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Development of biodegradable films based on blue corn flour with potential applications in food packaging. Effects of plasticizers on mechanical, thermal, and microstructural properties of flour films

Andrea Carolina Valderrama Solano [a], Cecilia Rojas de Gante [b,*]

[a] Tecnológico de Monterrey, Campus Monterrey, Centro de Biotecnología FEMSA, Escuela de Biotecnología y Alimentos, Ave. Eugenio Garza Sada 2501 Sur, Col. Tecnológico C.P. 64849, Monterrey, Nuevo León, Mexico
[b] Tecnológico de Monterrey, Campus Ciudad de México, Centro de Biotecnología FEMSA, Departamento de Ingeniería en Biotecnología, Calle del Puente 222 Col, Ejidos de Huipulco, C.P. 14380 Tlalpan, México Distrito Federal, Mexico

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ABSTRACT

In the present study, blue corn flour films were developed. The cereal grain's total composition (excluding the pericarp) is used to obtain the films. The plasticizing effects of two different polyols such as glycerol and sorbitol on the mechanical, thermal, and microstructural properties of flour films were researched. The results showed that films plasticized with sorbitol had better mechanical properties and less affinity for water than those plasticized with glycerol. The sorbitol-plasticized films were more rigid and did not lose their integrity when immersed in water. The ATR-FTIR spectra of blue corn flour plasticizer with sorbitol showed the presence of the additional band at 1745 cm^{-1} characteristic of the vibrational carbonyl peak, which confirms the chemical linkages between sorbitol and a polymeric matrix. The effect of the plasticizer on the glass transition temperature (T_g) was characterized using differential scanning calorimetry (DSC). T_g decreased as the plasticizer content increased. Plasticized glycerol films showed lower T_g values than those with sorbitol. SEM observations showed that it was necessary to add plasticizer to maintain film integrity. The sorbitol-plasticized flour films revealed better adhesion between phases, and these films showed a compact structure.

1. Introduction

Over the last few years, materials made from renewable and natural polymers such as polysaccharides, proteins, and lipids have received increasing attention from researchers and industry. These materials have several applications as interesting alternatives to food packaging (Tharanathan, 2003) and these materials have revealed promising properties envisaging their use in a wide range of biomedical applications (Malafaya et al., 2007). While the properties of synthetic polymers are limited, natural polymers provide many important benefits, including degradability, biocompatibility, and biological stability (Grenha et al., 2010). Thus, there is continuous ongoing research on natural materials with particularly desirable properties that can be used for many specific applications.

Several studies reported using proteins and polysaccharides from different sources to develop biodegradable films with different properties and have denoted that these biopolymers as promising materials in this regard. The important functional property of proteins and polysaccharides is their ability to form films in the presence of plasticizers (Mali et al., 2005). One of the main disadvantages of biodegradable polymers obtained naturally, particularly starch, is their predominant hydrophilic nature, which results in inherently fast degradation rates, but in many cases, poor mechanical performance. These properties can be significantly improved, in many cases, by blending the natural polymers with other biodegradable synthetic or natural polymers. Various studies have attempted to improve the functional properties of these materials by using mixtures of starch and proteins (Corradini et al., 2007; Habeych et al., 2009), and some lipids have also been added to improve water vapor permeability (Colla et al., 2006).

To produce such films, researchers have commonly used extracted and purified biopolymers that are then mixed during film

Abbreviations: AACC, American Association of Cereal Chemistry; ASTM, American Society for Testing and Materials; ATR-FTIR, attenuated total reflectance spectroscopy analysis; DSC, differential scanning calorimetry; K-TSTA, total starch assay kit; K-AMYL, amylosa/amylopectin assay kit; MC, moisture content; OH, hydroxyl group; RH, relative humidity; SEM, scanning electron microscopy; T_g, glass transition temperature; *v*, volume.

* Corresponding author. Tel.: +52 55 54832020; fax: +52 55 54832282.
E-mail address: crd@itesm.mx (C. Rojas de Gante).

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formation. Another attractive alternative is the use of flours prepared from agricultural crops, which are natural complex blends of starch, protein, and lipids. Schause-Purin (2002) developed biodegradable films from sorghum flour, Tapia-Blácido et al. (2005) and Colla et al. (2006) used amaranth flour, Tinoco-Pérez (2007) used blue corn flour and more recently, Dias et al. (2010) used rice flour and Pelissari et al. (2013) used flour from plantain bananas as the raw materials for producing biodegradable films. The use of natural blends directly obtained from agricultural sources takes advantage of each component in the original system and appears to be a new opportunity for developed new materials in the area of biodegradable films (Schause-Purin, 2002; Tapia-Blácido et al., 2005).

