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Evaluation of Some Properties of Starch and Starch Edible Films from Sub-Utilized Roots and Tubers from the Venezuelan Amazons

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Abstract
Biopolymers extracted from agricultural starchy commodities can be raw materials for edible, biologically degradable plastics. They have promising uses, having been proposed for replacing synthetic films. There are several starchy sources not yet quite exploited such as tropical roots and tubers that could be excellent starch sources to produce edible films with distinctive functional properties. The objective of this study was to formulate edible films from six tropical root and tubers starches. Starches were extracted and purified to 97-99% purity from *Ipomoea batatas*, and *Arracacia xanthorriza* roots, *Colocasia esculenta* and *Xanthosoma sagittifolium* corms and *Dioscorea trifida* tubers (white and purple) cultivated in the Venezuelan Amazons. The non-conventional starches were characterized for purity, amylose content and gelatinization profile by DSC, starch granular morphometry, and rheological properties. Film forming suspensions were formulated to produce the edible films using starch (2.5 and 5.00 g /100 g of solution) and glycerol (1.50 and 2.5 g/100 g of solution). Starch suspensions were gelatinized by heat, degassed, poured in plates and dried. In the films, the following studies were performed: Mechanical properties, thickness, and water vapor, oxygen and $C0_2$ permeability. Films were very good barriers to gases, had high water permeability and the botanical origin may affect the properties of the films. Non-conventional sources can be used for film preparation with barrier and mechanical characteristics that can be tailored for specific uses in the food industry. Next studies to conduct on films are Scanning Electron Microscopy, X-ray diffraction, and other supramolecular tests.

Keywords: Edible films, biopolymer, starch, non conventional starches, root and tuber starches

INTRODUCTION

Commercial starch extraction is carried out mainly in limited number of conventional sources (Ceballos et al., 2007), however tropical roots and tubers can be promising and unexploited sources of starch. Starches have a universal and long history of use in the food industry as raw materials to prepare different products due to their functional properties. On the other side, in the current search for alternatives to replace synthetic films, biopolymers extracted from agricultural starchy commodities have been considered as raw materials for edible, biologically degradable plastics, since it is a renewable source and abundant, inexpensive, widely available, relatively easy to handle and capable of forming a continuous matrix (Romero-Bastida et al., 2005; Famá et al., 2009). The edible film technology has been increasingly investigated for food coating since it acts as barriers to moisture and gases extending shelf life, minimizing sensory changes (texture, aroma, appearance), or improving handling characteristics of several foods. Films can be engineered as carriers of antimicrobials, antioxidants and other additives for development of innovative preservation food systems (Tapia et al., 2007). Tropical tubers like Dioscorea trifida tubers, corms like Colocasia esculenta and Xanthosoma sagittifolium, and root crops like

Arracacia xanthorrhiza Bancroft, and Ipomoea batatas, are staple food for indigenous peoples from the Caribbean coast and Amazon regions of Venezuela and have not been considered seriously as potential starch sources (Pérez et al., 2011). The objective of this study was to extract, purify and characterize starches extracted from six distinct tropical root, corms and tubers grown in the Venezuelan Amazons, to formulate edible films utilizing these non-conventional starches and study some of their mechanical and physicochemical characteristics.

EXPERIMENTAL

Starch extraction and characterization

Starches of cultivars grown in the Venezuelan Amazons of Ipomoea batatas and Arracacia xanthorriza roots, Colocasia esculenta and Xanthosoma sagittifolium corms, and Dioscorea trifida tubers (white and purple) were obtained from two different batches of each crop. The cleaned tubers/roots were peeled, and the edible portion sliced. Portions of the edible part were pounded for 2 min in a Waring blender with twice their volume of distilled water. The homogenate was passed through a 200 Mesh sieve. The grinding and screening operation was repeated four more times. The resulting slurry was centrifuged at 1500 rpm for 15 min. After removing the mucilaginous layer, the sediment was washed several times by suspending in distilled water and centrifuged until it appeared to be free of non starch material. The sediment then dried in a ventilated oven at 45 °C. Starches were blended, passed through a 60Mesh sieve and stored at room temperature in sealed plastic bags inside hermetic glass containers until subsequent analysis (Pérez et al., 2011).

