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Some properties of starch and starch edible films from under-utilized roots and tubers from the Venezuelan Amazons

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Abstract

Biopolymers 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 starchy crops. Starches were extracted and purified to 97–99% purity from *Ipomoea batatas*, *Arracacia xanthorriza* roots, *Colocasia esculenta*, *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 differential scanning calorimetry, starch granular morphometry and rheological properties. Starch-based films were processed by casting solutions prepared with each starch, glycerol, and distilled water. Starch suspensions were gelatinized by heat, degassed, poured in plates and dried. In the films, studies performed were water vapor, oxygen and carbon dioxide permeability, and mechanical properties in terms of tensile strength. Crystallinity patterns of native starches and films were also obtained. *Ipomoea batatas* and *Colocasia esculenta* exhibited

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polymorphism A+B type X-ray pattern, *Xanthosoma sagittifolium*, an A-type X-ray pattern, and *Arracacia xanthorriza* and both *Diosocrea trifida,* B-type patterns; while starch-based films had all a B-type X-ray pattern. 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. Films from these non-conventional starch sources with barrier and mechanical characteristics tailored for specific uses can be of interest as plastics for the food industry and results may be of significance also, for starch-based foams.

Keywords
edible films, biopolymer, starch, non conventional starches, root and tuber starches

Introduction

Commercial starch extraction is carried out in limited number of conventional sources;[1] however, tropical roots and tubers can represent unexploited sources of starch with interesting characteristics in terms of functional properties and potential uses as starch-based plastics. 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 from agricultural starchy commodities have been considered as resources for edible, biologically degradable plastics, since they are renewable, abundant, inexpensive, widely available, relatively easy to handle and capable of forming thermoplastic materials.[2,3] The edible film technology has been increasingly investigated for food coating since they act 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.[4] A good part of the literature published on edible films and coatings reports starch as the polysaccharide base and starch is being increasingly considered for films due to its biodegradability, availability and cost. Tropical starchy crops like *Dioscorea trifida, Colocasia esculenta*, *Xanthosoma sagittifolium*, *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.[5] The objective of this study was to extract, purify and characterize starches extracted from these six distinct tropical roots, corms and tubers grown in the Venezuelan Amazons, to formulate starch-based edible films, and study some of their main characteristics. Starch has also been considered as a matrix for foaming[6] using native and modified potato starch,[7,8] potato, tapioca, pea, maize, wheat, and rice starch,[9–11] and the information obtained in the present work may be of interest for this technological application.

Material and methods

Materials

Native starch extracted and purified from cultivars of *Ipomoea*, *Arracacia xanthorriza* roots, *Colocasia esculenta, Xanthosoma sagittifolium* corms and *Dioscorea trifida* tubers (white and purple) grown in the Venezuelan Amazons were used. Glycerol from Prolabo, Sweden, was employed as plasticizer in film formation (1.5 or 2.5 g/100 g of starch suspensions).

Starch extraction and characterization

Native starch was extracted 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 homogenates were passed through a 200-mesh sieve. The grinding and screening operations were repeated four more times. The resulting slurries were centrifuged at 1500 rpm for 15 min. After removing the mucilaginous layer, the sediments were washed several times by suspending in distilled water and centrifuged until appearing to be free of non starch material. The sediments were dried in a ventilated oven at 45°C. Each type of starch was passed through a 60-mesh sieve and stored at room temperature in sealed plastic bags inside hermetic glass containers until subsequent analysis.[5]

Proximate composition and % purity of starches

The proximate composition of each root/tuber starch (moisture, crude protein content (N × 6.25), fatty material and ash) was obtained as a percentage (w/w), using the procedures described in AACC.[12] The degree of purity was calculated from the difference between 100 and the percentage of moisture, crude protein, fatty material, and ash content using the following equation:[12]

$$\%\ \text{Purity} = 100 - (\%\ \text{moisture content} + \%\ \text{crude protein} + \%\ \text{fatty materials} + \%\ \text{ash})$$

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.[5] Granular shape and Maltese crosses were observed by optical microscopy using a polarized light filter. Starch was sprinkled onto a glass slide, 1 to 2 drops of distilled water were added and mixed with starch, 2 to 3 drops of Lugol solution were added, and the sample was left for 5 min. The slide was then covered with a slip cover glass, left for 2 more minutes, and then examined and photographed on a Nikon Optiphot-2microscope. Starch granule diameter range was estimated by measuring 20–30 randomly selected granules from microphotographs in duplicate.

Physicochemical properties of starch

Onset temperature and gelatinization enthalpy change determination. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC 7 device (Perkin-Elmer, Norwalk, CT, USA) using stainless steel sealed pans. The sample pan (10–11 mg of starch and 50 µL of lyso-phospholipid 2% w/v in water) and the empty reference pan were heated from 25°C to 160°C at a scanning rate of 10° C/min, held for 2 min at 160°C and cooled to 60 at 10°C/min. The gelatinization enthalpy variation (ΔH) and the onset gelatinization temperature (GT) of each sample were determined on each thermogram within the 55–90°C range of the linear baseline. The analysis was performed in duplicate, and mean values were calculated.[5]

DSC amylose determination. Amylose content was measured from the energy of amylose/lyso-phospholipid complex formation using DSC from the cooling stage of the thermograms previously used for the onset temperature determination. The analysis was performed in duplicate, and the mean values were calculated.[13,14]

