks of 20 mm of diameter in an oven at 100 °C for 24 h. To obtain the final dry weight values, the disks were immersed in 50 mL of distilled water for 24 h at 25 °C and dried at 100 °C for 24 h. The results reported are the average and standard error on 5 measurements per system.

2.4.8. Atomic force microscopy (AFM)

Films surfaces were analyzed by atomic force microscopy using an AFM-STM (NanoScope IIIa, Digital Instrument, DiVeeco, USA) equipment, operating in the tapping mode under the regime of nitrogen atmosphere. A three-dimensional image of a film surface of 5 μm x 5 μm was obtained and surface roughness (RMS) values were calculated using the WSxM 4.0 Beta 7.0 Image software Data Acquisition Wizard (Nanotec Electronic S. L., 2014). Determination was performed in duplicate.

2.4.9. Hydrophobicity of films surfaces (contact angle measurements)

Surface hydrophobicity of each film was determined following the methodology of (Stalder, Kulik, Sage, Barbieri, & Hoffmann, 2006), using a microscope MicroView (USB Digital Microscope) coupled with an image analysis software (Analysis Software 220 × 2.0 MP). A drop of distilled water (2 mL) was placed on the surface of each sample. The angle (θ) formed by the intersection of the liquid-solid interface (drop of water-surface of the film) and the liquid vapor interface (tangent on the boundary of the drop) was determined. The average of six measurements and the statistic error were reported.

2.4.10. Color change of the films in acidic and alkaline solutions

Taking into account that the films could be used as intelligent packaging, detecting deterioration of the product they cover from their own pH changes, color changes of the films in different aqueous media were observed. Pieces of ~ 16 mm of diameter were placed in petri dishes containing 10 mL of acidic and alkaline solutions (pH = 3 and pH = 12, respectively). Changes in the appearance of the samples (color) were recorded with a camera (Samsung model CMOS 8.0 mega pixels). Photographs of the samples at the previous moment and immediately after their immersion in the different pH media were reported.

2.4.11. Biodegradability in vegetable compost

Vegetable compost (soil) was poured into plastic trays (10 × 20 × 5 cm) up to a height of about 4 cm. Samples of each system (2 cm x 2 cm) were weighed and then buried in the soil to a depth of ~1 cm. The plastic trays were kept under ambient temperature and RH. Water was sprayed twice a day to sustain the moisture of the compost. At different times (first, sixth, and twelfth day), samples were carefully taken out, according to the method described by Dalev, Patil, Mark, Vassileva, and Fakirov, (2000) with some modifications (Dalev et al., 2000; Medina Jaramillo et al., 2015). Changes were recorded with a camera and representative photographs were reported.

3. Results and discussion

3.1. Total polyphenols content and migration of the extracts

Taking into account that the most important sources of antioxidants are polyphenols, the amount of these substances in the films containing tea (TPS-T) and basil (TPS-B) extracts was determined. Contents of polyphenols of ~ 2.97 mg PT/g and ~1.57 mg PT/g for TPS-T and TPS-B samples, respectively were observed (both values are expressed as Chlorogenic acid).

On the other hand, the mechanism of action of a coating with an antioxidant agent in direct contact with food is the release of the antioxidant into the product. The release of the extract in a medium that could simulate aqueous food, allow as to observe and determine the ability of the film to transfer its antioxidant property to certain foods, such as fruits and vegetables (80–90% moisture) (Fennema, Damodaran, & Parkin, 2008). Starch based films were applied to strawberries (Fragaria ananassa), showing that the products covered by the films were preserved over 21 days (Mali & Grossmann, 2003). Similarly, Ollé Resa, Gerschenson, & Jagus, (2016), obtained satisfactory results when using starch films as a coating on cheese. After evaluating the release of the extract in each system over 30 min, it was observed that the material with tea extract released ~17%, while TPS-B ~7%. The lower release of the film with basil was also reported by Suppakul et al. (2003), who demonstrated that the use of the active components of the basil led to a slow release of the antioxidant in a polymeric matrix (Suppakul, Miltz, Sonneveld, & Bigger, 2003). This result indicates that both films would be used as controlled-release products to coat food. However, TPS-T will release a higher amount of extract than TPS-B when in contact with a high water content food. Although there are no studies of the release of green tea extract incorporated into starch films, prevention of lipid oxidation in sausages coated by chitosan films containing this extract was already reported (Siripatrawan & Noipha, 2012).

