Evaluation of Biopolimeric Films of Cassava Starch with Incorporation of Clay Modified by Ionic Exchange and its Application as a Coating in a Fruit

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Coatings technologies with biopolymeric films are effective in maintaining the chemical and sensory characteristics of several fruits. Cassava starch is an attractive biopolymeric because of its renewable characteristics and low cost, but it has a high transfer rate of water vapor. Hydrophilic compounds of organically modified montmorillonite clay by ion exchange can be used to improve the limiting properties of starch in exchange for additives such as lipids. The solutions prepared with 5% m/v starch / 5% m/m cationic / anionic clay and uncoated were applied in caja fruit, harvested at physiological maturity, selected for absence of defects and color uniformity. The experimental design was performed with four storage times (0, 3, 6 and 9 days). For the maturation index, there was an isolated effect of the type of coating and storage time, showing the composite films of modified cationic clay with greater MI of the fruits in comparison to the control fruits.

Keywords: *Biopolymeric films, cassava starch, ion exchange, caja fruit, maturation index.*

1. Introduction

Edible films and/or biopolymeric are potentially known to reduce weight loss and humidity, improve respiration rate, maintain firmness and color characteristic of foods, retain, among other things, soluble solids, sugars and acidity, in addition to protecting the mechanical and maintaining them as fresh as possible[1].

Cassava starch is an attractive biopolymer due to its renewable, abundant and low cost characteristics, but it has limitations in the formation of films, such as high solubility in water, high transfer of water vapor, and low mechanical resistance. Hydrophilic composites of montmorillonite clay organically modified can be used as compatibilizing agents in the polymer network in order to improve the limiting properties of cassava starch in exchange for commonly used additives, such as lipids, which may negatively affect the properties of films[2].

The use of these coatings raises the maturation index (MI), which can be evaluated as the result of the alteration in the quantities of organic acids and sugar with changes that make possible the increase of sweetness, widely used in the food industry as a parameter associated to the degree of maturation and flavor reference for fruit, thus it is considered one of the indicators of the increase of the useful life, which consequently maintains the good characteristics in the fruits; the caja fruit, for example, is in constant process of expansion and of high commercialization. Its cultivation already covers

several areas of the North and Northeast regions, however, they are quite perishable, and there is a growing need to increase the useful life, maintaining the characteristics of acceptability[3,4,5].

In order to control the negative effects of lipid addition and increase the MI of the caja fruit, this work has the objective of evaluating the use of montmorillonite clay, organically modified with ion exchange, in addition to the biopolymeric matrix constituted of cassava starch, in maturation of caja fruit over nine days of storage.

2. Materials and Methods

2.1 Materials

The cassava starch of the Indústria Primícias do Brasil, Macaíba, Rio Grande do Norte, Brazil, was used in the preparation of the films. Glycerol PA (Synth) was used as plasticizer. Sodium bentonite clay, supplied by Armil Mineração Nordeste (AMN), Parelhas, Rio Grande do Norte, Brazil, with light cream color, in powder form, with a mean particle size of 0.074 mm and a cation exchange capacity of 75 meq/100 g .

The cation exchange was carried out in the presence of cetyltrimethyl ammonium bromide, manufactured by Sigma Life Science/USA, with 98% purity, ethyl alcohol (95.5º GL Absolute), brand Synth. The anion exchange was done in the presence of sodium dodecyl sulfate (SDS), manufactured

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by Inlab Confiança, and ethylene glycol, manufactured by Merck, with a molar mass of 62.07 g / mol and 99.5% purity.

The caja fruit (Spondias mombin L.) was taken from the university's own orchard (UFERSA).

2.2 Ionic exchange

In the anion exchange, 1g of clay was diluted in 80 ml of ethylene glycol. Then 1 g of sodium dodecyl sulfate (SDS) was added to 20 ml of distilled water. The mixtures were vigorously stirred for 2 hours at 100 º C. After stirring, the mixture was filtered and washed to remove excess of salt. The final product was dried in oven at 105 º C[6].

