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Corn Starch 80:20 "Waxy":Regular, "Native" and Phosphated, as Bio-Matrixes for Edible Films

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Abstract

Films made from starches are colorless, tasteless, non-toxic, biodegradable, and economical, besides having a low permeability to oxygen. Moreover, the cross-linking modification (phosphatation) could improve its physicochemical properties by reinforcing the hydrogen links inside the granules. The goals of this study were to elaborate and characterize starch corn films 80:20 "waxy":regular, from native and modified (cross-linked), to define their potential application. Results showed, that films with modified starch had highest hydrophilic properties which increased its thickness, permeability and solubility, and with mayor stability in acidic and alkaline medium. Finally, physicochemical properties and water vapor barrier data of the films denote the strong interaction phosphated starch-plasticizer.

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Keywords: Starch, Chemical modification, Corn, Edible films, Biomaterial.

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1. Introduction

The high consumer demand for natural products that do not cause environmental pollution has changed the food packaging and coating industries. Most synthetic products currently used are not degradable and its cost is very high because they come mostly from a nonrenewable resource such as oil.

In the last three decades several studies have been conducted on edible films from natural biodegradable polymers, such as cellulose, chitosan and starch as replacement for synthetic plastics.

Particularly, starch has been the focus of research because it is biodegradable, renewable, inexpensive, edible and readily available. Molecular, starch usually comprises amylose (linear structure) and amylopectin (branched structure). Amylose is responsible for the film-forming ability. Starches from various sources have different proportions of amylose/amylopectin ratio, which can induce different properties.

On the other hand, the starch of maize (*Zea mays* L.) represents 80 % of the starch produced worldwide. This is so because it is a low cost raw material, appropriate for several technical applications in products like soups and pasta flours, jams, chewing gum, meat fillings, sausage, thickened fruit juice, beer and spirits, bakery products, mayonnaise and margarines. Similarly, derivatives of the production of corn have numerous uses in industries: pharmaceutical, cosmetics, textiles, paints, paper, tannery and oil, among others.

In particular, corn starch is promising for formation of edible biodegradable films. However, its native structure is sometimes inefficient because certain conditions of technological processes may reduce their use for industrial applications. Additionally, some dispersions of native starch may impart a cohesive rubbery texture in foods where they are used as thickening agents.

In order to overcome the limitations of the use of starches, a number of techniques for modification have been developed. A common technique is cross-linking of starch. This method can improve some properties of the films generally used in the preparation of coatings for food processing. An important function of the films is to reduce the water exchange between the product and the environment.

Moreover, plasticizers are essential for the formation of many films and coatings based on polysaccharides. These components reduce the intermolecular interactions between adjacent polymer chains, increasing the flexibility of films.

The objective of this study was to evaluate the influence of chemical modification of starch, in the thickness, water vapor permeability, water solubility and stability in acidic and alkaline medium of edible films made from a corn (*Zea mays*) mix of 80:20 waxy:regular starch.

2. Experimental procedure/Methodology

2.1. Materials

Corn starch 80:20 "waxy":regular (*Zea mays*), provided by the company Alfonzo Rivas & Cia, Cagua, Aragua State, Venezuela. Food grade glycerol (Aldrich) as plasticizer.

2.2. Preparation of modified starch

The starch was chemically modified by wet cross-linking (phosphate), following the methodology described by Kerr and Cleveland, with modifications. Starch (150.3 g) was mixed distilled water (212 mL) at constant stirring and, then, sodium hydroxide (NaOH) to 2.5 % and pH 10.5 was added. Afterwards, 7.52 g of sodium sulfate (Na_2SO_4) was added maintaining constant stirring. pH was adjusted again to 10.5 with NaOH to 2.5 % and heated in a water bath at 45 ^oC with constant agitation. Once this temperature was reached, 4.51 g of sodium trimetaphosphate (STMP) was added. The mixture was stirred for three hours. Then it was neutralized to pH 7 with hydrochloric acid (HCl) at 2.5 %. The starch obtained was centrifuged (Damon CRU-500 centrifuge, USA) at 1000 rpm and washed three times with distilled water. Subsequently, the starch obtained was placed in aluminum pans and dried in a tray dehydrator mark Mitchell, Model 645159 for 24 h. After that time, the modified starch was ground with a food processor, and sieved through a 60 mesh screen. Finally the starch was placed into clean containers and stored at room temperature.

2.3. Preparation of edible films

For the preparation of film-forming solutions (FFS) 2 % W/V of each starch and 1.9 % W/V glycerol were mixed with 500 mL of distilled water. Then, the solution was heated for 30 min. at 90 °C with constant stirring in a water bath to ensure system gelatinization. The gel obtained was degassed by applying vacuum for approx. 30 min. The FFS were casted on 40 x 30 cm, stainless trays maintaining a uniform level and equal amount of mass, to compare the different properties of systems. Then, the material was transported to a brand Mitchell tray dehydrator (Model 645 159) for 24 h at 45 °C. Films from corn starch 80:20 "waxy":regular native (TPS-NC80:20) and phosphate (TPS-PC80:20) were obtained. The materials were stored in desiccators under a saturated solution of NaBr (equilibrium relative humidity, HRE, ~ 58 %) until analyzed. All assays were performed within 7 days of the production of films.

