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Development and characterization of flexible film based on starch and passion fruit mesocarp flour with nanoparticles

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ABSTRACT

Passion fruit mesocarp flour (MF) is a material of low-cost, because it can be produced from industrial processing of juices. The aim of this study was to develop flexible films based on MF, and to characterize their barrier, chemical, microscopic, thermal and mechanical properties, as well as to evaluate the rheological properties of the filmogenic solution used to produce them. The use of clay nanoparticles (NP) was also investigated. Films from MF were prepared by casting method, with glycerol as a plasticizer. The film forming solution of MF was more viscous than solutions of starch. The results of the contact angle values showed that films made from MF are more hydrophilic compared to starch, but there was no significant difference in water vapor permeability (WVP) and the thickness between these two different matrices. Regarding mechanical properties, the films made from MF proved to be tougher, stronger and less flexible. The formulation based on a mixture of MF and starch resulted in films less rigid and less resistant to tension, as compared to films based only on MF. The addition of NP did not influence the barrier properties, thermal and mechanical properties of films. Therefore, preparing films from MF, a cheap material, is a new alternative for taking waste from juice industries.

1. Introduction

Nowadays there is a need and a concern to reduce the use of synthetic plastic materials because of environmental issues. An alternative approach to this problem is to use films manufactured exclusively with natural polymers, which are able to be fully reincorporated to the environment in a short time and can be applied as a packaging material in various segments of the productive sector and consumer products.

The issue of environmental impact associated with a high cost of recycling plastic packaging has been a favored research on biodegradable flexible films that are made with natural polymers capable of forming adequately a cohesive and continuous matrix (Gontard & Guilbert, 1996). Biodegradable films do not generate solid waste and they could be consumed along with foods as they are easily degraded by the action of microorganisms occurring in the natural environment (Durango et al., 2006).

The increase of population and the high diversity of industrial production and consumption around the world have generated great production and accumulation of waste in several sectors. Agribusiness is one of the most important activities in various countries and the wastes generated have been studied for several applications. The interest of adding value to agricultural commodity waste has led to a search for new uses and applications, such as the use of residues from the juice industry to the development of biodegradable films (Arevalo, Aleman, Rojas, Morales, & Galan, 2009). The use of different types of food wastes as a carbon source for production of polymers reduces their accumulation and it is a good alternative to reduce the production cost of biopolymers. *Passiflora edulis* (passion fruit) is native from Brazil, the largest producer of this species in the world, where it is known popularly as "maracujá" and is widely cultivated, mainly for the use of its pulp in the food industry (processed juices and candies) (Zeraik & Yariwake, 2010). Several studies indicate the presence of polyphenolic substances (Zeraik & Yariwake, 2010), polyunsaturated fatty acids (Kobori & Jorge, 2005) and fiber (Córdova, Gama, Winter, Neto, Freitas, 2005), among other classes of substances, and the existence of these substances can indicate a potential use of passion fruit as a functional food. In fact, most of the data in literature still focus on the compounds in *Passiflora* leaves because of their pharmacological effects on the central nervous system and their use as a herbal medicine (Zeraik & Yariwake, 2010). However, investigations about the potential application of the residues have not been studied. The peel (mesocarp) of passion fruit is a co-product of industrial production of juices and its weight corresponds to approximately 90% of the fresh fruit that is discarded as a waste during processing. Several studies have pointed to the significant amount of pectin contained in the passion fruit mesocarp and its conversion into

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products offering a great opportunity for its use (Arvanitoyannis & Varzakas, 2008; Ferrari, Colussi, & Ayub, 2004; Kulkarni & Vijayanand, 2010).

Pectin is a complex carbohydrate, an amorphous substance, which occurs in fruits and certain vegetables, as a major structural component of cell walls and a good alternative to biodegradable materials (Mangiacapra, Gorras, Sorrentino, & Vittoria, 2006).

The formulation of films requires the use of at least one component capable to produce a structural matrix with a sufficient cohesion, while its operating efficiency depends strongly on the nature of the additional components (Mariniello et al., 2003).

When mixed with starch and glycerol, pectin forms biodegradable films that have good mechanical properties. Thus, based on the pectin content of the mesocarp, a flexible film can be obtained. According to Fishiman, Coffin, Onwulata, and Kostance (2004), a reduction in the particle size of the mesocarp of fruits, when mixed with starch and glycerol, allows the formation of films that also works as a potential reinforcement structure because of their high pectin content.

Recently, much attention has been given to polymer composites, where at least one of their components has nanometric dimensions (1–100 nm), especially those developed with layered silicates. These nanoparticles act as reinforcements in polymeric materials because they have an intercalation/exfoliation of silicate layers in a polymer matrix, as in the case of clays. Generally, to allow a better interaction of clay, that is inorganic, with organic polymers, the first needs to be organically modified (Brito, Oliveira, Araújo, & Melo, 2008). Besides, the use of charge at the nanoscale is an alternative to conventional polymer composites (Sorrentino, Gorrasi, & Vittoria, 2007).

The main aim of this study was to use passion fruit mesocarp flour in preparing thin flexible films by a casting technique and to analyze the influence of organoclay nanoparticle addition, by characterizing water vapor barrier, chemical, microscopic, thermal and mechanical properties of these films.

