



Influence of beet flour on the relationship surface-properties of edible and intelligent films made from native and modified plantain flour



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ABSTRACT

Different studies have been performed on edible films. However, the surface properties and the relationship with their properties has not been analyzed. Edible films were obtained from native and modified plantain flour, with and without the incorporation of beet flour. Moisture content, stability in acidic or alkaline solutions, thermogravimetric analysis (TGA), X-ray diffraction pattern (XRD), differential scanning calorimetry (DSC), attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM) and color parameters were determined. The systems evaluated with the incorporation of beet flour showed a plasticizer effect, which led to the obtaining of more transparent, smoother and wet films. This also was related with higher transmittance and slightest thermodynamic stability. Similarly, the modified plantain flour by cross-linking with sodium trimetaphosphate, allowed to obtain films transparent, smoother, more plastic and degradable. Considering the results, it was concluded that the minor interaction between the starch–starch chains, allowed to obtain films with lower development of the crystalline phase, which favored the obtaining of films transparent, smoother, more plastic and degradable.

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1. Introduction

Edible films have been regarded as environmentally friendly, since they degrade more easily compared with the common synthetic plastic (Famá, Flores, Gerschenson, & Goyanes, 2006; Famá, Goyanes, & Gerschenson, 2007; Famá, Rojas, Goyanes, & Gerschenson, 2005; Famá, Pettarin, Bernal, & Goyanes, 2011; Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007; García, Ribba, Dufresne, Aranguren, & Goyanes, 2009). So the same, the properties of these biopolymers can be modified by the addition of plasticizers, antimicrobials, pigments, among others; this with the purpose of improve their properties (García, Martino, & Zaritzky, 2000a, b). Another of the alternatives that have been employed

with the objective of improve the properties of the edible films is the chemical and/or physical modification of the starch (García-Tejeda et al., 2013). Gutiérrez, Guzmán, Medina, and Famá (2015), have reported in a recent paper that the incorporation of the beet flour to this type of biomatrixes, caused a plasticizer effect on films made from native and phosphated plantain flour. This due to sugars and proteins contained in beet flour, which can act as plasticizer, thus reducing the hydrogen-bonding interactions between the starch macromolecules. Additionally, the incorporation of the beet flour to this type of biomatrixes, allowed to obtain edible and intelligent films, this because the pigments found in beet flour (betalains), can act as front indicator to pH changes. In the particular case of the systems in study, are ripeness indicators and are based on pH changes caused by the deteriorative processes of the food.

It is worth noting, that intelligent films are an extension of the communication function of traditional packaging, and communicates information to the consumer based on its ability to sense, detect, or record external or internal changes in food product's

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environment (Restuccia et al., 2010). Therefore, the development of the intelligent and edible films poses new challenges compared to traditional packaging.

Nevertheless, despite the importance of these materials, the study of surface characteristics of the same have been few studied with the aim of relate the physico-chemical properties with the surface characteristics of these biomaterials. For this reason, the aim of this study was to evaluate the physico-chemical properties, and its relationship with the surface characteristics of these biopolymers. Additionally, it was evaluated if the films developed could be stable front to slight changes of pH acidic or alkaline, this due to that many food products could interact with the films.

2. Experimental

2.1. Materials

The plantain flour (*Musa ssp.*, group AAB, sub-group clone Harton) was obtained by the method described by Pacheco (2001). The plantain used had a degree of maturation of 1, according with the scale of Loesecke (1950) that was acquired at a local market in Caracas, Venezuela. Also, beet flour was obtained following the methodology of Pacheco (2001), but with some modifications: the beet was not immersed in a solution of citric acid (1%) before of dehydrate the tuber slices. The apparent amylose content in the flours used was determined by the methodology proposed by McGrance, Cornell, and Rix (1998). It was obtained an approximate apparent amylose content of 24% for native plantain flour and 10% for phosphated plantain flour (Gutiérrez, Guzmán et al., 2015). Glycerol from Prolabo, Sweden, was employed as plasticizer in the formation of the films.

2.2. Preparation of the modified flour

Phosphate-modified plantain flour was performed following the methodology described by Kerr and Cleveland (1959), modified by Lim and Seib (1993). Native plantain flour (300 g) and 15 g of sodium sulfate (Na_2SO_4) were suspended in 300 mL of distilled water, and the pH adjusted to 11 with 2.5% of NaOH solution. The slurry was then heated to 45 °C and 2 g of sodium trimetaphosphate were added. The mixture was then shaken for 3 h and the pH adjusted every hour so that it remained at 11. After 3 h, the pH was lowered to 7 with 2.5% HCl solution. The slurry was then washed three times by suspension in distilled water, centrifuged at 1500 r/min for 15 min and dried at 45 °C. The dried modified flour was milled and passed through a 60-mesh sieve. The maximum concentration of the modifying agent allowed by the FDA (2011) for starches intended for the food industry (3% w/w of sodium trimetaphosphate with respect to the weight of the starch) was used.

2.3. Film formation

Films containing 2% w/v of native or modified flour, 1.9% w/v glycerol and 500 mL distilled water were prepared following the methodology described by Gutiérrez, Guzmán et al. (2015), Gutiérrez, Morales, Pérez, Tapia, and Famá (2015), Gutiérrez, Tapia, Pérez, and Famá (2015a), Gutiérrez, Morales, Tapia, Pérez, and Famá (2015) and Gutiérrez, Tapia, Pérez, and Famá (2015b). In the case of the films with incorporation of beet flour, the same was added 10 min before the end of the process of obtaining the film forming solution (FFS), this in order to preserve the pigments of the beet, and give the opportunity of a homogeneous inclusion in the FFS. The incorporated quantity of beet flour was of 4% with respect to plantain flours used. The resulting thermoplastic flour films: native plantain flour (TPF-NPF), native plantain flour with

incorporation of beet flour (TPF-NPFB), phosphated plantain flour (TPF-PPF) and phosphated plantain flour with incorporation of beet flour (TPF-PPFB) were then carefully removed from the casting molds. Before characterization, the films were conditioned at ~57% relative humidity (RH) for a week at 25 °C.

2.4. Characterization of the films

2.4.1. Moisture content

The moisture content of the different films evaluated was determined by gravimetry. Three samples per formulation were considered. Water content was eliminated of the samples using a two-step process: first, they were dried the sample in a vacuum oven for 24 h at 100 °C, and then were stored in desiccators with silica gel until that was reached the constant weight. The results were expressed as % of moisture.

2.4.2. Stability in acidic or alkaline solutions

The stability of the films in acidic and alkaline solutions were evaluated, 25 × 25 mm pieces were immersed in plastic petri dishes with 20 mL of standard solutions of HCl (pH 1/0.1 M) or NaOH (pH 13/0.1 M). The containers were sealed and maintained at 25 °C for 24 days. Over this period the containers were protected of light at darkened rooms in order to avoid the photodegradation of the pigments. The changes in the appearance of the samples were recorded with a Cyber-shot Sony camera, model DSC-H3 with 8.1 mega pixels.