In the cation exchange, 1g of clay was diluted in 100 mL of distilled water, with constant agitation at 30ºC. In another container, cetremide or cetyltrimethyl ammonium bromide (CTAB) was added in 20 mL of 0.06M ethyl alcohol. The mixtures were vigorously stirred at 30 º C for 12 h. After stirring, the mixture was filtered and washed to remove excess of salt. The final product was dried in oven at 105 º C[7].

2.3 Preparation of the filmogenic solution

The film-forming solutions were prepared according to the modified methodology of Cyras et al[8], by adding 5g of cassava starch with 20% w/w of glycerol in relation to the dry mass of the biopolymer with heating up to 70 º C for 15 minutes in complete homogenization. Then, two different blends dispersed in distilled water were prepared: 5% w/w anionic clay and 5% w/w cationic clay in relation to the dry mass of the polymer. The concentrations of clay were previously tested in the preparation of films with polymeric matrix of cassava starch in varied concentrations following the indication of several authors Li & Guo[6]; Monteiro et al[9]; Romero-Bastida et al[10]. Preliminary results are not showed.

Finally, the solutions prepared were mixed and placed in an ultrasonic bath for 30 minutes to facilitate dissolution. The filmogenic solutions were arranged in rectangular plates and dried at 40ºC for 6 hours in the oven by the casting method.

2.4 Characterization of Clay

2.4.1 X-ray diffraction - XRD

The XRD analyzes were conducted at room temperature on a Shimadzu DRX-6000 equipment, using Cukα radiation (λ = 1.5418 Å), a voltage of 40 kV and a current of 30 mA. The samples were analyzed in a range of 2θ between 2 and 30º with a scan speed of 2º / min.

2.4.2 Fourier transform by infrared spectroscopy - FTIR

The infrared absorption spectra were obtained with a Shimadzu IRTracer-100 spectrometer, scanning from 7800 to 350 cm $^{-1}$ and 4 cm $^{-1}$ resolution. The samples were characterized directly by attenuated total reflectance, without any type of preparation.

2.5 Characterization of biopolymeric films

2.5.1 Thickness

The thicknesses of the films were measured using a Mitutoyo micrometer (Model MDC-25M, MFG / Japan). The measurements were taken at five different points throughout the film.

2.5.2 Scanning electronic microcopy - SEM

The samples were submitted to the SEM (model VEGA 3 TM, TESCAN-Czech Republic, 2013) applied at a voltage of 15kV, with a magnitude of 1kx.

2.5.3 Water vapor permeability - WVP

The water vapor permeability of the films was determined gravimetrically, according to the standard ASTM method E96-95[11] and Maran et al[12]. The films were cut into square pieces (2cm x 2cm) and sequentially deposited on top of the WVP measuring cells. The water level was up to 1 cm below the film. The weight of each cell was measured before being deposited in a desiccator which contained silica stones at the bottom, as well as a relative humidity of 60% and internal temperature of 28ºC. Cell weight was measured every hour over a period of 8 hours. The WVP of the films was calculated in g.mm/kPa.m[2].h as follows in Equation 1:

$$WVP = \frac{W.L}{A.t.\Delta P} \qquad (1)$$

Where W is the weight of water permeating through the film (g); L is the film thickness (mm); A is the permeation area (m[2]); t is the permeation time (h); ΔP is the pressure difference to water vapor between the two sides of the film (KPa).

2.5.4 Solubility

For solubility, the methodology adapted from Casariego et al[13] was used. Film disks with 2 cm of diameters were dried at 105ºC for 1 hour. The disks were immersed in distilled water at room temperature, shaken for 24 hours. Then they were dried again at 105ºC for 1h. The solubility was calculated from Equation 2:

$$S = \frac{mi - mf}{mi} \times 100 \qquad (2)$$

Where S is the solubility (%); m_i is the initial mass (g); m_f is the final mass (g).

