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Development and Active Biodegradable Film Evaluation Incorporated with Oregano Essential Oil and Nanoclay

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Biodegradable and active packaging comes against the industry wishes to offer innovative products and to help protect the environment, and avid consumers for food products with lower levels of additives, being thus healthier and safer. The objective of this work was to produce and characterize active biodegradable films, by extrusion blow processing, with 58% of thermoplastic starch (29g glycerol/100 g cassava starch), 40% poly (butylene adipate co-terephthalate), 1 to 2 % oregano essential oil, 1 to 2% of nanoclay. The three films were characterized sorption properties, films permeability to water vapor and mechanical strength. The nanoclay presence increased 11% in the tensile strength and did not alter the permeability to water vapor, however the presence of the oregano essential oil decreased hydrophilicity of the films. Further studies should be conducted to assess the stability of these packages and the antimicrobial effect.

1. Introduction

Plastics are the most used materials in the manufacture of food packaging due to its versatility, and because it is an excellent barrier to gases and water vapor, besides allowing visualization of the product (Avérous and Boquillon, 2004). But from the environmental point of view this material is disadvantageous, not only because it takes many years to decompose, but especially if we consider that the volume used is increasing and the portions offered to the consumer are becoming smaller, which increases even more the demand of these. In addition, the recycling of these wastes will give rise to a more restricted application material.

Thus these problems can be reduced or even solved if these packages are made from biodegradable polymers that do not cause environmental impact, especially if they are obtained from renewable sources (Avérous and Boquillon, 2004; Liu et al., 2009; Zullo and Iannace, 2009).

Many biodegradable synthetic polymers have good characteristics for the production of packages, but these polymers are much more expensive than conventional synthetic polymers such as polyethylene. Thus the agropolymers, which include polysaccharides, proteins and lipids, can also be used in the production of biodegradable packaging (Park et al., 2002).

These agropolymers have the advantages of high biodegradability and the lowest cost compared to synthetic biodegradable polymers. Among these, starch has been note for being the most abundant and the least cost but its use, as the only polymer for the production of packaging does not seem indicated. Several studies have shown that starch films are hygroscopic and low mechanical resistance, a feature that compromises the efficiency of the packaging and the quality of the product contained therein (Santos et al., 2014; Olivato et al., 2017).

The use of starch blends with biodegradable synthetic polymers can provide packages with lower costs, better biodegradability and performance. Among the synthetic biodegradable polymers it can be mentioned the poly (butylene adipate-co-terephthalate) (PBAT), that is a synthetic aliphatic-aromatic co-polyester derived from 1,4 butanediol, adipic acid, and dimethyl terephthalate, is biodegradable and compostable, is compatible with natural polymers such as starch and cellulose, and has excellent mechanical and optical properties (Witt et al.,

2001). The production of these packages can be carried out by extrusion, the technique used in industrial production of conventional flexible plastic packaging, which facilitates the adaptation of the laboratory scale to the industrial scale (Avérous and Boquillon, 2004; Mohanty and Nayak, 2012; Olivato et al., 2015).
In addition to being biodegradable, the packaging can contain in its structure additives that will make them more resistant and more efficient in food preservation. To improve the mechanical and permeation properties is the use of nanoclay, nanoparticles of layered mineral silicates, such as montmorillonite, is the most common nanoclay used because it is cheaper and does not present environment risks and human health (Azeredo, 2009).The incorporation of additives as preservatives, antioxidants, natural or synthetic, can make these packages active prolonging the useful life of the food and at the same time allowing the processing of foods with lower contents of these additives, contributing to a healthier diet (Bordes et al., 2009; Chivrac et al., 2010).
Thus, the objectives of the present study were to produce active biodegradable films by blow extrusion of blends of cassava starch, PBAT, glycerol, added of oregano essential oil and nanoclay, and study the effects in the mechanical and permeation properties.

