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Analysis of the Barrier and Thermogravimetric Properties of Cassava Starch Biopolymeric Films with Addition of Beeswax

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Abstract

Biopolymeric films have to appear as a viable technological alternative for two different strands, in order to replace the polymers of the petrochemical industry and to meet the growing world demand for fresh and healthy food, so the packaging is post-harvest technological solutions capable of reducing metabolic activity and preserve nutrients for long periods of storage. Biopolymeric films of cassava starch 2% were obtained; beeswax (BW) was added as a hydrophobic agent in the polymeric network at different concentrations relative to the dry biopolymer base (0%, 5%, and 10%). The contact angle of the systems containing beeswax indicated the hydrophobic behavior of the films, corroborating with the analysis of the Water Vapor Permeability (WVP) when it showed the behavior change between the films with and without BW for the shelf- life in fruits. The thermogravimetric analysis also evidenced that the addition of BW produced changes in the thermal decomposition behavior of the starch.

Keywords: Biopolymeric films; Cassava starch; Beeswax; Water vapor permeability; Thermogravimetric analysis

Introduction

Food preservation, quality optimization, and shelf-life extension are challenges in the food industry today, as the demand for fresh fruits and vegetables has risen steeply in recent years, often because consumers are looking for freshness and quality when they buy these products. Packaging has significant importance in the conservation of agricultural products and its proper use can reduce postharvest losses since these foods have a short shelf life, which is mainly attributed to mechanical and physiological damages and deterioration [1,2].

The development of edible coatings or film packaging has developed as a potential low-cost post-harvest technology and renewable diversity, attracting the attention of numerous researchers [3-10]. In addition to the primary functions of protecting content, facilitating transportation, storage, and handling, packaging influences consumer perception and expectation [11].

Within the vast possibility of using polysaccharides as the polymeric matrix of the films, the starch has been presented as one of the main materials used in the elaboration of these edible coatings, since it is a non-toxic, biodegradable polysaccharide obtained from natural sources of low cost, stability, and capacity to form gels [12].

Due to their high hydrophobicity, the coatings are susceptible to moisture since the water molecules can easily form hydrogen bonds and transport rapidly within chains of the polysaccharides. On the contrary, lipids, which are hydrophobic, have effective moisture barriers but are inferior to structural strength. In this context, beeswax is commercially known, with high hydrophobicity and is abundant, which makes its use well available [13].

This study seeks to guide the need to find economically viable and sustainable alternatives from the use of renewable sources of biopolymers extensively produced in several areas to obtain biopolymer films as post-harvest technology of fruits and vegetables, showing the films that have better barrier properties and thermo gravimetrically more susceptible to various uses, establishing comparative means from the use or not of hydrophobic agents.

Materials and Methods

Materials

Cassava starch used in the preparation of the films was supplied by Industria Primícias do Brasil Ltda., Macaíba, Rio Grande do Norte-Brazil. Glycerol, with the denomination of glycerin P.A-ACS (Synth), with molecular formula $C_3H_5(OH)_3$, was used as a plasticizer of the films. Beeswax was supplied by the Companhia de Apicultores Rurais of the city of Severiano Melo, the Rio Grande do Norte-Brazil. The surfactant used was Sunflower Saponified Oil (SSO), anionic surfactant produced from the saponification process of essential oil of sunflower in the Laboratory of Chemical Processes of the Universidade Federal Rural do Semi-Árido-UFERSA, Mossoró, the Rio Grande do Norte-Brazil.

Obtaining biopolymeric films

Three biopolymer films were obtained. One without the addition of hydrophobizing agent, and two more with the addition of beeswax. The methodology used follows what is described in Chiumarelli and Hubinger [14].

For Film 1 only one mixing phase was required. 2% cassava starch was added in distilled water and 20% glycerol in relation to the biopolymer dry mass. The mixture was kept under constant stirring at 75°C, with complete gelation.

To obtain Films 2 and 3 a second phase was necessary, from the addition of beeswax. In two separate containers, 5% and 10% of

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beeswax was added to 2.5% and 5% of anionic surfactant so (saponified sunflower oil), respectively. All addition percentages took into account the initial biopolymer dry mass. Also as described in Hromis [15], the blends were stirred at 85°C and complete solution formation.

To avoid bubbles or lack of standardization, the filmogenic solutions were placed in an ultrasonic bath for 10 minutes. Afterward, the solutions were deposited in a rectangular plate 13 cm wide, 23 cm long and 2 cm deep, and then dried at 28°C for approximately 36 hours, according to the casting method.

