International Food Research Journal 22(6): 2346-2351 (2015)
Journal homepage: *http://www.ifrj.upm.edu.my*

Influence of different starch sources and plasticizers on properties of biodegradable films

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Article history

Received: 11 June 2014
Received in revised form: 1 June 2015
Accepted: 11 June 2015

Keywords

Biodegradable polymers
Glycerol and sorbitol
Nanocomposites
Native starch renewable sources

Abstract

The concern with the accumulation of synthetic plastics in the environment is one of the reasons for the increasing interest in the development of biodegradable films. Among raw materials from renewable sources, starch is one of the most promising. In order to evaluate biodegradable films obtained from native starches (rice, potato and cassava), these were prepared by casting method with the addition of plasticizers (glycerol and sorbitol) and Montmorillonite clay (MMT). Thickness, mechanical properties and water solubility were evaluated. The rice starch and glycerol films were more flexible (elongation at break between 108 and 113%) and with a water solubility value between 18 and 24%, enabling their use as food packaging.

Introduction

The food industry is one of the major consumers of packaging, being responsible for consuming more than half of this segment market (Corradini *et al*., 2013). The food packaging is responsible for preserving the quality of food from its production until consumption. Synthetic polymers are the most used materials and the environmental impacts caused by its accumulation in the environment are reasons for growing interest and investment of researchers in the development of alternatives to minimize these problems (Ozcalik and Tihminlioglu, 2013). Biodegradable polymers are produced from natural and renewable raw materials therefore are easily decomposed in the environment, being an interesting alternative for the replacement of synthetic polymers. In addition, biodegradable films are a way of harnessing and adding value to waste materials in the food industry. Accordingly, the use of these raw materials, such as polysaccharides, proteins and lipids, has been growing in recent years (Masclaux *et al*., 2010; Yoon *et al*., 2012).

Starch is one of the most studied biodegradable polymers for film production for being abundantly present in nature as a reserve carbohydrate in most plants, and due to its low cost (Toral *et al*., 2002; Faria *et al*., 2012). This polymer consists essentially of amylose and amylopectin, and their applications are determined based on the proportions of these two macromolecules, which are dependent on their concentrations in starch (Toral *et al*., 2002). Starch may be obtained from various vegetable sources such as grains, roots and tubers, and also in fruits and vegetables, however, extraction of starch in a commercial level is restricted to cereals, roots and tubers (Young, 1984).

The use of starch in the preparation of biodegradable polymers is based on chemical, physical and functional properties of amylose to form gels and films (Young, 1984). When in solution, the amylose molecules tend to align themselves in parallel due to their linearity, get close enough that hydrogen bonds are formed between the adjacent hydroxyl polymers. Accordingly, the affinity of the polymer for water is reduced, which promotes the formation of opaque pastes and resistant films (Wurzburg, 1986).

The starch films have some disadvantages such as strong hydrophilic behavior, which makes these materials sensitive to contact with water, and inferior mechanical properties when compared to

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conventional plastic films due to low flexibility, yielding brittle materials (Avella *et al.*, 2005; Faria *et al*., 2012). In this sense, the addition of compounds such as nanoclays and plasticizers which, through intermolecular interactions with the polymer matrix, improves the characteristics and properties of films (Dean *et al*., 2011).

Clays such as Montmorillonite (MMT) are composed of silicate layers and when added to a polymer matrix can improve the mechanical, barrier, thermal, optical and transparency properties (Ray and Bousmina, 2005; Paiva *et al*., 2006). The plasticizers are added to the films in order to alleviate the rigidity making them more handleable, less brittle and more flexible (Vieira *et al*., 2011). The interaction between the plasticizer and starch occurs through hydrogen bonds and is affected by molecular size, configuration and total number of functional hydroxyl groups of the plasticizer, as well as its compatibility with the polymer (Yang and Paulson, 2000).

The starch, plasticizer and clay types as well as the proportions of each component present and the process conditions for obtaining the films are important because they determine the intermolecular interactions that occurred and their effects on the characteristics of the films. Given the above, the aim of this study was to develop and evaluate the physical properties of films of different native starches added with plasticizers (glycerol and sorbitol) and Montmorillonite clay.