2.5.5 Opacity

The opacity of the films was determined by the methodology adapted from Fakhouri et al[14] with the colorimeter (model CR 10, Minolta), calibrated with a standard white background and a standard black background. The opacity values were calculated according to Equation 3:

$$Op = \frac{Op_B}{Op_W} \times 100 \qquad (3)$$

Where Op_B is the opacity of the film against a black background; Op_W is the opacity of the film against a white background.

2.5.6 Mechanical properties

The mechanical properties were determined using an Testing Machine (model DL5000/10000, Paraná, Brazil), which operates according to standard ASTM method D882-83[15] at a test speed of 5 mm/min with application of total force of 5kN. The samples follow the same standard and are evaluated with length of 50mm, width of 5mm and maximum thickness of 0.25mm.

2.6 Characterization of Caja Fruit

The caja fruit was collected at the ideal physiological maturity, previously selected for absence of defects and color uniformity. The fruits were divided into three lots and three treatments, control (uncoated), and coated. The coatings were then applied to the caja fruit by the dipping technique and subsequently maintained at 15ºC ± 2ºC and 90% ± 2% RH for nine days.

The mass loss was considered by the difference of the initial weight and the final weight in the storage time[16]. The weighing was performed in analytical balance Marte (Model AY220, Minas Gerais, Brazil). In the determination of color, a Konica Minolta colorimeter (COLOR READ CR10, Japan) was used, the readings were expressed in index C, chromaticity a* and b*. The measurements were determined in three equidistant points, considering the average of the three readings.

2.7 Statistical analysis

In the biopolymeric films, a completely randomized design with two treatments and three replicates was used. The significant difference between the means was established by the Tukey test at 5% probability of error with the smallest minimum difference for the multiple comparisons.

The statistical design used in the storage of the fruits was completely randomized in subdivided portions with three treatments: control, anionic and cationic, with three storage times (3, 6, and 9 days), with three replicates of six fruits for each treatment and storage period. The data were submitted to analysis of variance with the aid of SISVAR software. A significant effect of the interaction between the factors under analysis was observed, and the means were compared using Tukey's test at 5% of probability.

3. Results and Discussion

3.1 Ionic Exchanges

3.1.1 FTIR

Figures 1A and 1B show the infrared spectra of the BT clay in its sodium form and after cation and anion exchange, respectively.

In Figure 1A it is possible to evaluate some changes between the two spectra and to observe that there was overlap in several regions between the transmittance bands of the two samples at the same frequency. This fact is related to the octahedral structure of bentonite, which is formed by elemental crystals of aluminum or silicon in the center and oxygen and hydroxyls at the vertices between two leafs of tetrahedrons[7,17].

In the region of high transmittance, in the peaks between 2845 cm^{-1} and 2925 cm^{-1}, there are the presence of the bands corresponding to the organic groups associated to the -CH and the cations of Al^{3+}, proving the ion exchange done in the BT clay by cationic surfactant. The peak near 1500 cm^{-1} proves the presence of bands that correspond to the functional groups of the quaternary ammonium salt -CH and -CN, and the region of transmittance at 1480 cm^{-1} indicates groups associated to the -CN and the presence of elements such as Si^{2+} cation and oxygen of the tetrahedral leaf; bands smaller than 1000 cm^{-1} were displaced to smaller values due to the presence of the hydroxyl at the vertices of the tetrahedral layer [7,18]. Similar results were presented by Marcel et al[19] and Sara et al[20].

In Figure 1B the spectra are formed between the characteristic peaks of 640 cm^{-1}, in addition to those, in points near 700 cm^{-1}. These characteristic peaks undergo a displacement, approaching 942 cm^{-1} and 1008 cm^{-1}, which corresponds to the electrostatic interactions between the silica, oxygen and aluminum bonds, which according to Sarier et al[21] this is due to fact that there is an intercalation of the MMT, forming sensitive bands in higher wave numbers.