Proximate composition and % purity of starches

The proximate composition was (moisture, crude protein content (N x 6.25), fatty material and ash) was analyzed as a percentage (w/w) using the procedure described in AACC (2003). The degree of purity was calculated using the following equation:

% Purity= 100- (% moisture content +% crude protein +% fatty materials + % ash) (Pérez, et al., 2011)

Onset Temperature and Gelatinization Enthalpy Change Determination

DSC analyses were performed on a Perkin-Elmer DSC 7 device (Perkin-Elmer, Norwalk, CT, USA) using stainless steel sealed pans. The gelatinization enthalpy variation (ΔH) and the onset gelatinization temperature (GT) of each sample were determined on the 55-90 °C range of the linear baseline (Pérez, et al., 2011).

Rheological (Functional) Properties of Starch

Clarity, starch pasting properties, and DSC-amylose determination were analyzed following the methods of Sanchez et al., 2010; Pérez, et al., 2011, and Amani et al., 2004, respectively.

Starch granular morphometry and optical microscopy

The determination of starch granule sizes were performed at room temperature using a Micrometrics International Co. Saturn Digisizer 5200 V1-08. Granular shape and Maltese crosses were observed by optical microscopy using a polarized light filter, and examined and photographed on a Nikon Optiphot-2 microscope. Starch granule diameter range was estimated by measuring 20-30 randomly selected granules from microphotographs in duplicate (Pérez et al., 2011).

Film formation

Film forming solutions were prepared in distilled water with 5% (w/v) Colocasia esculenta, or Xanthosoma sagittifolium or Arracacia xanthorriza starch and 2.5% (w/v) of glycerol, or 2.5% of Dioscorea trifida white, or Dioscorea trifida purple, or Ipomoea batatas starch, and 1.5% (w/v) of glycerol. Each was initially homogenized with an Ultra Turrax T25 (IKA ®WERKE), placed in a water bath at 95°C, and maintained at 95°C for 30 min with gentle magnetic stirring to gelatinize starch. After gelatinization, each gel suspension was degassed for 15

m with a vacuum mechanical pump. Aliquots of 60 mL of each film forming solution still hot and fluid were poured onto 14 cm diameter plastic petri dishes and dried in stove at 50°C during 24 h.

Water vapor permeability (WVP) Oxygen and carbon dioxide permeability measurement of starch-based films

WVP of films was determined gravimetrically at 25 °C using a modified version of the ASTM standard method E96-93 as described by Tapia et al., (2007). Water vapor transmission rates (WVTR) through the films under investigation and WVP were obtained. Oxygen and carbon dioxide permeability measurements were carried out according to the isostatic method as described by Gontard et al., (1996).

Mechanical properties

Tensile strength (TS) were determined with a texturometer Stable Micro Systems modelo TA-XT2i (Stable Micro Systems, Haslemere, Surrey, UK), (5kg) with Mini Tensile Grips. Initial grip separation and cross-head speed were set at 7,5mm and 2mm/s respectively. Strips of film samples (7,5cm x 2,5cm) were analyzed. TS was calculated by dividing the maximum load by the initial cross-sectional area of the sample and expressed in N.

RESULTS AND DISCUSSION

Results of the characterization of starch obtained from each of the six crops studied are shown in TABLES 1 to 4 and in FIGURE1, while results for starch-based edible films are shown in TABLES 5-6 and FIGURE 2.

FIGURE 1. Polarized optical light microscopy (100x) micrograph of starch isolated from *Dioscorea trifida* and *Ipomoea batatas* crops grown in the Venezuelan Amazons showing granular shape and Maltese crosses.

TABLE 1. Moisture contents of the edible portions and % purity (percent dry basis, except moisture) of starch from six varieties of roots, worms and tubers grown in the Venezuelan Amazon

Analysis	*Ipomoea batatas*	*Arracacia xanthorriza*	*Colocasia esculenta*	*Xanthosoma sagittifolium*	*Dioscorea trifida*	
					White	Purple
Moisture (%)	10.74±0.12	11.59±0.20	11.39±0.38	10.82±0.08	10.83±0.00	11.57±0.00
Crude protein (%)	ND	ND	ND	ND	0.09±0.001	0.09±0.001
Fatty material (%)	ND	ND	ND	ND	0.10±0.04	0.07±0.001
Ash (%)	0.50±0.09	0.56±0.05	0.24±0.04	0.09±0.02	0.03±0.00	0.005±0.00
*Purity (%)	99.5	99.4	99.8	99.9	99.8	99.8

Results are means of three determinations. Means with different letters in the same column within the same varieties differs significantly ($p < 0.05$). ND. It was not detected by the method used.*100 (%Crude protein+ %Fatty material+%Ash).