It is known that the main sources of phenolic compounds in the diet are fruits and vegetables (Moure et al., 2001), so the world health organization recommends a consumption of fruits and vegetables of at least 400 g/day. However, the intake of these products is very low, which makes it necessary to design new products that incorporate these compounds (Saura-Calixto & Goñi, 2006). In this context, the films containing green tea and basil natural extracts developed in this work are very promising to complement the necessary intake, considering not only that they release polyphenols to the food, but also that these films are edible.

3.2. Color change of the films in acidic and alkaline solutions

Taking into account that the change in acidity of foods is frequent when they begin to deteriorate, the reaction of the films containing tea and basil extracts was evaluated qualitatively by immersing them in different aqueous media (pH = 3 and pH = 12)

The film containing basil extract changed its appearance immediately after being placed in both media. Color change was more evident when the sample was immerse in pH = 3, where the matt greenish yellow became almost white with a very slight yellow tonality. In the basic pH medium, initial sample color changed to a bright clear yellow. When the sample with tea extract was immersed in both media, only in the medium with pH = 12 a change in the tonality was observed, resulting in a slight darkening of the film. Color changes of samples at basic pH medium probably suggest that the films have a basic turning range where the H_3O^+ ions of the extracts components are affected by the OH^- ions of the basic medium, producing an imbalance and a decrease in $[H_3O^+]$ (Chang, 2006). These results are relevant when considering the extracts as films components with the important ability to generate a color change of a coating that is in direct contact with food. This development is intended for the use of these films as primary packaging (the packaging which is in direct contact with food), which is contained in a secondary or tertiary packaging. In this case, pH effects of other materials contacted with the coated food during shipping and handling is avoided. In this sense, if a food coated with TPS-B changes its acidity due to the start of deterioration, the film would respond immediately by changing its hue. Therefore, the use of films containing basil extract with products that lowers their pH when deteriorate, could contribute to the consumer for a better food quality control.

On the other hand, it's very important that the films change their color in a basic medium as most of the pathogenic bacteria grow in foods of neutral to alkaline pH (Fennema, Damodaran, & Parkin, 2008). For example, during the storage of meat products, endogenous and microbial enzymes degrade the proteins and produce ammonia and amines, which raise the pH (Barrientos, Chabela, Montejano, & Guerrero Legarreta, 2006). In agreement with Veiga-Santos, Ditchfield, & Tadini, (2011), who investigated different natural extracts as pH indicators and attributed the pH changes to the anthocyanins and chlorophyll content of the extracts (Veiga-Santos, Ditchfield & Tadini, 2011), in our case, the pH indicator behavior is attributed to the chlorophyll content of green tea and basil (Fig. 1).

3.3. Biodegradability in vegetable compost

Images of the films as a function of time buried in vegetal compost (soil) are shown in Fig. 2. It can be observed that during the first 6 days of burial, both films rapidly degraded showing a high loss of mass. Moreover, samples exhibited significant degradation in vegetal compost after 12 days. Comparing the biodegradability results of TPS-T and TPS-B with the starch-based films reported in the literature (Cerruti et al., 2011; Maran, Sivakumar, Thirugnanasambandham, & Sridhar, 2014), it can be observed that the use of tea and basil extracts led to shorter degradation times in soil. In particular, we previously showed that a thermoplastic starch film similarly obtained degraded in approximately two weeks (Medina Jaramillo, Gutiérrez, Goyanes, Bernal, & Famá, 2016).

The results of biodegradability in soil are decisive when thinking about an environmentally friendly packaging. In this sense, both films developed here are very promising to be used as eco-friendly materials in the food industry.