Materials and Methods

Material

To obtain the starch, the raw materials used were potatoes *(Solanum tuberosum)*, cassava *(Manihot esculenta)* and rice (*Oryza sativa* L.). These were purchased at a local market in Rio Grande (RS). The organophilic clay used was Montmorillonite K10 (Sigma- Aldrich) with a particle size of 100 nm. The plasticizers used were glycerol (Vetec, Química Fina) and sorbitol (Vetec, Química Fina).

Extraction of potato and cassava starch

The extraction of potato and cassava starches was performed according to changes in the method described by Alvani *et al.* (2011). The vegetables were ground together with distilled water in a proportion of 1:1.5 (w/v). After filtration, the supernatant containing the starch was centrifuged at 2000 x g (Hitachi CT6EL, Taiwan) for 20 min, repeating this operation after successive washings of the precipitate with distilled water. The starch was dried at 40°C in an oven with forced air circulation (Fanem 520, Brazil).

Extraction of rice starch

The rice starch was extracted by alkaline extraction according to the method described by Wang and Wang (2004). The rice was milled in a knife mill, allowed to stand for 18 h immersed in 0.1% NaOH solution (1:2 w/v). Its particle size was then standardized in a 63 µm sieve (250 mesh) and the filtrate was centrifuged at 1400 x g (Hitachi CT6EL, Taiwan) for 10 min. The precipitate was resuspended in an equal volume of 0.1% NaOH solution and with repetition of the centrifugation operation under the same conditions. The precipitated starch was resuspended in distilled water, and the solution neutralized to pH 6.5 with 0.1 N HCl and then centrifuged again under the same conditions. Later on, the starch was washed with distilled water and again centrifuged with 2 repetitions of this operation. The starch was dried at 40°C in an oven with air circulation (Fanem 520, Brazil).

Preparation of the films

The films were prepared using the casting technique, with modifications to the method described by Majdzadeh-Ardakani *et al.* (2010). The starch (3% w/v) was dispersed in distilled water and the dispersion heated to 80°C under constant agitation (700 rpm) with propeller stirrer (Fisatom 713D, Brazil). The Montmorillonite clay (0.5 w/v) was vigorously stirred in a homogenizer (IKA Ultra-Turrax T25D, Germany) at 10000 rpm for 20 min. Subsequently, the nanoclay dispersion was added to the starch dispersion under heating, and this was maintained for 20 min, and later the plasticizer previously dissolved in distilled water was added (25% w/w starch) previously, maintaining the heating for 20 min longer. The solutions were then poured into acrylic plates (Ø = 9 cm) and dried at 40°C (Fanem 520, Brazil) until complete evaporation of the excess of water. To evaluate the influence of thickness, different volumes of film solution were used for the formation of the films (8, 10 and 12 mL/plate). The dried films were kept in an environment with controlled humidity (32%) for 24 h for further analysis.

Physical determinations in the films

Thickness

The thickness (mm) of the films was determined with a digital micrometer (Insize IP54, Brazil), from the average of 10 measurements at different points of the film.

Mechanical properties

The tensile strength and elongation at break were determined in texturometer (TA.XT plus Texture Analyser, UK) according to the official methodology (25°C, initial separation from the clutches = 50 mm and claw speed = 120 mm.min^{-1}) (ASTM, 2001). To determine the values of tensile strength (MPa) Equation 1 was used, where F is the force (N) and A is the area (m^2). To calculate the elongation at break (%) Equation 2 was used, where df (mm) represents the final distance of the stretching of the film, and dig (mm) is the initial distance between the claws (50 mm).

$$TS = \frac{F}{A} \qquad (1)$$

$$EB = \frac{d_f}{d_{ig}} \cdot 100 \qquad (2)$$

Solubility

For the determination of water solubility, the method described by Fakhouri *et al.* (2007) was used. The films were cut into standard size discs (2 cm diameter) and taken in a stove at 105°C for the determination of initial dry matter. Later, these were placed in containers with 50 mL of distilled water and kept at 25°C for 24 h under stirring at 100 rpm using an incubator shaker (CT-Cientec 712RNT, Brazil). After this period the samples were removed and dried at 105°C for determination of the dry matter that was not dissolved. For the calculation of the values, Equation 3 was used, where the solubility S (%) relates the initial difference in dry mass mi (g) and final dry mass mf (g) with the initial dry mass mi (g).