2. Materials and methods

2.1. Materials

Films were produced with native cassava starch obtained from Indemil (Paranavaí, Brazil). The plasticizer was glycerol (Synth, Brazil). The biodegradable synthetic polymer was poly (butylene adipate-co-terephthalate) (PBAT) (Ecoflex®, BASF, Germany). Nanoclay - Na-montmorillonite (Closite® Na+) was purchased from Southern Clay Products (USA) and oregano essential oil from Ferquima (São Paulo, Brazil)

2.2. Methods

2.2.1. Film preparation

The films was prepared according formulation described in Table 1 containing starch/glycerol/ oregano essential oil/nanoclay. After homogenization, these mixtures were extruded to obtain pellets of thermoplastic starch (TPS) using a twin screw extruder (model D-20, BGM, São Paulo, Brazil), with five heating zones (90^0C, 120^0C, 120^0C, 120^0C, 120^0C) at 100 rpm, and die with five holes the 2mm diameter. Thereafter, the films (Table 1) were obtained by blow extrusion using a mono screw extruder (model EL-25, BGM, São Paulo, Brazil).

Table 1. Formulation of the films containing starch + glycerol (29 g of glycerol/100 g starch) + biodegradable polymer (PBAT) + oregano essential oil and nanoclay .

Film composition	F1	F2	F3
Starch + Glycerol (TPs)	58%	58%	58%
PBAT	40%	40%	40%
Oregano essential oil	-	2%	1%
Nanoclay	2%	-	1%

2.2.2 - Thickness

The thickness of the films was measured using a manual micrometer (Mitutoyo, resolution 0,01 mm - Japan). For each formulation reported, the thickness value is the average of 3 measurements from each of 10 tested samples.

2.2.3 – Water sorption isotherms

Samples of about 0,5 g were predried for 20 days over anhydrous calcium chloride. After dried the samples them placed in desiccators containing saturated salt solutions de 11,3% (lithium chloride), 33% (magnesium chloride), 43% (potassium carbonate), 53% (magnesium nitrate), 64% (sodium nitrate), 75% (sodium chloride, 84% (potassium chloride) e 90% (barium chloride), at 25^0C, each sample were weighed until equilibrium moisture contend. All tests were conducted in triplicate. The model de Guggenheim-Anderson-de Boer (GAB) (equation1) to fit the data were used.

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

Where X_w (g de water/g de dry matter) is the equilibrium moisture contend; m_0 the monolayer value; a_w water activity; C e K, the constants of Guggenheim which represents the heat of sorption in the first layer and the heat of sorption of the multilayers, respectively. All the tests were conducted in triplicate.

2.2.4 Water vapor permeability

The water vapor permeability was determined by the gravimetric method following the protocol from the American Society for Testing and Materials (ASTM, 1995), all of the tests were carried out with three replications. The samples were pre-conditioned in desiccators with a saturated solution of $MgNO_3$ (53 ± 2% Relative Humidity - RH) and a temperature of 25 ± 2 °C for 72 h. Each sample of the film was fixed onto an aluminium capsule with an internal diameter of 60 mm using silicone wax, to guarantee that the migration of moisture only occurred via the film. Anhydrous calcium chloride was inserted into each capsule, and the capsules stored in desiccators at 25 ± 2 °C, with a saturated $MgNO_3$ solution (53% RH) to maintain the relative humidity gradient.

Periodic weighing was carried out until the rate of mass gain was constant.

The slope of each line was calculated by linear regression ($r_2 > 0.99$), and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the transport area (m_2). The WVP (g Pa^{-1} day^{-1} m^{-1}) was calculated using the expression WVP = [WVTR/S ($RH_1 - RH_2$)*D], where S is the saturation vapor pressure of water (Pa) at the given temperature (25 °C), RH_1 is the RH inside the desiccator, R_2 is the RH inside the permeation cell, and D is the thickness of the film (m). All the tests were conducted in triplicate.

2.2.5 Mechanical properties

Samples were stored under 53% relative humidity for seven days. The tensile properties were determined using a TAXT2i Stable Micro System texture analyzer (Surrey, England) in accordance with ASTM D – 882 – 91 (1995). The samples were cut into strips measuring 80 mm in length by 6 mm in width and were tied to the pneumatic grips of the texturometer. Initially, the grips were spaced 30 mm apart and the traction velocity was 500 mm/min. The properties investigated were maximum tensile strength (MPa), elongation at break (%), and elastic modulus (MPa). Ten measurements were collected for each sample.

2.2.6 Grammage

The determination of grammage followed the method cited by Sarantópoulos (2002) for flexible films. As samples were cut and aid of a template in the dimension of 100x100 mm. The specimens were cut 25 mm away from the edge of the coil. As samples were conditioned in a desiccator at 53% and 64% relative humidity, at 25ºC for 96 hours. After this period, samples were weighed and a thickness of each piece for 5 measurements taken at different points, 5 replicates were performed.

