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Comparative Analysis between Corn and Ramon (*Brosimum alicastrum*) Starches to Be Used as Sustainable Bio-Based Plastics

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Abstract**—**Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. Finding new uses for agricultural commodities is also an important area of research. Therefore, it is crucial to get new sources of natural materials that can be used in different applications. Ramon tree (*Brosimum alicastrum*) is a tropical plant that grows freely in Yucatan countryside. This paper focuses on the seeds recollection, processing and starch extraction and characterization in order to find out about its suitability as biomaterial. Results demonstrated that it has a high content of qualities to be used not only as comestible but also as an important component in polymeric blends.

Keywords**—**Biomaterials, biopolymer, starch, characterization techniques.

I. Introduction

GENERALLY, polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Starch is the most important carbohydrate in the human diet and serves as a major energy source [1]-[3]. Depending on the botanical source, carbohydrate is stored as starch granules in seeds, fruits, roots, tubers, and stems. Starch granules vary in size, shape, crystallinity, and amylose content, all of which can affect its functional properties [4]-[6] The most natural source of starch is corn, which is an important ingredient in human consumption and its usage should be limited to feed the population [7], [8]. Therefore, new sources of starch have been investigated lately in order to obtain its properties [9]-[12]. In Yucatan State, Mexico, Ramon tree (*Brosimum alicastrum*) can be found freely in the countryside. Its seeds were used by Maya people to be consumed in its diet due to the high protein content. However characterization of these seeds has been unknown.

Ramon tree (*Brosimum alicastrum*) belongs to moraceae family, is widely found in Yucatan State and it is considered as an important ingredient in antique Maya Civilization. It has been used also as seeds, forage, wood and a medicinal plant. The seeds from Ramon trees are used for human consumption since it has been demonstrate that it has a high value in nutrients. Mature seeds are collected either from the tree or even form the ground and are peeled in order to have the "bone" (Figs. 1 (a) and (b)).

Fig. 1 (a) Ramon seed, (b) Seeds recollection

Nowadays, local people submit the seeds to a dry process just by exposing them to the sun (temperatures in Yucatan are about 35°C most of the year) or in rustic wooden stoves in order to finally transform the dried seeds in flour (Figs. 2 (a) and (b)).

Fig. 2 (a) Wooden stove, (b) Dry process

Finally, Ramon seeds are converted into flour in order to be used as a main ingredient in the preparation of traditional food. Ramon flour has many additional benefits for human consumption:

- Controls high blood pressure (due to tryptophan, calcium and potassium content)
- Burns fat and avoids constipation
- Increments the milk production in breast feeding women
- Prevents anemia, arthritis and osteoporosis

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- Natural relaxant
- Complete protein content

Ramon starch has many benefits, but most of them are known empirically and scientific research is very limited. In this research Ramon seeds were collected, processed, and purified in order to obtain starch for analysis. Findings were compared with those obtained from cornstarch. One of the main goals of this research is to get information about the starch properties to be used as biomaterial in manufacture of biodegradable materials.

II. Experimental Methodology

When collected, Ramon fruits presented an average weight of 6.56±0.09 g and an average diameter of 2.44 ±0.67 cm. Ramon fruits were dried in a convection oven at 70 ◦C for 72 h, after which they were stored in a desiccator until the milling process. Then, seeds were milled, ground in an IKA MF-10 grinder (0.5 mm sieve) and sifted through 100-mesh screen to produce flour. Finally, the resulting flour was stored in hermetically sealed glass containers until use, in order to avoid moisture absorption. Starch extraction was carried out following the technique described by [13] and [14].

Starch was analyzed trough several analytic techniques such as Scanning Electron Microcopy (SEM), Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

III. Results

A comparison between granules morphology of corn starch (a) and Ramon starch (b) are shown in Fig. 3. The starches under study presented different shapes; corn starch granules were polygonal while those of the Ramon starch were oval–spherical. Granule size was heterogeneous, with an average diameter value of 15 µm, ranging from 3 to 26 µm for corn starch and an average value of 10.8 µm, ranging from 6.5 to 15 µm for Ramon starch.

