PAPER

DEVELOPMENT OF AN ACTIVE BIODEGRADABLE FILM CONTAINING TOCOPHEROL AND AVOCADO PEEL EXTRACT

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ABSTRACT

Thermoplastic starch (TPS) films and poly(butylene adipate co-terephthalate) (PBAT) (60/40 m/m) containing TOCO-70 (tocopherol/soybean oil 70/30 m/m) and avocado peel extract (ExA) were produced using blown film extrusion. The formulations of the 5 films (FC/F1/F2/F3 and F4) were established through mixture design with constraints maintaining constant PBAT and TPS proportion, and varying the antioxidant concentrations. Adding antioxidants reduced the water vapour permeability (K^w) of the films, with formulation F2 presenting higher decrease in relation to FC, 77.8%. The presence of ExA improved the mechanical properties of the films. The production of the films was determined to be viable after they presented good processability in a pilot extruder, as well as mechanical properties appropriate to production and utilization in industry. The presence of ExA and TOCO 70 provided the films with antioxidant activity; their application as active packaging requires further studies.

- Keywords: active packaging, antioxidant, biodegradable polymer, poly (butylene adipate co-terephthalate), thermoplastic starch -

1. INTRODUCTION

The fundamental function of food packaging is to delay the deterioration of the product in all physical, chemical, microbiological, sensory and nutritional aspects, ensuring the quality of the product until it is consumed (RESTUCCIA *et al.*, 2010). The oxidation of food sensitive substances form hydroperoxides that decompose into aldehydes, ketones, alcohols, acids, esters or hydrocarbons, altering the color, texture, smell and taste, as well as reducing the shelf life (MCCLEMENTS and DECKER, 2000). Active packaging interacts with the food to increase its shelf life, and materials containing antioxidants are a promising alternatives used to develop new active packaging (BYUN *et al.*, 2010; PEREIRA DE ABREU *et al.*, 2012; PEREIRA *et al.*, 2013).

Tocopherol is a liposoluble antioxidant that is widely applied in food as a primary antioxidant. Tocopherol is highly stable when applied in films of polyethylene and polypropylene, even under severe extrusion conditions. (AL-MALAIKA *et al.*, 1999; AL-MALAIKA *et al*, 2001). Recent studies regarding films elaborated from biodegradable polymers with tocopherol have generated positive results concerning antioxidant migration when applied to food (BYUN *et al.*, 2010; GRACIANO-VERDUGO *et al.*, 2010; LÓPEZ *et al.*, 2011; HWANG *et al.*, 2013; MARTINS *et al.*, 2012).

Several active principles originating from plants have been applied as anti-oxidants (DI-CASTILHO *et al.*, 2011; PEREIRA DE ABREU *et al.*, 2012; RUBILAR *et al.*, 2013), such as the avocado; the avocado is an oleaginous fruit native of Tropical America (Mexico) that is rich in phenol derivatives. Only 69% of this fruit are edible, the remaining is constituted of stone and skin. The use of the skin to extract antioxidants may add value to the residue and minimize environmental issues.

(WANG *et al.*, 2010) studied the antioxidant capacity of peels and seeds in various avocado species and concluded that these residues also contain large quantities of phenol compounds, among other antioxidants. RODRÍGUEZ-CARPENA *et al.* (2011) used avocado peel and seed extracts to inhibit lipid oxidation in meat products.

Active packaging can be manufactured using ecofriendly materials, such as biodegradable polymers. Starch has been used as an alternative to produce biodegradable films, but the materials present a low mechanical strength and are hygroscopic (MALI *et al*, 2005; REN *et al.*, 2009; SCAPIM, 2009). The conversion of starch into thermoplastic starch (TPS) involves heating and shearing with a plasticizer agent, such as glycerol.

