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# Nanocomposites of rice and banana flours blend with montmorillonite: Partial characterization

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ABSTRACT

Rice and banana flours are inexpensive starchy materials that can form films with more improved properties than those made with their starch because flour and starch present different hydrophobicity. Montmorillonite (MMT) can be used to further improve the properties of starch-based films, which has not received much research attention for starchy flours. The aim of this work was to evaluate the mechanical and barrier properties of nanocomposite films of banana and rice flours as matrix material with addition of MMT as a nanofiller. MMT was modified using citric acid to produce intercalated structures, as verified by the X-ray diffraction pattern. The intercalated MMT was blended with flour slurries, and films were prepared by casting. Nanocomposite films of banana and rice flours presented an increase in the tensile at break and elongation percentage, respectively, more than their respective control films without MMT. This study showed that banana and rice flours could be alternative raw materials to use in making nanocomposite films.



## 1. Introduction

There has been considerable development in the past decade in the use of starch resources in non-food applications, especially as substitutes to petroleum-based plastics because they have low cost and availability [1,2]. However, starch-based films have low permeability to gases and poor water vapor barrier properties due to the inherent hydrophilic characteristic of starch. Furthermore, mechanical properties of starch-based films, such as brittleness and strength, require substantial improvement if they are to be used as biodegradable packaging materials [3]. It is well known that the addition of plasticizers enhances the flexibility and extensibility of starch films for reduction of intermolecular forces, and increase in the mobility of polymer chains. Glycerol is the most common plasticizer used to prepare starch-based films [4], which can also be prepared by blending starch with other macromolecules such as proteins, lipids, and other polysaccharides. Flours have recently been studied as raw material for preparing films because they are obtained from food crops, and they are natural blends of starch, non-starch polysaccharides, proteins, and lipids [2,5–8]. Dias [2] reported similar mechanical properties of films made with rice flour and rice starch, plasticized by glycerol, but the film elaborated with rice flour presented poorer water vapor permeability (WVP) than the film of rice starch. Films containing between 4 and 8% of banana flour showed good mechanical properties [8]. We are interested in unripe banana flour as potential film forming material because it is a low-value product. Previously, unripe banana was used to isolate starch for film preparation [9]. However, unripe banana flour has a high level of non-starch [10] as well as proteins and lipids, and the resultant films may have unique properties. An additional material of interest is rice flour, it can be produced from broken kernels during milled rice, these kernels do not meet the quality parameters for the rice market, they are considered a by-product of the rice packing industry, and can be used for starch isolation [11]. The flour obtained from this by-product is a natural blend of proteins, lipids, and starch, and it can be employed for preparation of biodegradable films. However, the films prepared from rice flour have limited mechanical and barrier properties [2].

In addition to the search for low-cost film-forming materials, nanocomposites, by the incorporation of nanomaterials as fillers inside a biopolymer matrix, are an alternative to improve the mechanical and barrier properties of films. MMT is a nanoclay that has been used to produce nanocomposite films. Diverse methods are used to improve the properties of nanocomposites by enhancing the distribution of MMT in a polymer matrix. These methods include sonication of MMT, modification of MMT using different reagents, or extrusion of the polymer-MMT blend to obtain intercalation or exfoliation of the MMT layers [12–16]. Intercalated layers of MMT were observed after their reaction with citric acid with increased reactivity with

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polymers [17]. The aim of this work was to characterize nanocomposite films prepared from unripe banana and rice flours with the MMT treated with citric acid added.

## 2. Experimental section

### 2.1. Materials

Unripe banana fruit (*Musa paradisiaca* L.) and rice grains (*Oriza sativa*) were used to prepare flours. Unripe banana was purchased from a local store (Cuautla, State of Morelos, Mexico), and rice (A-98 variety) was purchased from Molino de Arroz Buenavista (Cuautla, State of Morelos, Mexico). Sodium MMT was a product obtained from Sigma-Aldrich Corp. (St Louis MO). All chemicals used were of analytical grade.

### 2.2. Banana flour preparation

Banana flour was prepared according to the method of Rodríguez-Ambriz et al. [10]. In brief, fruits were peeled and sliced (1 cm thick), then washed with a citric acid solution (0.5 g/L). Afterwards, they were dried in a convection oven at 45 °C for 24 h. Once dried, slices were ground in a manual grinder (Mapisa Internacional S.A de C. V., México, D. F.) to pass through a mesh number 100 (150 μm).

### 2.3. Rice flour preparation

Rice was ground using a IKA-WERKEmill (MF 10 basic, GMBH and CO KG, Staufen, Germany). The flour fraction that passed through a sieve with a mesh number of 100 (150 μm) was collected and was contained in a plastic bag sealed in a hermetic container prior to use.

