Physicochemical properties of biodegradable films of spine yam (Dioscorea rotundata), hydroxypropylmethylcellulose and clove oil (Syzygium aromaticum)

Propiedades fisicoquímicas de películas biodegradables de almidón de ñame espino (Dioscorea rotundata), hidroxipropilmetilcelulosa y aceite de clavo (Syzygium aromaticum)

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Abstract
The development of biodegradable films using sustainable and renewable raw materials that produce materials with improved and active properties are a necessity for the current food packaging industry. Also, these materials must be low cost and friendly to the environment. The objective of this study was to evaluate the effect of the addition of clove essential oil on the mechanical, optical and barrier properties of yam starch and hydroxypropyl methylcellulose-based films. A decrease in water affinity and improved water vapour resistance was appreciated due to the addition of the essential oil. Furthermore, it was observed that as the concentration of HPMC increases, more resistant and deformable films are obtained. The films with the highest concentration of HPMC showed more resistant and deformable capacity, with stress strength of 20 MPa and deformation capacity of 18% and the smallest elastic modulus with a value of 400 MPa. Besides, the films have a high barrier against UV light. The addition of clove essential oil and HPMC improved the physicochemical properties of yam starch-based films.

Keywords: Yam starch, Hydroxypropyl, methylcellulose, biodegradable films.

Resumen
El desarrollo de películas biodegradables usando materias primas sustentables y renovables que produzcan materiales con propiedades mejoradas y activas son una necesidad para la industria actual de empaque de alimentos, además estos materiales deben ser de bajo costo y amigables con el medio ambiente. El objetivo de este estudio fue evaluar el efecto de la adición de aceite esencial de clavo sobre las propiedades mecánicas, ópticas y de barrera de películas basadas en almidón de ñame e hidroxipropil metilcelulosa. Se apreció una disminución a la afinidad al agua y una resistencia al vapor de agua mejorada debido a la adición del aceite esencial. Además, se observó que a medida que la concentración de HPMC aumenta se obtienen películas más resistentes y deformables siendo la mezcla preparada con la mayor concentración de HPMC, la que mostró películas más resistentes y deformables, con un esfuerzo a la deformación de 20 MPa y una deformación del 18% y el menor módulo elástico con un valor de 400 MPa. Además, las películas poseen alta barrera contra la luz UV. La adición de aceite esencial de clavo e hidroxipropil metil celulosa mejoraron las propiedades fisicoquímicas de las películas basadas en almidón de ñame.

Palabras clave: Almidón de ñame, Hidroxipropil metilcelulosa, películas biodegradables.

1 Introduction

The environmental pollution caused by the excessive use of plastics in the food packaging industry has generated considerable interest in the implementation of natural, renewable and biodegradable raw materials in the production of packaging (Mohsenabadi et al., 2018).

Yam is a crop of small and medium farmers that constitutes in many regions of Colombia, the main source of rural employment and food supply to its inhabitants. In Colombia, around 500 thousand tons were cultivated in 2019, with a yield of 13.8 tons per planted hectare.

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On the Atlantic Coast, there are five species of yam (Creole yam (D. alata), Spine yam (D. rotundata), potato yam (D. bulbífera), sugar yam (D. esculenta) and yam (D. trifida). Among which are more than 100 varieties, D. alata and D. rotundata being those with the highest consumption and production. These starches have a high amylose content compared to cassava starch, being less susceptible to enzymatic degradation. Also, they have a higher gelatinization temperature requiring more energy for processing, but they are also less susceptible to thermal degradation. (Salcedo-Mendoza et al., 2018; Rodriguez-Lora et al., 2020; Villabona-Órtiz et al., 2020).