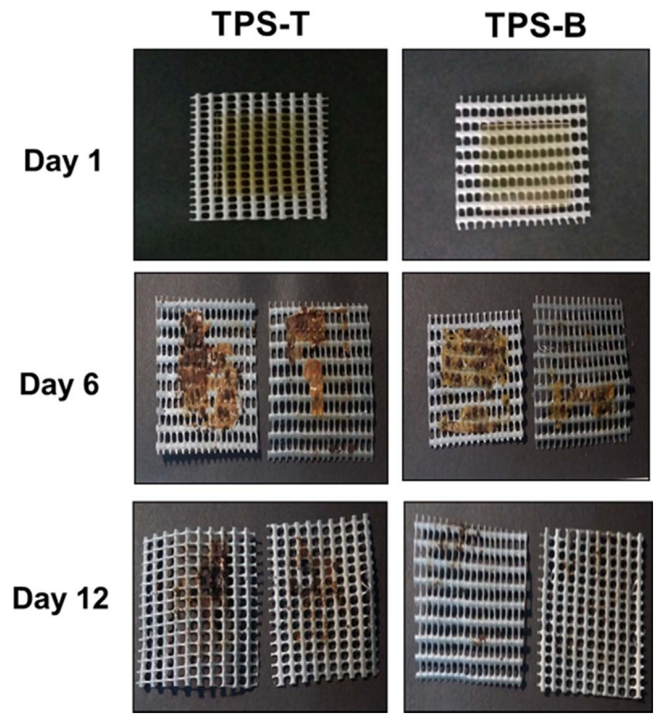

Fig. 2. Biodegradability in vegetal compost of cassava starch films with natural extracts.

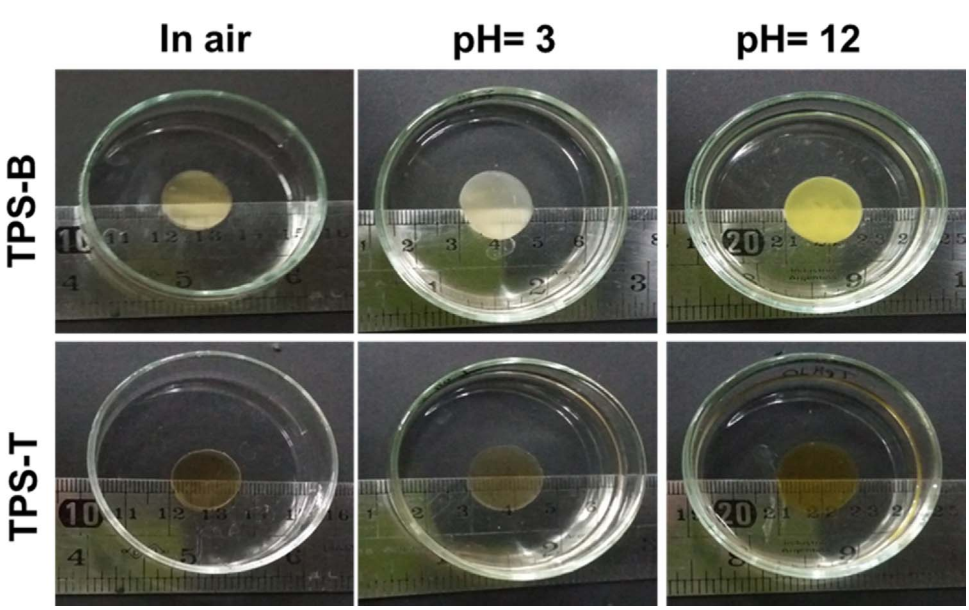

Fig. 1. Images of starch-natural extracts films in air and immersed in alkaline and acid medium.