These results confirm the hypothesis of anion exchange when it presents nanocomposites of starch and modified clay with a greater amount of hydrogen bonds established by the lower presence of free hydroxyl groups in relation to the unmodified clay, showing the electrostatic affinity of the functional groups of the surfactant with the structure of cassava starch[22]. Similar results were reported by Chiu et al[23] and Monteiro et al[10].
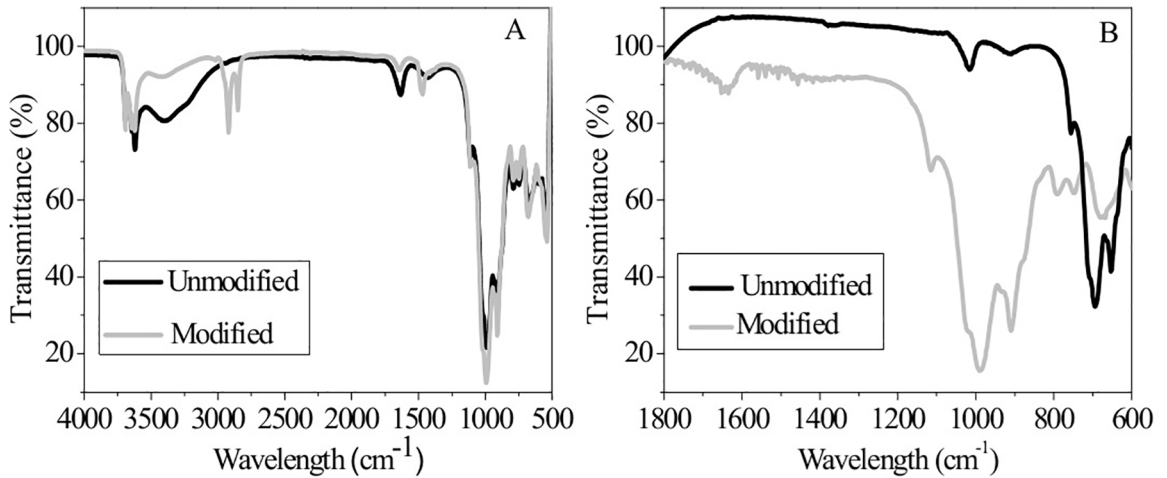
Figure 1. FTIR A) Unmodified clay overlapped with Cationic clay; B) Unmodified clay overlapped with anionic clay.

3.1.2 XRD

Figures 2A and 2B show the results of X-ray diffraction, of the BT clay in its sodium form and after cation and anion exchange, respectively.

In Figure 2A, the BT clay modified by cationic surfactant showed a characteristic displacement to lower values at 2θ, close to 5.5°, compared to the natural BT clay, at 6.5°, due to the influence of the functional groups on the contact surface between the layers of silicate, indicating an increase of the spaces between layers, even though, at the same time, they demonstrate a slight vulnerability of the polymer matrix when associating with the clay, not reaching a complete exfoliation, due mainly to the big interactions between the hydroxyl groups present in the chains, with a significant increase of the spaces between layers of BT and BT/CT[6,24]. Data obtained in

other studies present similar results (Romero-Bastida et al[11] and Alboofetileh et al[24]).

Figure 2B shows a particular characteristic of 2θ marked peaks, approximately 26.6°, when it overlaps with BT clay modified by anionic surfactant, confirming the increase of the basal space and the consequent increase of the region between layers when compared to the natural BT clay, displayed in 2θ, approximately 26.8°.

