FOOD PACKAGING AND SHELF LIFE 3 (2015) 1–8

Available online at www.sciencedirect.com

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Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches

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A R T I C L E I N F O

Article history:
Received 13 April 2014
Received in revised form 27 August 2014
Accepted 16 September 2014
Available online 29 October 2014

Keywords:
Biodegradable edible films
Cush-cush yam
Cassava
Cross-linking

A B S T R A C T

Edible, biodegradable films based on native and phosphated cush-cush yam and cassava starches plasticized with glycerol were developed by casting. The starches were chemically modified by cross-linking with sodium trimetaphosphate (STMP). The physicochemical properties of each of the different starch films were then evaluated and compared in order to determine their potential applications in the food industry. The amylose molecules in the cassava starch strongly interacted with glycerol resulting in an increase in the number of hydrogen bonds. This led to a slight shift upwards in the temperature required for the onset of the degradation of the cassava starch-based films, and even higher temperatures for degrading the films based on the modified starches. Films made from phosphated starches were more hydrophilic, producing an increase in solubility and crystallinity. Finally, the characteristics of the cassava films developed suggest that they would make good packaging materials, while films derived from cush-cush yam are more suitable as food coatings.

1. Introduction

The growing consumer demand for healthier products that do not cause environmental pollution has led to a change in the approaches used for the manufacture of materials by the food packaging industry. Most of the synthetic products currently used are not degradable and their cost is rising steadily as they are produced from non-renewable resources such as oil (Yang & Paulson, 2000).

In the last 30 years several studies on edible films derived from natural biodegradable polymers such as cellulose, chitosan and starch have been undertaken (Chillo et al., 2008; Famá, Goyanes, & Gerschenson, 2007; Famá, Rojas, Goyanes, & Gerschenson, 2005; Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007; Ghanbarzadeh, Almasi, Ali, & Entezami, 2010). In particular, starch has been the focus of a number of investigations due its biodegradable, renewable, inexpensive and edible nature as well as its wide availability (Lu, Tighzert, Berzin, & Rondot, 2005; Tharanathan, 2003).

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http://dx.doi.org/10.1016/j.fpsl.2014.09.002
2214-2894/

Molecularly, starch usually contains linear amylose and branched amylopectin. Although both components have the ability to form film, amylose is the most important (Romero-Bastidas et al., 2005). Starch from different sources has different amylose/amylopectin ratios, giving it specific properties depending on its origin (Famá, Bernal, & Goyanes, 2014; García, Famá, Dufresne, Aranguren, & Goyanes, 2009; Gutiérrez, Pérez, Guzmán, Tapia, & Famá, 2014; Krogars et al., 2003; Lawton, 1996).

Among the many naturally occurring starches, cush-cush yam (*Dioscorea trifida*) and cassava (*Manihot esculenta* C.) are very common in tropical latitudes and are used as food staples for some populations. A notable difference between these polysaccharides is their amylose content which is lower in cush-cush yam starches (Gutiérrez, Pérez, et al., 2014; Pérez et al., 2011). The molecular structure of native starches is often inefficient for the formation of films because of the invasive processes used in their extraction (Amani, Kamenan, Rolland-Sabaté, & Colonna, 2005; Bello-Pérez, Contreras, Romero, Solorza, & Jiménez, 2002; Kaur, Singh, & Singh, 2004). However, native cush-cush yam and cassava polysaccharides have shown promise for producing edible, biodegradable films (Gutiérrez, Pérez, et al., 2014; Pérez, Segovia, Tapia, & Schroeder, 2012). In addition, some native starch dispersions impart a cohesive rubbery texture to foods and are used as thickening agents (Wurzburg, 1986).

In order to overcome the limitations of native starches a number of techniques for their modification have been developed (Light, 1990; Swinkels, 1985, Chapter 8; Wurzburg & Szymanski, 1970). One common method is the cross-linking of the starch by phosphating which gives good results without generating large changes in its crystallinity or morphology (Matos & Pérez, 2003; Moorthy, 1994; Sívoli, 2009). This method can increase the tensile properties of starch films thus making them more adequate materials for, for example, food coatings (Hu, Chen, & Gao, 2009; Wurzburg, 1987). In addition, phosphating ensures that the films developed are actually edible and, consequently, considered safe by the FDA (2011).

