

**INFLUENCE OF STORAGE TIME ON MECHANICAL PROPERTIES OF FILMS MADE WITH MONTMORILLONITE/FLOUR (UNRIPE BANANA AND RICE) BLENDS****INFLUENCIA DEL TIEMPO DE ALMACENAMIENTO EN LAS PROPIEDADES MECÁNICAS DE PELÍCULAS DE HARINAS (PLÁTANO Y ARROZ)/ MONTMORILLONITA DE SODIO**M.L. Rodríguez-Marín<sup>1</sup>, J. Alvarez-Ramírez<sup>2</sup>, L.A. Bello-Perez<sup>1\*</sup><sup>1</sup>Centro de Desarrollo de Productos Bióticos, Instituto Politécnico Nacional. Km 6 carr. Yautepec-Jojutla, Calle Ceprobi No. 8, Colonia San Isidro, Apartado Postal 24, C.P. 62731, Yautepec, Morelos, México. +527353942020, Fax: +527353941896<sup>2</sup>Departamento de Ingeniería de Procesos e Hidráulica. Universidad Autónoma Metropolitana-Iztapalapa. Apartado Postal 55-534. Iztapalapa, D.F. 09340 México.

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**Abstract**

Films were made by blending either unripe banana or rice flour with sodium montmorillonite (MMT) by means of the casting method. Structural characterization by X-ray diffraction was performed to explain the interactions of the components between MMT and flour components. The effects of storage time on structure and mechanical properties of the films by X-ray diffraction, tensile at break and elongation were evaluated. Storage of the films produced reorganization of starch components (amylose and amylopectin). Addition of MMT modified the reorganization process, which was observed by X-ray diffraction pattern and mechanical properties of the films. Reorganization process was affected by flour type due to that starch present in those flours has different structural characteristics (e.g., granule size).

*Keywords:* film, montmorillonite, mechanical properties, banana, rice.

**Resumen**

Se elaboraron películas de harina (plátano y arroz) con montmorillonita de sodio (MMT) por el método de vaciado en placa. Se realizó la caracterización estructural mediante difracción de rayos X con la finalidad de explicar las interacciones de la MMT con los componentes de las harinas. Se evaluó el efecto del tiempo de almacenamiento en las propiedades mecánicas de las películas por tensión a la fractura y porcentaje de elongación. El almacenamiento provocó la reorganización de los componentes del almidón (amilosa y amilopectina); la adición de MMT modificó el proceso de reorganización, lo cual se vio reflejado en el patrón de difracción de rayos X y en las propiedades mecánicas. El proceso de reorganización dependió del tipo de harina, las cuales presentan almidón con diferentes características estructurales (e.g., tamaño de granulo).

*Palabras clave:* película, montmorillonita, propiedades mecánicas.

## 1 Introduction

Biodegradable materials are used for packing or covering of diverse products. Biopolymers such as starch, proteins, lipids and blends of these have been used to make biodegradable films, but some drawbacks of those films are their poor mechanical and barrier properties to the films of synthetic polymers (Dobircan *et al.*, 2009; Zamudio-Flores & Bello-Perez, 2013). Starch and proteins used to make biodegradable films require isolation or separation steps, increasing the cost of these biopolymers. An alternative to that is the use of flours from food crops since a natural blend of starch, proteins, lipids and

fiber can be exploited. The advantage of using this natural blend is that each component is present in its natural environment because the addition of those components in the composite could be a drawback in the mechanical and barrier properties due to the immiscibility of some of them. Additionally, the exploitation of some underuse food crops can be beneficial for the economy of small farmers (Tapia-Blacido *et al.*, 2007).

Unripe plantain flour presents high starch and non-starch polysaccharides content (Ovando-Martinez *et al.*, 2009), which can produce functional properties to films elaborated from this flour (De la Rosa-Millan *et al.*, 2014). Films made from biopolymers present

\* Autor para la correspondencia. E-mail: labellop@ipn.mx

poor mechanical and barrier properties that can be improved with the use of reinforcement materials such as sodium montmorillonite (MMT) (Kampeerapappun *et al.*, 2007). The laminate structure of MMT allows diffusion through the polymeric matrix, improving the properties of the film. Interactions between MMT and film matrix can be obtained due to the formation of new hydrogen bonds (Chiou *et al.*, 2005). Also, MMT presents high interfacial area that modifies the molecular mobility of the films components with the consequent change in the mechanical, barrier and thermal properties (Kampeerapappun *et al.*, 2007). Composites elaborated with biopolymers to different end-use are frequently stored, promoting re-association of the macromolecules. Re-association can be produced at different rate and depends of intrinsic factors (amylopectin structure), starch concentration, pH, and other components present in the composite such as proteins, lipids and plasticizer (Famá *et al.*, 2007).