2. Materials and methods

2.1. Materials

The cassava starch (CS), locally known as “polvilho doce” (Yoki Alimentos, São Paulo, Brazil), was purchased from a local market. Despite the commercial availability of the passion fruit mesocarp flour (MF), it was decided to produce it in this study as the method of production is unknown and it can also vary according to the manufacturer. Thus, the fresh passion fruit was purchased from a local market in Rio de Janeiro and used in the flour production. Montmorillonite nanoclays, purified and modified with quaternary ammonium salt (Dellite® 43B), were provided by Laviosa Chimica Mineraria (Livorno, Italy). Glycerol P.A. was purchased from Isofar (Rio de Janeiro, Brazil). Citric acid was purchased from Vetec Chemistry (Duque de Caxias, Brazil).

2.2. Preparation of passion fruit mesocarp flour

Yellow passion fruits (*P. edulis*), were selected, without any mechanical damage, with similar color and maturation. Initially, the fruits were selected by size, washed in tap water and peeled off (epicarp of yellow color) by using an electric peeler, model DB-10, Metvisa (Brusque, Brazil). The removal of the remaining peel was manually taken with the aid of a stainless steel knife. Then, the fruits were cut in half to remove the seeds and pulp. The mesocarp was then submerged in a solution of 0.5% citric acid for 10 min, drained to remove excess water and dried in a fan oven at 60 °C for about 18 h. After it dried, it was ground in a knife–hammer mill of 7.5 hp (Treu, Rio de Janeiro, Brazil), fitted with a 1 mm aperture sieve. In order to obtain a narrow size powder, a sieve shaker was used and the powder fraction between 0.106 and 0.212 mm sieve was used. The final product was packed in polyethylene bags and stored at room temperature until its use. One production was enough for the development of films. The following chemical analyses were carried according to the methodology described by AOAC (2005): moisture (method 925.09), protein (method 2001.11), fat (922.06), ash (method 923.03), dietary fiber (method 985.29).

2.3. Preparation of films

The films were prepared by a casting technique. Glycerol was used as a plasticizer at a concentration of 0.30 w/w (Jansson & Thuvander, 2004) of dry raw material (starch or mesocarp flour). An aqueous solution containing 5% (w/v) of raw material was prepared, with the addition of a plasticizer. An aqueous dispersion of nanoclay was prepared and added. The solutions were placed in a Viscoamylograph Brabender (Duisburg, Germany) under stirring, heated to 90 °C for 10 min and then cooled to 50 °C resulting in a total time of 60 min. After obtaining the solution, 41.7 g was poured into polystyrene plates of 140 mm diameter. The filmogenic solution was dried in an incubator BOD (Biochemical oxygen demand), Hydrosan (Belo Horizonte, Brazil), and set to 33% relative humidity (RH) at 30 °C for 48 h resulting in a film that was manually detached from the plate and placed in a hermetic chamber at 53% RH for 6 days.

2.4. Characterization of films

2.4.1. Rheology of the filmogenic solutions

The rheological behavior of the filmogenic solutions was conducted in a Thermo Haake rheometer MARS (Duisburg, Germany) in duplicate at 25 °C (±0.5). A plate–plate geometry (PP35Ti) of 35 mm diameter was used and the gap of 1 mm was set between the plates. In order to classify the fluid behavior and assess the influence of different raw materials on viscosity, flow curves and viscosity curves were generated. Consistency, k (Pa s), and behavior, n, indexes were estimated, by applying the Ostwald-de-Waele model, $\sigma = \kappa\gamma^n$, to experimental values of shear stress (σ in Pa) and γ the shear rate (s^{-1}).

2.4.2. Film thickness measurement

The film thickness was measured with a digital micrometer, Fowler IP 54 (Newton, USA), with a sensitivity of 0.001 mm, at five points: one at the center and four at opposite positions. All measurements were performed in triplicate.

2.4.3. Thermogravimetric analysis (TGA)

The thermal stability of the films was evaluated by a thermogravimetric analyser (TGA), Perkin-Elmer — Pyris 1 (Shelton, USA), using a nitrogen atmosphere with a flow rate of 30 mL/min^{-1} in the sample. The mass of the samples ranged from 15 to 20 mg. The experiments were carried out in duplicate, in a temperature interval of 30–700 °C at a heating rate of 10 °C.min^{-1}. The weight loss as a function of temperature (TG) and the differential of the TG curves (DTG) were analyzed.

2.4.4. Contact angle

The contact angle of films was evaluated using a contact angle meter CAM 101 (KSV Instruments, Finland) equipped with a type of a diffuse light and a camera model DMK 21AF04 (1 photo/s). A drop of distilled water (≈3 μL) was deposited on the surface of the films and images of the drop profile were converted by a computer. For each film, hydrophobicity was deduced by the mean value of contact angle measured on both sides of the drop as a function of time (20 s). All measurements were performed in triplicate.