According to Hua[25] and Moyo et al[26], this displacement in Figure 2B is associated to the vulnerability of the polymer matrix as to its intercalation between the layers of clay modified due to the presence of the salt, compatible with the polarity of the polymer structure, demonstrating accentuated characteristics in the diffraction peaks in these points. The peaks have high intensity and stable basal line, indicating a moderate crystal phase and regular structure with significant distancing and optimum aggregation between the clay and the surfactant.
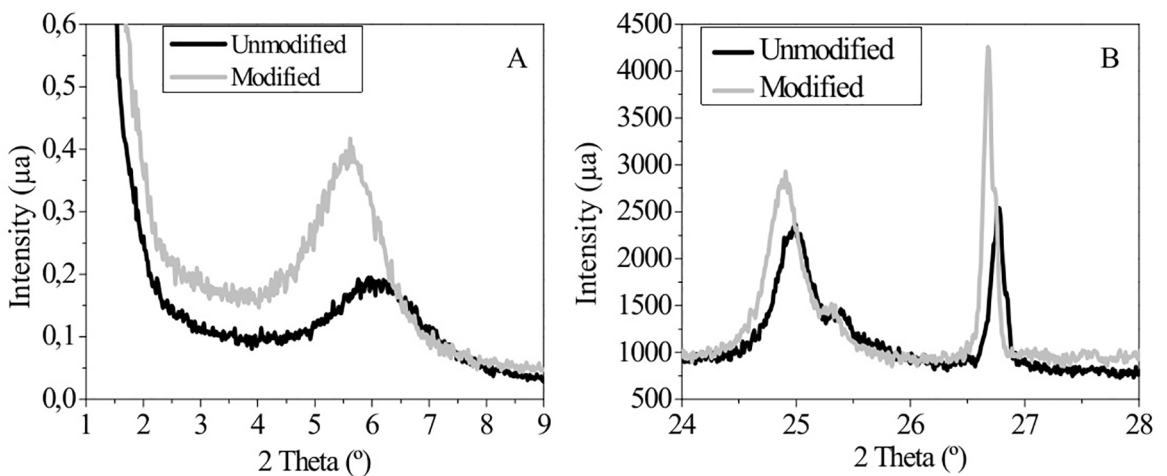

Figure 2. XRD A) Unmodified clay overlapped with cationic clay; B) Unmodified clay overlapped with anionic clay.

3.2 Biopolymeric films

3.2.1 SEM (Scanning Electron Microscopy)

In Figure 3 it is possible to evaluate the micrographs for the obtained biofilms.

Observing the Figure 3 it is possible to visualize the pattern of arrangement of the silicate layers on the surface of the biofilms before and after the ionic exchanges. In general, there is a clear formation and smooth morphology of the polymeric matrix of the biofilms in the presence of clay with ionic exchange, proving the adjustment of the polymer network with the incorporation of the modified clay, and also, showing good interaction between all the components, forming a very homogeneous mixture[27].

In Figure 3A, it is observed that the polymer network is disorganized with a more accentuated accumulation of unhomogenized natural clay, which, according to Casariego[13]; Zhu[28] and Tjong[29] are due to the fact that the starch-natural clay nanocomposites have little affinity between the structures, allowing the silicate layers to be stacked, which decreases the interaction forming an intercalated and brittle nanocomposite, showing a less favorable behavior of natural clay with starch.