2.4.3. Thermogravimetric analysis (TGA)

Thermogravimetric tests were performed using Shimadzu DTG-60. Pieces of 4–10 mg of each film were heated from room temperature to 500 °C at a rate of 10 °C/min and nitrogen flow 30 mL/min. The weight loss of the materials was recalculated on dry basis and the different degradation phases were noted. Analyses were performed in triplicate to ensure repeatability.

2.4.4. X-ray diffraction (XRD)

Film crystallinity was evaluated qualitatively by measuring the X-ray diffraction (XRD) with an X-ray diffractometer (Siemens D 5000) (radiation Cu $\alpha\text{K} = 1.5406 \text{ \AA}$, 40 kV and 30 mA). Scattered radiation was detected in an angular range of 3–33° (2θ) at a step size of 0.02° and scan speed of 2 s. The thicknesses of the samples on the slides were ~200 μm .

2.4.5. Differential scanning calorimetry (DSC)

A differential scanning calorimeter (Mettler Toledo Schwerzenbach) was used to determined changes in enthalpy (ΔH) and glass transition temperature (T_g) of the films. Indium and zinc were used to calibrate temperature and heat flux. Ten milligrams of samples contained in hermetically sealed aluminum pans was heated twice, in the temperature range –70 to 100 °C, at a scanning rate of 10 °C/min, under a nitrogen atmosphere. Changes of phase or state and the corresponding, the enthalpy were determined from the second heating thermogram. Glass transition was assigned to the middle temperature of the relaxation range (Biliaredis, Lazaridou, & Arvanitoyannis, 1999; Chartoff, 1981).

2.4.6. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR)

Absorbance spectrum of flour-based films were recorded on a Nicolet 8700 Fourier transform infrared spectrometer using the single reflection horizontal attenuated total reflectance (ATR) accessory Smart Orbit, with diamond crystal at an incident angle of 45°. The spectra were obtained by recording 40 scans performed with a resolution of 4 cm^{-1} between 700 and 4000 cm^{-1} . Each

sample was scanned three times observing good reproducibility.

2.4.7. Scanning electron microscopy (SEM)

The surface of the films exposed to drying were analyzed using a Philips XL series 30 (Holanda) scanning electron microscopy. For this, were mounted on bronze stubs and sputter coated with a thin layer of gold for 35 s.

2.4.8. Atomic force microscopy (AFM)

The topographic images of the films were obtained using an Agilent 5500 in the Acoustic AC Mode (AAC Mode) with silicon nitride (Si_3N_4) tips, which had a cantilever oscillation frequency of 155 kHz. Besides, this tips had a spring constant of 0.2 N m^{-1} and a V-shaped tip 2 mm long, which was positioned over the sample under ambient conditions. The AFM images were taken at the center and periphery of the surface of the films. The surface analyzed was the side of the surface exposed to the drying air during film preparation. The AFM images were processed with PicoView image software.

2.4.9. Color

CIE- $L^*a^*b^*$ coordinates of surfaces of the films evaluated exposed to drying: lightness (L^*), chroma (a^*) and hue (b^*), were measured according to the standard test method (ASTM D-1925, 1995) using a Macbeth® colorimeter in mode reflectance (Color-Eye 2445 model, illuminant D65 and 10° observer) standardized with a white reference plate ($L^* = 93.52$, $a^* = -0.81$ and $b^* = 1.58$). Color differences (ΔE) were calculated according to Valencia Rodríguez (2001), whiteness index (WI) was calculated according to Atarés, Bonilla, and Chiralt (2010), and the yellowness index (YI), according to ASTM D-1925 (MacFarlane, MacFarlane, & Billmeyer, 1936).

2.5. Statistical analysis

The analysis of data was performed through the analysis of variance (ANOVA) using the Statgraphics Plus 5.1. software (ManugisticsCorp., Rockville, MD). Fisher's least significant difference (LSD) procedure was used at the 95% confidence level.

3. Results and discussion

3.1. Moisture content

Table 1 shows the moisture content of the different films studied. The film made from phosphated plantain flour (TPF-PPF) had a decrease statistically significant ($p \leq 0.05$) in moisture content with respect to the native plantain flour-based film (TPF-NPF). This possibly was due to the modification by crosslinking of the plantain flour, which produced strong hydrogen bonding interactions between the phosphated flour and the plasticizer, thus limiting the possible water uptake by part of these polar compounds (Gutiérrez, Morales, Pérez et al., 2015). Likewise, these interactions between

the glycerol and the phosphated plantain flour, would weaken the intra and intermolecular interactions between starch macromolecules, which produces the increase in the movement and rearrangement of their chains (Gutiérrez, Tapia, Pérez, and Famá, 2015a). So the same, reduction of moisture content could be caused due a strong glycerol-phosphated plantain flour interaction, thus limiting the glycerol-water or starch–water interactions. These results agree with those reported by Gutiérrez, Morales, Pérez et al. (2015) in its study of films based on phosphated cassava starch.

Moreover, the films made from the native and phosphated plantain flour with the incorporation of the beet flour (TPF-NPFB and TPF-PPFB), they showed significantly higher moisture content values compared to the films without incorporation of beet flour (TPF-NPF and TPF-PPF). This, possibly due to the polar character of the sugars contained in the beet flour, which produced films more prone to water absorption from the environment (Gutiérrez, Guzmán et al., 2015). Similar results have been reported by Talja, Helén, Roos, and Jouppila (2007), in potato starch-based films with different contents of polyols.

3.2. Film stability in acidic or alkaline solutions

By definition, stability of a material is established according to its structure and chemical composition, which allow to the materials maintain their initial conditions against an external stimulus. In the case that we corresponds in this section, stability was analyzed according to the change in the dimensions of the tested films, which were caused by a pH change.

The aim of this study was to evaluate if the films developed could be stable front to slight changes of pH acidic or alkaline, this due to that many food products could interact with the films. For this reason, it is important determine whether the stability of the films employed is affected by pH.

For the purpose of the study the stability of flour-based films samples of all the systems were immersed in solutions of HCl (pH 1) or NaOH (pH 13). All the films left in the acidic solution (HCl) remained visually unchanged for at least 24 days, thus suggesting that they are stable in acid. Therefore, all the films developed could be used for food packaging slightly acidic as meats and citrus fruits. In addition, Gutiérrez, Guzmán et al. (2015), reported in a recent paper that these films have appropriate mechanical properties for food packaging, since these have a maximum stress $\sim 1.4 \text{ MPa}$ and strain at break $\sim 55\%$. Similar results were obtained by Hu, Chen, and Gao (2009) and Gutiérrez, Morales, Pérez et al. (2015) for thermo-plastic polymer films derived from potato starch and edible films based on cassava and cush–cush yam starches, respectively.

