

Chemical Modification and Characterization of Starch Derived from Plantain (*Musa paradisiaca*) Peel Waste, as a Source of Biodegradable Material

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Agriculture modernization and biomass processing generate millions of tons of waste per year containing different amounts and quality of polymeric components such as starch, sugar, lignin, cellulose and hemicellulose. The raw material for extraction was the green plantain peel (*Musa paradisiaca*), obtained from a local company that produces fried plantain snacks. This work presents the comparisons between the synthesis by wet extraction method and the modification of natural biopolymer with polyhydric alcohol (glycerin). Four blends were prepared at different concentrations of starch, glycerin and water to create a modified biopolymer. Later they were characterized with Fourier Transform Infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and Amylose-Amylopectin ratio. In the unmodified starch samples, the observed bandwidth at 3373 cm⁻¹ can be attributed to amylopectin O-H stretching (55%) and its width was attributed to the formation of inter- and intramolecular hydrogen bonds, also in the region known as the fingerprint (close IR), ranging from 400 to 1250 cm⁻¹, four characteristic peaks are observed in the spectra between 520 and 1020.16 cm⁻¹, which are attributed to the stretching of the C-O bond. For both unmodified starch and modified starch, the TGA tests showed that the weight loss started at a temperature of about 310 °C, but in modified starch the total degradation temperature increases to about 610 °C. Starch extraction from plantain peel wastes has demonstrated its potential for waste use and the production of value-added products, like degradable polymers. The mixtures of starch, glycerin and water (labeled 1, 2, 3, and 4) have different characteristics, shown in the FTIR spectra. Mixture number 4, with 35% glycerin, has a significant peak at 3425 cm⁻¹, corresponding to the OH group stretching. The bending peak at 1641 cm⁻¹, has less transmittance, since the percentage of water in the mixture is zero. The transmittance band between 1060 and 990 cm⁻¹, is characteristic of the polysaccharides, of amorphous structure.

1. Introduction

Since the synthetic polymers were discovered, more than 60 years ago, there have been hundreds of applications with which they have contributed to the development of humanity. Their most significant characteristics are the durability and manufacturing economy, which in turn affect the environment due to the variety of manufacturing methods and the many years needed for natural degradation (Ruiz-Avilés, 2006). Although recycling is an option to mitigate this problem, it is not entirely effective, because not all polymers can be recycled due to their composition or their usefulness.

The dispute about polymeric products against the environment continues to gain strength, and, as a result, new products have come to light, such as biopolymers, or biodegradable polymers. In this way, the use of the natural available resources plays a determining role in obtaining different raw materials (Di Donato et al., 2014; Nwokocha and Williams, 2009; Mazzeo et al., 2017). An example is the extraction of starch from banana and plantain peels, with appropriate properties for the development of different materials without

competing with food sources (Hernández-Carmona et al., 2017). Biopolymers from starch will be an economically and environmentally friendly way of obtaining polymers in the future, due to the abundance of plants that contain this type of material (Cruz et al., 2013). This research aims to obtain a biodegradable polymer from the starch of the green banana peel (*Musa paradisiaca*), based on a previously validated methodology (Hernández-Carmona et al., 2017), modified by using a polyol as plasticizer and also analyze some of its properties, as well as its physicochemical characteristics.

2. Metodology

2.1 Materials

The raw material for the starch extraction was the green plantain peel (*Musa paradisiaca*), obtained from commercial suppliers of this fruit. The original sample contained 1.5 kg of banana peel, which was processed immediately after peeling the fruits and separated into 150 g samples. The reagents (Sodium hypochlorite 1%, Ascorbic acid and Glycerine, analytical grade) were obtained from local suppliers (Panreac®, AppliChem® and Merck®, respectively).

2.2 Starch extraction method

The starch extraction method used is described in detail in a previous work (Hernández-Carmona et al., 2017) with the conditions that reported higher starch yields (Nwokocha and Williams, 2009; Mazzeo et al., 2017). The method basically consists of crushing the plant material of the green plantain peel in acid solution (with ascorbic acid), to promote the separation of the starch from the lignocellulosic fraction by decantation, and then dehydrate the starch at temperatures not higher than 40°C.