Functional properties of starch

Rheological starch properties. Hot starch dispersion viscosity profiles were obtained with a Rapid Visco Analyser–Series 4. (RVA-4), (Newport Scientific, Australia).[1,13–15] Starch (1.25 g db) was dispersed in distilled water (about 23 cm^3) to 5% suspension. Viscosity was recorded using the temperature profile: holding at 50°C for 1 min, heating from 50°C to 90°C at 6°C/min, holding at 90°C for 5 min, and then cooling down to 50 at 6°C/min. The gel was then maintained for 2 min at 50°C with continuous stirring at 160 rpm. Four parameters were measured: pasting temperature (PT), peak viscosity (PV), hot paste viscosity at the end of the plateau at 90°C (HPV) and the cool paste viscosity (CPV) at 50°C. Three additional parameters were calculated: breakdown (BD) estimated as PV-HPV, setback (SB) estimated as CPV-PV, and consistency (CS), estimated as CPV–HPV.[16]

Film processing

For production of films, starch was processed by casting solutions prepared with 5% (w/v) *C. esculenta or X. sagittifolium* or *A. xanthorriza* starch and 2.5% (w/v) of glycerol, or 2.5% of *D. trifida* white, or *D. trifida* purple, or *I. batatas* starch, and 1.5% (w/v) of glycerol and distilled water. The film formulations used in this study were determined by preliminary studies performed in the lab, assaying various concentrations of each starch and glycerol, and examining for non-friable films obtained after casting and drying – that peeled off from the plates without tearing – as well as for homogeneous appearance under the microscope and apparent integrity that allowed the determination of some physical properties. Film forming solutions were prepared in distilled water. 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 min with a vacuum mechanical pump. Aliquots of 60 cm^3 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. Films were peeled off the plates, stored at 25°C ± 2°C and conditioned under saturated NaBr (at 25°C and 57% relative humidity) in a closed chamber until used for analysis. Moisture content of the conditioned films was determined by AACC.[12] Water activity (a_w) of films was also determined using an Aqualab CX-3 water activity meter (Decagon Devices Inc., Pullman, WA, USA).

X-ray diffractometry

X-ray diffraction was performed on native starches obtained from the six crops investigated, as described by Pérez et al.,[5] and on the films formulated. Each starch was conditioned at an a_w of 0.90 and each film at an a_w of 0.57. The samples (20 mg) were sealed between two tape foils to prevent any significant change in water content during the measurement. The diffraction diagrams were recorded using a BRUKER (Karlsruhe, Germany) D8 Discover spectrometer. The X-ray radiation Cu $K\alpha_1$ (λCu $K\alpha_1 = 1.5405$ Å), produced in a sealed tube at 40 kV and 40 Ma was selected and parallelized using a double Gobël mirror parallel optics system, and collimated to produce a 500 µm beam diameter. Diffraction diagrams were collected with a two-dimensional GADDS detector, and recording time was set to 600 s. The distance from the sample to the detector was 100 mm and with an angle of 25° (2θ). Relative crystallinity was determined after normalization of all recorded diagrams at the same integrated scattering between 2θ values of 3° and 30°. A- and B-type recrystallized amyloses were used as crystalline standards after scaled subtraction of an experimental amorphous curve, in order to obtain null intensity in the regions without diffraction peaks. Dry extruded potato starch was used as the amorphous standard. The degree of crystallinity of the structures was determined using the method initially developed for cellulose.[17] The percentage of crystallinity was taken as the slope of the line $(I_{sample} - I_{amor})\ 2\theta = f(I_{crys} - I_{amor})\ 2\theta$, where I_{sample}, I_{amor} and I_{crys} are the diffracted intensities of the sample, the amorphous and the crystalline standards, respectively.

Oxygen and carbon dioxide permeability measurement of starch-based films

Oxygen and carbon dioxide permeability measurements were carried out according to the isostatic method as described by Gontard et al.[18] The permeation cell (arranged in a climatic chamber) consisted of two stainless steel chambers separated by a film sample and placed in a thermostatic chamber. The pure oxygen was injected continually into one chamber, and pure carbon dioxide gas into the other. Pressures in the chambers were equalized and maintained at atmospheric pressure. At steady state (constant oxygen and carbon dioxide concentration), the permeate gas that

passed through the film was deducted with a syringe and measured using a gas analyzer GC 800 (CE instrument, Italy) for oxygen and GC 1000 (Dani, Italy) for carbon dioxide. Flow rates were measured with an intelligent flowmeter ADM 1000 (J&W, USA). Oxygen or carbon dioxide permeability (P) was calculated as follows:

$$P = \frac{J(\Delta x)}{A(\Delta p)}$$

With P in amol/msPa (amol is 10^{-18} mol), J is the flow of oxygen or carbon dioxide though the film (in amol/s), Δx is the film thickness (m), Δp is the differential partial pressure across the film (Pa), and A is the surface area of the film (m^2). Three replicates of each film were tested.