Fig. 1 shows the photographs of the films after 1 days in an alkaline solution. As can be observed the film made from phosphated plantain flour (TPF-PPF) (Fig. 1c) suffered a similar swelling than native plantain flour-based film (Fig. 1a), so at this case does not show the greatest interaction glycerol-phosphated plantain flour.

Table 1
Moisture content and color parameters of the different films.

Parameter	TPF-NPF	TPF-NPFB	TPF-PPF	TPF-PPFB
Moisture (%)	29 ± 1^b	32 ± 1^c	27 ± 1^a	35 ± 1^d
L	20.20 ± 0.01^d	18.32 ± 0.09^c	16.47 ± 0.03^b	10.7 ± 0.1^a
a	1.16 ± 0.05^b	0.8 ± 0.1^a	3.81 ± 0.02^d	1.68 ± 0.03^c
b	5.2 ± 0.1^d	2.7 ± 0.1^a	5.02 ± 0.06^c	4.6 ± 0.2^b
Color differences (ΔE)	73.45 ± 0.01^a	77.09 ± 0.02^c	75.44 ± 0.09^b	83.0 ± 0.1^d
Whiteness index (WI)	20.02 ± 0.02^d	16.42 ± 0.02^b	18.08 ± 0.09^c	10.5 ± 0.1^a
Yellow index (YI)	31.0 ± 0.5^b	19.4 ± 0.5^a	38.6 ± 0.3^c	39 ± 2^c

Equal letters in the same row indicate no statistically significant differences ($p \leq 0.05$).

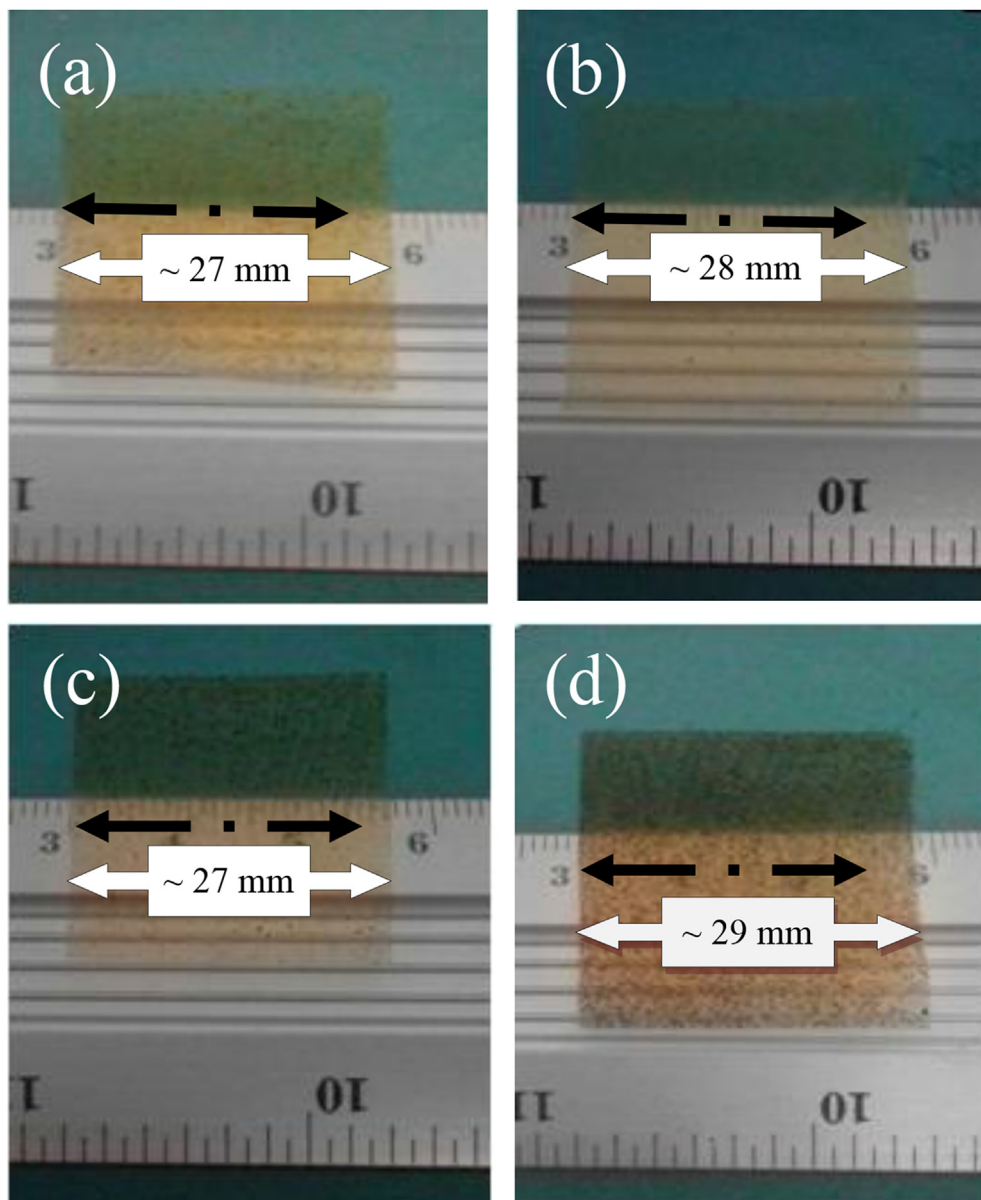


Fig. 1. Digital photographs of the thermoplastic flour films immersed in alkaline medium after 1 days: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFB), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB). Black line highlights initial length of the films. White line highlights final length of the films after 1 days immersed in alkaline medium.

However, a greater swelling was showed significantly in the films with incorporation of the beet flour (TPF-NPFB and TPF-PPFB), which could be related to the plasticizer effect of the sugars and the proteins found in beet flour, since this could destroy and reduce the hydrogen-bonding interactions and the intra and intermolecular interactions between the starch macromolecules, thus facilitating swelling and gelatinization of the starch contained in the native and phosphated plantain flour (Gutiérrez, Guzmán et al., 2015, Gutiérrez, Morales, Pérez et al, 2015). Although, it is worth noting that the greater swelling was registered for phosphated plantain flour-based film with incorporation of beet flour (TPF-PPFB). Whereby, the swelling of this film is due to the greater hydrogen bonding interaction between the beet flour and the phosphated plantain flour, which would allow greater mobility of starch chains contained in the phosphated plantain flour. In this way, the starch chains could be exposed to the disintegration and dissolution in

alkaline medium, due to the reaction of the sodium hydroxide with the hydroxyl groups of the starch molecules (Gutiérrez, Morales, Pérez et al, 2015; Hu et al., 2009).