2.4. Characterizations

2.4.1. Stability in acidic or alkaline solution

The stability of the films in acidic or alkaline solution was evaluated by immersing samples of 25 x 25 mm in containers with 10 mL of a standard solution of sodium hydroxide (0.1 mol/L) and 10 mL of a standard solution of hydrochloric acid (0.1 mol/L), respectively. The containers were sealed and kept at 25 °C for some time. Appearance changes of the samples were recorded with a Sony camera brand, model Cyber -shot DSC- H3 8.1 mega pixels, in order to evaluate the stability of the films in acid and alkaline solution.

2.4.2. Thickness

The thickness of the films was determined as described by Rojas-Grau et al., with a digital micrometer (Micromaster ®) with an accuracy of 0.001 mm. 18 measurements were taken at different points randomly selected from each film and an average was obtained, which was used to calculate the water vapor permeability.

2.4.3. Water vapor permeability (WVP)

The water vapor permeability was carried out following the ASTM E96-00 and the correction method described by Gennadios et al. For this, acrylic circular cells containing a piece of film (~ exposed area of 15.2 cm^2) were used introduced in desiccators under controlled relative Humidity.

WVP was calculated as:

$$WVP = \frac{G \times e}{S \times RH \times t \times A} \tag{1}$$

where G is the mass, e the thickness of the film, S the saturated vapour pressure at 25 °C, relative humidity RH, t the time, and A the area of each sample.

All assays were performed in triplicate, and the average and standard error were reported.

2.4.4. Solubility in water (SW)

The solubility of the films in water was measured according to the technique described by Romero-Bastidas et al., and using the modifications proposed by Hu et al.

SW was obtained using the following equation:

$$SW = \frac{m_i - m_f}{m_i} x100 \quad (2)$$

where m_i is the initial dry mass m_f, final dry mass.

3. Results and discussion

3.1. Stability in acid or alkaline solution

Films are biodegradable and edible; however, when they are used as packaging material, the wrapped items might be slightly acidic or alkaline, which would affect the stability of the starch based films. In that sense, it is important to study the stability of the films in an acidic and alkaline media.

All films studied in acidic solution (HCl 0.1 mol/L) were stable at least for 24 days, since they kept the same characteristics until the end of the test.

When the materials were evaluated in alkaline medium (NaOH, 0.1 mol/L); the modified starch films (Fig. 1 b) showed higher stability than native starch films (Fig. 1 a). It can be seen that the modification by cross-linking conferred an increased stability relative to the films, in an alkaline medium. Hu et al. studied the stability of potato starch-based films oxidized in an alkaline solution (with the same concentration as that used at this work), showing further deterioration after 24 h as compared to TPS-PC80:20 in the same period of time.

Although TPS-PC80:20 was the one with greatest stability, this film showed a swelling of almost 75 %.

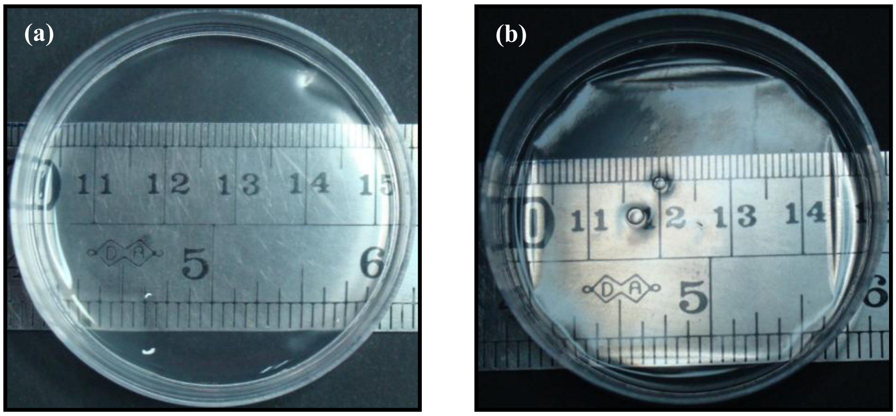

Fig. 1. Digital photographs of the thermoplastic starch films immersed in alkaline medium after 24 days: (a) native corn 80:20 (TPS-NC80:20) and (b) phosphatized corn 80:20 (TPS-PC80:20).

Results also suggest that the films developed in this study are more stable in an acidic medium. These observations may indicate that the sodium hydroxide could react with the hydroxyl groups of the starch molecules, destroying and thereby decreasing interactions of the hydrogen bond type and intra-and intermolecular interactions between starch macromolecules, facilitating swelling and gelatinization of starch. Furthermore, sodium ions may react with the carboxyl groups to form carboxylate groups, and this would increase the hydrophilicity and solubility of the starch. This could be the reason for the gradual disintegration and dissolution of the films in an alkaline medium.

3.2. Thickness

The film thickness is an important property because it affects barrier properties. For example, if the films are hydrophilic, the effect of film thickness on water vapor permeability is notorious. This effect is due to differences between the vapor pressures of water and humidity in the film-air interface.