The gelatinization temperatures (onset, To; peak, Tp; and conclusion, Tc), enthalpy of gelatinization (ΔHgel), peak height index (PHI) and gelatinization temperature range (GelTR) for corn and Ramon starches, measured using DSC are presented in Table I. Significant difference was observed in To, Tp and Tc among starches from corn and Ramon. The lowest To, Tp and Tc of 64, 71 and 80◦C, respectively, were oberved for corn starch, whereas Ramon showed the highest value for the same. These variations are influenced by various factors including the composition of the granule of starch (amylose: amylopectin), structure (relation crystalline: amorphous), shape and size, the molecular structure of amylopectin (bunch size, length chains) and the content of other components such as proteins, lipids and phosphorus. The values Gel_{TR} obtained show that there is a higher content of crystalline phases present in the Ramon (16.19◦C) in comparison with corn starch (14.16 ◦C). This implies that it is necessary a larger amount of heat to melt all the crystalline phase in Ramon starch. Fig. 4 exhibited the DSC curves for Ramon and corn starches.

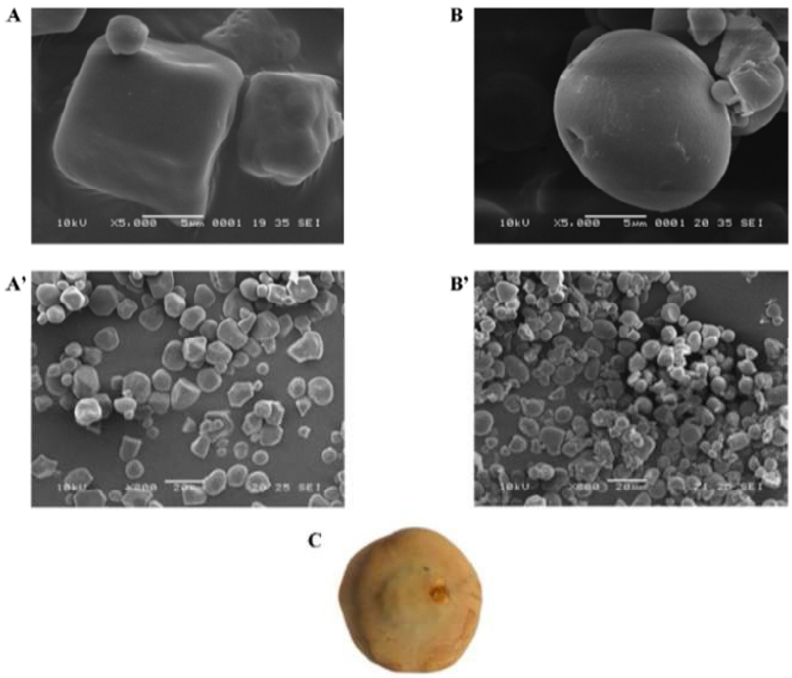

Fig. 3 Scanning Electron Microscopy (SEM) images. (A) and (A´) corn granules, (B) and (B´) Ramon granules, (C) Ramon seed

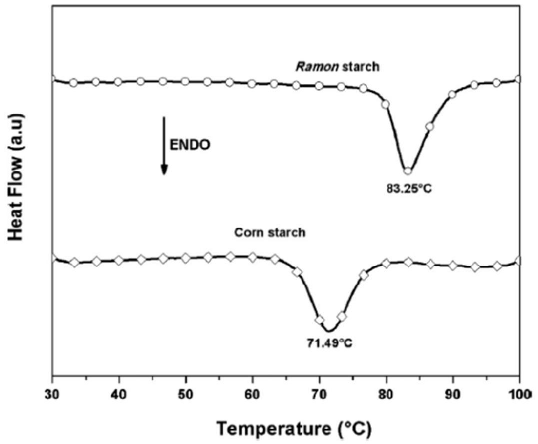

Fig. 4 DSC thermogram of corn and Ramon starches

TABLE I
THERMAL PROPERTIES OF CORN AND RAMON STARCH

	PARAMETERS					
Starch	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g)	GEL_{TR} (°C)	PHI (J/g°C)
Corn	64±1	71.08±.0.5	80±1	14.89±0.5	14.16	2.10
Ramon	75±1	83.05±0.5	95±1	21.42±0.5	16.10	2.66

To, onset temperature; Tp, peak temperature; Tc, conclusion temperature, ΔHgel, enthalpy of gelatinization range 2(Tp - To); PHI, peak height index ΔHgel /(Tp - To).

Figs. 5 (a) and (b) show the thermogram (TG) and its derivative (DTG), as a function of the temperature, for Ramon and corn starches, respectively. For the samples, the thermal decomposition process was developed in three steps. The first step, corresponding to a reduction in mass at temperatures below 150°C, can be associated to the loss of water of the samples. In the second stage (250 ± 10°C ≤ T ≤3 60 ± 10°C), mass loss is due to the main decomposition processes of starch macromolecules and the mass of the Ramon starch was diminished by 67%, while the mass of the corn starch was diminished by 72%. In the third stage (T > 400°C), inert carbonaceous residues were formed; mass loss became stabilized.