It is also worth mentioning, that all the systems studied showed lower stability after 24 days in alkaline medium compared to other thermoplastic starch films reported in the literature (Gutiérrez, Morales, Pérez et al, 2015, Gutiérrez, Tapia, Pérez, and Famá, 2015b). It is equally important to mention that the discussion of the stability of the films in alkaline medium was carried out based on the first day of the assay, because to the third day of the study were dissolved the films.

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed in order to analyze the thermal stability of the four film systems (Fig. 2).

According to the literature, the thermal decomposition of glycerol-starch biofilms occurs in three main stages (Ayala, Agudelo, & Vargas, 2012; García, Famá, Dufresne, Aranguren, & Goyanes, 2009; Gutiérrez, Morales, Pérez et al., 2015; Marques et al., 2006; Pelissari, Andrade-Mahecha, do Amaral Sobral, & Menegalli, 2013). The first stage corresponds to water evaporation, which occurs around of 100 °C, the second stage is associated to the evaporation of the glycerol-rich phase which also contains starch, and occurs between ~180 and 260 °C, and finally, the third stage occurs from the 330 °C, due to the oxidation that undergoes the partially decomposed starch (García, Famá et al., 2009; Liu, Xie, Yu, Chen, & Li, 2009; Sanyang, Sapuan, Jawaid, Ishak, & Sahari, 2015; Wilhelm, Sierakowski, Souza, & Wypych, 2003).

In Fig. 2, the first stage of the thermal degradation is not observed, since weight loss of the materials was recalculated on dry basis in order to avoid distortions as a result of the different moisture contents of the films. Likewise, it can be observed the evaporation of glycerol-rich phase in the following films: TPF-PPF, TPF-NPF and TPF-PPFB. However, the film made from native plantain flour (TPF-NPF) presented a double mass loss at this stage (Fig. 2a), which would be related with a phase separation, due to the low compatibility of the native plantain flour with the glycerol (Liu, Yu, Liu, Chen, & Li, 2008; Liu et al., 2009; Sanyang et al., 2015; Shi et al., 2007). This would explain the slight increase in moisture content in the native flour-based film (TPF-NPF) with respect to the phosphated flour-based film (TPF-PPF); since when being the glycerol-free, the same can absorb moisture from the environment, thus increasing moisture content. So the same, it can also observe that beet flour produced a plasticizer effect between the native plantain flour and the glycerol, which no allowed to observe phase separation in the native plantain flour-based film with the incorporation of the beet flour (TPF-NPF, Fig. 2b).

Similarly, the addition of the beet flour in the phosphated plantain flour-based film (TPF-PPFB, Fig. 2d) produced a degradation at temperatures lower than its analogous without the addition of the beet flour (TPF-PPF, Fig. 2c). This suggests that the incorporation of the beet flour in the film made from phosphated plantain flour (TPF-PPFB) reduces intra and intermolecular interactions between starch–starch chains and strengthens hydrogen bonding interactions between the hydroxyl groups of the starch chains and the sugars contained in the beet flour, thus confirming the results obtained through the study of the stability of these films in alkaline medium (Cyras, Tolosa Zenklusen, & Vazquez, 2006; García, Famá

et al., 2009; Gutiérrez, Guzmán et al., 2015, Gutiérrez, Morales, Pérez et al., 2015; Mathew & Abraham, 2008; Pelissari et al., 2013). Additionally, other studies have also reported a slight decreases in decomposition temperatures related with glycerol-rich phase in the starch-based polymers when a plasticizer is incorporated (Cerruti et al., 2011; Hwang et al., 2013; Mathew & Abraham, 2008).

Also, a decrease in the degradation temperature was observed in phosphated plantain flour-based film with addition of beet flour (TPF-PPFB, Fig. 2d) compared to the film made from native plantain flour with the addition of beet flour (TPF-NPF, Fig. 2b). Again, this would confirm the analysis performed by means of the results of the stability of these films in alkaline medium, where phosphate groups incorporated in the modified plantain flour reinforces the hydrogen bonding interactions with the sugars contained in beet flour, this compared to the films made from native plantain flour with addition of beet flour (TPF-NPF).

Finally, in the third stage were observed stable curves of thermal degradation up to 500 °C. So the same, at this stage was observed a lesser weight loss in the films that contained beet flour (TPF-NPF and TPF-PPFB), with respect to the films without the addition of this flour (TPF-NPF and TPF-PPF). This possibly due to the contribution of the minerals contained in the beet flour and to the products of the oxidation of aromatic rings (coal residues) of the betalains, which are part of chemical composition of the beet flour (Gutiérrez, Guzmán et al., 2015; Patel et al., 2010; Ruiz, 2006).

3.4. X-ray diffraction (XRD)

Fig. 3 shows the X-ray diffraction patterns of the developed films. Zullo and Iannace (2009), reported that the molecular order within starch granules is destroyed when is heated during processing of the films, i.e. an amorphous structure is obtained. According to this, it can say that the four films studied showed an important contribution of the amorphous phase, which have a small crystalline fraction. This would be consistent with the results reported in the literature (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Famá et al., 2006, 2007; Famá et al., 2005; Flores et al., 2007; García, Famá et al., 2009; Kristo & Biliaderis, 2007; Rindlav, Hulleman, & Gatenholm, 1997; Romero-Bastidas et al., 2005; Tapia et al., 2012).

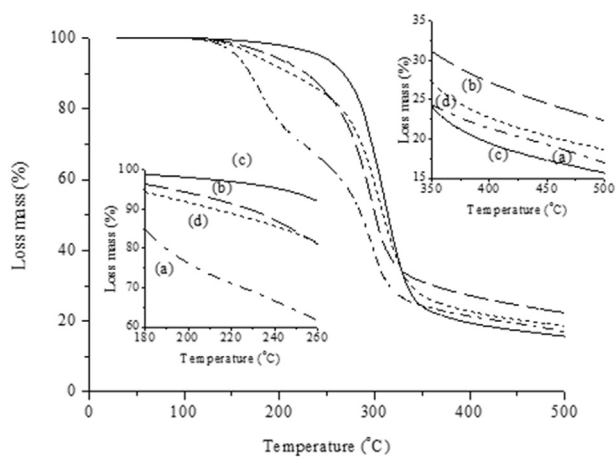


Fig. 2. TGA curves of the different films studied: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFb), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB).