2.4.5. Water vapor permeability

The water vapor permeability (WVP) of films was determined in adapted permeation cells of polycarbonate (5.0 cm in diameter and

5.7 cm in height), containing distilled water at 100% RH. The experiments were conducted at 25 °C (±0.5). The water vapor permeability was determined by the modified method proposed by Vicentini (2003), based on ASTM E96-80 (American Society for Testing and Materials, 1989) using the equation:

$$WVP = (g/tA) \times (X/\Delta P) \quad (1)$$

where (g/tA) is the mass flux; A is the permeation area, g is the weight gain and t is the total time in hours. The term g/t was calculated by linear regression between the points of weight gain and time in steady state; X is the average thickness of the films and ΔP is the difference between pure water and ambient containing silica gel vapor pressure.

2.4.6. Mechanical properties

Mechanical tests were performed using a texture analyzer TA XT Plus (Stable Microsystems, Surrey, England). For tensile testing, the film samples used were cut to 15 mm×50 mm with scissors. Before all analyses, the specimens were conditioned at 53% relative humidity for 72 h, provided by a saturated salt solution of magnesium nitrate. The tensile strength, the elongation at break and Young's modulus were determined with a minimum of 15 replicates for each film. The force and deformation were recorded during the span of 10 mm/s, with an initial distance between the claws of 30 mm.

For puncture test, the specimens were sized to 20 mm×20 mm and conditioned at 53% RH for 24 h before analysis. Later, they were perforated by a sphere probe tip of 5 mm diameter, moving at a speed of 1 mm/s penetration. The diameter of the area where film was placed was 10 mm. The strength in puncture and displacement of the probe were determined in curves of force and deformation. The puncture deformation was calculated according to the methodology described by Gontard, Guilbert, and Cuq (1993) with a minimum of 15 replicates for each treatment.

2.4.7. Scanning electron microscopy (SEM)

Samples of the films were placed in desiccators with silica gel for 1 h before analysis, and after this period, the samples were mounted on an aluminum stub with a double side adhesive. The images were taken using a Hitachi scanning electron microscope (Tokyo, Japan), TM 3000 model, using an accelerating voltage of 15 kV, and a magnification 200 times of the origin specimen size.

2.4.8. Statistical analysis

A 2^2 factorial design, with three central points, was carried out, resulting in a total of seven experiments (Table 1). Nanoparticles (NP) and mesocarp flour (MF) were the two factors. The levels were 0 and 2%, for NP, and 0 and 5%, for MF (or 5% and 0% of starch, respectively). The regression analysis and analysis of variance (ANOVA) were performed by using Statistica software for Windows v. 8.0 (Tulsa, USA) at a significance level of 5%.

Table 1
Design matrix used in the film preparation.

Experiment	Coded variables		Original variables	
	FM content	NP content	FM content (%)	NP content (%)
1	−1	−1	0	0
2	−1	+1	0	2
3	+1	−1	5	0
4	+1	+1	5	2
5	0	0	2.5	1
6	0	0	2.5	1
7	0	0	2.5	1

3. Results and discussion

The chemical composition of MF produced in this study and used in the development of the films is presented in Table 2. Published results of the chemical composition of the MF could not be found in the current literature; however the composition of the mesocarp and the pericarp of passion fruit flour is available (Ishimoto, Harada, Branco, Conceição, & Coutinho, 2007; Souza, Ferreira, & Vieira, 2008). Protein and ash values found by these authors were higher than the MF values, which could be attributed to a higher amount of structural protein and minerals found in the peel which were not removed during processing.

3.1. Rheological properties

Fig. 1 shows the curves of apparent viscosity as a function of shear rate for each formulation. It was observed as a pseudoplastic behavior for all curves, characterized by a decrease in apparent viscosity with increasing strain rate. The pseudoplastic model represents most of the non-Newtonian fluid behaviors, which can be explained by changes in the structure of long chains of molecules with increasing velocity gradient. These chains tend to align in parallel to streamlines, reducing the resistance to flow (Toneli, Murr, & Park, 2005). The viscosity was statistically different for all treatments and higher for the filmogenic solutions based on MF and NP (Fig. 1). This measurement is important for the final quality of the film formed. Low viscosity allows the uniformity of the film surface, affecting its appearance and efficiency of their protective properties (Peressini, Bravin, Lapasin, Rizzotti, & Sensidoni, 2003). High viscosities are undesirable because the dispersion of ingredients and the elimination of visible air bubbles are more difficult, and they could be responsible for discontinuities. The effect of a smooth surface may be necessary to achieve a uniform thickness (Peressini et al., 2003).

The rheological parameters, κ and n, from the Ostwald-de-Waele model were shown in Table 3. The values ranged from 1715.0 to 19,965 and 0.42 to 0.84 for κ (consistency value) and *n* (behavior index), respectively. Because $n<1$, this result confirms a pseudoplastic behavior of the films, which has been confirmed elsewhere in the literature for gelatinized starch dispersions and solutions for film formation based on polysaccharides.