3. Results and discussion

The sorption isotherms of a given material represent the equilibrium relation between the moisture content and the corresponding water activity, at a given constant temperature and pressure, and can be used to predict the hydration level of films containing plasticized polysaccharides and properties in different environments relevant to their application.

According to Figure 1, the F1 film showed a greater tendency to absorb water with increasing relative humidity, and F2 matched this film under more severe humid conditions. The calculation of the second derivative indicated a point of inflection relative to the percentage of 64.0% for all films, and it can indicate that from this humidity as Relative Humidity a decreasing effect can be observed in the water absorption, which can be explained by the relatively high anti-plasticizer effect of water (Figure 2).

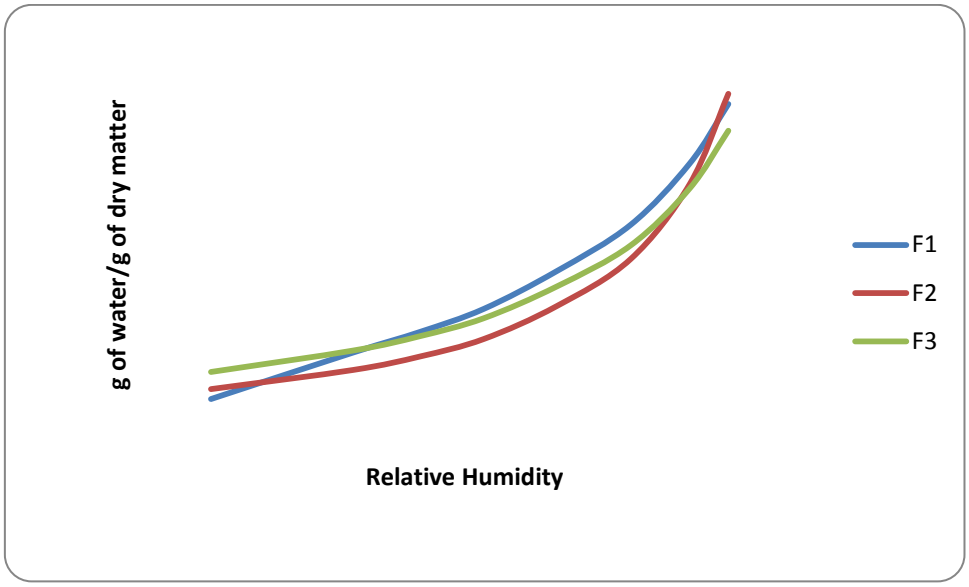

Figure 1. GAB-mode water sorption isotherms of the TPs + PBAT (58:40) films containing oregano essential oil and nanoclay under 25 °C.

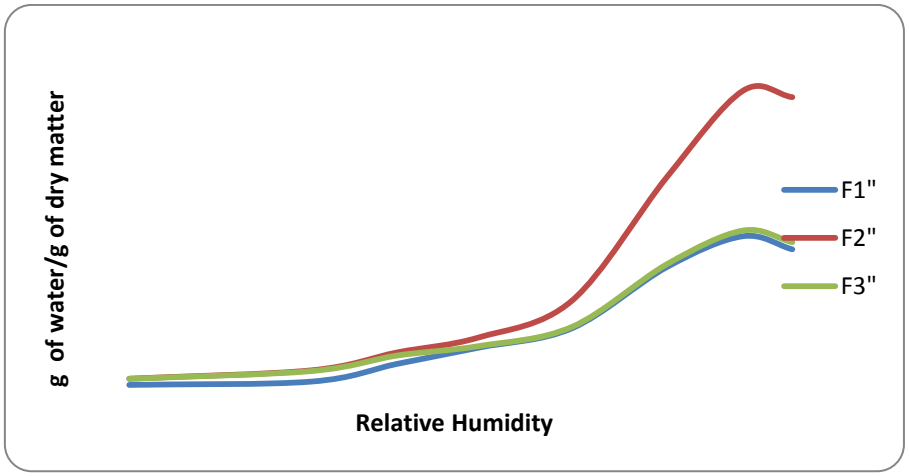

Figure 2. Second derivative of the GAB-mode water sorption isotherms of the TPs + PBAT (58:40) films containing oregano essential oil and nanoclay under 25 °C.