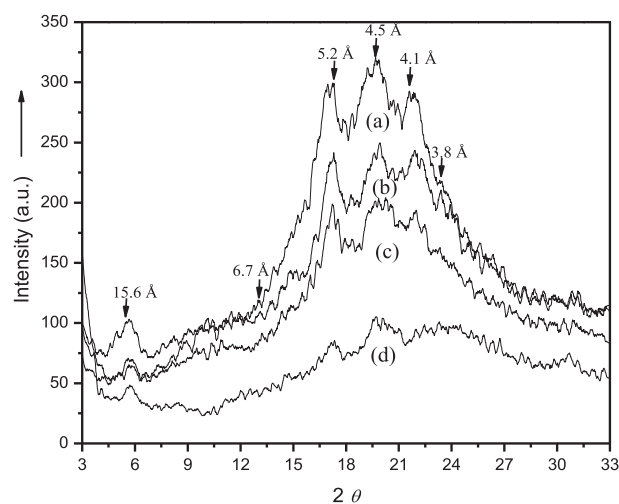


Fig. 3. X-ray diffraction pattern of the different films studied: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFb), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB).

According to Tapia et al. (2012) and Pérez, Segovia, Tapia, and Schroeder (2012), the crystallinity of the starch films is mainly associated with the amylose, since the same is almost linear, unlike the amylopectin than is highly branched. Hence, and as was demonstrated in this study, the native plantain flour-based films, showed a higher crystallinity (Fig. 3), due to the higher amylose content present in the native plantain flour, which was previously reported by Gutiérrez, Guzmán et al. (2015). This can be observed, since the areas under the crystallinity peaks are larger in the native plantain flour films than the phosphated plantain flour films.

Moreover, as can be seen in Fig. 3 all the films studied showed curves with diffraction peaks corresponding to the following d -spacings $\cong 3.8$ Å, 4.1 Å, 5.2 Å and 15.6 Å, associated with B-type structures (Pelissari et al., 2013). According to García-Tejeda et al. (2013) the signal observed for $2\theta = 17.2$, corresponding to d -spacing $\cong 5.2$ Å, is associated with interactions between the short external amylopectin chains and glycerol. Likewise, others diffraction peaks are located at the following d -spacings $\cong 4.5$ Å and 6.7 Å, which would be associated with V-type structure (Zobel, French, & Hinkle, 1967).

Additionally, the peaks localized at 4.5 Å are related to the hydrogen bonding interactions (Gutiérrez, Morales, Pérez et al., 2015; Zobel et al., 1967). Likewise, these interactions are stronger in the films made from the phosphated plantain flour (TPF-PPF and TPF-PPFB) compared to the native plantain flour-based films (TPF-NPF and TPF-NPFB), since the crystallinity of these films decreased. So the same, this behavior suggests that there is an increase in the number of the hydrogen bonding interactions, product of the

plasticizer effect of beet flour (TPF-NPFB and TPF-PPFB), which was recently reported by Gutiérrez, Guzmán et al. (2015).

3.5. Differential scanning calorimetry (DSC)

Fig. 4 shows the DSC thermograms of the studied films. As can be seen, all curves presented two falls in heat flow. According to the literature, the first located between -19 °C and -4 °C, would be attributable to the melting of water, and the second fall in heat flow localized in the range of 16 – 46 °C, would be related to the glass transition of the starch-based films (Chang, Karim, & Seow, 2006; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002; Mitrus, 2005; Pelissari et al., 2013).

Moreover, a decrease in the T_g has been associated with the greater mobility of the starch chains, caused by the greater interaction between the hydroxyl groups of the starch chains and the molecules of the plasticizer (glycerol) (Mali, Grossmann, García, Martino, & Zaritzky, 2006). Additionally, lower enthalpy values (ΔH) associated to the glass transition have been related to the weakening of the inter and intramolecular interactions between starch–starch chains (García et al., 2000a, b; Mali et al., 2002; Mitrus, 2005; Pelissari et al., 2013). According to Bair (1981), García et al. (2000b), and Bertuzzi, Vidaurre, Armada, and Gottifredi (2007), this leads to a decrease in growth of the crystal phase in these semi-crystalline biomaterials, since this impedes the alignment and recrystallization of starch molecules.

The DSC curves of the thermoplastic films derived from native and phosphated plantain flour with the incorporation of beet flour

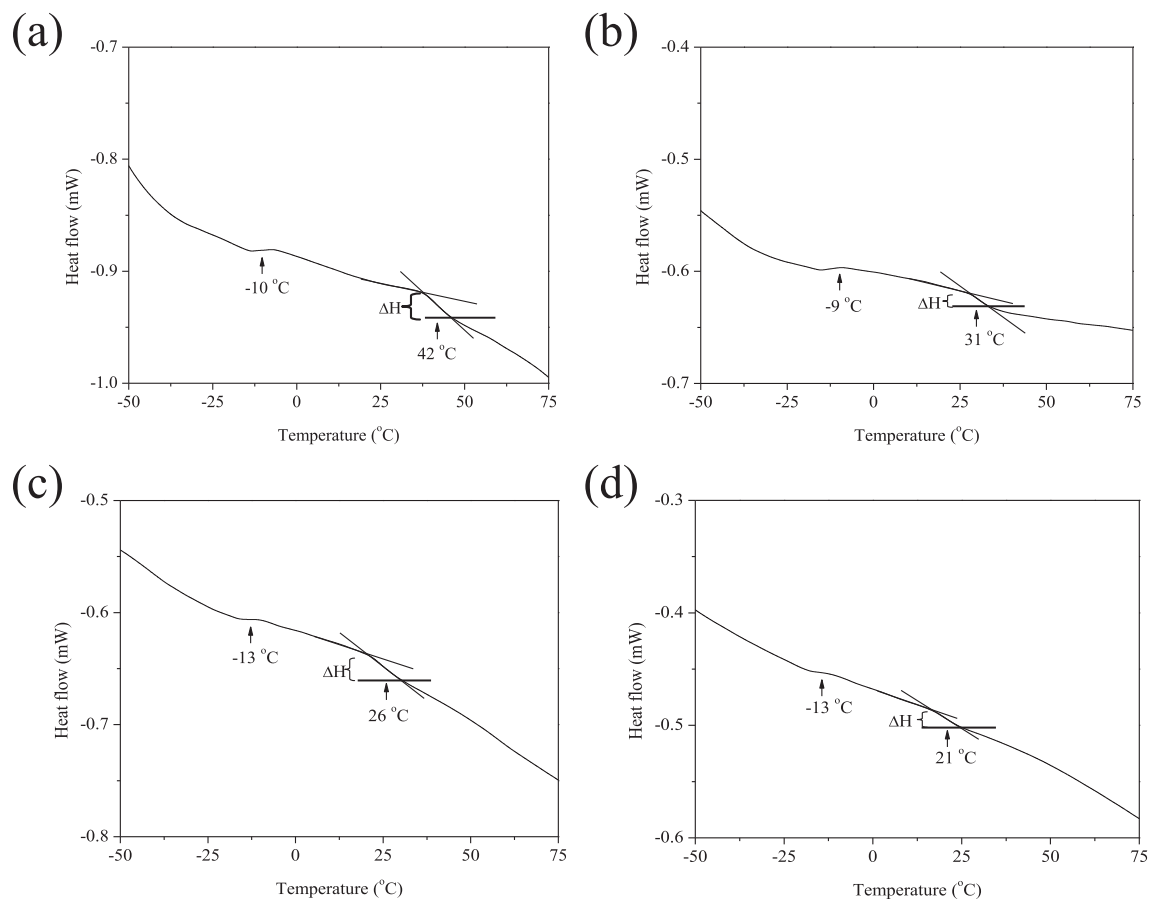


Fig. 4. Heating thermograms of the films based on: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFB), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB).