The consistency index (κ) values were very high for all formulations, especially for the formulations based on MF. This could be explained by the presence of a high content of soluble fiber in this composition, such as pectin. This polysaccharide is a colloid of strong hydrophilic character, which is owing to the presence of polar groups, a property that binds large amounts of water, increasing thus its volume and reducing the free volume between the macromolecules and consequently increasing the viscosity of the medium. According to Branco and Gasparetto (2003), the consistency index and apparent viscosity are directly influenced by the presence of insoluble solids, such us insoluble fiber and also by soluble fibers such us pectin, which is increased in their presence. In starch-based solutions, the viscosity is the result of structural changes, such as irreversible swelling of starch granules, melting of crystals formed by molecules of

Table 2
Proximate chemical composition of mesocarp passion fruit flour (g/100 g).

	g/100 g
Moisture	5.19
Ash	5.56
Protein	3.24
Fat	2.26
Dietary fiber	57.8
Carbohydrate[a]	26.0

[a] By difference.

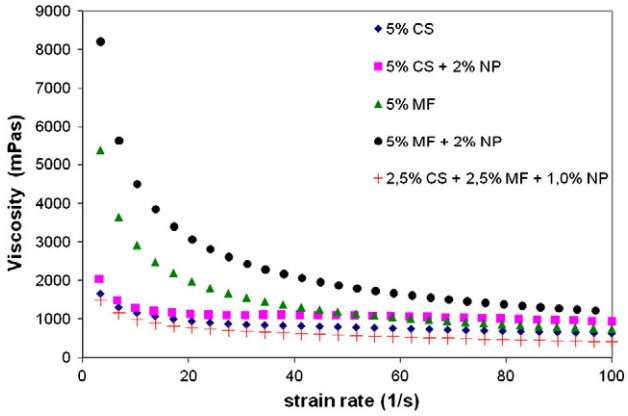

Fig. 1. Viscosity versus shear rate for film-forming solutions. CS (cassava starch), MF (mesocarp passion fruit flour) and NP (nanoparticle).

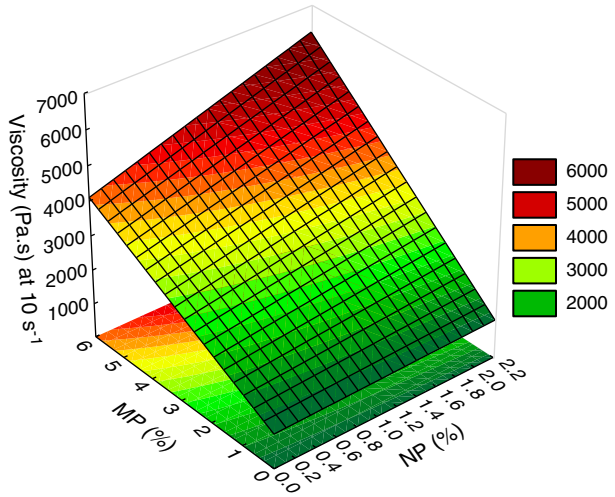

Fig. 2. Response surface for viscosity at 10 s^{-1}.

amylopectin and leaching out of amylose molecules from the amorphous region of the starch granule that occurs during gelatinization. When the maximum swelling is reached, it starts to break the bead, which is associated with decreased viscosity, which can be expanded under high shear stress (Lagarrigue & Alvarez, 2001; Li & Yeh, 2001). With the addition of NP, there was an increase in the consistency index (κ) to the suspensions based on MF. However, this did not occur to the suspensions produced only with starch. This behavior can be attributed to changes in the orientation of silicate layers and polymer conformation during the mixing/shearing, and the possible interactions that can be established between the clay and pectin present in the passion fruit flour.

Figs. 2 and 3 present the response surfaces for the viscosity at 10 s^{-1} (beginning of the viscosity curve) and 80 s^{-1} (end of viscosity curve), respectively, as a function of MF and NP contents. By using ANOVA at 5% of significance, a statistical difference among the treatments for both cases was shown. The plane curvatures were statistically significant and a center composite design should be carried out in a future work in order to consider a quadratic term of one or both factors used.

3.2. Film thickness

The values found for the thickness of the films ranged from 0.133 to 0.185 mm. Thickness was not a statistically significant concern for NP and MF contents ($P>0.05$). It is worth noting that despite the higher viscosity of MF solutions (Fig. 1), this did not lead to an increase in thickness of the MF formed films. Because of the low coefficient of variation (around 10%) found in the measurements, one can conclude that the spreading technique used in the development of the films allowed a satisfactory control of its thickness, by fixing the mass (weight) of the solution deposited on plates. The uniformity in film thickness is important to evaluate the results of the mechanical tests with good repeatability; it also serves as a basis for determining several functional properties of the films.

3.3. Thermal stability of the films

The thermal stability of the films was studied by thermogravimetric analysis (TGA). The curves are shown in Fig. 4.

For films based on starch, basically two thermal events were observed. The first occurs immediately after the temperature increase and ends before 100 °C, which refers to the elimination of water and low molecular weight compounds present in the sample by evaporation/dehydration. Part of this water is contained in the starch molecules because of their hydrophilicity caused by hydrogen bonds formed by hydroxyl groups of glucose units (Cyras, Zenklusen, & Vázquez, 2006; Liu, Xiea, Yua, Chena, & Li, 2009; Wilhelm, Sierakowski, Souza, & Wypych, 2003). The second level is the highest stage of decomposition of starch, which corresponds to the elimination of hydroxyl groups, decomposition and depolymerization of the carbon chains. The maximum decomposition temperature (T max) was the peak temperature shown on the curve. The degradation of the starch film and the starch film with nanoparticles were 164.05 °C and 161.38 °C, respectively.