The materials produced from blends of thermoplastic starch and other biodegradable polymers may be used to develop low-cost biodegradable packaging with better mechanical and barrier properties (BRANDELERO *et al.*, 2012; OLIVATO *et al.*, 2011; REN *et al.*, 2009; SCAPIM, 2009). Poly(butylene adipate co-terephthalate) (PBAT) is a biodegradable polyester with mechanical properties similar to the those of polyethylene films with resistance to fat and humidity and temperature variations (BASF, 2013). Previous studies have studied biodegradable materials produced using blends of thermoplastic starch and PBAT (BRANDELERO *et al.*, 2012; OLIVATO *et al.*, 2011; REN *et al.*, 2009; SCAPIM, 2009). The objective of this study was to characterize and assess the mechanical and structural properties of biodegradable films composed of thermoplastic starch, PBAT and antioxidants (tocopherol and bark extract avocado) seeking better interaction among these compounds in order to suggest further studies on the application of these films in active packaging.

2. MATERIALS AND METHODS

2.1. Materials

The film production utilized native cassava starch (Indemil Com. Ind. Ltda, Brasil), glycerol (Synth P.A, Brasil), poly(butylene adipate co-terephthalate) (Ecoflex®, BASF Chemical Company, Brasil) and TOCO-70 (tocopherols solution/soybean oils 70/30 m/m) (Danisco, Brasil). The avocado fruits (Persea americana Mill) were utilized at an intermediate maturity stage as moderately tender and green peel derived from São Paulo state after being purchased in Maringá PR.

2.2. Production and characterization of avocado peel extract

The peels were separated from fruits, cut into 2-cm squares, dried in a greenhouse at 60°C for 24 h, ground in an analytical mil and sieved. The extracts were prepared according to SANTOS *et al.* (2011) with some modifications. The previously dried and ground peels were soaked in ethanol at 95% v/v (proportion 1/10 m/v) with stirring for 4 h. The solution was vacuum filtered and concentrated via rotary evaporation at 40°C. The dry extracts (ExA) were stored in amber flasks at -18°C, under nitrogen atmosphere (N_2) until the analyses.

The compounds in ExA were characterized and quantified using Ultra-High Performance Liquid Chromatography coupled to Electrospray Ionization Mass Spectrometry in negative ion mode (UPLC-ESI(-)-MS) (Acquity UPLC-TQD, Waters, EUA). Approximately 10.0 mg of dry ExA and 1.0 mg of standard in HPLC grade methanol were injected (3 μL) into UPLC-ESI(-)-MS equipped with an Acquity column UPLC BEH C^{18} (2,1 x 50 mm) with 1.7 μm particles at 30°C. A gradient elution at 0.20 mL/min with solvent A (formic acid at 0.1%, in Milli-Q water) and B (methanol) was used with the following

method: from 95% of A and 5% of B to 100% B in 8.00 min, and the system was stabilized at 10.00 min. The spectra were acquired under the following conditions: capillary and cone stress of -3000 V and -30 V, respectively, with a source temperature of 150°C and a temperature of desolvation of 350°C.

2.3. Preparation of the biodegradable films

We produced 5 different types of biodegradable films, where the film Control (FC) was used as a reference and was composed of starch/glycerol/PBAT the proportions 42/18/40 (w/w/w). In the other films concentrations TOCO-70 and ExA were determined using a mixture design with constraints (Table 1), were proportion of starch/glycerol/PBAT was maintained at 42/18/40 (m/m/m). The results were analyzed using the STATISTICA 7.0 software (Statsoft, EUA).

The films were processed in the Technology Laboratory of Food Science and Technology Department of State University of Londrina (UEL - Brazil). The antioxidant compounds were mixed with glycerol. Initially, the pellets were produced in a pilot twin screw extruder (BGM, model D-20, Brazil) equipped with screws measuring 20 mm in diameter and 680 mm in length. The speed of the screws was set at 100 rpm, and the temperature profile in all five heating zones was 90/120/120/120/120°C. The film was produced in a pilot single-screw extruder (BGM, model EL-25, Brazil) equipped with a screw measuring 250 mm in diameter. The speed was maintained at 35 rpm, and the temperature profile in all four heating zones and in the matrix for balloon formation was 90/120/120/130/130°C.

2.4. Biodegradable Films

2.4.1. Thickness (δ) *and density* (ρ)

The thickness (δ) of the films was determined using a digital micrometer (0.001 mm resolution, Mitutoyo, Japan). Twelve random points on each film formulation were assessed. For the density (ρ), the average masses of 10 square samples (25 mm x 25 mm) of film were calculated after being conditioned in desiccators with anhydrous calcium chloride for 20 days.