(TPF-NPFB and TPF-PPFB, Fig. 4b and d respectively), evidenced a lower enthalpy (ΔH) than their analogous without the incorporation of beet flour. For this reason, it can be said that the incorporation of beet flour makes to these thermoplastic films (TPF-NPFB and TPF-PPFB) more susceptible to be degradable. This corroborates the lower stability in alkaline medium and the lower thermal resistance observed in TGA curves of the systems with the incorporation of beet flour. Likewise, the decrease in the T_g in the systems that contained the addition of the beet flour (TPF-NPFB and TPF-PPFB, Fig. 4b and d), confirmed the plasticizer effect of the sugars contained in the beet flour (Gutiérrez, Guzmán et al., 2015; Hulleman, Janssen, & Feil, 1998; Talja et al., 2007). Similar results have been reported by García et al. (2000a), in films based on corn starch with and without addition of sorbitol or glycerol. Also Bergo et al. (2008), observed the same phenomenon in films based on cassava starch plasticized with different concentrations of glycerol.

Then according to observations by means of DSC, the addition of beet flour could destroy the intra and intermolecular interactions between starch–starch chains, thus strengthening hydrogen bonding interactions between the hydroxyl groups of the starch chains and the polar compounds of the beet flour, which allows greater mobility of the starch chains. Talja et al. (2007) and Gutiérrez, Guzmán et al. (2015), suggest that this effect could be due to the addition of any low-molecular-weight compound, such as the sugars contained in beet flour, which would entail to an increase of the free volume, thus modifying the structure of these biomaterials (Van der Berg, 1991).

On other hand, a decrease in the T_g was observed in the modified plantain flour-based films (TPF-TPP and TPF-PPFB, Fig. 4c and d) with respect to its analogous native (TPF-NPF and TPF-NPFB, Fig. 4a and b). This would be related to the lower amylose content that presented the phosphated plantain flour (Gutiérrez, Guzmán et al., 2015). Previous studies have considered that this occurs due to the better interaction between the linear chains of the amylose, which induces its crystallization (Bizot et al., 1997; Cowie & Henshall, 1976; Orford, Parker, Ring, & Smith, 1989). This would explain the lower values of T_g in films elaborated from native plantain flour (TPF-NPF and TPF-NPFB, Fig. 4a and b). Similar results have been reported by Liu, Yu, Xie, and Chen (2006) and Li et al. (2011), in starch-based edible films with different amylose contents.

3.6. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR)

Fig. 5A shows FTIR spectra of the different films studied in all the range absorption. The spectra of the films presented absorption peaks around 3298 cm^{-1} (OH stretching) corresponding to C–O group, own of the polymer and of the absorbed water (Pereira, de Arruda, & Stefani, 2015; Xu, Kim, Hanna, & Nag, 2005), and bands that can be identified corresponding to: CH_2 modes at ~ 2938 and 2887 cm^{-1} , C=O bending at $\sim 2359\text{ cm}^{-1}$, OH bending at $\sim 1646\text{ cm}^{-1}$ (Silva-Pereira, Teixeira, Pereira-Júnior, & Stefani, 2015; Vicentini, Dupuy, Leitzelman, Cereda, & Sobral, 2005; Xu et al., 2005). Bands appearing between 1300 cm^{-1} and 1430 cm^{-1} are assigned to C–O angular deformations (Reis et al., 2015). Specifically, the band detected at $\sim 1428\text{ cm}^{-1}$ is associated with the symmetric stretching of the carboxyl group ($-\text{COO}$) (Kizil, Irudayaraj, & Seetharaman, 2002). The absorbance band around 1648 cm^{-1} is sensitive to both the H-bonding and amount of hydroxyl interactions (Famá, Bittante, Sobral, Goyanes, & Gerschenson, 2010). So the same, differences in terms of band shape and intensity can be observed concretely in the region between 3750 and 3000 cm^{-1} (Fig. 5B), where the plasticizer effect of beet flour caused an increase in transmittance in the films derived

from native and phosphated plantain flours (TPF-NPFB and TPF-PPFB), which was more significant in phosphated plantain flour-based film with incorporation of beet flour (TPF-PPFB). This would be related with an increase in the degrees of freedom of OH groups, which itself would be attributable to the greater mobility of the starch chains. Similar results have been reported by Medina, Gutiérrez, Goyanes, Bernal, and Famá (2015), on the study of plasticizer effect of the yerba mate extract. For this reason, an increase in transmittance is related to the decrease of the T_g . Likewise, a slight increase in the transmittance of the phosphated plantain flour-based film (TPF-PPF) with respect to the film made from native plantain flour (TPF-NPF) was associated with decreased of the T_g , product of the lower amylose content in the phosphated plantain flour.

3.7. Scanning electron microscopy (SEM)

Fig. 6 shows the SEM micrographs of the surface of the different films studied. It can be seen that the films produced were non-porous and compact. Although a growth of the crystalline phase was observed on the surface of the films based on native plantain flour (TPF-NPF and TPF-NPFB, Fig. 6a and b), was probably evidenced by the recrystallization of the starch, which was originated from the cocrystallized amylose during the film-forming process (Chang, Cheah, & Seow, 2000; Miles, Morris, & Ring, 1985; Rindlav-Westling, Stading, & Gatenholm, 2002; Rindlav-Westling, Stading,

