Carbohydrate Polymers 81 (2010) 839–848

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Development of films based on quinoa (*Chenopodium quinoa*, Willdenow) starch

Patricia C. Araujo-Farro[a,*], G. Podadera[b], Paulo J.A. Sobral[b], Florencia C. Menegalli[a]

[a] Department of Food Engineering, DEA/FEA/UNICAMP, P.O. Box 6121, 13083-862, Campinas, SP, Brazil
[b] Deparment of Food Engineering, ZEA/FZEA/USP, P.O. Box 23, 13635-900, Pirassununga, SP, Brazil

ARTICLE INFO

Article history:
Received 10 February 2010
Received in revised form 4 March 2010
Accepted 29 March 2010
Available online 3 April 2010

Keywords:
Quinoa starch edible films
Chenopodium quinoa
Willdenow
Mechanical properties
Response surface methodology (RSM)

ABSTRACT

The filmogenic solutions (FS) composed of quinoa starch (4.0 g/100 mL) were prepared, containing various concentrations of glycerol (GC; 16.6–33.4 g glycerol/100 g of quinoa starch, dry weight basis) and alkaline pH values (9.7–11.3). To obtain quinoa starch films (QSF), the FS were dried using different temperature/time combinations (T°C/h) denoted as the drying conditions (DC; 30 °C/20 h–50 °C/5 h). The influence of GC, pH and DC on the mechanical properties and solubility of QSF was evaluated using response surface methodology (RSM). According to the statistical analyses, the optimized conditions corresponded to 21.2 g of glycerol/100 g of quinoa starch, a pH value of 10.7 and 36 °C/14 h for the DC. The films produced under these conditions exhibited superior mechanical properties (7.05 ± 0.37 N puncture force, 7.56 ± 0.95 MPa tensile strength, and 58.14% ± 3.16 elongation at break), low solubility (15.9%), and optimal barrier properties (WVP of 0.204 ± 0.012 g mm m^{-2} h^{-1} kPa^{-1} and oxygen permeability of 4.34 ± 1.03 cm^3 μm m^{-2} d^{-1} kPa).

1. Introduction

Starch, a renewable biopolymer consisting of amylose and amylopectin, is the most commonly used agricultural raw material for edible film manufacture, since it is inexpensive, relatively easy to handle, totally biodegradable and widely available in nature from sources such as cereals, roots, tubers, palms and more recently the rediscovered pseudocereals such as amaranth and quinoa (Araujo-Farro, Podadera, Sobral, and Menegalli, 2006; Colla, Sobral, & Menegalli, 2006). The quinoa seed (*Chenopodium quinoa*, Willdenow) is a small grain (~3 mm diameter) found typically in the South American Andean highlands, and is composed of significant amounts of starch (up to 80%), which has an amylose content of ~10–21% (depending on the variety) and a small starch granule size (~1 μm), characteristics that allow for easier dispersion, which make this starch a promising material for film production (Ahamed, Singhal, Kulkarni, & Pal, 1996). In addition, according to Araujo-Farro et al. (2006), quinoa starch is able to form transparent edible biodegradable films without any previous chemical treatment. On the other hand, in order to increase the workability and flexibility of edible films based on different starches, various plasticizers, usually polyols, have been widely used, glycerol being one of the most preferred and most studied. Glycerol is a hydrophilic plasticizer, and when added at the correct level with respect to the biopolymer content, can interfere with chain to chain hydrogen bonding and the water solubility of the biopolymer (protein/starch mixtures), a process generally used to improve the mechanical properties of edible films (Sobral, Menegalli, Hubinger, & Roques, 2001; Sothornvit & Krotcha, 2001). Edible plasticized films are thin, flexible materials made from biopolymers and capable of forming a continuous matrix by adding food grade plasticizers. They are usually manufactured by the wet method, which is based on the drying of a film-forming solution or dispersion by casting on a convenient support. Furthermore, the wet process is generally preferred in order to form edible preformed films or to applied coatings directly onto food products (Colla et al., 2006; Guilbert, 2000; Sobral et al., 2001). According to Alcantara, Rumsey, and Krotcha (1998), Jangchud and Chinnan (1999) and Perez-Gago and Krotcha (2000), the barrier and mechanical properties of edible biodegradable films have been shown to improve when the drying temperatures were increased. In all the situations, the results were attributed to structural changes in film morphology. Thus the drying conditions used during the drying process of the filmogenic solution can be considered as an important factor in obtaining homogeneous films, and have a great influence on their performance.