Water vapor permeability of films

Water vapor permeability (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.[4] Water vapor transmission rates (WVTR) through the films under investigation and WVP were obtained. Two circular specimens were cut from each film after conditioning and were mounted over methylmethacrylate test cups (with an internal diameter of 3 cm, an outer diameter of 4.5 cm and a depth of 2.0 cm) and sealed using a cap with a rubber O-ring, leaving a known area of the film exposed. Diameters of the specimens were slightly larger than the diameter of the cups. The cups were filled with 5 cm^3 of distilled water, leaving a 1 cm air gap between the film's underside and the water surface. Cups were placed in airtight desiccators containing saturated $MgCl_2.6H_2O$ solutions at the bottom; RH was kept at 33.3% at 25°C. Cup weights were recorded at 30-min intervals over 24 h. The water vapor transfer through the films (m_1, slope of the curve of weight loss compared with time in grams per second) was estimated by regression analysis. WVTR through the films under investigation and WVP were obtained as described by Kaya and Kaya[19] and Chinnan and Park.[20]

$$\mathrm{WVTR} = \frac{m}{A}$$

$$\mathrm{WVP} = \frac{\mathrm{WVPR}\, x\, L}{pi - pa} \quad 10^{-10}\mathrm{g/(m \cdot s \cdot Pa)}$$

Where, m is the constant of linear regression from the values of mass loss against time during a constant period, A is the exposed film area, L is the average (m) thickness of the film and pi–pa is real vapor partial pressure (saturated air and air with 33% RH, respectively, at 25°C) difference (Pa) across the film.

Mechanical properties of films

A texturometer Stable Micro Systems model TA-XT2i (Stable Micro Systems, Haslemere, Surrey, UK) (5 kg), and a tension grip system (mini tensile grips) was

used for determination of tensile strength (TS) and percent elongation (PE) at break that were calculated as outlined in ASTM D882.[21] Initial grip separation and cross-head speed were set at 7.5 mm and 2 mm/s, respectively. The dimensions of the samples were 75 mm length × 25 mm width × 0.28 ± 0.04 mm thick. At least 10 samples of each film type were analyzed. TS was calculated by dividing the maximum load by the initial cross-sectional area of the sample and expressed in megapascals. Percent elongation at break was expressed as percentage of change of the original length of a specimen between grips at break.

Results and discussion

Native starch

Starch characterization. Results of the characterization of starch obtained from each of the six crops studied are shown in Tables 1 to 4 and in Figure 1. Starches were efficiently extracted and purified from the six Venezuelan crops, showing a high degree of purity, varying from 99.4% to 99.9% (Table 1). These are important aspects when considering commercial production of starch from plants. As an example from a conventional starch root resource, cassava represents one of the most important sources of starch because of its ease of extraction and the high purity of its starch, with less protein and other associated compounds.[2]

Starch granule characterization

Figure 1 presents a polarized optical light microscopy (100 ×) micrograph of starch isolated from *I. batatas*, *A. xanthorriza*, *C. esculenta*, *X. sagittifolium* and *D. trifida* grown in the Venezuelan Amazons. The microphotographs show the granular shape and typical Maltese crosses of the starches. The granular size varied from 2 to 12.5 μm for *X. sagittifolium*, 4.8 to 26.1 μm for *I. batatas*, 4 to 35 μm for *A. xanthorriza*, 16 to 36 μm for the two *D. trifida* (white and purple), and 0.5 to 22 μm for *C. esculenta,* showing a variable granular structure such as, shells, rounded, egg-truncated, and bells. In the native starch granules, amylose and the branching points of amylopectin are considered to be amorphous, but the linear branches of amylopectin and some amylose, combine in crystalline double helixes that arrange in parallel, forming a crystalline structure.[22–24] Due to the orderly arrangement of the crystalline areas, starch granules shown birefringence, with an interference patron of the Maltese cross under polarized light.[25]

Amylose content and crystallinity pattern of starch

Table 2 present the amylose content, the crystallinity pattern, and percentage crystallinity of starches from the six different sources studied. *X. sagittifolium* had the highest amylose content (26.2 ± 0.34%), followed by *I. batatas*, *A. xanthorriza*, *C. esculenta*, while both, white and purple *D. trifida*, were almost amylose-free

Table 1. Compositional characteristics and purity of starch from six varieties of roots, corms and tubers grown in the Venezuelan Amazon

Analysis	*Ipomoea batatas*	*Arracacia xanthorriza*	*Colocasia esculenta*	*Xanthosoma sagittifolium*	*Dioscorea trifida*	
					White	Purple
Moisture (%)*	10.7 ± 0.12^{a}	11.6 ± 0.20^{b}	11.4 ± 0.38^{b}	10.8 ± 0.08^{a}	10.8 ± 0.00^{a}	11.6 ± 0.00^{b}
Crude protein (%)**	ND	ND	ND	ND	0.09 ± 0.001^{a}	0.09 ± 0.001^{a}
Fatty material (%)	ND	ND	ND	ND	0.10 ± 0.04^{a}	0.07 ± 0.00^{b}
Ash (%)**	0.50 ± 0.09^{d}	0.56 ± 0.05^{d}	0.24 ± 0.04^{c}	0.09 ± 0.02^{b}	0.03 ± 0.00^{b}	0.005 ± 0.00^{a}
Purity (%)***	99.5^{a}	99.4^{a}	99.8^{a}	99.9^{a}	99.8^{a}	99.8^{a}

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.
*wet basis; **dry basis; ***100 = (% Crude protein + % Fatty material + % Ash).