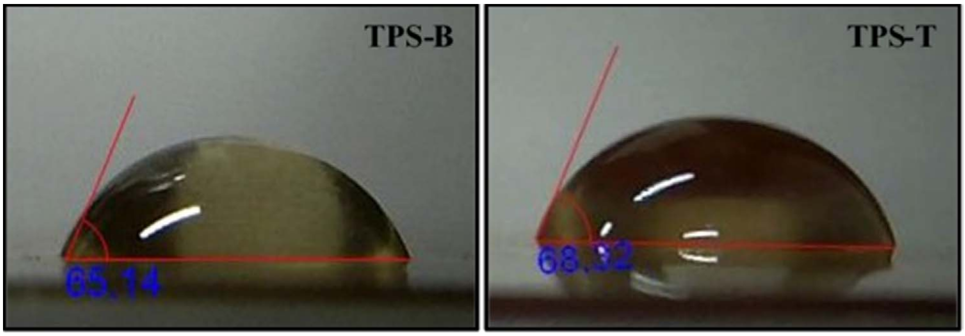

Fig. 3. Contact angle of the different starch-natural extracts films.

3.4. Contact angle, moisture content and solubility of the films

From tests of wetting of a drop of water on the surface of the films (Fig. 3), it was observed that both films presented contact angles (θ) between 60° and 70° (63 ± 3 and 68 ± 3, for TPS-B and TPS-T, respectively). Following the terms 'hydrophobic' and "hydrophilic", defined for θ > 65° and θ < 65°, respectively (Vogler, 1998), the evaluated films may be taken as hydrophobic materials. Although there are no significant differences between the contact angle (θ) values, there is a trend towards greater hydrophobicity in the film containing tea extract. Based on our previous results for films of starch and yerba mate extract, the increase of hydrophobicity in the materials having natural extracts was expected (Medina Jaramillo et al., 2016).

When films moisture content (*MC*) was evaluated (Table 1), a decreasing trend in the film containing green tea extract was observed. This result is in agreement with the slightly higher hydrophobicity of this film and with the results obtained from water solubility measurements (Table 1), in which a tendency to lower solubility in TPS-T compared to TPS-B was observed. It is important to remark that solubility tests revealed great integrity of all films until the end.

3.5. Atomic force microscopy, scanning electron microscopy and water vapor permeability

The surfaces that were in contact with air during the drying step of the films were analyzed through 3D topographical analysis (Fig. 4). The images revealed different behavior in both materials investigated. In the TPS-T surface, a very homogeneous distribution of small and close peaks was observed, whereas the film with basil extract presented a more heterogeneous distribution of higher and wider peaks, which were also more separated from each other. The roughness of TPS-B surface could be due to the lower integration of basil extract to the matrix during processing compared with tea extract (Ghasemlou et al., 2013; Jiménez, Fabra, Talens, & Chiralt, 2012).

This could be attributed to the presence of some solids of basil extract, which are not soluble in water. Then, due to their low molecular weight, they probably migrated to the surface of the film. This finding could not be obtained in the SEM micrograph of TPS-B (Fig. 5b) because it was taken from the cryogenic fracture surface of the film. The AFM micrograph, in contrast, was directly obtained from the film surface. Despite the differences in the topographies of the materials, roughness values (RMS) for both films (Table 1) did not show significant differences but RMS of TPS-T tended to increase over that of TPS-B.

It is well known that there is a strong relationship between the material surface roughness and its hydrofibicity (Erbil, Demirel, Avcı, & Mert, 2003; Kim et al., 2014; Miwa, Nakajima, Fujishima, Hashimoto, & Watanabe, 2000). In particular, Miwa, (2000) basically attributed this fact to the air spaces generated between the peaks on the surface, independently on the shape, size and distribution (Miwa et al., 2000). Specifically, we demonstrated previously that as the roughness increased, the contact angle was higher (Medina Jaramillo et al., 2016).