The increased demands placed on materials for both currently approved and novel emerging applications continues to stimulate interest in improving the performance of existing polymers for food packaging and in developing new polymeric systems. Blue corn (*Zea mays* L.) flour can be considered an interesting source of raw material for this application. Besides its advantages in terms of sustainability, the interest in using this source to produce materials is adding value to traditional crops and products. Blue corn varieties represent a niche market due to their low level of commercial exploitation and higher price. Blue corn has been utilized in Mexico for human consumption for centuries. The chemical composition of blue corn has been noted as superior in certain phytochemicals and minerals when compared to yellow and white corn genotypes (Ultrilla-Coello et al., 2009). The protein present in the endosperm consisted of 8.3% for the blue corn genotypes while the white genotype contains approximately 7.5%. Apparent amylose content ranges from 23.1% to 26.3% for blue corn and white corn, respectively. Starch content is 84.1% for the blue corn genotype and 78.7% for the white corn (Ultrilla-Coello et al., 2009). These confirm that the blue corn is an important source of biopolymers with excellent filmogenic properties, particularly, proteins and starches.

Blue corn polymers can be employed for biodegradable and edible packaging due to their excellent antioxidant properties and the added value of oxidation protection for the food they contain. Rojas de Gante et al. (2010) developed flexible blue corn flour films using glycerol as a plasticizer (0.3 g/g of dry flour). The films showed interesting mechanical properties (tensile strength between 0.17 to 0.28 MPa and 22% to 33% of elongation at break) with potential applications in food packaging with intermediate water activity; they also showed that blue corn flour materials can also control the release of bioactive molecules (Tinoco-Pérez, 2007). However, these films had inferior mechanical properties with respect to other films made from the flour of other plant species and when these films were used as packaging for foods with high water activity, the materials exhibited high water absorption and caused food dehydration, food texture changes, and a loss of the packaging's structural integrity.

The purpose of this research was to study the possibility of using blue corn flour films with suitable properties as material for food packaging. The aim of the present work focused both on improving the mechanical properties as well as improving the water resistance of blue corn flour films by using glycerol and sorbitol as plasticizers. This preliminary report presents the mechanical and thermal properties and the characterization of the corn flour film's microstructure and the influence of plasticizer on these properties.

2. Materials and methods

2.1. Materials

Commercially-available blue corn (*Zea mays* L.) kernels were utilized in this research. The kernels were obtained from Guanajato (Mexico). The blue corn flour was obtained according to the methodology described by Rojas de Gante et al. (2010). The obtained flour was passed through a 150-mesh sieve to standardize the final granulometry and stored at 5 °C in sealed containers until it was used. The glycerol and sorbitol used were of reagent grade.

2.2. Chemical analysis

The water content, ash, protein, and fat of the blue maize flour samples, were analyzed according to respectively AACC (2000) methods 44-15A, 08-01, 46-13, and 30-25. The total starch content and amylose/amylopectin relation were determined using the commercial Megazyme kit (K-TSTA and K-AMYL, Megazyme International Ltd., Ireland).

2.3. Film development

The flour-based films were developed using the casting method described by Rojas de Gante et al. (2010). An important technical advantage is that this method avoids the process of purifying proteins and starches from cereals. Therefore, the cereal grain's total composition (excluding the pericarp) is used to obtain the film. Glycerol and sorbitol were used as plasticizers at concentrations of 0.3, 0.35, and 0.40 g/g of dry flour. The procedure was realized as follows: Initially, 50 ml of ethanol solution (70% v/v) containing 3 g of blue corn flour was prepared. This dispersion was maintained 20 min at 82 °C ± 2 °C under magnetic stirring to dissolve the protein. After that, hot distilled water (50 ml 89 °C ± 1 °C) was added, it gelatinized at 89 °C ± 2 °C for 20 min under magnetic stirring, and finally the plasticizer was added. When the filmogenic solution temperature was around 65 °C, solution was poured on plastic Petri dishes (10 cm diameter). For each film, 35 ml of the filmogenic solution was used. The films were dried at 65 °C in an oven and 55% relative humidity (RH) to a final water content that allowed for easy peeling from the plates. All the films were preconditioned for at least 48 h in desiccators containing a saturated solution of Mg $(NO_3)_2$ (53 ± 1% RH) prior to the characterization. An average of 10 measurements were taken at different points on the film sample using a digital micrometer (Digimatic Outside Micrometer Mitutoyo, Japan) to measure the thickness of the sample.

2.4. Film characterization

2.4.1. Tensile properties of the films

A standard method D882-02 (ASTM, 2002) was used to measure the tensile properties of the films. Films were cut into strips with a test dimension of 66 × 16 mm. All films were conditioned for 48 h at 23 ± 2 °C and 50 ± 2% RH before testing. The strips were mounted on a TA.XT2i texture analyzer (SMS, Surrey, U.K.) with a 5 kg load cell. The initial gauge length was set to 40 mm and films were stretched using a crosshead speed of 2 mm/min. The parameters of tensile strength and elongation at break were determined. Measurements were performed on five replicates.

2.4.2. Moisture content (MC) and water stability of films

The water content of the films was calculated according to AACC (2000) method 44-15A after being stored at controlled relative humidity (50 ± 2% RH). Water stability was measured as the percentage of the film's dry matter solubilized in water during a period of 24 h. Films with and without plasticizer were analyzed. The initial dry matter of each film was obtained after drying film specimens in desiccators containing P_2O_5 for a week. Samples (2 cm diameter) were weighed and immersed in 20 ml of distilled water at 23 ± 2 °C, sealed, and periodically agitated. Films not solubilized in water were removed and dried to determine the weight of dry