2.4.2. Water vapour permeability (K^W)

The films were conditioned at 64±2% RH and 25±2°C for 72 h. The film samples were fixed to a circular opening of a permeation cell (area of 60 mm2) with silicone grease. The interior of the cell was filled with magnesium chloride saturated solution (33% RH) and was stored at 25±2°C in a desiccator that contained sodium nitrate saturated solution (64% RH) to maintain a 31% RH gradient across the film. The sample were weighed every 3 h during 72 h of testing time. The changes in the weight of the cell or mass gain (m) were plotted as a function of time (t). The slope of each line was calculated using linear regression, and the water vapour permeation ratio (K^wR) was obtained using Equation (1):

$$K^wR = (m/t).(1/A)$$

where m/t is the angular coefficient of the curve and A is the sample permeation area.

The K^w was calculated as Equation (2):

$$K^w = K^wR.st/sp(RH_1-RH_2)$$

where st is the mean sample thickness (m), sp is the water vapour saturation pressure at the assay temperature (Pa), RH1 is the relative humidity of the desiccator and RH2 is the relative humidity in the interior of the permeation cell. The tests were conducted in triplicate.

Table 1 - Formulation of biodegradable films according to mixture design and the constraints.

Film formulation	Films component (m/m/m)		
	Starch + Glycerol + PBAT	ExA	TOCO-70
	x_1	x_2	x_3
FC	1.000	-	-
F1	0.994	0.006	-
F2	0.992	-	0.008
F3	0.986	0.006	0.008
F4	0.993	0.003	0.004

° $x_1 + x_2 + x_3 = 1$

2.4.3. Sorption isotherms

The sorption isotherms of the films were determined according to the methodology described by SCAPIM (2009) using the following relative humidities at 25°C: 11.3, 33, 43.2, 52.9, 64.5, 75.3, 84.3 and 90.2%.

The isotherms were modeled according to the Guggenheim-Anderson-de Boer (GAB) model (Equation 3) using the Quasi-Newton method in Statistica 7.0.

$$X_w = \left(\frac{m_0.C.K.a}{[(1-K.a_w).(1-K.a+C.K.a_w]}\right)$$

where X_w (g of water/g of dry matter) is the relative humidity of balance, m_0 is the water content in the monolayer (g of water/g of solids), a_w is the water activity, and C and K are constants from the GAB model that represent the sorption heat in the first layer and sorption heat of the multilayer.

2.4.4. Determination of solubility (β) and diffusion (D^w) coefficients

The method used to calculate the solubility coefficient (β) was proposed by LAROTONDA *et al.* (2005) using the first order derivative of the GAB. This model is correlated with the water activity and water vapor pressure (P_s) at 25°C according to Equation 4.

$$\beta = \frac{C k m_o}{p_s}\left[\frac{1}{(1-ka_w)(1-ka_w+Cka_w)} - \frac{a_w}{[(1-ka_w)(1-ka_w+Cka_w)]^2}[-k(1-ka_w+Cka_w)+(1-ka_w)(-k+Ck)]\right]$$

where β(g/g.Pa)is the solubility coefficient, C, K, and m_0 are the GAB model parameters and Ps (Pa) is the water vapor pressure at 25°C. The a_w was the average of the relative humidity gradient used in K^w(g/m.Pa.day) (item 2.4.2).

The coefficient of water vapor diffusion (D^w) was calculated according to Equation 5 using the values of β and K^w, as determined in section 2.4.2, where ρ is the film density:

$$D^w = K^w/\rho.\beta\,\frac{PVA}{\rho.\beta}$$

2.4.5. Mechanical properties

The mechanical properties (ultimate tensile strength and elongation at rupture) were assessed according to ASTM D 882-91 (ASTM, 1996) using a texturometer (Stable Micro Systems, model TA.TX2i, England) with a 30-mm distance between the clutches and a traction speed of 500 mm/min. The samples were 80 mm long and 6 mm wide; they were conditioned under 64.5% RH at 25°C for seven days before the analyses. For each formulation, 10 repetitions were performed.