In a previous study of films elaborated either with unripe plantain flour or rice flour, the combinations of high MMT concentration and low glycerol concentration produced high stiffness and consequently better mechanical properties. Also, the addition of MMT to the films of unripe plantain flour and rice flour increased tensile strength and elongation percentage, respectively (Rodríguez-Marín *et al.*, 2013b). However, the effect of storage time was not evaluated. The aim of this study was to evaluate the effect of storage time on structural characteristics and mechanical properties of films elaborated with unripe plantain and rice flours.

## 2 Materials and methods

### 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 (Cauatla, State of Morelos, Mexico), and rice (A-98 variety) was purchased from Molino de Arroz Buenavista (Cauatla, State of Morelos, Mexico). A description of the flour obtaining process can be found in Rodríguez-Marín *et al.* (2013a). Sodium MMT was a product obtained from Sigma-Aldrich Corp. (St Louis MO). All chemicals used were of analytical grade.

### 2.2 Modification of the MMT

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. In this regard, the MMT was modified using a mixture (2:1) of citric acid and sulfuric acid following the method described by Rodríguez-Marín *et al.* (2013a).

### 2.3 Preparation of nanocomposites films

In a previous work (Rodríguez-Marín *et al.*, 2013a), surface response method was used to optimize the component fractions of edible films made of flour, MMT and glycerol. While the addition of MMT promoted the film stability, its excess content can lead to breakable material. The surface response method provided a procedure for choosing adequate amounts of the film components in order to maximize stability in the face of storage conditions. This work departs from our previous report by considering the optimal film formulations already obtained.

The nanocomposite films were prepared by means of the casting method. 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 nanoclay (5% of flour mass or 0.1g) was dispersed at room temperature in 40 mL distilled water and sonicated (Bransonic, ultrasonic cleaner, 2510R-MTH, Danbury, CT, USA) for 30 min. Afterwards, modified nanoclay dispersion was added into the flour suspension at 70° C, held at this temperature for 10 min, heated to 85 °C for 15 min to complete starch gelatinization and incubated in an oven at 35 °C for 24 h. The dried films were peeled off for analysis.

### 2.4 Methods for films characterization

The films were conditioned at 57% relative humidity (RH) for 48 h. Films were immediately analyzed and other films were stored at room temperature for 90 days to evaluate the effect of storage time on mechanical properties and X-ray diffraction pattern. The tensile test was performed using a texture analyzer (Stable Micro Systems, Ltd in Godalming, Surrey England, model TAXT2i) and an A/TG tensile grips

system, according to the standard method ASTM-882-95. XRD analyses were performed to the MMT and the nanocomposite films. The X-ray diffractometer from Bruker advance D8 (model 2100, Amsterdam, Netherlands) was equipped with  $\text{CuK}\alpha$  radiation (35 kV,  $\lambda = 0.154$  nm). The samples were scanned at  $1^\circ/\text{min}$  in the  $2\theta$  range of  $3\text{--}70^\circ$ .

## 2.5 Statistical analysis

One-way analysis of variance (ANOVA) was applied to analyze the data using Sigma-Stat program (SYSTAT software, Chicago, IL, USA). Mean comparisons were conducted using the Tukey's test at a significance level of 5%.

## 3 Results and discussion

### 3.1 X-ray diffraction

Recrystallization of starch molecules in the films due to storage time was analyzed by the changes in the X-ray diffraction pattern. Unripe plantain flour films with glycerol and MMT recently elaborated (0 days) and stored for 90 days (Figure 1) showed similar X-ray diffraction patterns, mainly amorphous patterns

because one peak at  $2\theta = 17.3^\circ$  was observed. The amorphous pattern in the recently elaborated film is due to starch granule disorganization. After storage for 90 days, no appreciable changes in the X-ray diffraction pattern were found, indicating that the plasticizer (glycerol) reduced the reorganization of the starch components (retrogradation) (Ma *et al.*, 2006).