Water vapor permeability (WVP) value for the starch-based film containing basil extract was lower than that for the film with green tea (Table 1). However, both values were in the same order of magnitude. The lower WVP value obtained for TPS-B was expected, taking into account the hydrophobicity behaviors and AFM topographies of both systems. On the one hand, it is well known that water vapor transfer usually increases in a material with pores and/or with higher hydrophilicity (Dhanapal et al., 2012; Gennadios et al., 1994; Kavoosi, Dadfar, & Purfard, 2013). In this sense, cryo-fractured surfaces of both films did not present pores (Fig. 5), and TPS-B showed a greater tendency to hydrophobicity than TPS-T. On the other hand, topographical analysis of TPS-B led to the idea that this film had probably more restrictions to the passage of water molecules through it, decreasing WVP (Dai, Qiu, Xiong, & Sun, 2015; Sinha Ray & Okamoto, 2003). From another point of view, the use of tea and basil extracts led to materials with greater barrier to water vapor compared with typical thermoplastic starch films (Kechichian, Ditchfield, Veiga-Santos, & Tadini, 2010; López-de-Dicastillo, Gómez-Estaca, Catalá, Gavara & Hernández-Muñoz, 2012). This concept is remarkable taking into account that beyond the advantage of using natural extracts to provide antioxidant properties, they can also contribute to the improvement of other important properties for food coating such as water vapor barrier properties.

3.6. Differential scanning calorimetry (DSC)

The thermograms (DSC) of both materials are shown in Fig. 6. Well-distinguished endothermic processes can be observed. The first, in the range of 50 °C to 150 °C, with a peak temperature (melting temperature, T_m) around 90 °C (Table 1), is attributed to the melting of the crystals formed during starch retrogradation (Chang, Cheah, & Seow, 2000; López-de-Dicastillo et al., 2012; Medina Jaramillo et al., 2016). The use of the different natural extracts did not lead to changes in this thermodynamic process. Hence, it can be concluded that the type of extract used does not affect the process of retrogradation of starch due

Table 1
Surface roughness (RMS), moisture content (MC), water vapor permeability (WVP), water solubility (S), melting temperature (T_m) and fusion temperature (T_f).

Material	RMS	Moisture Content, %	WVP, g/smPa ($x10^{-10}$)	S (%)	T_m (°C)	T_f (°C)
TPS-T	4.5[a] ± 0.3	25.3 ± 1.6	5.2 ± 0.4	28[a] ± 1	89[a] ± 1	306 ± 2
TPS-B	4.3[a] ± 0.3	28.6 ± 1.2	3.4 ± 0.2	30[a] ± 1	90[a] ± 1	287 ± 1

[a] Similar letters in the same column indicate non-significant differences (p ≤ 0.05).

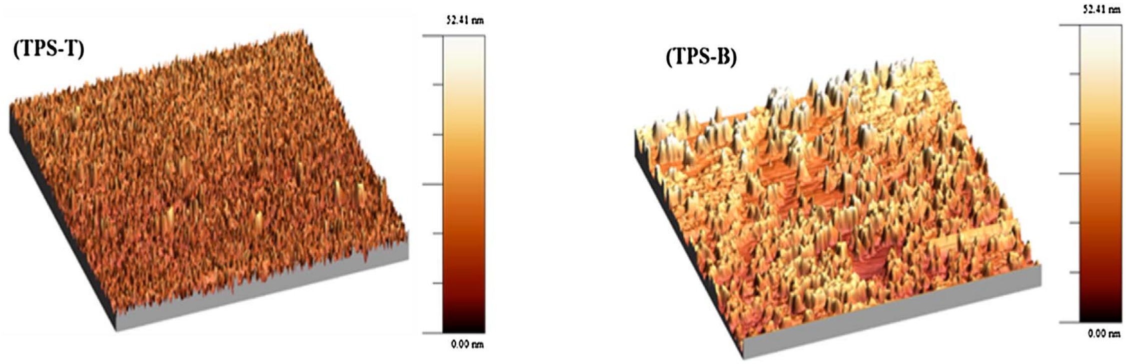

Fig. 4. AFM three-dimensional topographic images of the surface of the films.