2.4.6 Microstructures analysis

The analyses were conducted using scanning electron microscope (Shimadzu, model SS-550N, Japan) based on the methodology descripted by SCAPIM (2009). The samples were immersed in liquid nitrogen and fractured with the aid of tweezers before being conditioned in a desiccator with calcium chloride to remove any humidity for three weeks. The samples were subsequently overlaid with two golden covers through a metallizer (Shimadzu IC-50 Ion Coater, Japan). After preparation, the samples were visualized through electronic scanning microscope to have its fracture area surface analyzed.

2.4.7. Antioxidant capacity of avocado peel extract and films

The analyses were carried out according to the method described by SERPEN *et al.*, (2012). Sample of 10.0 mg of avocado peel extract and each film formulation was reacted with 5 mL of 2.2-diphenyl-1- picrilhidrazil (DPPH•) in ethanol/water (50/50, v/v) over 1, 2, 3 and 4 hours under magnetic stirring and protection from light. Afterward, the blend was centrifuged for 1 min at 300-400 rpm (8 G) and the absorbance of the supernatant was measured through a spectrophotometer (ThermoScientific, model Genesys 10 UV, USA) at 525 nm. Methanolic solutions of (±)-6-hydroxy-2,5,7,8-tetramethylcromano-2-carboxylic acid (Trolox) in different concentrations were used to obtain the calibration curve for 5 mL (y = 29.448x + 5.4989, R^2 > 0.99) with the oxidant capacity expressed in μmol of Trolox equivalents (ET)/g for each film formulation.

3. RESULTS AND DISCUSSION

3.1. Antioxidant compounds and antioxidant capacity of avocado peel extract.

The following antioxidant compounds were identified and measured in the avocado peel extract: citric acid (133±10 μg/100 g extract), catechin hydrate (82±3 μg/100 g extract), malic acid (75±2 μg/100 g extract), epicatechin (62±3 μg/100 g extract) and tartaric acid (11.8±0.1 μg/100 g extract). Prior studies have revealed positive results for active packaging developed using plant extracts with compositions similar to ExA (DICASTILHO *et al.*, 2011; LÓPEZ *et al.*, 2011; PEREIRA DE ABREU *et al.*, 2012).

The antioxidant capacities of ExA and TOCO-70 were 188±8 mmol ET/g o and 162±8mmol ET/g, respectively. WANG *et al.* (2010) assessed different avocado species and concluded that both the seed and peel contain copious quantities of phenolic compounds and high antioxidant capacities. The authors found variations from 38 to 189.8 μmol of ET/g in peels from different species; the peel contributes 38% of the antioxidant capacity of the entire fruit. Therefore, the extraction concentrated the relevant compounds, presenting an antioxidant capacity more than a thousand times higher than that reported by (WANG *et al.*, 2010).

3.2. Films characterization

3.2.1. Sorption isotherms

The films all exhibited practically constant water sorption until 60% UR, and above 60%

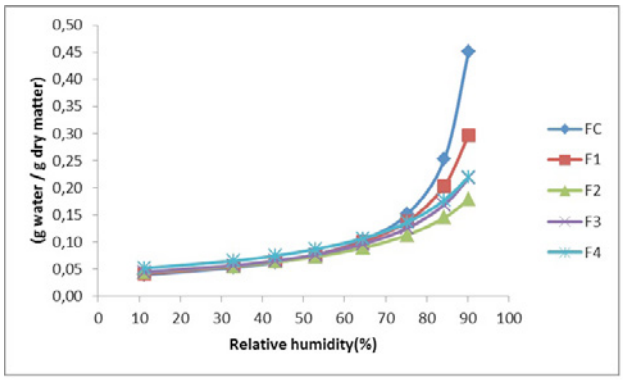

Fig. 1 - Water sorption isotherms of biodegradable films at 25 °C.

an increase in sorption occurred (Fig. 1) due to the hydrophilic nature of the starch. According to TALJA *et al.* (2008), for relative humidities above 60%, a replacement of starch-starch and starch-glycerol interactions with starch-water and water-glycerol interactions may occur, justifying the increase in water sorption from the humidity.