During film elaboration, glycerol penetrates (due to its small size) to the starch chains, avoiding their association by intra- and inter- hydrogen bonds. Hydrogen bonds between glycerol and starch chains hinder reorganization of starch chains during storage and consequently the recrystallization (Chen and Evans, 2005). Similar patterns were previously found in fresh starch films with glycerol where the plasticizer retarded or avoided reorganization of starch chains (Van Soest *et al.*, 1996; Ma *et al.*, 2006; Mali *et al.*, 2002; Chung *et al.*, 2010). This pattern above mentioned depends of starch source, plasticizer type and process to make the film (extrusion or casting). In films elaborated with flours (rich in starch) the presence of other macromolecules such as proteins, lipids and non-starch polysaccharides can avoid or retard starch chain reorganization. When starch chain reorganization is avoided or retarded during storage the film maintains the initial characteristics (mechanical and barrier properties).

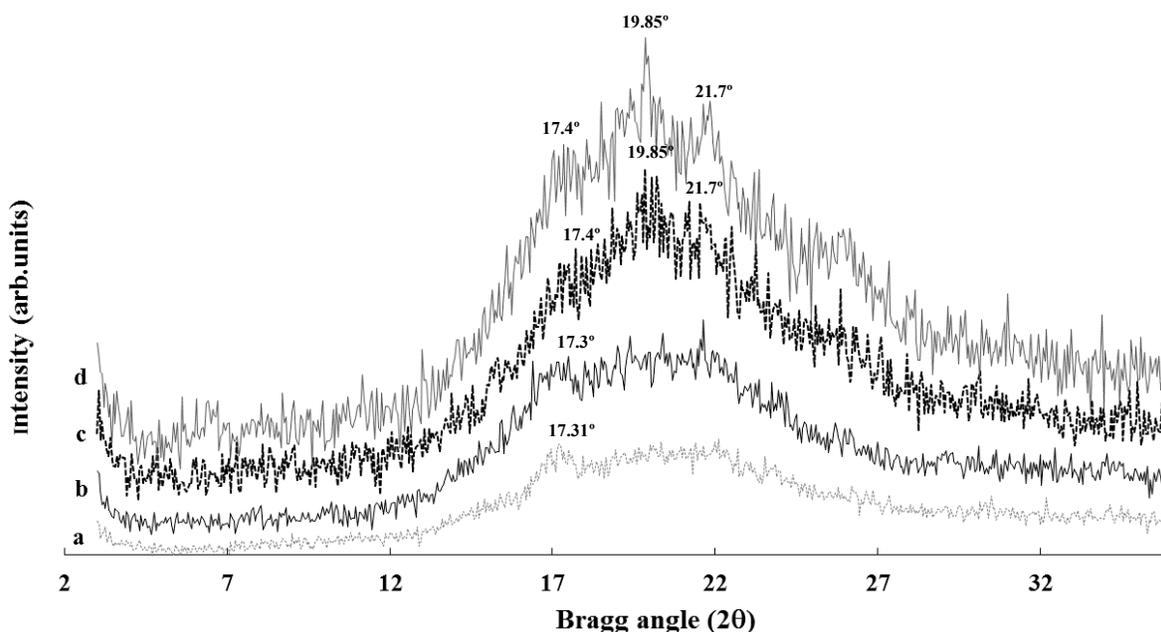


Fig. 1. X-ray diffraction pattern of nanocomposite films based on unripe banana flour for different storage time: a) 0 days without montmorillonite (MMT), b) 90 days without MMT, c) 0 days with MMT, d) 90 days with MMT.