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

Parameter	*Ipomoea batatas*	*Arracacia xanthorriza*	*Colocasia esculenta*	*Xanthosoma sagittifolium*	*Dioscorea trifida*	
					Purple	White
DSC-Amylose (%)	20.4 ± 0.28	18.5 ± 1.08	12.7 ± 0.08	26.2 ± 0.34	1.4 ± 0.34	3.8 ± 0.34
Amylopectin (%)	79.2 ± 0.28	81.5 ± 1.08	87.3 ± 0.08	73.8 ± 0.34	98.6 ± 0.34	96.2 ± 0.34
A/Ap relation	0.26	0.23	0.15	0.35	0.02	0.04
Crystallinity pattern	Polymorphism A+B	B	Polymorphism A+B	A	B	B
Crystallinity (%)	30	40	35	43	40	40

A: Amylose; Ap: amylopectin; A/Ap relation: Amylose/Amylopectin ratio.

(1.44 ± 0.34 and 3.8 ± 0.34, respectively), being reported as a new promising waxy yam starch.[5] As for the diffraction patterns of the native starches, *I. batatas* and *C. esculenta* exhibited a polymorphism A + B, *X. sagittifolium,* a A type crystallinity, and *A. xanthorriza,* and both *D. trifida*, a B type crystallinity. According to Garcia et al.,[26] since amylopectin accounts for the crystalline regions in the native starch granules, a higher crystallinity should be expected for starches containing more amylopectin. Table 2 shows that starch from the purple and white *D. trifida* (3.8 and 1.4% amylose), along with *A. xanthorriza* (18.5% amylose), present high degrees of crystallinity (40%). However, the crystallinity value for the *X. sagittifolium*, showing the highest amylose amount (26.2%), is the highest (43%) and, on the opposite, the crystallinity value for the *C. esculenta*, exhibiting relatively low amylose content (12.7%), is moderate (35%). Among the starches exhibiting a polymorphism A+B, i.e. *I. batatas* and *C. esculenta,* the crystallinity increased when the amylose content decrease and in the case of pure B type starches

Table 3. Pasting temperature range and gelatinization enthalpy obtained by differential scanning calorimetry of starch from six varieties of roots, corms and tubers from the Venezuelan Amazon

Crop		Pasting temperature range (°C)	ΔH Gelatinization (J/g)
Ipomoea batatas		69.5–74.4	15.0 ± 0.60
Arracacia xanthorriza		48.7–53.7	14.3 ± 1.04
Colocasia esculenta		75.5–80.0	19.0 ± 1.44
Xanthosoma sagittifolium		67.1–74.9	15.22 ± 1.03
Dioscorea trifida	'White'	71.4–76.3	22.2 ± 0.03
	Dioscorea trifida 'Purple'	69.1–73.7	22.19 ± 1.64

Table 4. Rheological properties (Pas) and initial gelatinization temperature (°C) of starch from six varieties of roots, corms and tubers from the Venezuelan Amazon

Crop	Initial gelatinization temperature	Maximun viscosity (PV)	Breakdown (BD)	Setback (SB)	Consistency (CS)
Ipomoea batatas	76.9 ± 0.2	2.01 ± .09	0.56 ± 0.2	−0.18 ± 0.2	0.37 ± 0.1
Arracacia xanthorriza	60.5 ± 0.1	2.38 ± 0.6	0.98 ± 0.2	−0.74 ± 0.4	0.24 ± 0.6
Colocasia esculenta	80.1 ± 0.4	1.25 ± 0.1	0.24 ± 0.3	−0.16 ± 0.2	0.40 ± 0.8
Xanthosoma sagittifolium	78.4 ± 0.0	1.45 ± 0.3	0.59 ± 0.9	−0.34 ± 0.3	0.25 ± 0.2
Dioscorea trifida 'White'	75.7 ± 0.1	4.10 ± 0.1	2.45 ± 0.6	0.24 ± 0.8	0.01 ± 0.2
Dioscorea trifida 'Purple'	75.1 ± 0.6	3.98 ± 0.8	2.38 ± 0.3	2.34 ± 0.3	0.03 ± 0.1

(*A. xanthorriza* and *D. trifida)*, the crystallinity remained stable whatever the amylose content. These results are in line with the data reported in literature for maize[27,28] and cassava starches[28] and with the results reported for waxy potato starches (pure B type) which exhibits the same crystallinity as normal ones.[28]

It has been postulated[29] that different conformations of amylose and amylopectin are present at the crystalline or amorphous state. Then, differences in the potential correlation of the amylose content and crystalline degree may be produced by other factors such as the chain longitude or the branch numbers, among others.