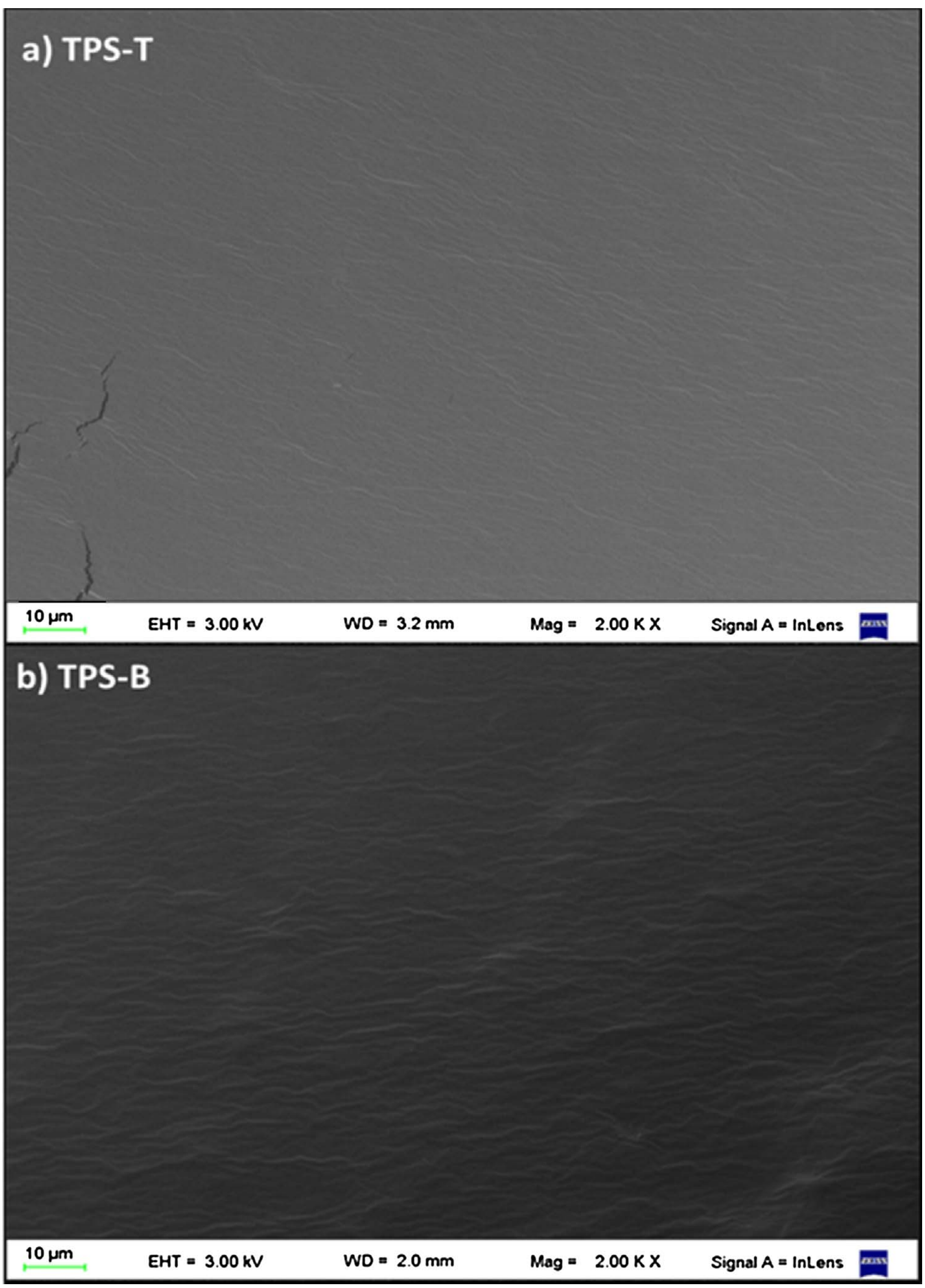

Fig. 5. SEM Micrographs of the cryogenic fracture surface of the films.