Adding TOCO-70 and ExA decreased the hydrophilicity of the films under UR above 75% while formulations F2, F3, F4 and F1 presented reductions of 34, 21, 11 and 10%, respectively, concerning water sorption in the control film (FC). The formulation containing only TOCO-70 (F2) presented the lowest water sorption in high relative humidities most likely due to the compatibility between the tocopherol and the soybean oil present in the compound with the starch and PBAT blend (BRANDELERO *et al.*, 2012).

Table 2 - Parameters for the GAB equation at 25°C for the biodegradable films.

Parameters for GAB model	Films formulations				
	FC	F1	F2	F3	F4
m_0	0.0348	0.0370	0.0394	0.0399	0.0465
C	168.52	159.57	150.49	163.361	139.76
K	1.02	0.97	0.86	0.91	0.87
R^2	0.97	0.99	0.89	0.94	0.96

The GAB model was satisfactorily adjusted to the experimental isothermal data, and the determination coefficients (R^2) varied from 0.89 to 0.99 (Table 2). The constant values of sorption for the multilayer (K) are correlated with the isothermal behavior in relative humidity above 65% (Fig. 1); specifically, the higher the water sorption for the films in that area are, the higher the K values are.

3.2.2. Water vapour permeability (K^W), the coefficient of solubility (β), the coefficient of diffusion (Dw), the thickness (δ) and the density (ρ)

The films containing antioxidants presented values for the water vapour permeability *(K^W)*, the coefficient of solubility (β) and the coefficient of diffusion (Dw) lower than for the control film (FC) (Table 3) due to the hydrophobic nature of ExA and TOCO-70. Film F2 contained only TOCO-70 and presented the lowest hydrophobicity, with a decrease of 77.8% in relation to the control formulation (CF). Considering that the hydrophilicity of the cassava starch is a major obstacle for its application in packages, the addition of antioxidants may also contribute to improve this characteristic (AVÉROUS and BOQUILLON, 2004; BRANDELERO *et al.*, 2011; OLIVATO *et al.*, 2011; REN *et al.*, 2009).

According to the model generated using the mixture design (R^2=0.83) that was correlated with the K^W in accordance with the film components (Fig. 2), the films containing only one type of antioxidant present a reduced K^W that has proven to be more effective than the blends. This behavior may be verified using the positive interaction model $+5.x_2.x_3$; specifically, when the film contains both antioxidants (x_2 = avocado extract; x_3 = TOCO-70), an increase in K^w occurs.

BRANDELERO *et al.* (2012) verified that the presence of soybean oil in the ATP/PBAT blends facilitated an interaction between the carboxyl group of the fatty acids and the PBAT, as well as film compaction promoted by the starch, which explains why formulation F2 presented the lowest β e D^w coefficients. Both ExA and TOCO-70 acted as compatibilizers, helping polymers interact and enabling the formation of a more compact structure that gives the molecules less

Table 3 - *Water vapour permeability (K^W)*, thickness (δ), density (ρ), coefficient of solubility (β) and coefficient of diffusion (D^w) for the biodegradable films.

Formulation	K^W (x10^{-6}) (g/m.Pa.day)	Δ (μm)	ρ (g/cm³)	β (x10^{-5}) (g/g.Pa)	D^w (x10^6) (m²/day)
FC	14.51±0.47	196±37	1.278	4.50	0.25
F1	6.75±0.46	149±19	1.475	4.12	0.11
F2	3.21±0.52	146±13	1.165	3.24	0.08
F3	6.03±0.81	130±17	1.279	3.69	0.13
F4	7.53±0.98	161±17	1.153	3.95	0.17