2.3 Chemical modifications of crude starch

The starch extracted from the banana skin was modified using the process described by Averous et al. (2000) and Ruiz-Avilés (2006). It was implemented through the preparation of different mixtures of starch, glycerin and water in the proportions by weight stated in Table 1.

Table 1: Experimental conditions for modification of the obtained starch.

Modification	1	2	3	4
Starch (wt %)	72	70	67	65
Glycerine (wt %)	12	18	24	35
Water (wt %)	16	12		9
				0

2.4 Characterization

Crude starch and Modified starch

The crude starch was extract according to the procedure described by Hernández-Carmona et al. (2017), and tested for purity using AOAC methods 920.44 and 906.03. In addition, the amylose-amylopectin ratio was calculated using the colorimetric method described by Morrison and Laignelet (1983). Samples of raw starch were analyzed in a FT-IR SHIMATZU 8400S spectrophotometer, using the KBr pellet method according to the ASTM-E168 and ASTM-E1252 standards, with the objective of obtaining information on the characteristic functional groups (Hernández-Medina et al., 2008; Lin, 2016).

To obtain information about the composition of the samples and their thermal stability, a Thermogravimetric Analysis (TGA) test was carried out in accordance with the ASTM E1131-98 standard. Each sample of raw and modified starch is heated at a rate of 50°C/min, in a nitrogen atmosphere between 50 and 550°C and in an oxygen atmosphere between 550 and 900°C. The weight loss over specific temperature provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability.

3. Results

3.1 Purity of the raw sample and Amylose/Amylopectin ratio

The purity percentage (wt) of the crude starch reached a maximum value of 70% ± 0.76%, under optimum extraction conditions. The amylose/amylopectin ratio of the raw samples was 17/55%, these results agree with

what is reported in the literature (Enríquez et al., 2013), also, taking into account the purity of the starch extracted, the values are very close to those reported in other publications (Ruiz-Avilés, 2006).

3.2 FT-IR spectra of crude starch from *Musa paradisiaca* peel

Figure 1 shows the FT-IR spectrum of the raw starch sample. To simplify its interpretation, this spectrum can be divided into regions. The mid-infrared spectrum ($4000\text{--}400\text{ cm}^{-1}$) is approximately divided into four regions. The nature of a group frequency is determined by the region in which it is located. The bands in the region between 3300 cm^{-1} and $3000\text{--}2800\text{ cm}^{-1}$ characterize the stretches of the OH and CH bonds, respectively, then the triple bonds region ($2500\text{--}2000\text{ cm}^{-1}$), followed by the region of double bonds ($2000\text{--}1500\text{ cm}^{-1}$) and the so-called fingerprint region ($1500\text{--}600\text{ cm}^{-1}$). The results show a wide and strong absorption band with transmittances between 3520 and 3217 cm^{-1} corresponding to the stretches of the OH groups. The amplitude of the band indicates the presence of intermolecular hydrogen bonds. The transmittances between 2920 and 2930 cm^{-1} correspond to the extension vibrations C-H. At 1643 cm^{-1} there is a band of flexion of the OH of the water, which indicates that the polymer is hygroscopic. At 1459 and 1350 cm^{-1} are the C-H bending vibrations and the transmittance band between 1060 and 990 cm^{-1} , is characteristic of the polysaccharides and is attributed to the strain deformations of the C-O-C and flexion of the OH. The results showed a representation of amylose and amylopectin, characteristic molecules of starches. The ratio of the absorbances to 970 cm^{-1} represents the order of the starches and the band of 1020 cm^{-1} is related to the amorphous component.