Similar situations can be considered for the films produced with the MF; the mass loss from ambient temperature to 100 °C with release of water molecules formed from the broken OH bonds present in the structures of pectin and additives in the first stage. However, it should be noted that the hemicellulose/pectin has a lower molecular weight, which could explain the reduction of the carbon chains at lower temperature, at least up to 230 °C, which can be attributed to an organic decomposition of relative low molecular mass (Andrade, 2010). There was no effect of NP addition in the thermograms. The amount of clay and the relative degree of exfoliation may be responsible for this result. The amount of exfoliated silicate layers may not have been enough to change significantly the thermal stability. According to Wilhelm et al. (2003), in general, the presence of clay does not affect the thermal

Table 3
Rheological parameters (κ and n) for film-forming solutions, contact angle (θ) and water vapor permeability of films.

FM content (%)	NP content (%)	(κ ± SD) (Pa.s)	n ± SD	Contact angle (θ ± SD) (°)	(WVP ± SD) ($g.mm.h^{-1}.m^{-2}.kPa^{-1}$)
0	0	1837.9 ± 474.56	0.75 ± 0.036	84.3 ± 1.27	0.307 ± 0.000123
	2	1715.0 ± 407.80	0.84 ± 0.0041	64.3 ± 1.13	0.334 ± 0.00502
5	0	14,345 ± 3931.1	0.41 ± 0.0037	38.0 ± 2.01	0.351 ± 0.00357
	2	19,965 ± 3704.1	0.43 ± 0.0018	41.6 ± 2.59	0.332 ± 0.00295
2.5	1	2227.0 ± 232.32	0.64 ± 0.0041	41.8 ± 2.77	0.305 ± 0.000861
2.5	1	1827.4 ± 373.01	0.64 ± 0.0043	34.8 ± 2.38	0.361 ± 0.00655
2.5	1	1707.7 ± 462.39	0.65 ± 0.0051	39.0 ± 0.401	0.294 ± 0.00212

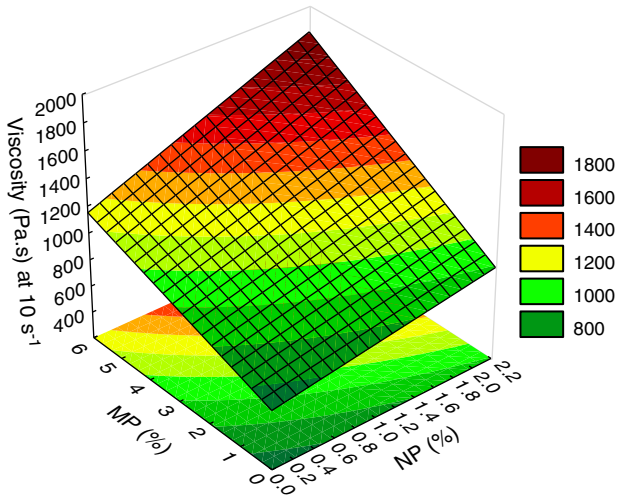

Fig. 3. Response surface for viscosity at 80 s^{-1}.

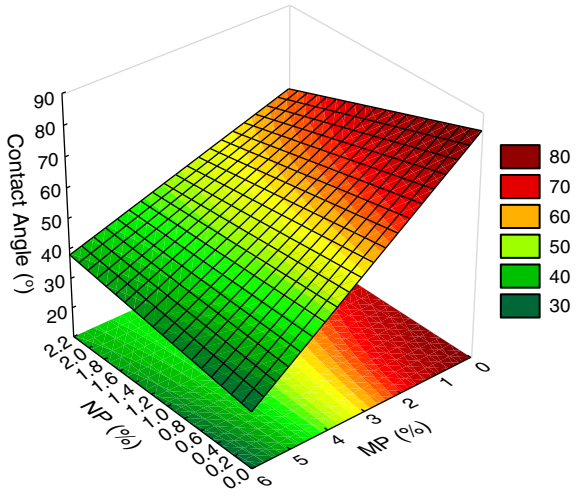

Fig. 5. Response surface for contact angle.

stability of plasticized starch films. Mausclaux, Gouanvé, and Espuche (2010) found similar results for potato starch films in the thermal stability that was not significantly affected by 2.5 to 7.0% of clay. No factor was statistically significant ($P>0.05$), indicating that the degradation temperature was not affected by the addition of nanoparticles nor the type of matrix used for the film.

3.4. Surface hydrophobicity

The values of contact angles are shown in Table 3. These results were statistically different only in relation to the MF content ($P<0.05$) and the response surface can be seen in Fig. 5. As before, the plane curvature was statistically significant and a center composite design should be carried out in a future work in order to consider a quadratic term of one or both factors used.