### 2.4. Chemical analysis of flours

The following methods of the American Association of Cereal Chemists [18] were used for compositional analyses: Kjedahl method for the protein content (Method 46–13); Soxhlet extraction method for the lipid content, with petroleum ether as a solvent (Method 30–25); dry incineration method at 550 °C for the ash content (Method 08–01); oven desiccation at 100 °C for 3 h for the moisture (Method 44–19); acid hydrolysis and alkali hydrolysis (boiling point) for the fiber content (Method 978.10). Alkaline hydrolysis and determination of glucose using the glucose–oxidase–peroxidase GOD/POD method were used to determine the total starch content following the procedures of Goñi et al. [19].

### 2.5. Modification of the MMT with citric acid

The MMT was modified using citric acid, and a mixture of citric acid and sulfuric acid, following the method of Huang et al. [17]. About 1.68 g of citric acid (8.75 mmol) was added to 230 mL water at 80 °C in a 500 mL beaker. A separate clay dispersion was prepared by mixing 5 g MMT in 100 mL water and heated to 80 °C. The acid solution was added to the clay dispersion, and the mixture was stirred at 80 °C for 3 h. After cooling down to room temperature, the dispersion was filtered through Whatman no.4 filter paper, and the cake was washed with distilled water. After centrifugation at 3000 rpm for 30 min, the pellet (the modified clay, named as MMT-II hereafter) was dried at 60 °C for 24 h, and then ground into a fine powder. The MMT modified with the acid mixture, referred as MMT-III, was prepared using similar procedure, except the above citric acid solution was added with 0.8 mL of 98% sulfuric acid.

### 2.6. Preparation of the MMT/flour nanocomposites films

The nanocomposite films were prepared by casting. About 2 g of flour was first dispersed in 60 mL distilled water with glycerol equivalent to 50% mass of flour (1 g). The suspension was heated to 70 °C for 1 h under vigorous stirring. A specified amount of dried clay (5% of flour mass or 0.1 g) was dispersed at room temperature in 40 mL distilled water and sonicated (Bransonic, ultrasonic cleaner, 2510R-MTH, Danbury, CT, USA) for 30 min. After that, the nanoclay dispersion was added into the flour suspension at 70 °C, held at this temperature for 10 min, heated to 85 °C, and held at 85 °C for 15 min to complete starch gelatinization. The final slurry was cast into Petri dishes, cooled at 60 °C and incubated in an oven at 35 °C for 24 h. The dried films were peeled for the following analysis.

### 2.7. X-ray diffraction (XRD)

XRD analysis was studied for the MMT and the nanocomposite films. The X-ray diffractometer from Bruker advance D8 (model 2100, Amsterdam, Netherlands) was equipped with CuKα radiation (35 kV, $\lambda = 0.154$ nm). The samples were scanned at 1°/min in the 2θ range of 3–70°. The basal spacing of the silicate layer, $d$ (001), was calculated using the Bragg's equation ($\lambda = 2d \sin\theta$), where θ is the diffraction angle and λ is the wavelength.

### 2.8. Thickness measurement

Thickness was measured with a manual micrometer (Mitutoyo, Brazil). Measurement was performed on ten different points randomly along the specimen. The thickness obtained was 0.18 mm, which is average of ten measurements.

### 2.9. Mechanical properties

The tensile test was performed using a model TAXT2i texture analyzer (Stable Micro Systems, Ltd in Godalming, Surrey England) and an A/TG tension grip system. The distance between grips was 8 cm, and the speed used in assay was 10 mm/min. The films with 0.18 mm thickness were trimmed to rectangular specimens 10 cm long and 1 cm wide that were conditioned at 57% relative humidity (RH) and 25 °C for 48 h before testing. The maximum breaking force (N) and the deformation at break (extension at the moment of rupture, mm) were obtained from the force vs. deformation curves. Ten determinations were measured for each sample.

### 2.10. Water vapor permeability (WVP)

The WVP test was conducted using E 96–66 ASTM [20]. The films were trimmed to circular shaped specimen. Each film was sealed over the circular opening of a permeation cup (13-338Q, Fisher Scientific, Pittsburg, PA, USA) with a diameter of 10 cm that was stored at 25 °C in a desiccator. To maintain a 75% relative humidity (RH) gradient across the film, silica gel (0% RH) was placed inside the cup, and saturated sodium chloride solution (78% RH) was used in the desiccator. The RH inside the cup was always lower than the outside, and the water vapor transport was determined from the weight gain of the permeation cup. Data were recorded as a weight gain vs time plot. The coefficient of the straight line, obtained by linear regression, was determined, and the water vapor transmission rate was calculated ($WVT = g/t \cdot A$), where g/t is the coefficient of the straight line and A is the permeation area ($m^2$). WVP was calculated using the equation $WVP = (WVT \cdot x)/\Delta P$, where x is the average thickness of the material and ΔP is the difference of vapor pressure of the environment containing thickness of the material and ΔP is the difference of vapor pressure of the environment into the desiccators. The films with 0.18 mm thickness were conditioned at 57% relative humidity and 25 °C for 48 h before testing. Tests were conducted in triplicate.