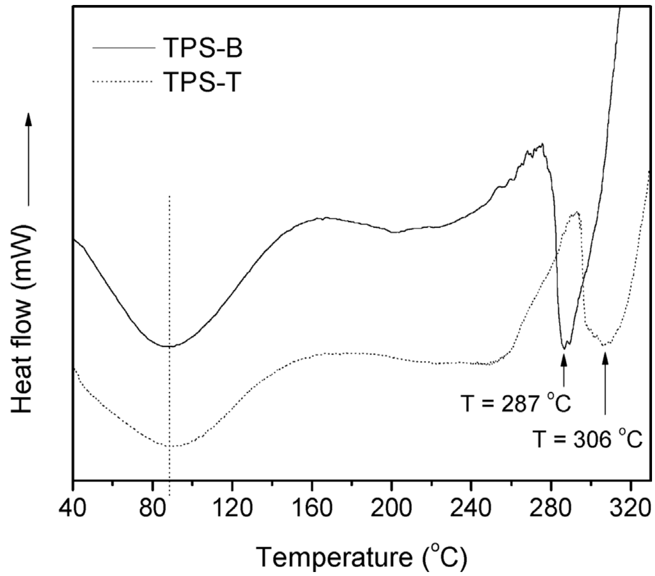

Fig. 6. DSC of the different developed films.

to the complex formed by the starch-glycerol-extract. It is interesting to note that melting temperature values for the films presented in this work are lower than those for typical thermoplastic starch films without extracts (Ferreira, Grossmann, Mali, Yamashita, & Cardoso, 2009; López-de-Dicastillo, Gómez-Estaca, Catalá, Gavara, & Hernández-Muñoz, 2012; Medina Jaramillo et al., 2016). According to the literature, some additives or components can lead to a decrease in the melting temperature of thermoplastic materials (Mathew & Abraham, 2008; Rachtanapun & Tongdeesoontorn, 2009; Robertson, 2016). In particular, (Wu, Chen, Li, & Li, 2009) reported the decrease of T_m in rice starch films with tea extract. The authors attributed this effect to the interaction of the polyphenols of the extract with the amylopectin side chains, changing the coupling forces between the crystallites and the amorphous matrix. Therefore, the addition of tea and basil extracts limited the growth of crystals by their intermolecular interaction with the polymer chains, hindering their alignment (Medina Jaramillo et al., 2016).

A second endothermic process observed as a broad peak from approximately 160 °C occurred also in both samples but its temperature peak is not well defined. According to the literature, this phenomenon could be also due to the melting of the crystalline phase of starch (Bergo et al., 2008). Nordmark and Ziegler (2002) analyzed high amylose starch by DSC and observed a small but wide endothermic peak occurring from 160 °C and they associated it to higher melting crystallites of starch. This thermal process is slightly shifted to higher temperatures in TPS-T, probably due to the better integration of tea extract to the matrix, causing that higher temperatures were needed to melt these crystals.

The third endothermic process observed is related to the thermal degradation of starch (T_d) (Reddy & Yang, 2010; Shogren, Fanta, & Doane, 1993). In both cases, the films withstood temperatures of at least 280 °C before their decomposition (Table 1). The decomposition values of these samples are in agreement with those reported in the literature for highly plasticized starch films (Bergo et al., 2008; Chang et al., 2000).

The beginning of the thermal degradation of TPS-T resulted in slightly temperatures than T_d of the film containing basil extract TPS-B (~5 °C). Taking into account AFM behavior, this fact may be attributed to the greater introduction of the extract of tea in the starch matrix, generating greater interactions through hydrogen bonding between starch and tea extract and leading to a higher degradation temperature.

Thermal results suggest that starch films with tea or basil extracts seem to be attractive as coatings for any food able to be cooked at a temperature lower than 280 °C.

4. Conclusions

From the results of this investigation, it can be concluded that biodegradable thermoplastic films based on cassava starch and natural extracts such as green tea and basil can be used as smart and active food packaging. First, high contents of polyphenols capable of acting as antioxidants were observed in the films containing the different extracts, leading to coatings able to delay the oxidation of food products, and avoiding their fast deterioration. On the other hand, chlorophyll and carotenoids present in both green tea and basil extracts undergo changes in the color when exposed to different pH, resulting in materials able to be used as indicators of food quality. In addition, fast films degradation in soil (less than two weeks) was observed, resulting in environmentally friendly materials. In addition, with the use of tea and basil extracts, films water vapor permeability was reduced respect to typical thermoplastic starch based materials, also keeping their flexibility to facilitate the handling. Finally, excellent thermal properties were obtained for both types of films, making them able to withstand temperatures up to 240 °C without degradation.

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