Hydrophobicity (larger angle) is higher for films prepared without nanoparticles and are starch-based. The contact angle for the film was much lower for MF compared to the film of starch (Experiment 1); it may be attributed to a greater number of affinity sites to the water soluble fibers present in the MF. Another interesting aspect is that the addition of nanoparticles has the opposite effect for the two raw materials. Depending on application, if a hydrophobic film is needed, a film without nanoparticles and starch should be chosen. This can be explained by the high concentration of pectin in the mesocarp of passion fruit, which has groups of high polarity bonds that can interact with water molecules and hence reduce the contact angle by increasing diffusion water on the surface of the film. However, the addition of NP had no effect, maybe because of some NP dispersion issue in the polymer matrix. Higher amounts of clay tend to limit the penetration of the drop inside the film, resulting in a reduction of surface hydrophobicity (Tunc et al., 2006). Kampeerapappun, Aht-Ong, Pentrakoon, and Srikulki (2007) found similar results for films of starch and chitosan, as the addition of clay did not affect the hydrophobicity of the film. The interaction effect between MF and NP was marginally significant ($0.05<P<0.1$).

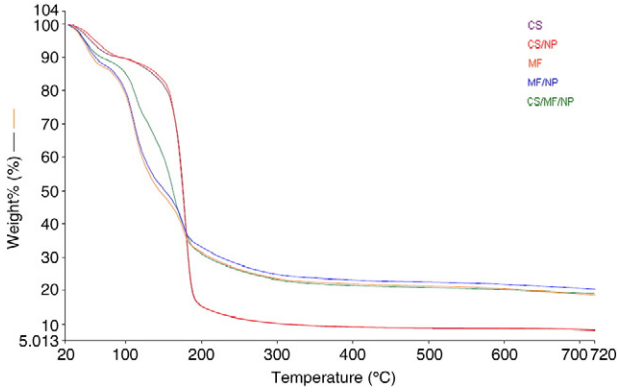

Fig. 4. Thermogravimetric analysis curves of the films produced. CS (cassava starch), MF (mesocarp passion fruit flour) and NP (nanoparticle).

3.5. Water vapor permeability (transmission rate of water vapor)

The WVP films in this study varied from 0.29 to 0.36 g.mm.h^{-1}.m^{-2}.kPa^{-1} (Table 3). Rocha (2009) found values between 0.16 and 0.37 g.mm.h^{-1}.m^{-2}.kPa^{-1} for starch-soy protein films, while Ortiz (2009) found values between 1.52 and 2.53 g.mm.h^{-1}.m^{-2}.kPa^{-1} for films made of cassava flour and soy protein produced by extrusion, using the same method of determination of this study. For the WVP, no significant difference ($P>0.05$) among the formulations was found (Table 3). The nanocomposites did not show changes with respect to WVP when films without clay are compared, which can be explained by an incompatibility between the hydrophilic polymer and highly hydrophobic clay, preventing a good dispersion and consequent formation of aggregates which promote the diffusivity of water vapor and accelerate the transmission of water vapor (Park et al., 2002). According to Coelho, Santos, and Santos (2007), if the particles of clay act in the matrix forming aggregates, we will still have traditional or conventional polymers and we will not obtain specific properties of nanocomposites. The final properties of the material are the result of the present structures and their relative percentages.

3.6. Mechanical properties

Table 4 shows the results of tensile tests. It was observed that increasing MF led to an increase in the modulus of elasticity and in tensile strength, as well as to a substantial reduction of elongation at break. The formulation based on the mixture of starch and MF resulted in films less rigid and less resistant when compared to starch films only. No significant differences were found for the film with nanoparticles ($P>0.05$). This may be due to the fact that the low addition of nanoparticles (2%) was not sufficient to promote improvements in the mechanical properties of the films studied nor the clay nanoparticles were well exfoliated causing a lack of polymer inclusions

Table 4
Mechanical properties: tensile test determined for the films produced.

FM content (%)	NP content (%)	Tensile test (Young's modulus ± SD) (MPa)	(Elongation at break ± SD) (%)	(Tensile strength ± SD) (mPa)
0	0	51.3 ± 1.12	118 ± 7.96	2.46 ± 0.0992
	2	54.8 ± 1.43	118 ± 9.05	2.22 ± 0.0987
5	0	182 ± 10.8	13.7 ± 0.912	7.56 ± 0.179
	2	203 ± 12.5	13.5 ± 0.844	8.12 ± 0.208
2.5	1	164 ± 10.1	11.3 ± 0.676	1.30 ± 0.0761
2.5	1	146 ± 9.21	12.0 ± 0.605	1.01 ± 0.0656
2.5	1	160 ± 9.90	16.0 ± 1.02	1.36 ± 0.0690

within the layers reducing their effect as a reinforcing material. Cyras, Manfredi, Ton-That, and Vázquez (2008), working with starch nanocomposites containing 2, 3 and 5% of sodium montmorillonite, observed an increase of 5% in tensile strength of the films. The samples analyzed by Cyras et al. (2008) with 2% of nanoparticles presented no significant difference in mechanical parameters (tensile strength, Young's modulus and elongation at break) when compared with the samples of plasticized starch.

The Young's modulus or modulus of elasticity is an indicator of the rigidity of the film, and the higher the modulus, the more rigid is the film, which was verified for the films made from MF (Table 4). Higher value for the Young's modulus was found for films based on 5% MF with nanoclay. But at lower contents of MF and of nanoclay, the Young's modulus decreased. However, the effect of nanoparticles was not significant ($P > 0.05$). This may be because of the formation of an interface between the layers of clay and modified pectin molecules, caused by the presence of an organic modifier (dimethyl benzyl hydrogenated tallow ammonium), preventing or reducing the formation of hydrogen bonds between them. Probably, for the nanocomposites, the improvement of the Young's modulus depends not only on the degree of dispersion of the clay particles in the matrix but also on the interaction between the matrix and nanoparticle (clay); that is a relevant parameter for improved rigidity.