The parameters of the adjustment of the GAB model to the sorption equilibrium data are presented in Table 2. The model adjusted satisfactorily with the coefficient of determination (R^2) varying between 0.96 and 0.99. The value of mo was not influenced by the films composition, this parameter indicates the amount of water that is strongly bound in sites of sorption in the monolayer (MALI et al., 2005). The mean value obtained for mo was approximately 50% lower than that found by Olivato et al. (2017) for cassava starch/glycerol/pbat/sepiolite film.

The decrease in the nanoclay content of the films caused an increase in the values of the parameter C, the Guggenheim constant. This parameter is related to the difference in the enthalpy between the monolayer and the multilayers and the values found in this work were much higher than those found by Olivato et al. (2017).

The parameter K is a measure of the sorption heat of the water in the multilayers, presented values lower than 1.0 (one) similar to those found in the literature for cassava ATP film and showed no correlation with the formulation of the films (MALI et al., 2005).

All films presented values for K <1 and C> 2, characteristic of Type II isotherms (BLAHOVEC, 2004), which was verified by other authors for films of biodegradable polymers (MALI et al., 2005; Olivato et al. 2017). The

films had an average thickness of less than 100 micrometers and could be considered flexible film. The addition of oregano essential oil and nanoclay did not alter the permeability to water vapor (Table 3).

Table 2. GAB model parameters for water sorption isotherms toof the films de TPs + PBAT (58:40) with oregano essential oil and nanoclay.

GAB model parameters	F1	F2	F3
m_0	0,8305	0,9268	0,8512
C	128,62	160,77	166,93
K	0,08	0,04	0,62
R^2	0,96	0,99	0,95

Table 3. Mean values for thickness and water vapor permeability (WVP), for films of TPs + PBAT (58:40) with oregano essential oil and nanoclay.

Formulations	F1	F2	F3
Thickness (mm)	$0,0828^a$	$0,0846^a$	$0,0854^a$
WVP($x10^6$) (g/m.Pa.day)[a]	$2,37^a \pm 0,26$	$2,75^a \pm 0,18$	$2,21^a \pm 0,19$

[a] Different letters in the same line indicate significant differences ($p \leq 0.05$) between means (Tukey test).

Samples contained nanoclay in the formulation showed higher tensile strength, demonstrating the resistance amplification capacity of the films (Table 4). The mean values obtained in this paper for tensile strength were very close to those obtained by Olivato et al. (2015), or films with thermoplastic starch and PBAT 50/50, and in relation to elongation at break the values obtained were up to 22 times higher than those cited by the same authors.
The young's modulus of the films evaluated in this paper are less rigid than those obtained by Olivato et al. (2015).

Table 4. Mechanical properties of TPs + PBAT (58:40) with oregano essential oil and nanoclay.

	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (MPa)
F1	$6,67^a \pm 0,25$	$378,25^a \pm 20,34$	$33,78^a \pm 12,87$
F2	$5,99^b \pm 0,28$	$338,44^b \pm 19,94$	$42,38^a \pm 14,37$
F3	$6,11^a \pm 0,62$	$299,50^c \pm 69,12$	$38,33^a \pm 13,80$

[a,b,c]Different letters in the same column indicate significant differences ($p \leq 0.05$) between means (Tukey test).

The addition of oregano essential oil and nanoclay did not alter the grammage of films (Table 5), this result is quite interesting to increase film thickness and higher production costs.

Table 5. Grammage of films of TPs + PBAT (58:40) containing oregano essential oil and nanoclay, conditioned at the relative humidity of 53 and 64%.

Films	Grammage (g/m^2)	
	53% URE	64% URE
F1	$103^a \pm 4$	$100^a \pm 5$
F2	$97^a \pm 5$	$105^a \pm 3$
F3	$108^a \pm 9$	$99^a \pm 2$

[a]Different letters in the same column indicate significant differences ($p \leq 0.05$) between means (Tukey test).

4. Conclusion

The presence of nanoclay increased the tensile strength but did not alter the stiffness of the films. The addition of oregano essential oil and nanoclay did not alter the water vapor permeability, hydrophilicity and grammage of the films. Further studies must be carried out to verify the application of these films as active packaging for food.

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