In Figure 3B and 3C, the compounds of starch with modified clay, in both cases, presented better agglomerations forming a cohesive polymer matrix, which, according to Veiga-Santos et al[30] and Tan & Thomas[31], is due to the organic modification of the clay through functional groups of the surfactants used, which are electrostatically compatible with the molecules of the starch, allowing the wide penetration of
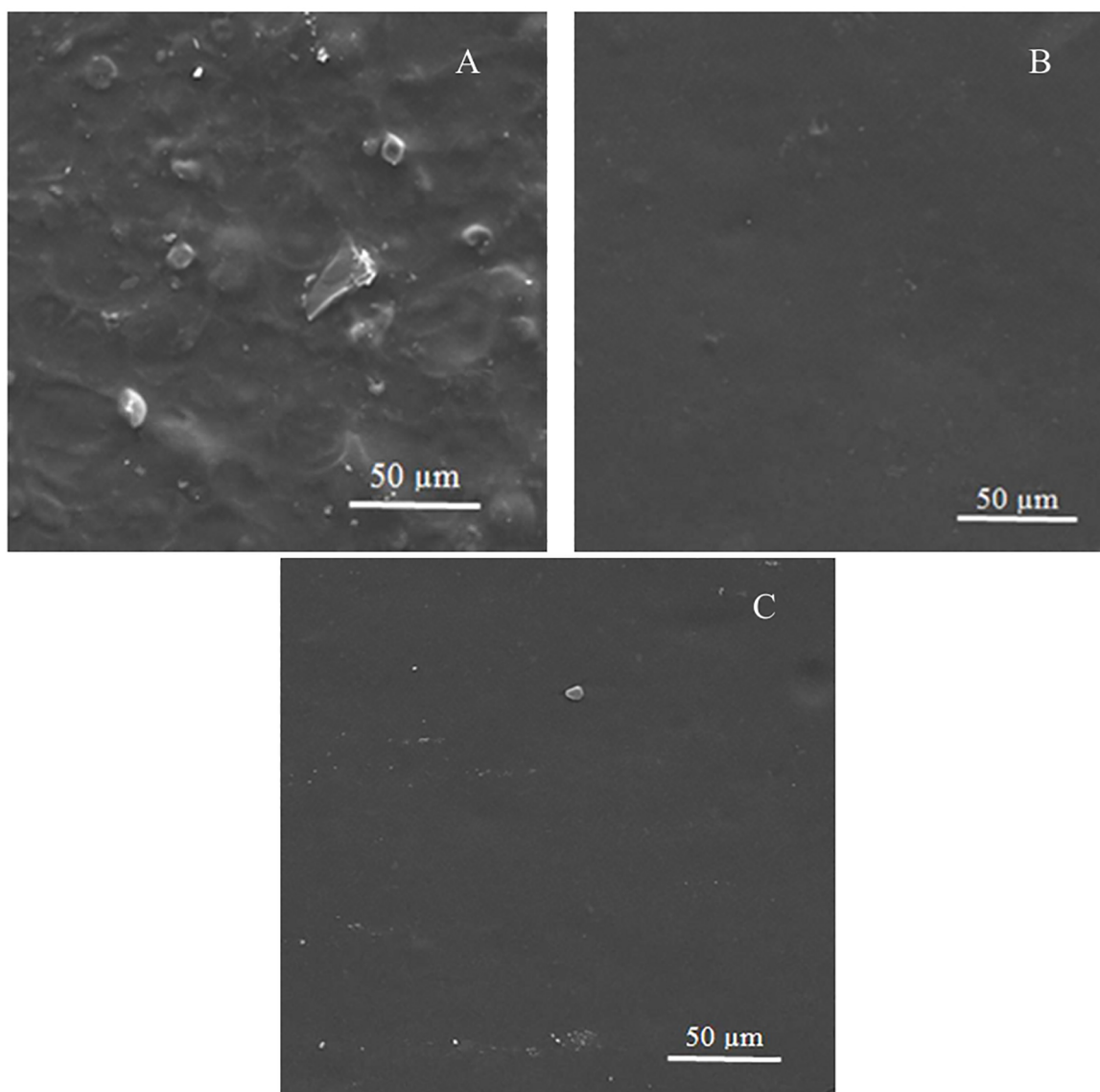

Figure 3. SEM A) Cassava starch biofilm with unmodified clay B) Cassava starch biofilm with cationic clay C) Cassava starch biofilm with anionic clay. Magnitude 1kx.

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the biopolymer between the layers of silicate, characterizing the formation of a exfoliated nanocomposite.

3.2.2 WVP, Solubility, Opacity and Mechanical Properties

The thickness of the films obtained in this study ranged from 0.14 mm to 0.16 mm, and did not present statistical difference (p <0.05) between treatments.

The results of WVP, solubility, opacity and mechanical properties of the biopolymeric films are shown in Table 1.

As shown in Table 1, the decrease of the WVP values of natural BT clay and BT clay with treatment was satisfactorily decreased with statistical difference (p <0.05) between the three treatments, with emphasis on the cation exchange treated films, which showed lower WVP results than films treated with anion exchange.

According to the studies of Kavoosi, Dadfar & Purfard [32] and Acosta et al[33] these results of WVP are explained by the fact of the better organization of the components of the mixture, which benefit the polymer adjustment, facilitating the increase of the contact area, observed in Figure 2, when a greater basal space in the clay structure with cationic treatment, evident in the greater distancing of the peaks of equivalence in this clay, which are larger than the distance of peaks of the clay with anion treatment, leading to a lengthening in the route of the water vapor molecules along of the film.