Plasticizers are essential for the formation of many polysaccharide-based films and coatings (Krochta & De Mulder-Johnston, 1997). These components weaken the intermolecular interactions between adjacent polymer chains thus increasing film flexibility (Jongjareonrak, Benjakul, Visessanguan, Prodpran, & Tanaka, 2006; Sobral, dos Santos, & García, 2005).

One important and desirable feature of edible films and coatings is that they reduce moisture exchange between the product and its surrounding environment. The diffusivity and water solubility of these films are thus important characteristics which need to be controlled for their successful use as packaging materials (Gontard, Guilbert, & Cuq, 1993; Krochta, Baldwin, & Nísperos-Carriedo, 1994; McHugh & Krochta, 1994).

The aim of this study was to evaluate the stability, water content, water solubility and crystallinity of edible films prepared from cush-cush yam and cassava starches, and the effects of their modification by phosphating on these characteristics.

2. Experimental

2.1. Materials

Native starch was obtained from a variety of dark purple cush-cush yam (*D. trifida*) found in the Venezuelan Amazon (12 ± 3% apparent amylose) and from a variety of cassava (*M. esculenta* C.) (21 ± 3% apparent amylose) on sale at a local market in Caracas, Venezuela (Gutiérrez, Pérez, et al., 2014). The extraction of the starch from the cush-cush yam and cassava tubers was carried out using the methodology described by Pérez et al. (1993), obtaining in both cases a yield of approximately 30% (Gutiérrez, Pérez, et al., 2014). Modified starches were prepared from native starches by cross-linking (phosphating the starches). The apparent amylose content of the modified dark purple cush-cush yam starch and the cassava starch was ~11% and ~22%, respectively (Gutiérrez, Pérez, et al., 2014). The degrees of substitution (DS) of the starches were: 0.0006 ± 0.0002% and 0.017 ± 0.009% for native and modified dark purple cush-cush yam, respectively, and 0.0015 ± 0.002% and 0.008 ± 0.001% for native and modified cassava, respectively (Gutiérrez, Pérez, et al., 2014). Glycerol from Prolabo, Sweden was employed as a plasticizer.

2.2. Modification of the starches

The starches were modified using sodium trimetaphosphate (STMP) according to the method described by Kerr and Cleveland (1959) with some small adjustments following (Lim & Seib, 1993). Native starch (300 g) and 15 g of sodium sulfate (Na_2SO_4) were suspended in 300 mL of distilled water, and the pH adjusted to 11 with 2.5% of NaOH solution. The slurry was then heated to 45 °C and 2 g of STMP were added. The mixture was then shaken for 3 h and the pH adjusted every hour so that it remained at 11. After 3 h, the pH was lowered to 7 with 2.5% HCl solution. The slurry was then washed three times by suspension in distilled water, centrifuged at 1500 r/min for 15 min and dried at 45 °C. The dried modified starch was milled and passed through a 60-mesh sieve. The maximum concentration of the modifying agent allowed by the FDA for starches intended for the food industry (3%, W/W of sodium trimetaphosphate with respect to the weight of the starch) was used.

2.3. Film preparation

Biodegradable films were prepared from each of the four starches using 2% (W/V) of starch, 1.9% (W/V) of glycerol and 500 mL of water. The films were heated for 30 min at 90 °C in a water bath with constant stirring to ensure gelatinization (Hernández, 2006). After gelatinization the film-forming solutions (FFS) were degassed for 30 min by applying a vacuum. The FFS were then poured into 40 × 30 cm stainless steel trays, maintaining a constant level and uniform thickness, and left in a tray dehydrator (Mitchell, USA, Model 645159) for 24 h at 45 °C. Once dried the four thermoplastic starch film systems (TPS): native cush-cush yam (TPS-NY), phosphated cush-cush yam (TPS-PY), native cassava (TPS-NC) and phosphated cassava (TPS-PC) were peeled off the trays.