Characterization of biopolymeric films

Thickness: The technique used to measure thickness followed the studies of Luchese [16] the films were measured using a Mitutoyo micrometer (Model MDC-25M, MFG/Japan). Measurements were taken at five different points throughout the films.

Barrier properties: For the contact angle analysis, an experimental apparatus consisting of a mobile base with sample port with a light source attached to a camera (VP 540 s, Intelbrás) was necessary, according to the adapted methodology of Boinovich [17] based on the sessile drop technique, with images formed by the intersection of the liquid-solid. The software used to calculate the contact angle was Surftens 4.5.

The water vapor permeability of the films was determined gravimetrically, according to Monteiro [18]. The films were cut into square pieces (2 cm × 2 cm) 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 desiccators which contained silica stones at the bottom, as well as a relative humidity of 50% and the internal temperature of 29°C. Cell weight was measured every hour over a period of 8h. The WVP of the films was calculated in g.mm/m.h.kPa as follows in Equation 1:

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

Where W is the weight of water permeating through the film (g); L is the film thickness (m); 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).

Thermogravimetric analysis

A thermogravimetric analyzer and simultaneous calorimeter, model TG209F1 Libra and manufacturer NETZSCH were used for the analysis. All the tests were carried out obeying the following parameters: alumina crucible; nitrogen purge gas; bleed gas flow rate of 50 mL/min; heating rate of 10 °C/min; final temperature of 600°C and sample mass of 5 mg.

Statistical analysis

All qualitative analysis data were collected in triplicate. The significant difference between means was established by the Tukey method with a level of statistical significance lower than 5%.

Results and Discussion

Thickness

The thicknesses of the developed films ranged from 0.05 mm to 0.09 mm. The cassava starch 2%films were 0.05 mm thick, followed by cassava starch 2% films with beeswax 5%, 0.075 mm and cassava starch 2% with beeswax 10%, which presented 0.09 mm, so that the concentration of beeswax increased the surface area, generating thicker films.

Barrier properties

Table 1 shows the results of the barrier properties (contact angle and WVP) for the obtained films in order to investigate the results from the incorporation of beeswax into the polymeric matrix.

In general, the films that presented higher values of θ exhibit behavior of greater surface hydrophobicity, a fact also verified in the analysis of WVP. The quantitative differentiation between "hydrophilic" and "hydrophilic" surfaces is based on θ> 65 or θ<65, respectively [19]. Only Film 1 presented hydrophilicity characteristics so that the addition of BW was essential for the superficial maintenance of Films 2 and 3.

This behavior can be explained by the hydrophobicity of the main bioactive compounds found in BW, the carboxylic acids, such as the certic and palmitic acids, responsible for reducing the water vapor exchange when added to the polymer matrix [20]. The importance of these compounds is mainly tied to the attraction between the water molecules and the surface of the biopolymer film, so that the adhesive forces of the film become much smaller with respect to the cohesive forces of the liquid in order to hinder the penetration of the liquid, forming angles greater than 90°C between a drop of water and the surface [21,22].

The same behavior is visualized in the WVP results, the addition of BW and the surfactant ended up reducing the water vapor exchange. The hydrophobicity of the main bioactive compounds found in the BW caused a decrease in the diffusion of water vapor, probably because it affected the bonding forces of the chains in the network, in order to raise its potential [14]. The addition of the surfactant probably caused an increase in the contact angle between the functional groups of the other components, both the polymer matrix and the BW, increasing the affinity between them, contributing to the reduction of the forces of the polymer network, and when there is a loss of matrix cohesion, water vapor transport is limited, so these intermolecular interactions have improved the water resistance and stability of the films (Table 1) [9,15,23,24].

Thermogravimetric analysis

Figure 1 shows the behavior of thermogravimetric curves related to the loss of mass of cassava starch film 2% (Film 1) and starch films with the inclusion of beeswax 5% and 10% (Films 2 and 3, respectively).

Film	Barrier properties data	
	θ	WVP × 10^{-4} (g/m.h.KPa)
1	61.9 ± 1.00^{c}	2.88 ± 0.04^{a}
2	90.1 ± 0.98^{b}	2.58 ± 0.05^{b}
3	93.8 ± 0.95^{a}	2.41 ± 0.03^{c}
Different letters in the columns indicate statistical difference. All comparisons were performed by the Tukey test at 5%		

Table 1: Profile of the barrier properties of Films 1, 2 and 3; (Film 1: polymer base with 2% of cassava starch, Film 2: polymer base with 2% of cassava starch with addition of 5% beeswax and Film 3: polymer base with 2% of cassava starch with addition of 10% of beeswax).