TABLE 2. Amylose content and gelatinization profile by DSC of starch from six varieties of roots, worms and tubers from the Venezuelan Amazon

Parameter	*Ipomoea batatas*	*Arracacia xanthorriza*	*Colocasia esculenta*	*Xanthosoma sagittifolium*	*Dioscorea trifida*	
					White	*Purple*
DSC-Amylose (%)	20.38±0.28	18.52±1.08	12.69±0.08	26.17±0.34	1.44±0.34	3.78±0.34
Amylopectin (%)	79.2±0.28	81.48±1.08	87.31±0.08	73.83±0.34	98.56±0.34	96.22±0.34
A/Ap relation	0.26	0.23	0.15	0.35	0.02	0.04

TABLE 3. Rheological properties by Rapid-visco analysis (RVA) results of starch from six varieties of roots, worms and tubers from the Venezuelan Amazon

Crop	*Initial gelatinization (°C)*	*Maximun Viscosity (PV)*	*Breakdown (BD)*	*Setback (SB)*	*Consistency (CS)*	*Cooking ability (CA)*
Ipomoea batatas	76.9±0.2	2007±9	555±20	-183±18	372±1	1±0
Arracacia xanthorriza	60.5±0.1	2378±56	978±21	-737±35	241±55	4±0

Colocasia esculenta	80.1±0.4	1252±1	235±28	-163±21	398±8	1±0
Xanthosoma sagittifolium	78.4±0.0	1449±32	591±9	-344±30	247±21	1±0
Dioscorea trifida "white"	75.7±0.1	4102±121	2474±59	-2375±76	99±18	1±0
Dioscorea trifida "purple"	75.1±0.6	3983±75	2376±27	-2342±28	34±1	1±0

TABLE 4. Pasting temperature range and gelatinization enthalpy obtained by Differential scanning calorimetry (DSC) of starch from six varieties of roots, worms and tubers from the Venezuelan Amazon.

Crop		Pasting Temperature Range (°C)	ΔH Gelatinization
Ipomoea batatas		69.5-74.4	15.01±0.60
Arracacia xanthorriza		48.7-53.7	14.28±1.04
Colocasia esculenta		75.5-80.0	19.01±1.44
Xanthosoma sagittifolium		67.1-74.9	15.21±1.03
Dioscorea trifida	White	71.4-76.3	22.20±0.03
	Purple	69.1-73.7	2219±1.64

TABLE 5. Oxygen and carbon dioxide permeability (amol/m s Pa) of six starch-based edible films (starch extracted from six varieties of roots, worms and tubers from the Venezuelan Amazon.

Edible film from starch extracted from roots, worms and tubers (% starch and % glycerol in the formultion)	O_2 permeability (amol/m s Pa)	CO_2 permeability (amol/m s Pa)
Ipomoea batatas (2.5% starch, 1.5% glycerol)	18,06±0.08	----
Colocasia esculenta (5% starch, 2.5% glycerol)	85,12±0.09	----
Xanthosoma sagittifolium (5% starch, 2.5% glycerol)	14.03±0.07	----
Arracacia xanthorriza (5% starch, 2.5% glycerol)	9.72±0.15	11.14±0.27
Dioscorea trifida "White" (2.5% starch, 1.5% glycerol)	4.05±0.06	11.66±0.17
Dioscorea trifida "purple" (2.5% starch, 1.5% glycerol)	3.82±0.03	6.44±0.32

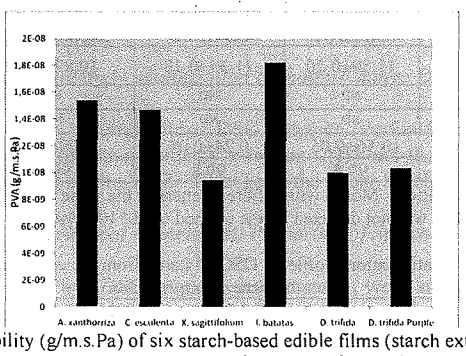

FIGURE 2. Water vapor permeability (g/m.s.Pa) of six starch-based edible films (starch extracted from six varieties of roots, worms and tubers from the Venezuelan Amazon. (1. *Ipomoea batatas* (2.5% starch), 2. *Colocasia esculenta* (5% starch) 3. *Xanthosoma sagittifolium* (5% starch), 4. *Arracacia xanthorriza* (5% starch), 5. *Dioscorea trifida* white (2.5% starch), 6. *Dioscorea trifida* purple (2.5% starch)