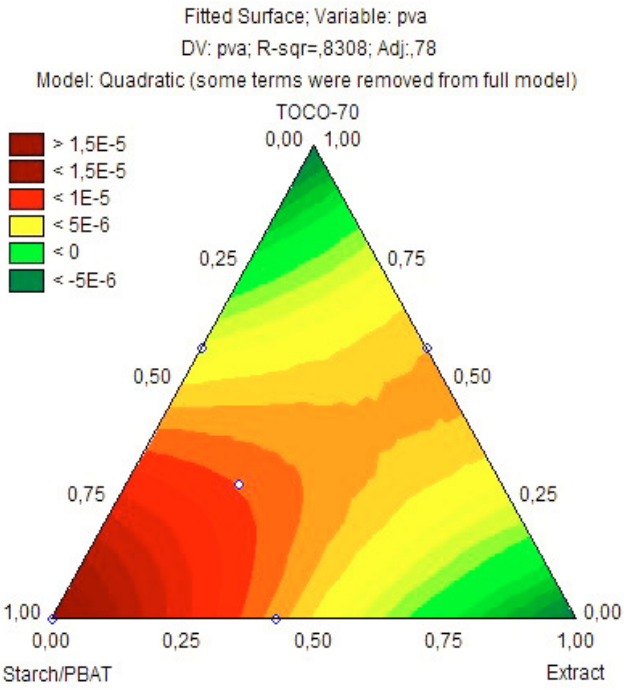

Fig. 2 - Permeability of water vapour of films according to starch/PBAT, ExA and TOCO-70 contents.

space to move, as shown by the coefficient of diffusion. These additives also provide lower hydrophilicity, as the coefficient of solubility indicates. Possibly, such improvement in the interaction of polymers promoted by the presence of antioxidants contributed to the lower thickness of the films since all of the formulations with an antioxidant presented reduced thickness compared with the control formulation, FC, with higher

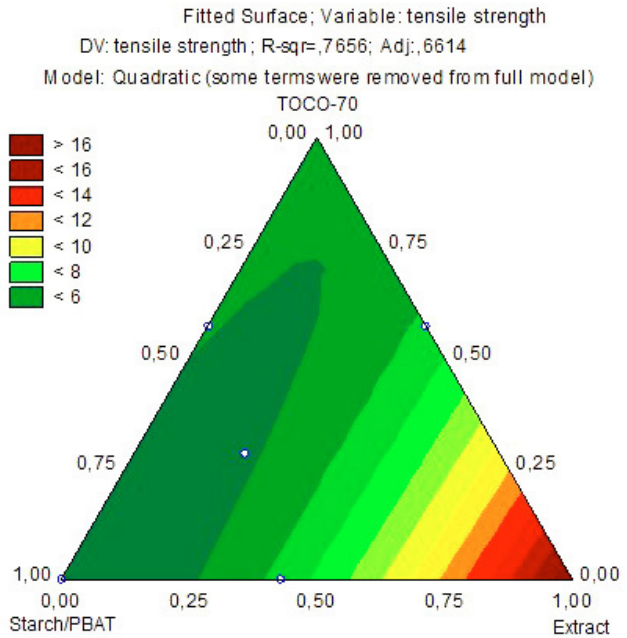

Fig. 3 - Tensile strength of the films according to Starch/PBAT, ExA and TOCO-70 contents.

mean value, 196±37μm, and F3 with the lower mean value, 130 ±17μm.

3.2.3. Mechanical properties

According to the model generated using the mixture design (R^2=0.77) to correlate the mechanical properties with the film components, the avocado extract (ExA) had a larger effect than TOCO-70 concerning the tensile strength (Fig. 3) and the elongation of the films (Fig. 4). According to OLIVATO *et al.* (2012), both citric and malic acids promote reticulation (*crosslinking*) between thermoplastic starch

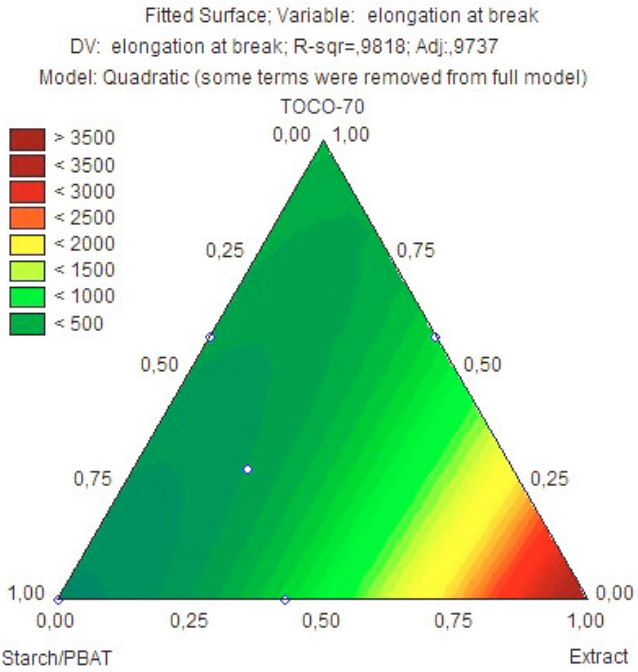

Fig. 4 - Film elongation at break according to Starch/PBAT, ExA and TOCO-70.

and PBAT, making the films resistant toward traction. ExA contains both acids in its composition, improving the mechanical properties of the films.