Starch is the most abundant polymer in nature, and for many years it has been considered one of the most widely applied natural polymers in the packaging industry (Cao and Song, 2019). Biodegradable starch-based films can act as a barrier to the transfer of oxygen, carbon dioxide, and lipids, thus preventing deterioration of quality and increasing the shelf life of food products (Sullca et al., 2018). The use of starch in the production of films is limited due to its nature; the films produced have poor mechanical properties. For this reason, binary blends with different polymers are used, such as hydroxypropyl methylcellulose (HPMC). HPMC is a semi-synthetic polymer used as a pharmaceutical excipient and is commonly used in the development of films due to the excellent mechanical properties that these present. It is easy to use, it is inexpensive, highly available, and its non-toxicity makes HPMC the most widely used cellulose derivative. However, HPMC films are highly permeable to water vapour, which is a significant problem for different applications. In order to improve the barrier properties against water, lipid and fatty acid components, agro-industrial residues, surfactants and resins are commonly incorporated (Bodini et al., 2019). Different authors have extensively studied the use of starch from different sources (cassava, corn, potatoes, wheat, yams, etc.) to obtain biodegradable plastics (Mohsenabadi et al., 2018; Cao and Song, 2019; Sullca et al., 2018; Bodini et al., 2019; Evangelho et al., 2019; Fitch-Vargas et al., 2019; Ramírez-Hernández et al., 2015; Rodríguez-Soto et al., 2019). Plant essential oils are recognized as a safe source for bactericidal, viricidal, fungicidal, anti-parasitical, insecticidal, medicinal and cosmetic applications, especially nowadays in pharmaceutical, sanitary, cosmetic and agricultural and food industries. Essential oils are natural, volatile, complex compounds characterized, strong odour and are formed by aromatic plants as secondary metabolites, they are used in the preservation of foods and as an anti-inflammatory, antimicrobial, analgesic, sedative, spasmolytic and locally anaesthetic remedies. These oils have antioxidant and antifungal activity due to their phenol and terpenoid content, and this makes them potential additives in the production of food preservation packaging (Arezoo et al., 2019; Acosta et al., 2016; Peláez and Rodríguez, 2016; Valderrama, 2018; Mehdizadeh et al., 2020; Jahani et al., 2020; Piñeros-Guerrero et al., 2020).

Jamróz et al. (2018) used lavender essential oil in polymeric films composed of starch, furcellaria and gelatin in concentrations of 2%, 4% and 6%. They found that the addition of lavender essential oil increased the thickness of the films, while the solubility, water absorption and the degree of swelling decreased significantly as the oil concentration increased, the antioxidant and antimicrobial properties also increased as the oil concentration increased. In another study, Acosta et al. (2016) added essential oil of cloves and oregano to polymeric films based on starch and gelatin, the addition of these oils generated a significant reduction in the barrier to water vapour and oxygen permeability. However, they also increased the transparency of the films but reduced their gloss. In a similar study, Campos-Requena et al. (2017) analyzed the physicochemical properties of starch and montmorillonite-based films containing oregano essential oil for the packaging of strawberries. They concluded that the addition of essential oil significantly improved the preservation of strawberries, in addition to improving the mechanical and thermal properties of the films. The objective of this work was to study the physicochemical properties of films made from yam starch and HPMC in different proportions with the addition of clove essential oil.

2 Materials and methods

2.1 Materials

Yam tubers of the Dioscorea rotundata variety were provided by local growers from the Montes de María region in the department of Bolívar, Colombia. HPMC E15 was purchased from Shanghai Honest Chem. Co., Ltd. (China) with a viscosity of 15 cps and clove oil was purchased from Now Foods (United States) with 100% of purity.
2.2 Starch extraction

For the extraction of starch, 10 kg yams were used following the methodology previously described by Vargas et al. (2016). The received tubers were washed with water to remove residual dirt and any other type of impurities. The tubers were manually peeled with the help of knives. The peeled material was cut into small pieces for further processing in an industrial blender. In the liquefying process, the yam was added in a ratio 1/10 by weight with distilled water to promote the formation of a fluidized mixture. This mixture was filtered by passing it through a canvas. The residual fibre was washed with abundant water to optimize the extraction of starch. After sedimentation, the residual water was removed, and the starch was washed with a solution of NaOH 0.1M, drying at a temperature of 50 ºC for 24 hours, ground and packed in airtight bags until later use.

2.3 Film preparation

Films were prepared using 2% total solids and different starch/HPMC ratios (1:0, 0:1, 1:0.25, 1:0.5, 1:1). Clove essential oil was incorporated in a concentration of 5% concerning the sum of both polymers. The films were prepared by the casting technique described by Talón et al., with some modifications, two different film-forming dispersions were formed based on the pure polymers (S and HPMC).

The starch was pre-gelatinized by mixing starch, and distilled water in a 2% starch dispersion, the dispersion was heated to a temperature of 95 ºC with constant stirring for 30 minutes. After this, the dispersions were allowed to cool to approximately 40 ºC, the amount of water lost was added, and the amounts of glycerol, essential oil and Tween 80 were added indicated in Table 1.