TABLE 6: Tensile strength (N) of six starch-based edible films (starch extracted from six varieties of roots, worms and tubers from the Venezuelan Amazon

Arracacia xanthorriza	*Colocasia esculenta*	*Xanthosoma sagittifolium*	*Ipomoea batatas*	*Dioscorea trifida white*	*Dioscorea trifida purple*
9,348	4,556	9,808	11,6875	14,775	12,72

Alternative sources for obtaining starch with better physicochemical and functional characteristics are continuously sought for the food industry. Starch has also caught attention for an area that exhibits an extraordinary potential for multiple applications in food preservation and food packaging: the edible

films/coatings field. A good part of the literature published on edible films and coatings contain a polysaccharide base, and starch is being increasingly considered for films due to its biodegradable nature, availability and cost. Amylose and amylopectin content and their physical organization into the starch granule are responsible for the functionality of starch. Amylose is responsible for the film-forming capacity of starches. Addition of plasticizers such as glycerol, however, are used to modify functional, sensory, nutritional and mechanical properties of edible films (Romero-Bastidas et al., 2005).

In this work, starches extracted and purified from six Venezuelan-grown root and tubers crops showed a high purity varying from 99.4 to 99.9% (TABLE 1). They exhibited different functional properties, and amylose contents (TABLE 2). *Xanthosoma sagittifolium* had the highest amylose content (26.17±0.34%), followed by *Ipomoea batatas* (20.38±0.28), *Arracacia xanthorriza* 18.52±1.08, *Colocasia esculenta* (12.69±0.08) and finally, *Dioscorea trifida*, almost amylose-free (1.44±0.34/3.78±0.34), representing a new promising waxy yam starch (Pérez et al., 2010). It was demonstrated however, that all of the six starches could be used as matrix for edible films adding glycerol as plasticizer. A thermal analysis of the native starches showed that *Colocasia esculenta* had the highest gelatinization temperature and *Arracacia xanthorriza* the lowest one. This parameter is important in the gelatinization process for film preparation. The granular size have varied from 2 to 12.5 μm for *Xanthosoma sagittifolium* ; 4.8 to 26.1 μm for *Ipomoea batatas* ; 4 to 35 μm for *Arracacia xanthorriza* ; 16 to 36 μm for the two *Dioscorea trifida* varieties, and 0.5 to 221 μm for *Colocasia esculenta*, showing a variable granular structure such as, shells, rounded, egg-truncated, and bells.

As expected, all six films exhibited high WVP due to the hydrophilic character of the starch molecule, even higher than values reported for cassava and waxy maize starch-based films: 4.5 ± 0.6 and 3.8 ± 0.3 $gm^{-1}\ s^{-1}\ P^{-1}\ x10^{-10}$ respectively by García et al., (2009) and for banana, okenia, and mango starch-based films reported by Romero et al., (2005) that ranged between 20-25 $gm^{-1}\ s^{-1}\ P^{-1}\ x10^{-11}$. Both, the waxy *Dioscorea* and *Xanthomonas* exhibited the lower WVP of the six starches: 9.9 ± 0.4 and 9.45 ± 0.3 $gm^{-1}\ s^{-1}\ P^{-1}\ x10^{-9}$. This is considered one of the major drawbacks encountered for the applications of starch-based edible films. However, this property could be modified by adding lipids to the formulation (Tapia et al., 2007).

Also as expected, the six films were good barriers to O_2 and CO_2. TABLE 5 shows values in the permeability of films to oxygen and carbon dioxide. Only the films made from *Arracacia xanthorriza* starch (5%) and the white and purple waxy starch from *Dioscorea trifida* (2.5%) had some detected but low, permeability to CO_2.

The tensile strength (TS) of the films prepared from diverse starch sources (TABLE 6) is comparable to those reported in the literature for starch films, but differences attributable to botanical origin should be studied in more depth since thickness values exhibited no statistical significant differences among the six types of films.

More studies are needed to correlate the amylose content to X-ray diffraction patterns of starch films and to other properties of the films, as well as the differences imparted by the starch source, and to perform Scanning Electron Microscopy on films.

CONCLUSIONS

It is feasible to use non-conventional starches with high purity, granular structure, and appropriated rheological properties for the elaboration of edible films with physicochemical, mechanical and barrier properties that can be adequate for certain type of foods, and can also be engineered to improve them. As expected, the potential for these types of films are more in the area of decreasing gas exchange rather than retardation of water loss due to their hydrophilic nature.

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