Solubility showed an opposite aspect to WVP. The anionic treatment caused the maximum reduction, about 45% in relation to the untreated clay film, possibly due to the NH_2-MMT amino groups type, which made the films more hydrophobic or more hydrophilic, according to the amount disposed in each quaternary salt. A larger number of these groups affects decreasing the solubility [34].

The studies of Mu et al[35] presented similar results and pointed out that the more hydrophilic nature of the unmodified BT clay than the modified BT clay acts as a barrier between the starch and the solvent when analyzing the basal space and the increase of the modified area by the quaternary salt in both cases. Thus, the use of unmodified clay interferes with an increase in solubility.

The opacity of the films of natural or modified (cationic and anionic) clay did not differ statistically (p <0.05) between them. Other authors such as Cyras et al[8] and Monteiro et al[10] evaluated the use of biofilms with a polymeric matrix constituted only of cassava starch and obtained values similar to those found in this study. It is possible to infer that the addition of natural or modified clay did not give the biofilms a more opaque appearance and could be considered transparent when compared to cassava starch coatings on fruits.

The control film, with untreated clay, presented lower tensile strength, while the treated films showed an increase, with a statistical difference (p <0.05) between the three

Table 1. WVP, solubility, opacity and mechanical properties of the films.

Film	WVP ($\times 10^{-2}$g.s^{-1}.m^{-1}.Pa^{-1})	Solubility (%)	Opacity (%)	Tensile Ttrength (MPa)	Elongation at break (%)
Control	4.18±0.02^a	66.15±0.15^a	45.47±1.09^a	0.74±0.02^c	31.59±0.14^a
Cationic	2.52±0.01^c	42.10±0.24^b	46.16±1.06^a	0.88±0.02^b	20.76±0.12^b
Anionic	2.98±0.02^b	36.31±0.04^c	43.49±1.06^a	1.43±0.08^a	17.49±0.11^c

CAT: Clay with cationic treatment; ANI: Clay with anionic treatment. Different letters in each column indicate the statistical difference (p < 0.05) between treatments.

Table 2. Mass loss (%) of the caja fruit.

Treatment	Storage Days		
	3	6	9
Control	6.50±0.06^a	6.94±0.03^a	7.45±0.02^a
Cationic	4.85±0.02^c	5.74±0.03^c	6.07±0.03^c
Anionic	5.14±0.01^b	6.63±0.02^b	7.01±0.01^b

Different letters in each column indicate the statistical difference (p < 0.05) between treatments.

Table 3. Parameters a*, b* and chroma index for the color of the caja fruit.

Treatment	Days of Storage								
	3			6			9		
	a*	b*	c*	a*	b*	c*	a*	b*	c*
Control	-8.6^{cA}	48.9^{bA}	49.6^{bcA}	-0.2^{bA}	50.7^{abA}	50.7^{bcA}	6.0^{aA}	52.7^{aA}	53.0^{aA}
Cationic	-12.4^{cC}	44.0^{bcBC}	45.7^{bcBC}	-7.6^{bB}	44.2^{bcBC}	45.8^{bcBC}	-1.7^{aBC}	47.1^{aBC}	47.2^{aBC}
Anionic	-11.3^{cBC}	43.3^{abBC}	44.8^{bcBC}	-7.0^{bBC}	45.0^{bcBC}	45.6^{bcBC}	-1.5^{aBC}	48.4^{aBC}	48.4^{aBC}

*Different lowercase letters in each parameter indicate the statistical difference (p < 0.05) for the storage time. * Different capital letters compare in the column in each parameter, and indicate the statistical difference (p < 0.05) for the type of coating.

treatments, and with emphasis for the films treated with anion exchange, which presented higher resistance, reinforcing the study of other authors, such as Chen & Evans[36] and Cyras et al[37], which point to increased stiffness of the material when added MMT clay in cassava starch films.