For HPMC dispersion, 1/3 of water was heated to a temperature of 70 ºC, and the HPMC amount was added to form a 2% dispersion with the total water and stirred for 30 minutes. When the dispersion time ended, the 2/3 of missing water were added to promote the solubilization of the polymer. With the solubilized polymer, the temperature was adjusted to approximately 40 ºC and the corresponding amounts of glycerol, essential oil and Tween 80 indicated in Table 1 was added. With the pure polymer mixtures made, we proceeded to mix in the proportions mentioned above. All the mixtures were homogenized using a rotor-stator kit. (Ultraturrax Yellow Line DL 25 basic, IKA Janke and Kunjel, Germany) for 3 minutes at 10,000, 20,000 and 30,000 rpm continuously and degassed using a vacuum pump. After the mixtures were poured into square Teflon plates (20cm side), the amount of polymer was kept constant to obtain an area density of 140g of polymer/m². After, formulations were dried in an oven with air circulation at 40 ºC for 48h. Films were removed from the mould and conditioned in desiccators at 30 ºC with an oversaturated solution of NaCl (RH 75%) for two weeks.

2.4 Thickness

Film thickness was measured with a micrometre (Insize, IP54, accuracy 0.001mm) in ten different positions for each film sample. Average thickness values were considered in the calculations of tensile strength and water vapour permeability (WVP).

2.5 Mechanical properties

Mechanical properties were determined using a texture analyzer (TA.XTplus, Stable Micro Systems, England) based on the method ASTM D-882-02. Films were cut into 25-by-100-mm specimens. The initial grip clearance and cross speed were set at 50mm and 1mm/s, respectively. The maximum stress force (TS), elongation at the fracture point (E) and Young’s modulus (MY) were determined from stress-strain curves.

Table 1. Mass fraction on a dry basis of studied formulations.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>0.763</td>
<td>0</td>
<td>0.61</td>
<td>0.509</td>
<td>0.382</td>
</tr>
<tr>
<td>HPMC</td>
<td>0</td>
<td>0.763</td>
<td>0.153</td>
<td>0.254</td>
<td>0.382</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.191</td>
<td>0.191</td>
<td>0.191</td>
<td>0.191</td>
<td>0.191</td>
</tr>
<tr>
<td>Essential oil</td>
<td>0.038</td>
<td>0.038</td>
<td>0.038</td>
<td>0.038</td>
<td>0.038</td>
</tr>
<tr>
<td>Tween 80</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
</tbody>
</table>
2.6 Water solubility

The water solubility (%) of the mixtures was measured according to the method described by Gontard et al. (1992) with some modifications. The samples (2 cm in diameter) were dried in an oven (DeLeo, A15E, Brasil) at 105 °C to determine the initial dry weight. The mixtures were immersed in 50ml of distilled water, and the mixtures were continuously stirred (100 rpm) at 25 °C for 24h. After immersion, the mixtures were dried at 105 °C to determine the final dry weight. Film solubility (%) was defined as the ratio of the water-soluble solid content to the initial dry solid content.

2.7 Moisture content

Films previously conditioned at 75% RH were dried for 24 h at 60 °C in an oven with air circulation and subsequently placed in a desiccator with P2O5 at 30 °C for two weeks. The reported results represent the mean values of at least three samples.

2.8 Water vapour permeability

Water vapour permeability was determined gravimetrically according to the Standard Method ASTM E96-00, with some modifications. The mixtures were sealed in a permeation cell containing distilled water (100% RH). The cells were placed in desiccators with a saturated solution of magnesium nitrate (53% RH) and weighed at intervals of 1 h for 24 at 25 °C. The WVP (g mm kPa⁻¹ h⁻¹ m⁻²) was calculated as follows:

\[
WVP = \frac{W \times L}{A \times t \times \Delta P}
\]

where \(W\) is the weight increase of the permeation cell (g); \(L\) is the thickness of the film (mm); \(A\) is the exposed area of the film (m²); \(t\) is the time of weight gain (h); \(\Delta P\) is the difference in vapour pressure across the film (kPa).

2.9 Internal transmittance

The transmittance of the films was determined in a range of UV-VIS light to specimens (1cm x 3cm) that were conditioned at 20 °C and 53% RH, using a UV-VIS spectrophotometer (Thermo Scientific, Evolution 300), within a wavelength range of between 190nm to 1100nm.