Pasting temperatures and gelatinization enthalpy change determination

Table 3 presents the results of the thermal analysis of the native starches studied. The starch gelatinization profiles measured by DSC showed a pasting temperature range between 48.7–53.7°C and 75.5–80.0°C, with *C. esculenta* exhibiting the highest gelatinization temperature and *A. xanthorriza* the lowest one. This parameter is important

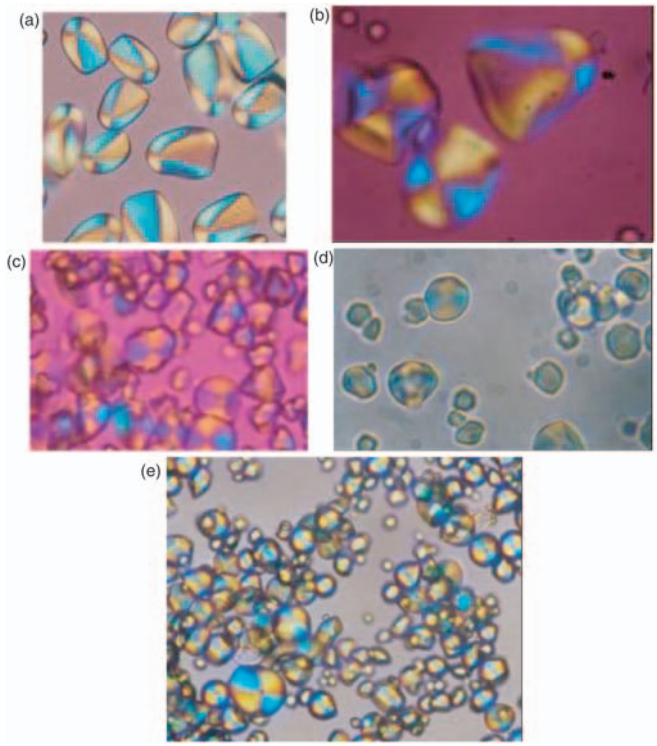

Figure 1. Polarized optical light microscopy (100×) micrograph of starch isolated from (a) *Dioscorea trifida*, (b) *Ipomoea batatas*, (c) *Arracacia xanthorriza*, (d) *Colocasia esculenta* and (e) *Xanthosoma sagittifolium* crops grown in the Venezuelan Amazons showing granular shape and Maltese crosses.

since the gelatinization temperature is an inflection point in the process of conversion of the molecular structure of starch, to 'thermoplastic'starch in film preparation.

Amani et al.[13] studied the pasting behavior of a 4% starch suspension of different yam varieties from the Ivory Coast. They measured the highest pasting temperature at 87°C on *D. dumetorum* starch and the lowest pasting temperature on *D. esculenta* starch (78.7°C), whereas starches from *D. alata* and from *D. cayenensis-rotundata* complex exhibited an intermediate pasting temperature (around 83°C). In this study, the pasting temperatures of starches from *D. trifida*, white and purple varied from 71.4 to 76.3 and 69.1 to 73.7, respectively. Considering the characterization of various West African yams, a large onset variation has been observed in the range 69.9–76.5°C, whereas some other authors have reported variations between 69.0 and 78.8°C.[30] The gelatinization enthalpy variation (ΔH) was in the 14.3–22.2 J/g range, with the highest enthalpy change for both *D. trifida,* white and purple starch genotype (Table 3). A gelatinization enthalpy variation (ΔH) in the range of 22.4–25.3 J/g has been the highest values reported in the literature for

Dioscorea species.[5] With the same method, a great diversity of yam starch from Ivory Coast was screened earlier, and the authors reported variation from 13.7 to 20.3 J/g.[13] The gelatinization characteristics of starch depend on the molecular structure of amylopectin, starch composition, and granular architecture. It has been postulated[31] that DSC parameters are influenced by the proportion of crystalline region and the type of crystallinity which are linked to the distribution of amylopectin short chains and to the amylose:amylopectin ratio.[32] The gelatinization temperature and gelatinization enthalpy variations are of the most important parameters to be determined in order to set up the cooking process of starch, because they are the index of the energy necessary to complete the process of gelatinization. Moreover, the starch crystallinity raises the gelatinization temperature and the endothermic enthalpy. Enthalpy of gelatinization reflects the loss of molecular order; therefore starch with high crystalline structure requires higher energy for gelatinization. As can be seen in Table 3, both D. trifida, which have the highest amylopectin contents, a pure B type X-ray pattern and a high crystallinity, showed the highest ΔH gelatinization values. ΔH were generally higher for low amylose starches among starches exhibiting the same polymorphic type (Table 3) in line with results already reported for maize[28,33] and cassava.[28] Crystallinity and DSC results suggest that *D. trifida* have a more organized structure than the other four starches. All these parameters affect the type of plastic films that can be obtained from specific starch sources.

Rheological starch properties

Table 4 presents some rheological properties by rapid-visco analysis (RVA) results of starch from the six varieties studied. The overall values are different from each other, with the maximum viscosities developed at 5% suspension by the *D. trifida* starches (white and purple), presenting values of 4.10 ± 0.12 and 3.98 ± 0.75 Pas, respectively. However, the viscosities developed by the other starches from the Venezuelan Amazon investigated are also high, or in the case of *C. esculenta* starch, analogous to potato starch, when comparing with viscosities values reported for normal and waxy potato starch (2.55 and 2.44 Pas), maize and waxy maize (0.18 and 0.97 Pas), rice (0.34 and 0.50 Pas), and cassava starches (0.95 and 1.12 Pas).[5] Similarly to potato starch, these starches exhibit high viscosities with high pasting temperatures. The starches from the six crops have these viscosity peaks, and also exhibit high breakdown during the holding stage at 90°C, between 0.24 ± 0.03 and 2.47 ± 0.06 Pas, the former being the high values of *D. trifida*. Breakdown values of 1.2 Pas have been reported for potato starch and 0.5 Pas for cassava starch.[15]