3.2.4. Antioxidant capacity of biodegradable films

According to the model generated while using the mixture design (R^2=0.98) and correlating the antioxidant capacity with the film components, the effect of the avocado peel extract (ExA) on the antioxidant capacity of the films was higher than that of tocopherol (TOCO-70) (Fig. 5).

The antioxidant capacity of the ExA extract and the TOCO-70 solution are similar, however, the films containing ExA presented a higher antioxidant capacity compared to the films containing TOCO-70, most likely due to the higher thermal stability of the ExA.

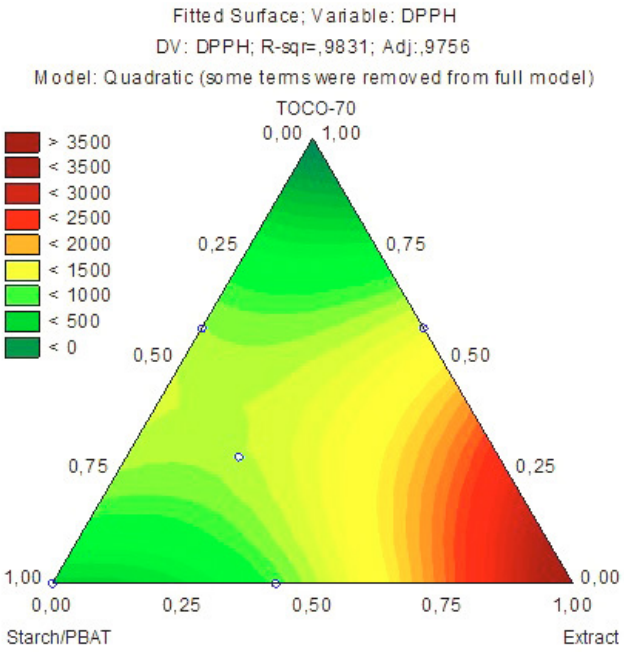

Fig. 5 - Antioxidant capacity of the films according to Starch/PBAT, ExA and TOCO-70 contents.

3.2.5. Desirability function

As observed in the analyses of K^w the presence of TOCO-70 provided better result when compared with formulation FC, with 77.8% decrease. However, by assessing the contour surfaces of the mechanical properties and the antioxidant capacity, it is possible to observe the occurrence of a tendency to have these characteristics improved when ExA is more present than TOCO-70. The desirability function indicated that the formulation that maximizes the ultimate tensile strength, elongation at rupture, and the antioxidant capacity while minimizes the permeability to water vapor (K^w) is a film whose composition should consist of 98.95% starch + PBAT + glycerol, 0.556% EXA, and 0.494% TOCO-70. After these results, further studies are going carry out with the same composition defined by Desirability function.

3.2.6 Microstructure

In the surface and film fracture micrographs neither pores, non-gelatinized granular neither starch nor phase separation were detected, thereby indicating good interactions between the components of the films for all formulations.

4. CONCLUSIONS

The production of biodegradable films composed of thermoplastic starch, PBAT and antioxidants (tocopherol and avocado peel extract) is viable since the films presented good processability in a pilot extruder, as well as the appropriate mechanical properties for industrial production and applications. The presence of ExA provided the films with antioxidant activity enabling their application as active packaging. It is required to conduct further studies to test the application of this blend of polymers and antioxidants in biodegradable and active packaging for products rich in lipids, such as hamburguers, nuggets, peanuts and soy, to verify the occurrence of antioxidant action of the package produced using such film on the product stored. Still, we suggest the development of a film with composition established through the desirability function to carry out the application tests.

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