The tensile strength was higher for the film of MF. Fishiman et al. (2004) observed that in increasing the content of albedo (mesocarp) of orange, which has a comparable content of pectin to passion fruit mesocarp, there was an increase in the tensile strength, which is a similar finding to this study when only MF was used to prepare the films.

Elongation at break is a measurement of flexibility of the film and it is defined as the ability of the film to deform before breaking (Moraes, 2009). The starch film was much less brittle than the MF film, and the latter showed a lower elongation. According to Bastos (2010), pectin is more hydrophilic than starch and absorbs more water, decreasing the mechanical properties of the material. Batista (2004) also noted that the increase in pectin content in the films, produced in their study, promoted a decrease in elongation of the films. The interaction effect between MF and NP was not statistically significant when considering the tensile test.

Table 5
Mechanical properties: puncture test determined for the films produced.

FM content (%)	NP content (%)	Puncture test (Force ± SD) (N)	(Deformation ± SD) (%)
0	0	17.28 ± 0.68	4.77 ± 0.097
	2	14.82 ± 0.34	4.80 ± 0.099
5	0	9.86 ± 0.19	4.39 ± 0.078
	2	11.19 ± 0.23	4.42 ± 0.082
2.5	1	5.01 ± 0.10	4.39 ± 0.077
2.5	1	4.89 ± 0.099	4.38 ± 0.075
2.5	1	3.70 ± 0.085	4.35 ± 0.069

For the puncture test, the maximum force at break and the puncture deformation were lower for the films made from MF (Table 5). There are few studies that conducted puncture test on flexible films; therefore, there is little evidence that these measurements are important in determining the force required to penetrate the film. Mali, Grossmann, García, Martino, and Zaritzky (2004) found, for yam starch films, values of 6.03 N and 15.96 N for force in puncture and 3.44% and 4.78% for puncture deformation, which are similar to this work.

For all mechanical properties analyzed herein, the plane curvature was statistically significant and a center composite design should be carried out in a future work in order to consider a quadratic term of one or both factors used. Fig. 6 presents the Young's modulus. The response surfaces for the tensile strength and elongation at break were exactly the same as the Young's modulus.

3.7. Scanning electron microscopy (SEM)

Surface morphology of films was investigated under scanning electron microscopy. The scanning electron microscopy allowed an overview of the structure of the film, but did not allow an analysis of nanostructures, which is possible by transmission electron microscopy. It was possible to note that in the starch based films the starch granules were broken down and formed a continuous phase with glycerol. A homogeneous surface with no cracks or visible air pockets (Fig. 7) is clearly seen. In the micrographs of the MF films, it is possible to identify the presence of fibrous structures and the presence of clusters (Fig. 8). The composites of starch and MF group showed a smooth surface without the presence of clusters, showing a good interaction between the used polymers (Fig. 9).

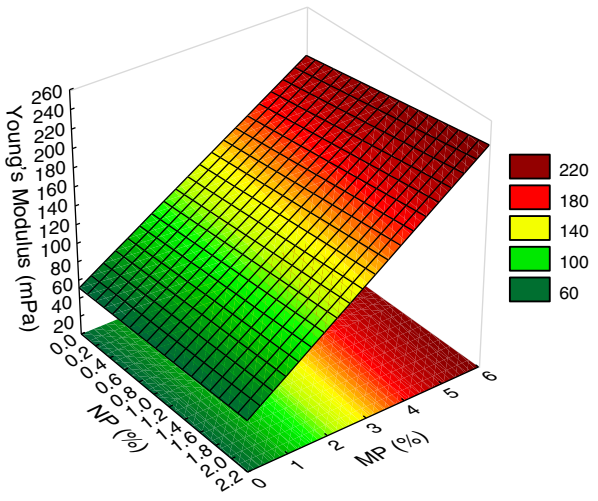

Fig. 6. Response surface for Young's modulus.