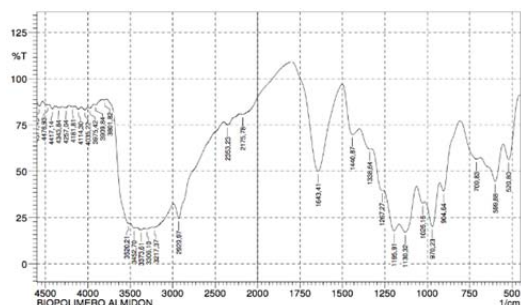


Figure 1. FT-IR spectrometry from raw samples of starch without any modification, extracted from plantain peel (*Musa paradisiaca*).

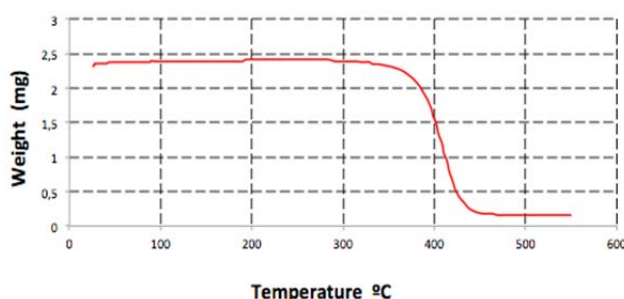


Figure 2. TGA curve from crude starch ($25\text{--}600^{\circ}\text{C}$, 4°C/min)

3.3 Thermal decomposition of crude starch (TGA)

According to the thermogravimetric analysis of crude starch (Figure 2), the weight loss can be observed from the temperature of 318°C , in addition the graph shows that the polymeric material decomposes in a proportion of 93.3% at a temperature of 470°C . The thermal decomposition of the sample without modifications, can be divided in three phases: Stage 1: ($25\leq T\leq 290^{\circ}\text{C}$) mass loss (about 0.9%) due to the weightlessness caused by the evaporation of volatile substances, mainly the evaporation of water; Stage 2: ($291^{\circ}\text{C}\leq T\leq 410^{\circ}\text{C}$) mass loss (about 60%) largely resulted from the decomposition of organic matters like starch; Stage 3: ($411^{\circ}\text{C}\leq T\leq 600^{\circ}\text{C}$) mass loss (about 35%) mostly because of carbonization of organic matters and non-volatile.

3.4 FT-IR spectra of crude starch and modified mixtures

The FT-IR spectrum for the four modified mixtures as well as the starch sample can be divided into regions as shown in Figure 3. The first region (fingerprint region) of the spectrum corresponds to the stretching of the functional group C-O below the line of 2000 cm^{-1} . In M-2, the bands in the region between 1250 and 2000 cm^{-1} characterize the formation of proteins, fatty acids and the formation of the C-H bonds. In M-3, the bands in the region between 1200 and 1500 cm^{-1} correspond to the contribution of proteins (amides III), asymmetric stretching of the P-O bond of phosphate groups and the formation of the C-H bonds. This can also be seen in 1417.73 and 1454.38 cm^{-1} in M-4, where these bands are associated with the symmetric stretching of the carboxyl group -COOH (Kizil et al., 2002). According to Van Soest et al. (1995) and Huang et al. (2006), the region relative to the stretching of C-C, C-O and C-O-H bonds of starch can be analyzed through the absorption bands lying between 848.71 and 1332.86 cm^{-1} .

In the mid-infrared spectrum region, between 1300 and 2900 cm^{-1} , different functional groups can be observed which are the C-H (fatty acids), the lipids (corresponding to cell walls), as well as proteins and formation of the C-H bond. Based on the fact that the free hydroxyl groups absorb energy between 3650 and 3584 cm^{-1} , the

bands observed in the region $3000 - 3600 \text{ cm}^{-1}$ in the spectra can be assigned to the stretching of the $-\text{OH}$ groups, caused by formation of the hydrogen bonds (Silverstein et al., 2007). All the mixtures presented bands in this spectrum range corresponding with the presence of hydroxyl and amino bonds. It is noted that in the crude starch spectra, maximum value at 3571.45 cm^{-1} is presented related with the stretching of the functional group C-H as well as the presence of IV carbohydrates.