According to Rometo-Bastida[11] these results are due to the exfoliated structure obtained by the addition of modified clay in the polymer matrix, which benefit the transport of the tension applied by the better dispersion of the reinforcing elements.

The elongation at break has an opposite effect, when there is an increase of tensile strength and stiffness of the films, there is a reduction of the elastic properties, observed with the decrease of this parameter of elongation in films with anion exchange. Similar results were obtained by Romero-Bastida et al[11] and Farahnaky et al[38]. This can be attributed to the fact that the filling materials decrease the deformation of the polymer structure due to the formation of a layer of immobilizing biopolymer at the polymer-filling material interface and reduce the flexibility of the smooth surface of starch [39].

3.3 Properties of Caja Fruit

3.3.1 Mass loss

In Table 2, it is possible to evaluate the mass loss of the caja fruit during the period of storage.

At the end of the nine days of storage, the fruits coated with the coverage of the cationic treatment had a much lower mass loss (6.07%) to the fruits conditioned with the coverage of the anion treatment (7.01%) and control fruits (7.45%), with statistical difference ($p < 0.05$) among the three treatments throughout the storage time.

The results of Table 2 demonstrate that the loss of mass was satisfactory for the coatings used with treated clay in the polymer network, as they restricted the diffusion of water vapor, reducing, transpiration, loss of water throughout the days of treatment and consequent decrease of mass loss[40,41].

According to the studies of Lee et al[7] and Limchoowong et al[42], the lower WVP presented in films with modified clay (Table 1) indicates that the polymer matrix with this composition has a low transfer of water vapor that ends up extending the transfer distance of the water molecules, thereby reducing the rate transfer of water.

3.3.2 Color

In Table 3, it is possible to evaluate the color of the caja fruit throughout the days of storage.

Changes in the color of the peel is a natural indicator of maturity. The change in the color of the peel, from green to yellow, is due to the degradation of chlorophyll and to the synthesis and development of carotenoids. Color is used to select many products in commercial classes and categories and is related to consumer perception of appearance[43].

The values of the index C, Chroma, is a representation of the appearance visible to the eyes of an infinity of colors, and, the greater, the more intense the observed color. Hence, an increase in C indicates a distance from the center of the coordinates of C, where the colors are more vivid and strong, typical of yellowing. As seen in Table 3, the chroma index of the peel or the intensity of this color was influenced by the coating, being significant ($p < 0.05$) during the days of storage between the coated fruits and the control, and not significant for the coated fruits with ion exchange films. Chroma was also influenced by storage time from day 3 to day 9.

Taking into consideration the treatments, the coated fruits presented chroma values inferior to the control fruits, evidencing that the color intensity is more accentuated in these fruits, that, predominantly, acquire the strong yellow color, typical of the maturation of the caja fruit throughout the period of storage[44].

The values a^* and b^* represent the color itself; the values of a^* vary from green when negative ($-a^*$) to red when positive ($+a^*$). The values of b^* change from yellow when positive ($+b^*$) to blue when negative ($-b^*$), this indication proves the result of the Chroma index, as seen in Table 3, showing significant changes in treatment time, and effect of coatings. Coated fruits showed significant differences ($p < 0.05$) between values of these with the control.

A peak in the production of ethylene may have caused the difference in the color of the peel in these fruits, since such a transformation is closely linked to the biosynthesis of this product, which is responsible for the increased activity of the enzymes chlorophyllases. These enzymes act by degrading chlorophyll, inducing the synthesis of enzymes from the maturation period, which produce carotenoids, in a marked way in the control fruits, confirming the satisfactory result of the application of the coating with treated clay[45,46].

4. Conclusion

The incorporation of quaternary salts in clay modified its hydrophilic characteristics and altered the basal space of these, making satisfactory its use in the polymer matrix of cassava starch, which facilitated the increase of the contact area and a marked improvement in the barrier properties of the coatings used in caja fruits, resulting in a restriction on the diffusion of water vapor, which reduced the transpiration and loss of mass, consequently increasing the storage time and preserving the ideal characteristics of the fruit.

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