$$SA = \frac{m_i - m_f}{m_i} \cdot 100 \qquad (3)$$

Statistical analysis

The effects caused by the use of different native starches on properties of the films were evaluated by analysis of variance (ANOVA), and the Tukey test was used at $p < 0.05$ to verify the significant differences between the values.

Results and Discussion

Thickness

Thickness of the films prepared ranged from 0.06 to 0.08 mm (Figure 1), with no differences between the means obtained with the different plasticizers. From Figure 1, it is also observed that thicker films were obtained when were prepared films with a greater volume of film solution. Thickness is an important physical characteristic of the films since to be used as packaging the type, volume and weight of the food to be packaged are considered (Embuscado and Huber, 2009). Moreover, the thickness is important to evaluate the homogeneity of the film and it is also related with the strength and barrier properties. Thickness variations cause problems on the mechanical performance of the films and variations in the barrier properties (Oliveira *et al.*, 1996).

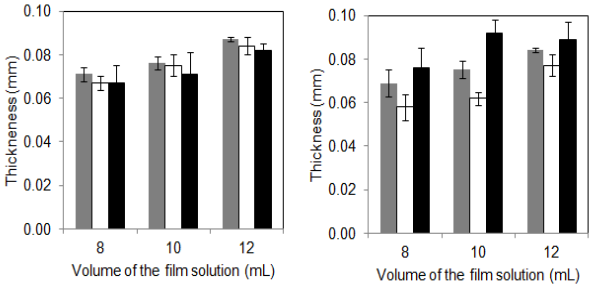


Figure 1. Film thickness of native starch and: (a) glycerol and (b) sorbitol. Gray column: Rice starch, white column: potato starch, black column: cassava starch

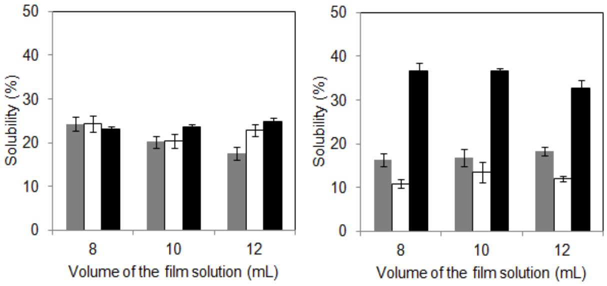


Figure 2. Solubility in water of native starch films and: (a) glycerol and (b) sorbitol. Gray column: Rice starch, white column: potato starch, black column: cassava starch

Solubility

The water solubility of the films is shown in the graphs illustrated in Figure 2. For those films prepared using glycerol as plasticizer, water solubility ranged between 18 and 25%, with little variation when compared to the films of the various starches and various volumes of the film solution. On the other hand, films prepared with sorbitol, those obtained from cassava starch showed to be considerably more soluble than others, with this figure reaching a maximum of 37%. This result may have been due to phase separation and crystallization of sorbitol by making the film more soluble. Although glycerol and sorbitol are alcohols, the difference in the properties of the films is due to their structural characteristics, resulting in different types of interaction with the polymer matrix.

The molecule of sorbitol is formed by a chain of six carbon atoms, which makes its insertion between

Table 1. Film properties of different starches with glycerol and nanoclay in different volumes of film solution

Volume	Properties	Rice starch	Potato starch	Cassava starch
8 mL	Tensile strength (MPa)	$1.0\pm{<}0.1^{c}$	9.9 ± 1.1^{a}	3.1 ± 0.1^{b}
	Elongation at break (%)	112.8 ± 6.9^{a}	1.8 ± 0.3^{b}	3.0 ± 0.8^{b}
10 mL	Tensile strength (MPa)	1.2 ± 0.9^{c}	8.0 ± 0.7^{a}	3.2 ± 0.2^{b}
	Elongation at break (%)	118.1 ± 2.6^{a}	2.9 ± 0.5^{b}	3.9 ± 1.1^{b}
12 mL	Tensile strength (MPa)	1.2 ± 0.2^{c}	11.0 ± 1.0^{a}	4.4 ± 0.3^{b}
	Elongation at break (%)	108.0 ± 7.1^{a}	2.0 ± 0.2^{b}	4.9 ± 0.9^{b}

Same superscript letters in the same row indicate that the results are not significantly different ($p \leq 0.05$, Tukey test).