The bands between 3600 and 4600 cm^{-1} (M-2, M-3 and M-4) confirm the presence of certain functional groups such as hydroxyls, ammoniums, carbohydrates (IV) and the flexing and stretching of the C-H molecules. In these mixtures the % water by weight is lower than the crude starch, which is why said functional groups do not present as strong in the modified starch mixtures as in the crude one.

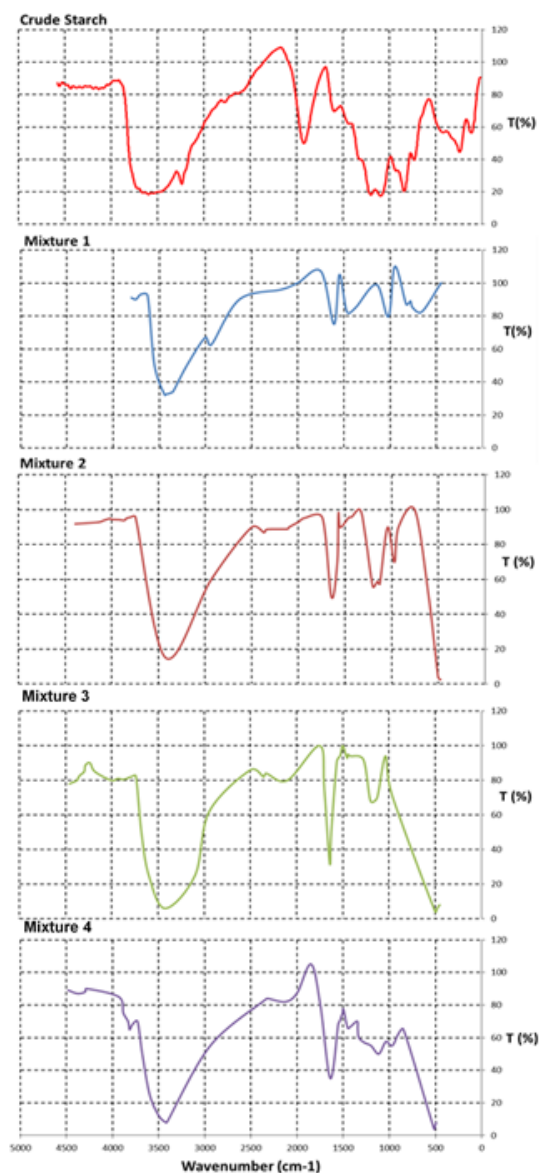


Figure 3. FT-IR spectrometry from raw sample of starch (*Musa paradisiaca*) and several modifications