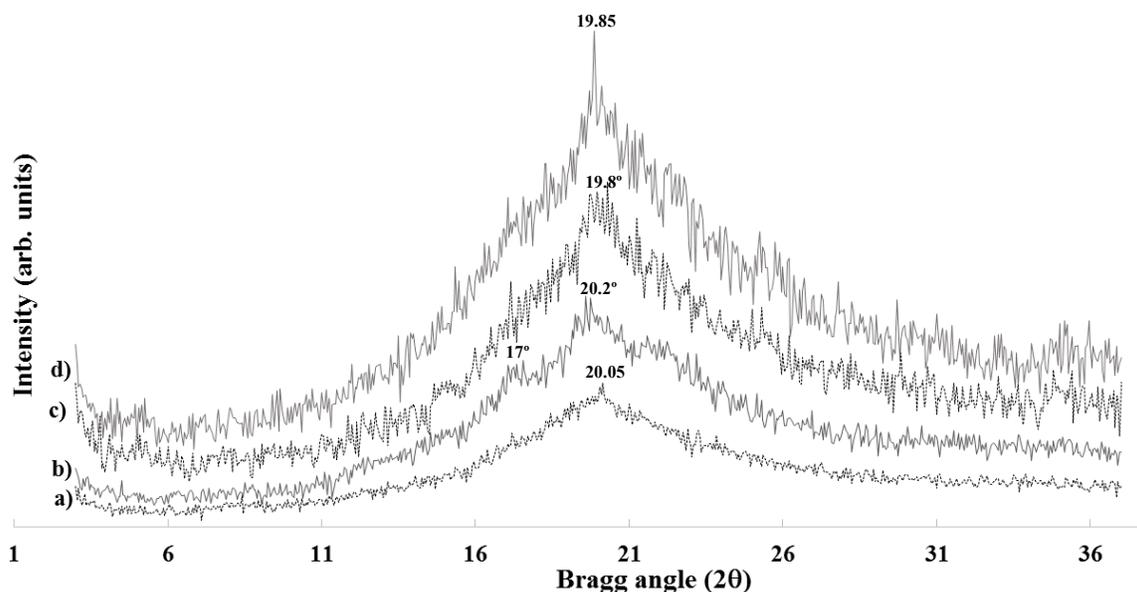


Fig. 2. X-ray diffraction pattern of nanocomposite films based on rice flour for different storage time: a) 0 days without montmorillonite (MMT), b) 90 days without MMT, c) 0 days with MMT, d) 90 days with MMT.

Unripe plantain flour film with MMT showed X-ray diffraction peaks at  $2\theta = 17.4^\circ$ ,  $19.85^\circ$  and  $21.7^\circ$  (Figure 1c and 1d). The presence of MMT stimulates crystallization of starch chains even in the films without storage (immediately elaborated). This pattern could be caused by some particles of MMT that were not completely dispersed in the film matrix and some crystals. A slight increase in the crystallinity peaks was found in the films stored for 90 days. This pattern can be explained from small crystals present in the film without storage that play the role of nucleation sites. However, glycerol restricted the crystallite growing. The intercalated structure in the MMT and the plasticizer can interfere in the structural re-arrangement of starch chains (Chung *et al.*, 2010). Potato starch films with nanoclay and glycerol and stored for 80 days presented similar behavior (Chen and Evans, 2005).

Rice flour film without storage showed an amorphous pattern (Figure 2a) with a small crystallinity peak at  $2\theta = 20^\circ$ , which increased with storage (Figure 2b) and other peak was produced ( $2\theta = 17^\circ$ ). The difference between unripe plantain and rice flour film is related to starch structure (Espinosa-Solis *et al.*, 2009; Palma-Rodríguez *et al.*, 2012). Rice flour film with MMT and no storage showed the peak at

$2\theta = 20^\circ$ , which is slightly higher than its counterpart without MMT. This result indicates the presence of some remnant crystals by the incomplete dispersion of MMT particles. Rice flour film without MMT and stored showed increase in the peak at  $2\theta = 20^\circ$ , indicating perfection of remnant crystals, but without appreciable growing.

The moisture content of films decreased during storage, which can be due to Van der Waals interactions between starch and other macromolecules of the flour (e.g., proteins), promoting or inducing that re-crystallization rate of starch components (amylose and amylopectin) increase (Bello-Perez *et al.*, 2005). In turn, this produced a slow formation and/or growing of crystallites (Galdeano *et al.*, 2009). It has been reported that under storage conditions interactions protein-starch in the flour provoked slow re-crystallization process (Wu *et al.*, 2010).

### 3.2 Effect of storage time on mechanical properties

Unripe plantain flour film without storage presented higher tensile at break (TB) than its rice flour film counterpart.

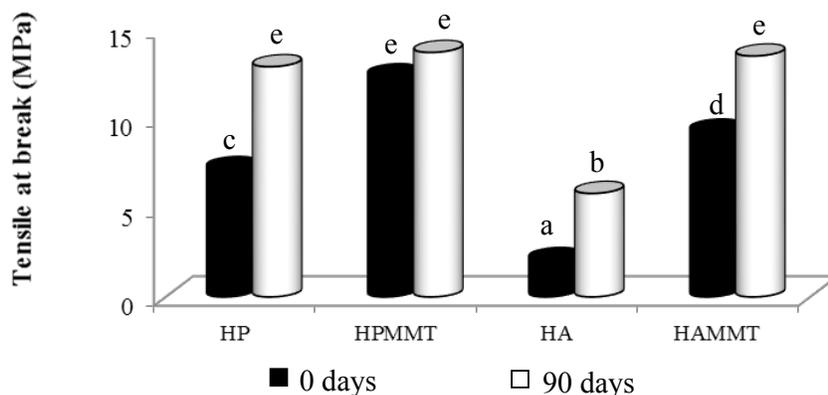


Fig. 3. Tensile at break (TB) after 90 days of storage time for films made of unripe banana flour without montmorillonite (MMT) (HP), unripe banana flour with MMT (HPMMT), rice flour without MMT (HA) and rice flour with MMT (HAMMT). Data were obtained from the average of 10 measurements  $\pm$  standard error. Same letters indicate no significant differences with  $p < 0.050$ .