Starch-based plastic films

X-ray diffraction

X-ray diffraction patterns were obtained for each of the six types of films prepared. The six films studied had a B-type diffraction pattern. The diffraction patterns

obtained for four of them are shown in Figure 2. The diffraction of the B-crystalline structure appears in all the diagrams, with not sharp differences in the peaks intensity. All diagrams exhibit contributions of the amorphous phase, with a small crystalline fraction (the higher the amorphous zone, the lower the crystallinity of the sample), which is in agreement with results reported in the literature. Romero-Bastidas et al.[2] report B-type crystallinity for films made from for banana, okenia and mango starch, as well as Rindlav et al.[34] for films prepared from potato starch. Since amylose is nearly linear, whereas amylopectin is highly branched, the crystallinity of starch films is primarily associated with amylose, even if amylopectin accounts for the crystalline regions in the native starch granules.[35,36] Consequently, starch films containing more amylose, should show higher crystallinity. Since the molecular order within the granules is destroyed when the granular starch is mixed with plasticizers and heated for film processing, a conversion of the molecular structure to thermoplastic starch is obtained, and much of the starch changes from a crystalline to an amorphous structure, even if a granular native structure or a new crystalline form induced by the process remains in the thermoplasticized material.[37] X-ray diffraction (XRD) patterns for plasticized tapioca starch films generally are reported to present highly amorphous or B-V-type patterns.[38–40]

Water vapor permeability of films

As can be seen in Figure 3, 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 g/m·s·Pa $\times 10^{-10}$ respectively by García et al.,[36] and for banana, okenia, and mango starch-based films reported by Romero-Bastida et al.,[2] that ranged between 20 and 25 g/m·s·Pa $\times 10^{-11}$. Both, the waxy *Dioscorea* and *Xanthomonas* exhibited the lower WVP of the six starches: 9.9 ± 0.4 and 9.45 ± 0.3 g/m·s·Pa $\times 10^{-9}$. This is considered to be 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.[4,26]

Gas permeability of films

The six films were good barriers to O_2 and CO_2. Table 5 shows values of the permeability of films to oxygen and carbon dioxide. Films made from *I. batatas* (2.5% starch, 1.5% glycerol), *C. esculenta* (5% starch, 2.5% glycerol) and *X. sagittifolium* (5% starch, 2.5% glycerol), had no detectable CO_2 permeability, while films from *A. xanthorriza* (5% starch, 2.5% glycerol) *D. trifida* 'White' (2.5% starch, 1.5% glycerol), *D. trifida* 'purple' (2.5% starch, 1.5% glycerol) exhibited values of 2.73 ± 0.37, 2.86 ± 0.19 and $1.58 \pm 0.21 \times 10^{-10}$ cm^3 /m·s·Pa, respectively. O_2 permeabilities were significantly higher than those for CO_2. García et al.[26] when using plastizicers (glycerol and sorbitol) and lipids (sunflower oil) for improving barrier properties of edible starch-based films and coatings, using commercial corn starch and high amylose corn starch, found that O_2 permeabilities were much lower, in the order of 10^{-10}

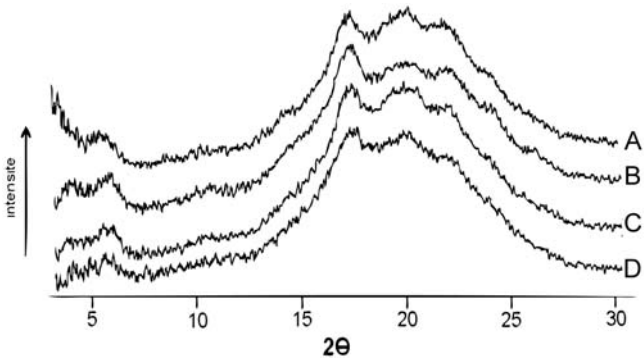

Figure 2. X-ray diffraction patterns of starch-based films: A: *Dioscorea trifida* (purple); B: *Dioscorea trifida* (white); C: *Xanthosoma sagittifolium*; D: *Ipomoea batatas*.

$cm^3/m{\cdot}s{\cdot}Pa$, than those for CO_2, in the order of 10^{-9} $cm^3/m{\cdot}s{\cdot}Pa$, indicating a selective action of these films on gas permeabilities, which the authors attributed to a higher solubility to CO_2 in the starch films. The lowest values of CO_2 permeability were obtained for amylomaize films either with sorbitol or glycerol (3.85 ± 1.28 and $2.96 \pm 0.46 \times 10^{-9}$ $cm^3/m{\cdot}s{\cdot}Pa$). They also observed that CO_2 and O_2 permeabilities of films without plasticizer were significantly higher than plasticized films, results attributed to the presence of pores and cracks in the surface of unplasticized films. In the present study, all six films had plastizicers, and all films were significantly more permeable to O_2, in the order of ten fold, (10^{-9} $cm^3/m{\cdot}s{\cdot}Pa$), than to CO_2 (10^{-10} $cm^3/m{\cdot}s{\cdot}Pa$). The different degree of plasticization, the moisture content of the films even if all were conditioned to an equilibrium RH of 57% and the degree of crystallinity might affect permeability to gases of the films. In films containing 1.5% glycerol and 2.5% starch (made with starch from both *D. trifida* and *I. batatas*), the percentage of glycerol over the weight of the mixture glycerol/starch represents 37.5% (1.5/4.0), while in films with 2.5% glycerol and 5% starch, (made with starch from *C. esculenta, X. sagittifolium* and *A. xanthorriza*), the proportion of glycerol in the formulation represents 33.3% (2.5/7.5). Despite this high proportion of plasticizer a phase separated microstructure was never observed. In Table 5 it can be seen that films with higher glycerol proportion (37.5%) have higher moisture contents. This difference in moisture could be in part responsible for the higher permeability to O_2, exhibited by those films, even if this moisture effect is not so clear regarding the permeability of the films to CO_2.