Fig. 6 shows the FTIR spectra corresponding to Ramon and corn starches. Absorption at 3389-3420 cm-1 was observed in both starches, corresponding to the stretching vibrations of the hydroxyl groups (-OH) and contributing in the inter and intra-molecular interactions of OH-; which is a particular characteristic of starch structure. The water absorbed by the starch appears in the spectrum with a characteristic medium band between 1640 and 1650 cm-1. In the region known as "fingerprint", characteristic peaks of starch can be observed at 1155, 1087 and 1019 cm-1, corresponding to the vibrations of glucose C-O-C bonds, and at 928, 862, 764, 709, 605 and 573 cm-1, attributed to the pyranose. In starch there is an amorphous region and a crystalline region; the quantity of each is important in predicting the response of this polysaccharide when it is processed or that of the products that contain starch when they are stored. It was observed that Ramon starch had greater ordering (more crystalline areas) than corn starch.

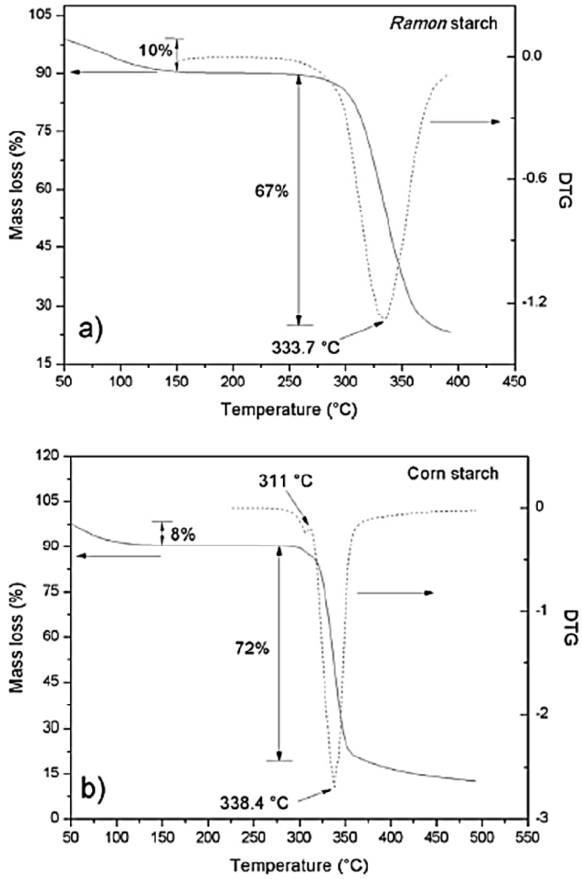

Fig. 5 TGA results of the thermal decomposition and its derivative (DTG); a) Ramon starch; b) corn starch

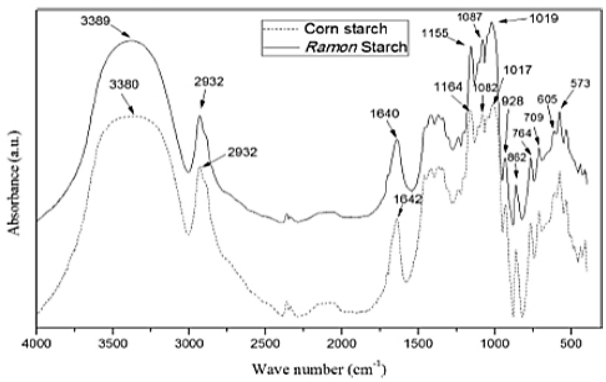

Fig. 6 FTIR spectra of Ramon and corn starches

IV. CONCLUSIONS

The chemical composition and functional properties of starch from Ramon seed, a non-conventional source, suggest it may have numerous possible uses as an ingredient in food systems and other industrial applications. Ramon seeds produced a starch yield of 300 g per kg. The extracted Ramon starch showed a high degree of starch purity (92.57%), a granule size ranging from 6.5 to 15 µm and an oval–spherical-shaped granule. The amylose/amylopectin ratio was 1:2.94, indicating a predominance of amylopectin, which results in a low tendency to retrograde. Raw flour and fiber residue resulting from Ramon starch extraction showed high contents of crude fiber (8.14%) and proteins (10.81%). According to thermic properties, the Ramon starch exhibited higher resistance to heat and heat stability than corn starch, therefore it can be widely used as main component in products that need to be exposed to high temperatures. Such materials could be employed in the elaboration of food supplements. The results of this study suggest that Ramon starch could be used in food systems requiring high processing temperatures and that it is a promising material for application in the manufacture of biodegradable materials.

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