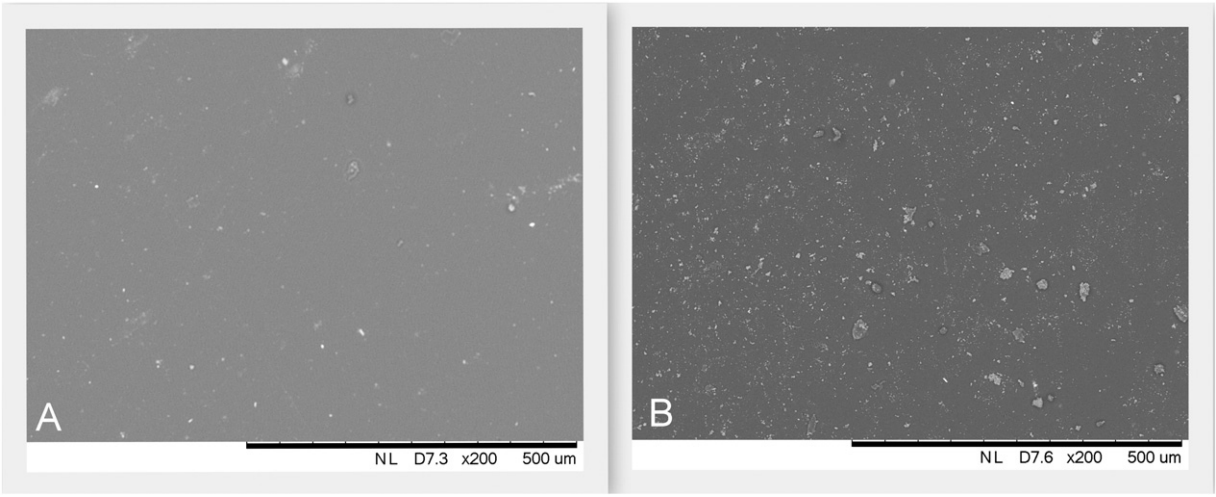

Fig. 7. Micrographs of starch films. (A) without addition of nanoparticles. (B) with 2% of nanoparticles.

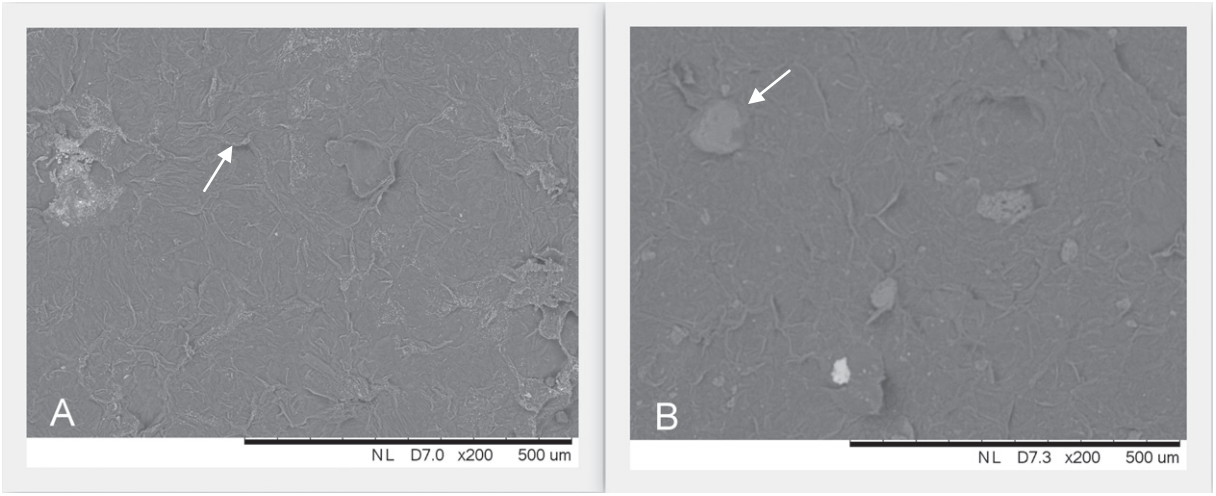

Fig. 8. Micrographs of the MF films. (A) Without addition of nanoparticles. (B) with 2% of nanoparticles.

4. Conclusions

In this study the capacity of MF to form flexible films by a casting technique has been shown. The film forming solution of the base passion fruit flour mesocarp was more viscous than the solutions of cassava starch. In relation to the hydrophobicity of the films, the results of the contact angle values showed that the films made from MF are more hydrophilic than cassava starch, but there was no significant difference in water vapor permeability and thickness. Regarding mechanical properties, the films made from MF proved to be tougher, stronger and less flexible than the starch films. The formulation based on the mixture of flour and starch resulted in films less rigid and less resistant to traction, as compared to the films based only on MF.

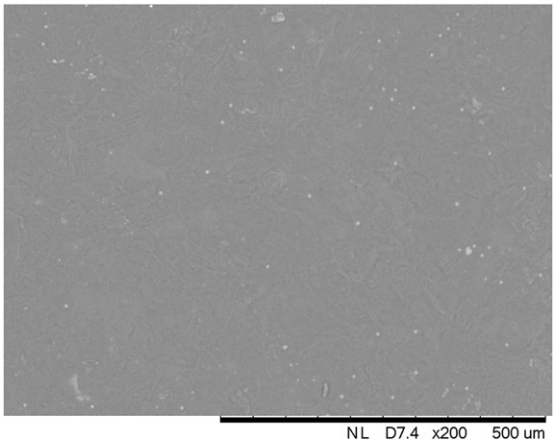

Fig. 9. Micrograph of starch, MF and NP composites by SEM.

The addition of organoclay (NP) did not influence the barrier properties, and the thermal and mechanical properties of films. The results of this study indicate that the use of MF allows the preparation of films with similar properties to cassava starch films. Further studies are needed to improve their properties and application uses. The statistical analysis showed that the MF content modifies the mechanical properties, the contact angle and the viscosity.

As the plane curvature was statistically significant for all mechanical properties and contact angle, a work is being developed using a center composite design in order to have predictive models.

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