2.10 Gloss

The gloss was measured on the surface of the film, with an incidence angle of 60°, according to the standard method ASTM D523, using a flat surface gloss meter (Multi Gloss 268, Minolta, Alemania). Measurements were taken in triplicate for each sample, and three films of each formulation were considered. All results were expressed as gloss units (GU), relative to a highly polished surface of standard black glass with a value close to 100GU.

2.11 Statistical analysis

Statistical analyzes of results were performed through an analysis of variance (ANOVA) using Statgraphics Centurion XVI software (Manugistics Corp., Rockville, MD). The Fisher’s least significant difference (LSD) procedure was used with a 95% confidence level.

3 Results and discussion

3.1 Mechanical properties of the films

The results obtained from the evaluation of the tensile strength, the deformation capacity and elastic modulus for all the formulations are shown in Figure 1. Different letters on the bars mean significant differences among the formulations (p < 0.05). Trends of improvement in tensile strength and deformation are shown as increases the concentration of HPMC. The mechanical properties of films, including tensile strength, elongation, and modulus of elasticity, are fundamental because the packaging material must possess adequate mechanical strength to maintain its integrity during handling and storage (Romani et al., 2016). The mechanical properties of the films are strongly influenced by the different proportions of S/HPMC.

The mixture prepared with the highest concentration of HPMC (1:1) showed more resistant and deformable films, with pure HPMC films showing the highest tensile strength, elongation and modulus of elasticity. Romani et al. (2017) described obtaining stronger and more flexible films using high protein contents in the development of films based on rice starch and fish protein. Wang et al., developed films based on HPMC and hydroxypropyl starch (HPMS), where it was concluded that the modified starch reduces the stiffness of the film and improves
flexibility. Song et al. (2018) evaluated the effect of adding lemon essential oil to corn starch films. They concluded that tensile strength decreased with increasing concentration of essential oil and conversely increased elongation at break compared to control film.

The decrease in tensile strength can be attributed to the change from polymer-polymer interactions to polymer-oil interactions. According to these authors, and the data obtained show tendencies to obtain less rigid and more deformable materials and these effects due to the change in the molecular interactions caused by the addition of essential oils and the mixture of both polymers. These less rigid and more deformable materials may apply to the production of bags as food packaging.

3.2 Interaction of films with water

The results obtained for the measurement of thickness, water content, solubility in water and water vapour permeability of the films are shown in Table 2. The thickness of the starch/HPMC mixtures was statistically less (p<0.05) when 25% of HPMC was used in the development of films. This behaviour is probably due to molecular rearrangement during the drying process, which is different for starch and HPMC independently.

Regarding solubility, this is an essential property of films for food protection applications in high water activity products, for example, to prevent oozing of frozen or fresh food during processing and to maintain product integrity (Gontard et al., 1992). Films may require low solubility or insolubility to improve moisture barrier properties and shelf-life stability (Zavareze et al., 2012).

It is observed that pure HPMC is the formulation with the highest moisture content and solubility in water.

These two properties are strongly affected with the concentration of HPMC in blends, as HPMC increases the water content and solubility increase, this due to the hydrophilic nature of HPMC and interactions with S/HPMC generate a more hydrophobic behaviour at low concentrations of HPMC. Yam starch has lower solubility, only 18%, compared to that reported by Chen et al. (2019) in which it reports a solubility for hydroxypropyl starch films of 64.62%. The obtained results are comparable with that reported by Romani

Table 2. Mean values and standard deviation of water content (Xw: g water/g dried film) and solubility in water (g solubilised film/g initial dried film) of studied formulations conditioned at 75% R.H.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Xw</th>
<th>Solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.071 ± 0.005&lt;sup&gt;a&lt;/sup&gt;</td>
<td>20.181 ± 0.007&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>F2</td>
<td>0.094 ± 0.003&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>F3</td>
<td>0.041 ± 0.005&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.211 ± 0.004&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>F4</td>
<td>0.068 ± 0.006&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.322 ± 0.003&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>F5</td>
<td>0.075 ± 0.007&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.612 ± 0.009&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Table 3. Mean values and standard deviation of the thickness (µm) and water vapour permeability (WVP: g·mm·kPa⁻¹·h⁻¹·m⁻²) of studied formulations conditioned at 75% H.R.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Thickness (µm)</th>
<th>WVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>244 ± 4b</td>
<td>6.5 ± 0.2c</td>
</tr>
<tr>
<td>F2</td>
<td>250 ± 4ab</td>
<td>11.3 ± 0.5a</td>
</tr>
<tr>
<td>F3</td>
<td>230 ± 9c</td>
<td>6.9 ± 0.3bc</td>
</tr>
<tr>
<td>F4</td>
<td>245 ± 8abc</td>
<td>7.5 ± 0.4b</td>
</tr>
<tr>
<td>F5</td>
<td>260 ± 5a</td>
<td>8.1 ± 1.1ab</td>
</tr>
</tbody>
</table>