Table 2. Film properties of different starches with sorbitol and nanoclay in different volumes of film solution

Volume	Properties	Rice starch	Potato starch	Cassava starch
8 mL	Tensile strength (MPa)	11.2 ± 1.1^{ab}	12.7 ± 0.6^{a}	10.1 ± 0.4^{b}
	Elongation at break (%)	$0.4\pm{<}0.1^{b}$	1.4 ± 0.1^{a}	0.5 ± 0.1^{b}
10 mL	Tensile strength (MPa)	13.5 ± 1.0^{ab}	12.7 ± 1.8^{b}	15.9 ± 0.7^{a}
	Elongation at break (%)	1.0 ± 0.3^{a}	1.3 ± 0.5^{a}	1.5 ± 0.1^{a}
12 mL	Tensile strength (MPa)	16.5 ± 5.2^{a}	23.7 ± 3.5^{a}	20.5 ± 0.3^{a}
	Elongation at break (%)	1.3 ± 0.5^{b}	2.5 ± 0.3^{a}	1.7 ± 0.1^{ab}

Same superscript letters in the same row indicate that the results are not significantly different ($p \leq 0.05$, Tukey test).

chains of polymers difficult. While the glycerol contains only three carbon atoms bonded together, with lower molecular weight and being more easily inserted and positioned within the three-dimensional polymer network, which results in higher mobility of the chains of the film-forming matrix, higher water absorption capacity and therefore a more effective plasticizing effect (Yang and Paulson, 2000; Shimazu *et al*., 2007).

When using sorbitol as a plasticizer it was also verified that there was a difference in solubility of the films prepared with different starches, mainly potato and rice starch as compared to cassava starch. This difference may be due to interactions between the starch and plasticizer, which vary according to the composition of the starch that is different for each vegetable source.