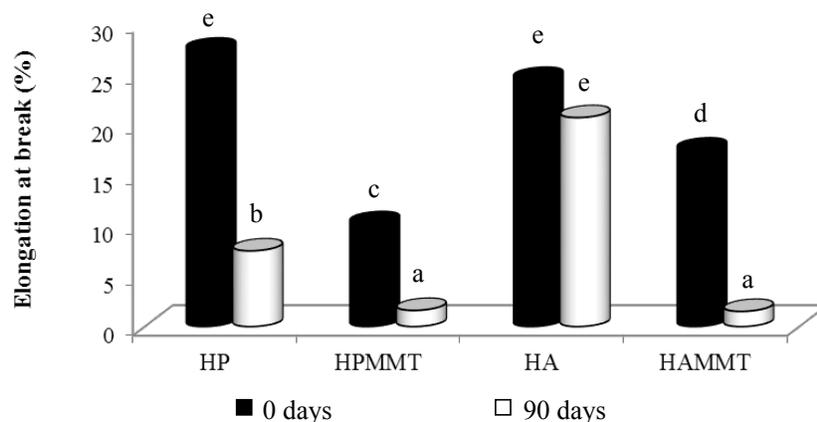


Fig. 4. Elongation ( $\epsilon$ ) after 90 days of storage time for films made of unripe banana flour without montmorillonite (MMT) (HP), unripe banana flour with MMT (HPMMT), rice flour without MMT (HA) and rice flour with MMT (HAMMT). Data were obtained from the average of 10 measurements  $\pm$  standard error. Same letters indicate no significant differences with  $p < 0.050$ .

This pattern is related to the starch type in the flours (Figure 3), with Type A crystallinity for rice starch and Type B crystallinity for unripe banana starch. Storage produced an increase in the TS value in both films (unripe plantain and rice flours). This pattern is due to re-arrangement of starch in the film matrix as was observed by X-ray diffraction B.

The addition of MMT in the non-stored films increased the TB value due to interfacial interaction between polymeric matrix and the silicate layers of MMT. This interaction is induced by the high surface area exposed by the MMT (Cyras *et al.*, 2008). The effect of addition of MMT on TB value was higher

in rice flour film. This effect can be related to the smaller size and lower amylose content of starch rice than plantain starch (Espinosa-Solis *et al.*, 2009; Palma-Rodríguez *et al.*, 2012). Stored unripe plantain flour film showed a TB value similar to non-stored counterpart. This figure is related to starch chains reorganization that agrees with the X-ray diffraction pattern. Stored rice flour film presented a slight increase in the TB value, indicating that remnant crystallites in the film were perfected during storage, which agrees with the decrease in moisture content of the film in storage (Famá *et al.*, 2007). The water in the films work as plasticizer; high water content

in the film produced weakness of interactions among starch chains and more fragile materials are obtained; similar behavior is produced with low water content (Van Soest *et al.*, 1996).

Fresh films (non-stored) of both flours showed similar  $\varepsilon$  (%) value (Figure 4). Stored films of unripe plantain flour presented a reduction in  $\varepsilon$  value compared with its non-stored counterpart, although the rice flour did not exhibit this effect. The decrease in  $\varepsilon$  value indicates a more rigid film. The addition of MMT produced a decrease in the  $\varepsilon$  value in the non-stored film compared with its counterpart without MMT. Reinforcement of the film with addition of MMT was due to the nanoclay was distributed inside the polymeric matrix. Stored films with MMT presented lowest E value due to reorganization of starch chains.

## Conclusions

Storage of the films produced structural changes as revealed by X-ray diffraction. Such effects were caused by the reorganization of starch chains. Addition of MMT to filmogenic solution left some crystalline zones in the starch that were perfected during storage. Storage time increased tensile strength and decrease  $\varepsilon$  value. Addition of MMT did not modify the tensile strength value in unripe plantain flour film, but a slight increase was found in the rice flour film. Stored films with MMT showed the lowest  $\varepsilon$  values.

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## Nomenclature

$2\theta$  diffraction angle  
 $\lambda$  wavelength

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