Donhowe and Fennema[41] stated that permeability to gases increases with decreasing crystalline-amorphous ratio, since crystalline structures are extremely tightly packed and tend to be impermeable but fragile. In theory, starch films containing less amylose, should show lower crystallinity, but in the present study, the waxy starch-based films (*D. trifida* (white and purple) presented the lowest permeability to O_2, as opposed to the results of García et al.[26] who found that amylomaize films, with higher amylose, content showed higher crystallinity and lower permeabilities than corn starch films. As stated by García et al.[26] permeability to gases depends

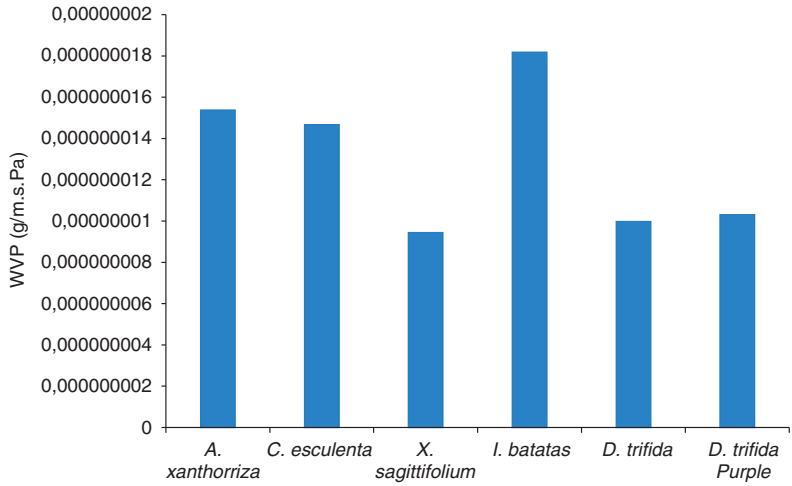

Figure 3. Water vapor permeability (g/m·s·Pa) of six starch-based edible films (starch extracted from six varieties of roots, corms and tubers from the Venezuelan Amazon. 1: *Ipomoea batatas* (2.5% starch, 1.5 % glycerol); 2: *Colocasia esculenta* (5% starch, 2.5% glycerol); 3: *Xanthosoma sagittifolium* (5% starch, 2.5% glycerol); 4: *Arracacia xanthorriza* (5% starch, 2.5% glycerol); 5: *Dioscorea trifida* white (2.5% starch, 1.5% glycerol); 6: *Dioscorea trifida* purple (2.5% starch, 1.5% glycerol).

Table 5. Moisture content, oxygen and carbon dioxide permeability of six starch-based edible films of starch extracted from six varieties of roots, corms and tubers from the Venezuelan Amazon

Starch-based film forming solution (% starch and % glycerol in the formultation)	Moisture content (%) Wet basis	O_2 permeability 10^{-9} (cm^3/m·s·Pa)	CO_2 permeability 10^{-10} (cm^3/m·s·Pa)
Ipomoea batatas (2.5% starch, 1.5% glycerol)	37.83	4.42 ± 0.08	–
Colocasia esculenta (5% starch, 2.5% glycerol)	27.54	2.09 ± 0.09	–
Xanthosoma sagittifolium (5% starch, 2.5% glycerol)	30.83	3.44 ± 0.07	–
Arracacia xanthorriza (5% starch, 2.5% glycerol)	31.60	2.38 ± 0.15	2.73 ± 0.27
Dioscorea trifida 'White' (2.5% starch, 1.5% glycerol)	35.46	9.92 ± 0.06	2.86 ± 0.17
Dioscorea trifida 'Purple' (2.5% starch, 1.5% glycerol)	35.11	9.36 ± 0.03	1.58 ± 0.32

All film samples were conditioned at a a_w of 0.59 ± 0.02.

strongly on the interaction between the polymer matrix and the permeating gas and the environmental conditions such as temperature and relative humidity. So, more research is needed in order refine the experiments of gas permeability of the films studied. It is known that addition of plasticizers and absorption of water molecules

by hydrophilic polymers increase polymer chain mobility and generally lead to increased gas permeability,[42] thus, increasing the RH levels around the films, could lead to increase the gas permeability, which along with addition of components to improve water resistance and other desirable film physical properties would allow to design starch-based films for specific foods and uses, as alternative secondary packaging, for controlling respiratory exchange and improving the conservation of fresh or minimally processed vegetables.[43–46]