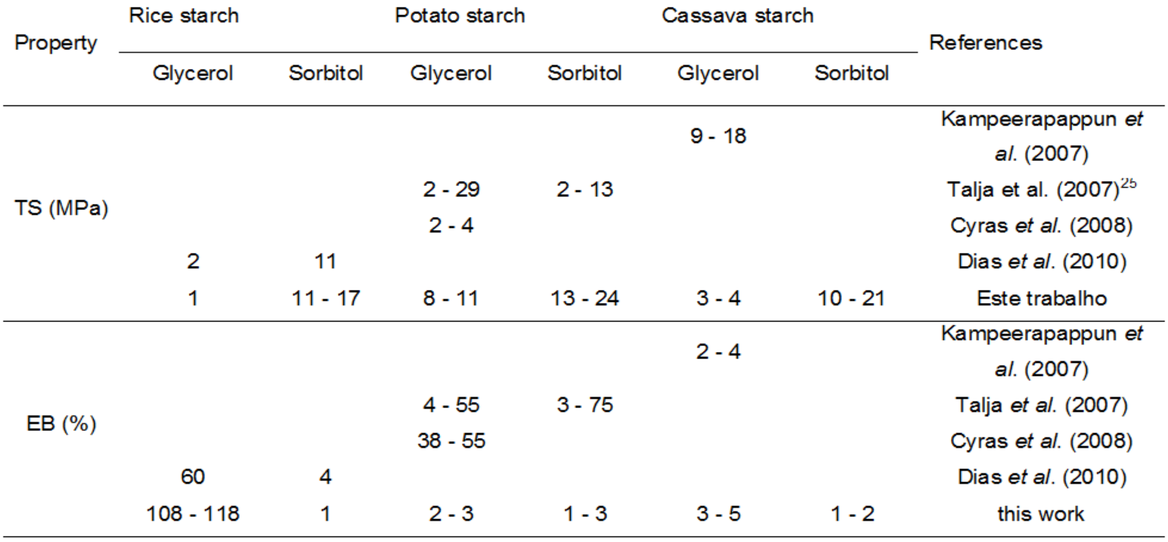
Mechanical properties

The rice starch films produced using glycerol as plasticizer (Table 1) showed tensile strength values lower than those produced with sorbitol (Table 2), and elongation at break values over 100 times higher. Higher values of tensile strength and lower elongation at break were also found for the films from potato and cassava starch when prepared with glycerol (Table 1). Due to the high tensile strength presented, the films with the use of sorbitol proved to be brittle and difficult to handle after drying. This behavior is explained by the structure of sorbitol, which due to the difficulty in interacting effectively between the polymer molecules, results in a reduced ability to disrupt the interactions that occurs in starch (Yang and Paulson, 2000). Furthermore, sorbitol has low affinity for water, a fact that also limits their ability to reduce the hydrogen bonds between starch chains compared to glycerol chains (Bourtoom, 2008).

This suggests that glycerol is the more suitable plasticizer for preparing starch films when compared to sorbitol. The better performance of glycerol in biodegradable films from starch is probably due to its small size, which allows it to exert a greater influence on the mechanical properties than the molecule of sorbitol. In addition, water acts as a plasticizer in starch-based materials, so due to the high glycerol moisture the films are also plasticized by water, explaining its lower tensile strength and greater elongation at break (Dias *et al.*, 2010). Data in the literature show inferior and superior values to those found in this study (Table 3).

In films prepared with glycerol and sorbitol, it is possible to note significant difference ($p < 0.05$) in the mechanical properties for the different starches. Depending on the characteristics of each starch (e.g.,

Table 3. Film properties from different starches and plasticizers



Property	Rice starch		Potato starch		Cassava starch		References
	Glycerol	Sorbitol	Glycerol	Sorbitol	Glycerol	Sorbitol	
TS (MPa)					9 - 18		Kampeerapappun *et al.* (2007)
			2 - 29	2 - 13			Talja et al. (2007)[25]
			2 - 4				Cyras *et al.* (2008)
	2	11					Dias *et al.* (2010)
	1	11 - 17	8 - 11	13 - 24	3 - 4	10 - 21	Este trabalho
EB (%)					2 - 4		Kampeerapappun *et al.* (2007)
			4 - 55	3 - 75			Talja *et al.* (2007)
			38 - 55				Cyras *et al.* (2008)
	60	4					Dias *et al.* (2010)
	108 - 118	1	2 - 3	1 - 3	3 - 5	1 - 2	this work

TS: tensile strength; EB: elongation at break

vegetal source, degree of maturity of the vegetal during the extraction of starch, purity of starch, amylose:amylopectin ratio), the interactions with the plasticizer occur differently, leading to variations in the properties of the films obtained from starches from different sources.

According to Vieira *et al.* (2011) the polymer-plasticizer interactions in the crystalline regions of amylose and amylopectin are similar and occur more slowly compared with the interactions occurring in the amorphous regions of amylopectin. The hydrogen bonds between the starch and plasticizer occur as the temperature is increased, both with the crystalline regions of amylose and amylopectin as well as with the amorphous region of amylopectin (Vieira *et al.*, 2011). Thus, variations in the proportions of amylose and amylopectin contents may be largely responsible for differences in the mechanical properties of the obtained films of rice starch (amylose: 15-25%; amylopectin: 75-85%), potato (amylose: 23%; amylopectin: 77%) and cassava (amylose: 16-20%; amylopectin: 80-84%) (Mali *et al.*, 2010).

Conclusion

The rice starch, for resulting in films with higher elongation values and low water solubility; and glycerol, for resulting in more flexible films, presented themselves as the most suitable starch and plasticizer for the preparation of films with potential for coating foods.

Acknowledgement

The authors of this study would like to thank the PDE - FURG (Institutional Program for Student Development) for fellowship support for this work.

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