et al. (2017). They observed that the increase in the ratio of starch/protein increases the solubility in water, for a 75/25 ratio, a solubility of 16.7% was obtained. Jamróz et al. (2018) reported that the more significant reduction in the solubility of the films based on starch, furcellaria and gelatin was attributed to the higher concentration of oregano essential oil (6% w/w), the results obtained. Those reported in the literature agree that the addition of essential oils significantly reduces the solubility of films, this reduction in solubility prevents films from collapsing on contact with wet food, improving its application in the food packaging industry.

3.3 Water Vapour Permeability (WVP)

The WVP of films is one of the most critical factors in their application for food packaging. The film must be able to prevent, or at least decrease, the transfer of moisture between the environment and food (Sukhija et al., 2016). Higher HPMC contents, in general, are responsible for a higher permeability to water vapour, being the mixture of pure HPMC the one that presented a higher value of WVP and the mixture with ratio S/HPMC (1:0.25) presented higher resistance to the passage of water steam. This behaviour is directly related to the affinity of HPMC and water. Song et al. (2018) reported that the addition of lemon essential oil decreased water vapour permeability and attributed the observed behaviour to the reduced water binding capacity and increased tortuosity of the vapour diffusion path through the film as a result of the presence of lipid globules. Romani et al. (2017) observed that high protein contents are responsible for the low water vapour permeability. The increase in WVP is associated with the polarity of the chains. This behaviour is evident in the results because of the tendency of the WVP increase with increasing the HPMC concentration the mixtures. Reducing water vapour permeability is a desired condition in food packaging as this will prevent food from dehydrating easily, thereby extending the shelf life of products.

3.4 Internal transmittance and gloss

The internal transmittance and gloss values of the films studied are shown in Figure 2.

It was observed that the internal transmittance values increase as the HPMC concentration increases and conversely the gloss values decrease as the HPMC concentration increases. Song et al. (2018) reported that incorporation of essential oils in HPMC films yielded lower gloss values than in pure HPMC films. This phenomenon is probably due to an increase in light scattering induced by oil drops in the film network. Light scattering phenomena mainly depend on the content and particle size of the dispersed phase. The more drops, the higher the intensity of the light scattering and the lower the transmittance (Alibadi et al., 2014). In another study, Lee et al. (2019) reported that the internal transmittance of the films decreases as the oregano essential oil content increases, indicating an improvement in the barrier against ultraviolet light. The internal transmittance indicates that the packages generated with these materials would offer protection to foods that quickly oxidize with light, besides the packages would be opaque due to the decrease in brightness caused by the addition of essential oil.

Conclusions

In the present study, clove essential oil was incorporated into films based on yam starch (S) and hydroxypropylmethylcellulose (HPMC), the effect of the variation of the S/HPMC ratio on the mechanical, optical and barrier properties was studied. It is remarkable that as the concentration of HPMC increases, more resistant and deformable films were obtained, according to the mechanical properties of
pure HMPC films. When the starch and HPMC were blended, an appreciable decrease in water content and solubility, compared to control formulations, were observed. Regarding water vapour permeability, blends show intermediate values between starch and HPMC films. Also, films possess a significant barrier against UV light. The formulation with S/HPMC ratio of 1:0.25 is the most suitable for the development of materials when the intended application requires a material with significant insolubility. These materials would offer protection against oxidation (UV light) and dehydration (water vapour barrier) of products in the food industry, as well as being low cost and friendly to the environment. For future tests, it is necessary to evaluate the effect of the concentration of the essential oil on the properties of the films and evaluate antioxidant and antibacterial properties to generate a higher spectrum of applicability of these materials.

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References


Cao, T.L. and Song, K.B. (2019). Effect of gum karaya addition on the characteristics of loquat seed starch films containing oregano essential oil. *Food Hydrocolloids* 97, 105198.