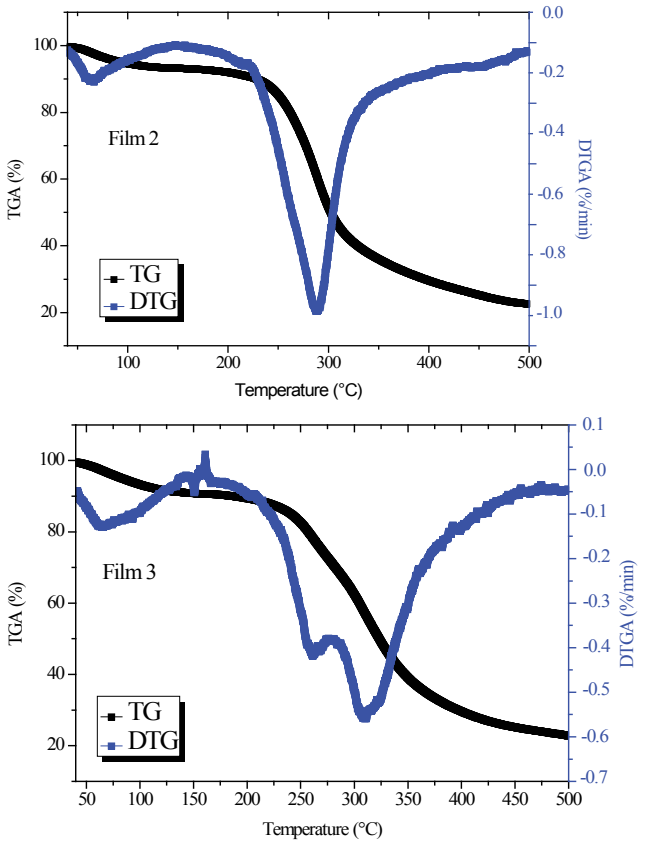

Figure 1: TGA and DTG for Films 1, 2 and 3; (Film 1: polymer base with 2% of cassava starch, Film 2: polymer base with 2% of cassava starch with addition of 5% beeswax and Film 3: polymer base with 2% of cassava starch with addition of 10% of beeswax).

The thermogravimetric analysis of biofilms was performed to determine how the addition of beeswax influenced the thermal decomposition behavior of cassava starch. Films 1, 2 and 3 were subjected to temperatures between 25°C and 600°C.

In the evaluation condition, two steps were observed through the curve formed by mass loss. The first phase, or the initial phase of degradation, corresponds to the evaporation of the water adsorbed by the starch from the first temperature movements up to about 200°C for Film 3, approximately 215°C for Film 2, and up to about 230°C in Film 1, suggesting lower water desorption in Film 3. This is due, in particular, to the different crystalline structure of the beeswax, which is a complex material, and contains about 300 different substances, mainly esters of fatty acids alcohols, possibly decreasing the water fraction and increasing the possibility of crystallization [24,25]. It is possible to evaluate lower desorption while the concentration of BW is increasing.

The second step corresponded to the decomposition of starch. This main stage of degradation occurred initially at 315°C, according to the peak indicated in the DTG until near 340°C for Film 1, initially at 295°C up to near 380°C in Film 2, and at 305°C, according to the peak indicated in the DTG until about 400°C for Film 3, corresponding to about 70%-80% mass loss.

The presence of beeswax, according to the increase of the concentration of the same in the polymer matrix gave to the cassava starch film a smaller loss of mass, about 10% if compared to Films 1 and 3, as well as the retardation of the decomposition point of the same, indicating an improvement in thermal stability, represented by a higher peak in a lower temperature range. A similar trend was reported by Haq [26], Jafari [27], Rocca-Smith [28], Zhu [29].

After the decomposition stage, the residual mass should be related to the nature of the starch, impurities and inorganic components. The degradation mechanism consisted of the elimination of polyhydroxyl groups accompanied by depolymerization and decomposition, with the final carbon production [30-32].

Conclusion

The films of cassava starch submitted to the addition of beeswax presented a more hydrophobic behavior in relation to the films only constituted of the polymeric matrix. The results obtained suggest that the addition of beeswax is effective in reducing the loss of water vapor and is superficially less attractive to the absorption of water. Besides that, the addition of beeswax caused a decrease in the decomposition capacity of the films, improving their thermo gravimetric profile. It is possible to infer that the films obtained from cassava starch with CA addition are a potential post-harvest technological alternative for fruits and vegetables.

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