Table 1 shows that the films thickness of the different samples studied; the films did not exhibit statistically significant differences ($p \leq 0.05$). However, there is a slight increase in the thickness of films based on phosphated corn starch 80:20. It is noteworthy that the same amount of mass was used for the preparation of the different systems. Therefore, this behavior could be attributed to modification by cross-linking of the starch. Pérez et al. reported a significant increase in the thickness of films of cross-linked starch from white *cush-cush* yam (0.26 ± 0.01 mm) with respect to films made from native starch of white *cush-cush* yam (0.13 ± 0.01 mm).

Table 1. Thickness, water vapor permeability (*WVP*) and water solubility (*SW*) of the films evaluated, of the films from corn starch 80:20 “waxy”:regular native (TPS-NC80:20) and phosphate (TPS-PC80:20).

Parameter	TPS-NC80:20	TPS-PC80:20
Thickness (mm)	0.15 ± 0.01^a	0.17 ± 0.03^a
WVP (x 10^{-11} g/ m·s·Pa)	1.9 ± 0.1^a	3 ± 1^a
Solubility (%)	31 ± 5^a	32 ± 3^a

Values in a column followed by the same letter are not significantly different (*$p \leq 0.05$*).

Cross-linking apparently strengthens internal bonds of the starch granule which, together with a greater interaction of the plasticizer (glycerol) at the time of starch gelatinization, affects the starch-starch interactions, which would increase the thickness. These results assume that the highest degree of substitution introduced inside the corn starch phosphate 80:20 has a favorable influence on the interaction glycerol and starch.

3.3. Water vapor permeability (WVP)

The water vapor permeability (WVP) is one of the most important properties studied in edible films, because one of the main functions of a food packaging is to prevent or reduce the transfer of moisture from the surrounding environment into the product. Its determination can predict the loss or gain of water by weight in food where films are applied. Moreover, the WVP is affected by numerous factors, including: film thickness, water activity, humidity, concentration of components used in the formulation of the films, among others.

Likewise, the coatings and/or edible films based on polysaccharides are characterized by being a good oxygen barrier, because of its ordered structure, formed by hydrogen bonds; however, such films have limited capacities as water vapor barrier due to their hydrophilic nature. However, one advantage of having poor water vapor barrier is that they allow movement of water through the film, thus preventing condensation of water, which is a potential source of microbial spoilage.

Based on this fact, it may indicate a trend of increasing WVP for TPS-PC80:20 with respect to TPS-NC80:20, with no significant differences ($p \leq 0.05$) (see Table 1).

Mali et al. determined the WVP of films based on yam starch, founding that it is influenced by the thickness, concentration of glycerol and starch concentration. Similarly, Mc Hugh et al. studied the effect of thickness on WVP of hydrophilic films; they reported that to greater thickness greater resistance to mass transfer and consequently the partial pressure of water in equilibrium, on the inner surface of the film, would be increased. Thus, hydrophilic films exhibit an increase in water vapor permeability with increased thickness. This is due to the changing conditions of the partial pressure of water vapor to which the inner part of the films is exposed.

This would explain the highest WVP for the TPS-PC80:20 with regard to the TPS-NC80:20, since as can be seen in Table 1, the latter tends to a smaller thickness compared to the TPS-PC80:20. It should be noted that this is not conclusive in this study, because differences in both figures were not statistically significant ($p \leq 0.05$).

3.4. Water solubility

The solubility of edible films indicates its integrity in an aqueous medium, i.e., a higher solubility represents a lower water resistance.

Table 1 shows the values obtained for the solubility in water at 25 °C of the systems studied. The results indicate that the water solubility of the starch based films corn "native" 80:20 was slightly lower compared to the calculated value for the film based on the cross-linked starch. These values have the same trend as those reported by Pérez et al., for edible films based on *cush-cush* yam starch.

As discussed, the film prepared from cross-linked starch (TPS-PC80:20) had higher hydrophilic characteristics. Therefore, it is suggested that an increase in the degree of substitution of starches makes increase in turn, the solubility of the films tested.

The values reported in this study were comparable with those found by other authors.

Sothornvit and Krochta indicate that the application of edible films with high solubility in water could be edible sweet wrappers as they can dissolve and melt easily in the mouth.

4. Conclusions

Edible biodegradable films were developed from corn starch 80:20 "waxy":regular "native" and modified. The influence of modification of starch by cross-linking on the stability in an acidic and an alkaline media, as well as thickness, water vapor permeability and water solubility of the films were investigated.

Both "native" and cross-linking systems were stable in acidic media, but the technique used for the modification of starch was more effective for the stability of the films in an alkaline media.

Water vapor permeability and water solubility results showed no significant differences between both systems, however, there was a trend of increasing them in the films containing modified starch, showing that these materials would be more hydrophilic.

Finally, taking into account the trend obtained, it can be conclude that both native and modified starches 80:20 "waxy":regular studied had qualities as thickeners for food products. Similarly, these starches may be employed in the formulation of biodegradable materials and packaging in the food industry.

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