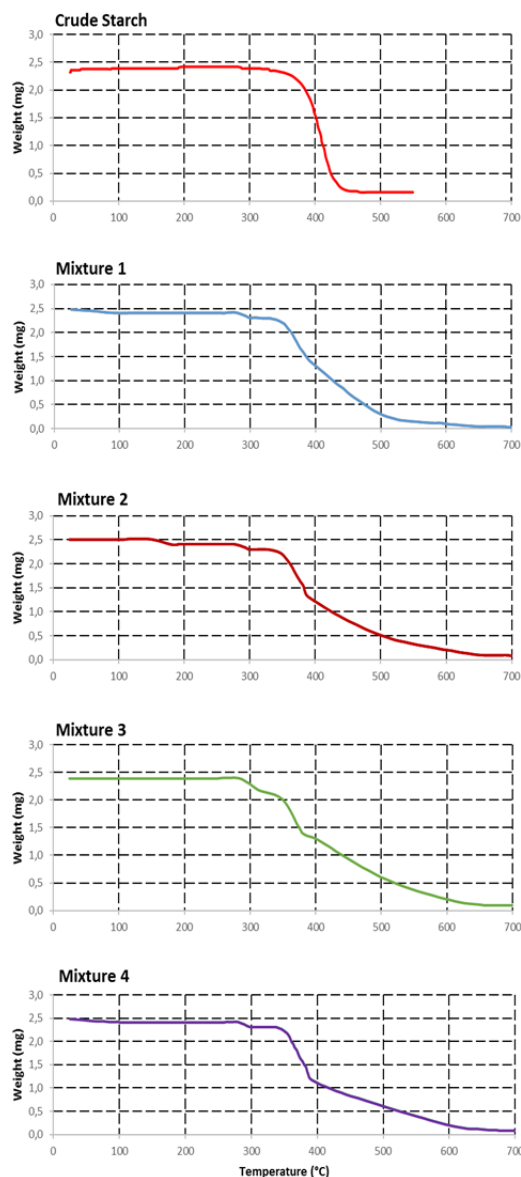


Figure 4. TGA curve from crude starch and modified mixtures (25-600°C, 4°C/min)

3.5 TGA of crude starch and several mixtures

TGA profiles of crude starch and several mixtures are present in Figure 4. In general terms, the behaviour of the different modified starch mixtures follows a 4-stage degradation trend. The first stage showed a significant weight loss corresponding to the starch drying (4% in mass) between ca. 100-150°C (M-1, M-2 and M-4). The second degradation stage occurs between ca. 280-330°C. In the third phase of degradation about 50% of the

sample was consumed for all the mixtures where most of the carbohydrates are eliminated. The last phase, corresponding to the final decomposition phase in the crude starch occurs at ca. 470°C, while in the modified mixtures occurs between ca. 600–700°C ($150^{\circ}\text{C} < \Delta T < 200^{\circ}\text{C}$) in M-2, M-3 and M-4. From mixture 2 it can be observed that unlike crude starch, the samples with modifications began to show evident resistance to the temperature and all the samples presented 4% of inorganic waste. In general, the decomposition of the four mixtures is prolonged as the temperature increases and differs from crude starch due to the addition of glycerine in them. These results were consistent with previous reports (Qiao et al., 2017) which indicate that starches with high amylopectin content have high thermal stability and present higher thermo-stability than starches with amylose-rich ones (Buléon et al., 1998; Tester et al., 2004).

4. Conclusions

Starch extraction from plantain peel wastes has proven potential source due to the diverse number of functional groups present in it, as well as the presence of amylose and amylopectin in appropriate concentrations, 17% and 55% respectively. In this work was implemented through the preparation of different mixtures of starch, glycerin and water in different proportions by weight. Using FT-IR analysis the differences and similarities of the spectra between the crude starch and the modified starches were determined, the thermal resistance of modified biopolymers was identified by TGA.

All the modified biopolymers present absorption bands corresponding to the wavelengths of the functional groups in the structure of amylose and amylopectin. In all cases, the content of amylopectin was greater than amylose, this can be attributed to the increase of the carbons in the starch matrix, by the generating of more free radicals in the molecular chains of starch. This similarity in the infrared spectra, both of the crude starch and the mixtures, allows us to conclude that the interaction between starch and glycerin is not chemical. The glycerin acts as a good plasticizing agent, providing different properties to modified starches, such as resistance to high temperatures and higher absorbance for the reading of new functional groups, observing the presence of proteins, asymmetric stretching of the P-O bond of phosphate groups and the formation of the C-H bond. The degree of decomposition was determined by TGA. It was observed that as the starch content decreases and the glycerin content increases, a higher temperature profile is required. The decomposition starts around 310 °C until a higher value of 600 °C with approximately 93% degradation in all biopolymers.

Finally, mixture 1, presents greater similarity with crude starch when compared with the rest of modified starch mixtures, due has the highest percentage of starch (72%). The biopolymer that showed the best results in FT-IR and TGA analysis was the mixture 4 (65% starch – 35% glycerin). For future studies, it is recommended to evaluate the mechanical properties of the synthesized biopolymer and their biodegradability. Use physical characterization techniques (Scanning electron microscopy and thickness and density) and compare the effectiveness of the starch extraction method with others.

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