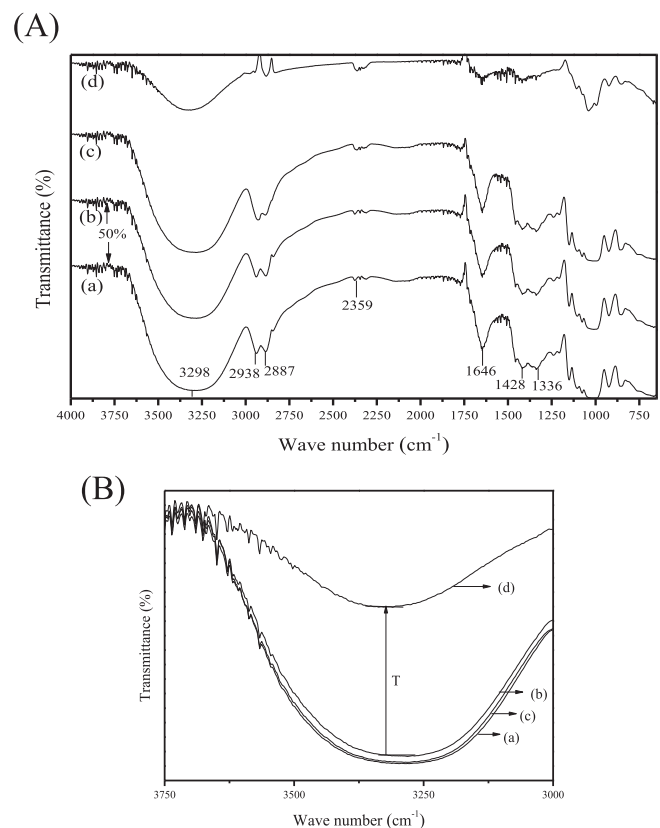


Fig. 5. Panel A – FTIR spectra of the different films studied in all the range absorption: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFB), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB). Panel B – FTIR spectra in the range of absorption corresponding to C–O group (OH stretching) of the different films studied: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFB), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB).

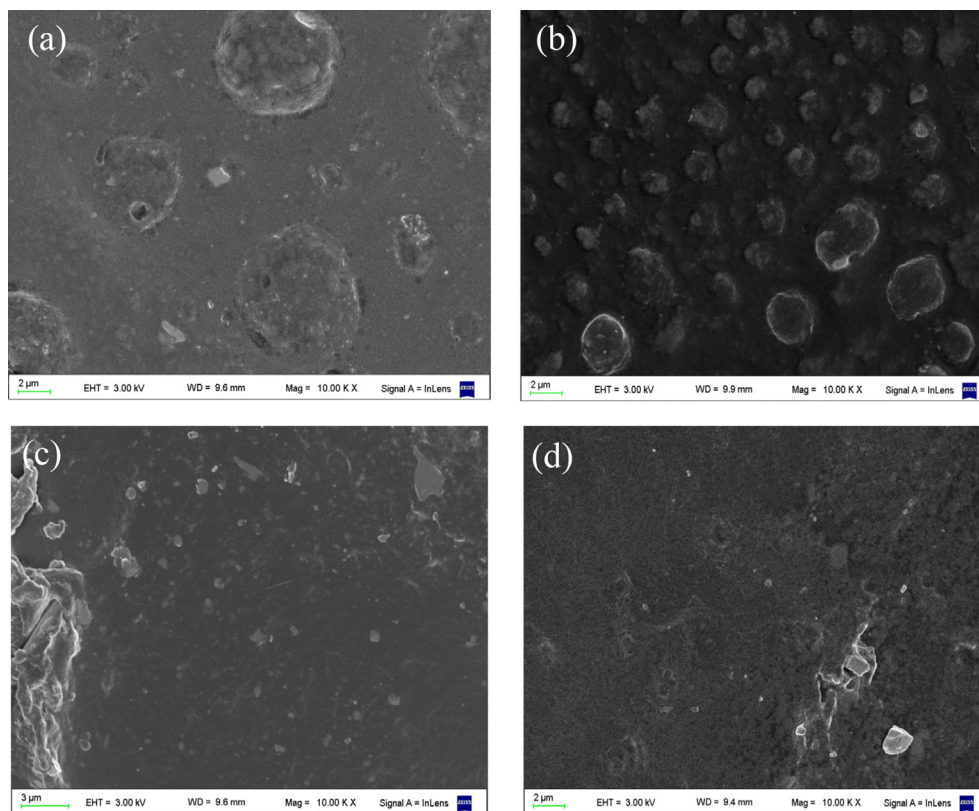


Fig. 6. SEM micrographs of the surface of the films based on: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFB), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB). At 10 k \times of magnification.

Hermansson, & Gatenholm, 1998). This would correspond to the higher amylose content present in native plantain flour (Gutiérrez, Guzmán et al., 2015). Similar structures have been reported by Gutiérrez, Izquier, González, and Famá (2015), in films developed from the cassava starch with and without the exposure to pulsed light. Likewise, smaller granules were observed in the native plantain flour-based film with incorporation of the beet flour (Fig. 6b, TPF-NPFB) compared to their analogous without the addition of the beet flour (Fig. 6a, TPF-NPF). This possibly due to plasticizer effect of the beet flour, which was opposed to the recrystallization of the starch that it found contained in the native plantain flour. Following the literature, the growth of the crystalline phase has been associated with the increase in the Tg (Bair, 1981; Bertuzzi et al., 2007; García et al., 2000b). Therefore, this behavior is consistent with the SEM micrographs of the surface of the different films studied and with the X-ray diffraction patterns.

3.8. Topography of edible films assessed by Atomic Force Microscopy (AFM)

The topography of the edible films assessed by AFM are shown in Fig. 7. Films made from native plantain flour (TPF-NPF, with a higher amylose content, Gutiérrez, Guzmán et al., 2015) showed greater surface roughness than those made from phosphated plantain flour (TPF-PPF). This behavior is consistent with the luminosity results obtained (Table 1). Reyes (2013) and Gutiérrez, Izquier, et al. (2015), mentions that films with a high roughness profile are more opaque, i.e. less transparent. This is probably due to the fact that a rougher surface texture does not permit the reflection of light which is thus absorbed by the film. This could also explain the increase in the transmittance in phosphated plantain

flour-based film (TPF-PPF) in relation to the film made from native plantain flour (TPF-NPF). Following to Karbowski, Debeaufort, Champion, and Voilley (2006) and Gutiérrez, Izquier, et al. (2015), indicate that surface roughness can be explained by an increase of the molecular re-organization of the polymer matrix. In the native plantain flour-based films (higher amylose content) the hydrogen bonding interaction acts in opposition to retrogradation. This creates twisting forces in the starch macromolecules generating crater-like holes in the surface. The holes increase the surface roughness of the films (Fig. 7, TPF-NPF and TPF-NPFB) by creating physical obstacles (Fig. 6, TPF-NPF and TPF-NPFB) product of the retrogradation of the amylose.

On the other hand, the incorporation of the beet flour generated a smoother surface in the systems evaluated (Fig. 7, TPF-NPFB and TPF-PPFB), this due to the plasticizer effect of the beet flour, which was opposed to the retrogradation of the starch, thereby avoiding the creation of holes. Similarly, a smoother surface was related to the increased of the transparency of these systems (TPF-NPFB and TPF-PPFB), this compared to the films developed without the addition of beet flour (TPF-NPF and TPF-PPF).