Textural properties

The tensile strength (TS) and the percentage of elongation at break (Eb) of the films prepared from diverse starch sources are presented in Table 6. Tensile strength is the maximum tensile stress that a film can sustain. Elongation is the maximum change in length of the test specimen before breaking.[46] TS varied from 4.56 ± 0.12 MPa for *C. esculenta*, which is the lowest value obtained, to values of 14.78 ± 0.30 and 12.72 ± 0.13 MPa for both *D. trifida* films which are the highest TS values, followed by *I. batatas* films (11.69 ± 0.23 MPa). These films have the highest moisture content and the highest glycerol proportion (37.5%) (Table 5). Myllarinen et al.,[47] investigating the effect of glycerol on behavior of amylose and amylopectin films, found that a highly plasticized amylose film was rather strong showing a tensile strength of 10 MPa, while the corresponding amylose film, lost all strength, and addition of 30% glycerol to amylopectin films resulted in a liquid-like behavior. Lourdin et al.[48] studying the influence of amylose content on starch films, when mixing different ratios of amylose and amylopectin, with 20% glycerol found that the amylose films were only slightly stronger than the amylopectin films. The authors report TS of 38 MPa for pure amylopectin film and up to 69 MPa for pure amylose film. In this study however, highly plasticized films made from a waxy *Dioscorea* starch (very low amylose content) were the more resistant exhibiting the highest TS. Romero-Bastidas et al.[2] report for banana starch films with tensile strength values of 25 MPa and around 20 MPa for okenia and mango starch films. A tensile strength of 10 MPa is comparably as strong as a polyethylene film.

As for the Eb, both types of *Dioscorea* films (highest TS) and films from *X. sagittifolium* exhibited the lowest values, $10.41 \pm 0.55\%$ and $9.48 \pm 0.37\%$ for white and purple *Dioscorea*. The highest Eb values are found in *C. esculenta* ($26.46 \pm 0.45\%$), and *A. xanthorriza* ($23.37 \pm 1.5\%$) which correspond to the lowest TS values (4.56 ± 0.12 and 9.35 ± 0.28 MPa, respectively). These values are higher than maximum elongations values reported by Lourdin et al.[48] for potato and wheat starch films, and comparable to some of the starch-based films investigated by Romero-Bastidas et al.[2] As stated by these authors the starch source plays an important role on this mechanical property (Eb). Kim et al.[49] reported that glycerol concentration increased Eb values, an inverse pattern to that found for TS. In our case, even if both *D. trifida* films and *I. batatas* have higher glycerol proportions, all films can be considered highly plasticized. Osés et al.[50] working with composite films based on whey protein isolate and mesquite gum found that films that were most resistant

Table 6. Tensile strength and elongation at break of six starch-based edible films (starch extracted from six varieties of roots, corms and tubers from the Venezuelan Amazon)

Starch-based film forming solution (% starch and % glycerol in the formulation)	Elongation at break (%)	Tensile strength (MPa)
Ipomoea batatas (2.5% starch, 1.5% glycerol)	15.24 ± 2.11	11.69 ± 0.23
Colocasia esculenta (5% starch, 2.5% glycerol)	26.46 ± 0.45	4.56 ± 0.12
Xanthosoma sagittifolium (5% starch, 2.5% glycerol)	14.75 ± 1.12	9.81 ± 0.03
Arracacia xanthorriza (5% starch, 2.5% glycerol)	23.37 ± 1.5	9.35 ± 0.28
Dioscorea trifida 'White' (2.5% starch, 1.5% glycerol)	10.41 ± 0.55	14.78 ± 0.30
Dioscorea trifida 'Purple' (2.5% starch, 1.5% glycerol)	9.48 ± 0.37	12.72 ± 0.13

presented the lowest Eb as well as the highest elasticity modulus. The differences in the mechanical properties attributable to botanical origin and amylose content have to be investigated in more depth. Parameters like thickness values exhibited no statistical significant differences among the six types of films.

Conclusions

It is feasible to use non-conventional starches with high purity, defined granular structure (shape and typical Maltese crosses), 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 which also can be engineered and improved. The relationship between the starch properties and those of its corresponding films is a broad and interesting field of investigation especially for non-conventional sources of starch. The purity, the amylose/amylopectin ratio, the granule size, the crystallinity pattern, and the pasting, gelatinization, and retrogradation pattern (rheological properties) of the starch affect the conversion of its molecular structure to 'thermoplastic' starch in the films produced. This work attempted to make an initial contribution with these under-utilized starchy crops. 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. Both *Dioscoreas* studied – starch and films – should be investigated in more depth due to its 'waxy' nature. Starch-based films from *I. batatas*, *C. esculenta* and *X. sagittifolium* yielded films that were totally impermeable to carbon dioxide, which can be of interest in some food science applications for shelf-life extension. Regarding the other starch-based films investigated made from *A. xanthorriza* and both *D. trifida* (white and purple), it is noteworthy that its permeability to CO_2 is higher than its permeability to O_2. As for the mechanical properties investigated, both the *D. trifida* films exhibited the highest TS values and the lowest Eb values. More studies are needed on molecular properties of the films investigated. A study of the specific role of molecular weight should also be addressed as well as the

correlation of the amylose content to X-ray diffraction patterns of starch films, to botanical origin, to degree of plasticization, moisture content and to other properties of the films.

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