3.9. Color

Table 1 shows the results of the color parameters of the films studied. *L* and *W* values were higher for the native plantain flour-based films (TPF-NPF and TPF-NPFB) than for the films made from phosphated plantain flour (TPF-PPF and TPF-PPF). Thus, the native plantain flour-based films were whiter and more opaque than the phosphated plantain flour-based films. These results are similar to those reported by Gutiérrez, Izquier, et al. (2015), which confirm that films with a higher amylose content are more opaque. Fakhouri

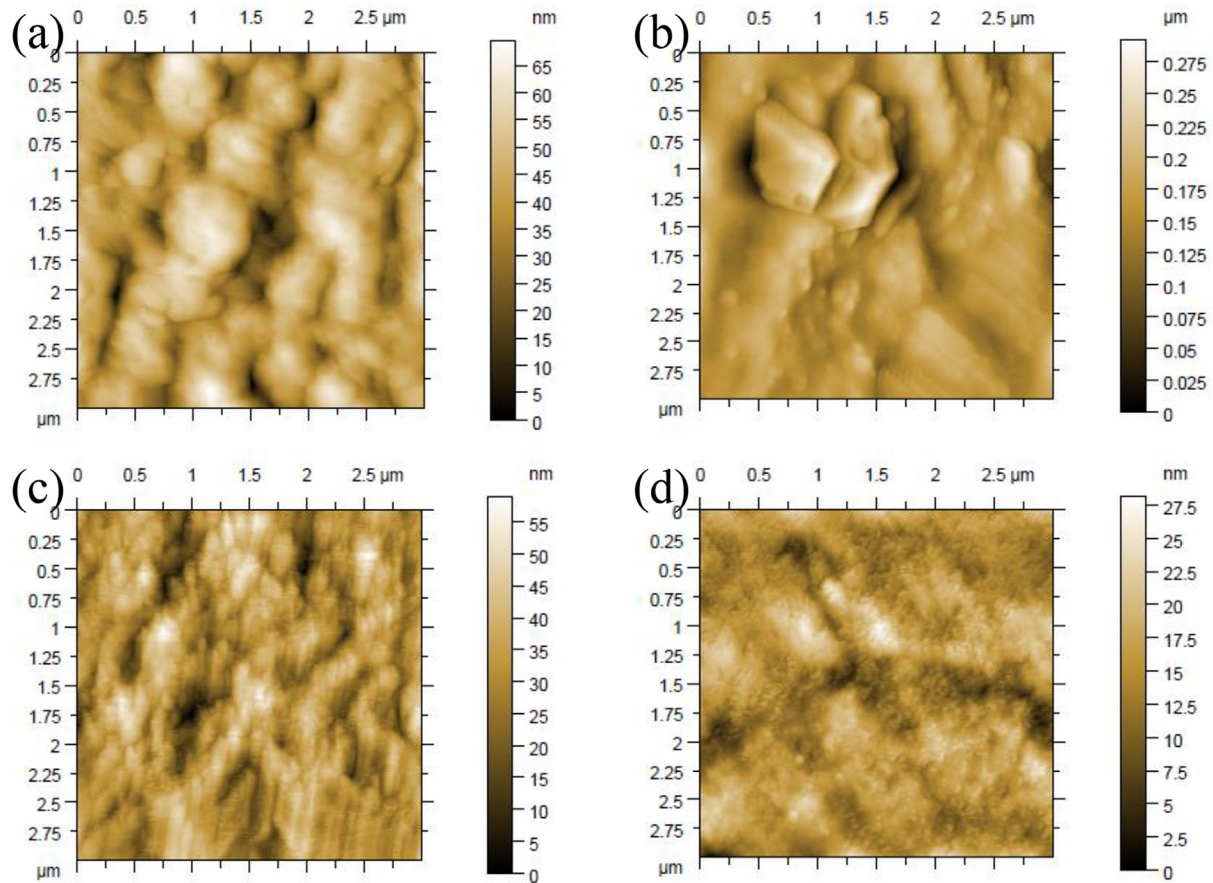


Fig. 7. AFM images of the films: (a) native plantain flour (TPF-NPF), (b) native plantain flour with incorporation of beet flour (TPF-NPFB), (c) phosphated plantain flour (TPF-PPF) and (d) phosphated plantain flour with incorporation of beet flour (TPF-PPFB).

et al. (2007) and Gutiérrez, Izquier, et al. (2015) indicate that opacity can vary depending on amylose content of the starch, since its molecules in solution, tend to be oriented parallel, approaching enough to form hydrogen bonds between the hydroxyl groups of adjacent chains, thus causing the retrogradation of the starch. Therefore, the results obtained were adequately correlated, such as was predicted in the literature. So the same, despite the differences between L and WI , it is important to note that all materials showed excellent transparency and would thus be acceptable to customers. The more opaque films (TPF-NPF and TPF-NPFB) they could be more appropriate when protection against incident light is necessary, especially for wrapping products that are sensitive to degradation reactions catalyzed by light (Pelissari et al., 2013). In contrast, the more transparent films (TPF-PPF and TPF-PPFB) could be particularly useful for foods that benefit from being seen through their wrappings to attract consumers (Gontard, Guilbert, & Cuq, 1992).

In addition, the incorporation of the beet flour in the systems studied (TPF-NPFB and TPF-PPFB), produced more transparent films, which in turn was associated again with the less roughness of the films. Thus confirming, that the lower interaction between the starch–starch chains (product of the plasticizer effect) generated films with surface smoother and more transparent.

All the samples evaluated showed a values of around zero, nevertheless, the values indicating a tendency towards red in the all systems, even films based on phosphated plantain flour were redder.

A positive b value indicates a tendency towards yellow. All the films studied showed this tendency.

The combination of all the changes observed in the chromatographic parameters L , a and b produced slightly greater changes in color, ΔE , in the films with incorporation of beet flour. The results of the yellow index YI shows that films made from phosphated plantain flour were more yellow.

4. Conclusions

Edible films were developed from native and phosphated plantain flour with and without incorporation of beet flour. The addition of the beet flour, allowed the minor interaction between the starch–starch chains, bringing as a result: 1) decrease in the T_g and the enthalpy, 2) minor thermodynamic stability, 3) smoother surfaces, 4) lower crystallinity and 5) more transparent films. Whereby, the films with smoother surfaces and with greater tendency to be degraded thermodynamically were related to the plasticizer effect of beet flour. The same behavior was observed in films elaborated from chemically modified plantain flour by cross-linking with sodium trimetaphosphate. Finally, it is concluded that greater interaction glycerol–starch produced films smoother, more biodegradable and transparent.

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