Edible films based on starch from conventional crops and roots have been extensively studied, and several researchers (Averous & Boquillon, 2004; Bader & Goritz, 1994; Follain, Joly, Dole & Bliard, 2005; Garcia, Martino, & Zaritzky, 2000; Lourdin, Della Valle, & Colonna, 1995; Mali, Grossman, Garcia, Martino, & Zaritzky, 2002; Mali, Grossmann, García, Martino, & Zaritzky, 2005; Mali, Sakanaka, Yamashita, & Grossmann, 2005; Muller, Yamashita, & Borges, 2008; Parris, Dickey, Kurants, Moten & Craig, 1997) have reported the

* Corresponding author. Tel.: +55 19 35214025; fax: +55 19 35214027.
E-mail addresses: pcaraujof@yahoo.com, patricia@fea.unicamp.br (P.C. Araujo-Farro).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.03.051

characteristics of the materials formed (starch, edible starch films, plasticized or not, chemically modified or not, used alone or in combination with non-renewable sources) and the different techniques used for the manufacture of such films. However, no previous work was found in the specialized literature on the production of edible biodegradable films based on quinoa starch using the wet method. Thus the aim of this work was to develop biodegradable films based on quinoa starch, and evaluate the combined effects of the glycerol content (16.6; 20; 25; 30; 33.4), pH (9.7; 10; 10.5; 11; 11.3) and drying conditions (30 °C/20 h; 34 °C/17 h; 40 °C/10 h; 46 °C/9 h; 50 °C/5 h;) on the mechanical properties and water solubility of the films using response surface methodology (RSM). The equations resulting from the RSM analysis were used to optimize the quinoa starch film (QSF) formulations, and finally the optimized QSF was characterized with respect to its mechanical, optical, solubility and barrier properties.

2. Materials and methods

2.1. Quinoa seeds

Polished mature seeds of quinoa (*C. quinoa*, Willdenow) cultivar "Real" were purchased in Municipal Market of Ayacucho – Perú. The seeds were cleaned up and stored at 3 °C in sealed containers until they were tested. Glycerol, NaOH, KOH and HCl were analytical reagent grade and were purchased from Merck (São Paulo, Brazil).

2.2. Quinoa starch production

Quinoa starch was produced using the methodology involving a short contact time with dilute alkaline solutions developed by Araujo-Farro (2008). The grains (1 kg) were first washed at least four times in an excess of deionized water in order to remove the saponins that cover the quinoa seeds and which are totally soluble in water. The seeds were then steeped in deionized water at 3 °C (1 kg seed/2 kg deionized water) for 8 h. The softened grain suspension was then milled in a kitchen blender and the resulting slurry screened and washed through a series of sieves (80, 200 and 270 mesh) with deionized water. The sieving-washing procedure was repeated five times until there was no further starch-like color associated with the material retained on the sieves. The spent material retained on the sieves then being discarded. The material that passed through the sieves was centrifuged (600 g, 20 min, 4 °C), and the upper layer containing the protein and fine fiber found on top of the sediment, was removed. The remaining starch cake was resuspended in deionized water, centrifuged, and the dark upper layer removed, repeating this process five times in all. The starch collected at the end of this process was suspended in aqueous 0.20% (w/w) NaOH at an alkaline pH value of 10.5, and gently stirred for 5 min at 15 °C to avoid any rise in temperature during this process. The suspension was then centrifuged, resuspended in deionized water and neutralized carefully by adding 1 M HCl. After centrifugation, the starch cake was resuspended in deionized water, centrifuged and removed (five times) in order to remove any traces of the mucilaginous layer (residual protein material) in the upper layer and any ionic components of the NaCl resulting from the neutralization process. The purified starch was then frozen in liquid nitrogen and freeze dried (HETO, CT 60E, Denmark), which took a week. The dried starch was gently ground by hand with a pestle and mortar and passed through a 270 mesh sieve. The obtained quinoa starch was stored at 3 °C in sealed containers until it was used.

2.2.1. Proximate analysis

The content of protein, ash, ether extractable lipids, total fiber and water was analyzed following the standard methods of the AOAC (1995).

Amylose content was determined using a colorimetric method (Juliano, 1971) modified by Martinez and Cuevas (1989).

2.3. Preparation of quinoa films and sample conditioning for the mechanical and solubility tests

All film-forming solutions (FFS) composed of quinoa (*C. quinoa*, Willdenow) starch were prepared, according to the experimental design shown in Table 1. The quinoa starch content, glycerol concentration, pH values, drying conditions and quinoa film- technique were established according to preliminary tests (Araujo-Farro, 2008). To obtain quinoa starch FFS, starch quinoa powder (4 g/100 g total film solution) was dispersed in deionized water (18 meq) at room temperature and stirred for at least 1 h on a magnetic stirrer (TECNAL-TE085). The pH value was then adjusted to the alkaline values shown in Table 1 using a 1N NaOH solution, in order to dissolve the protein and facilitate starch granule disruption during the gelatinization process. After adjusting the pH, magnetic stirring was continued for at least one more hour, and the dispersion then heated to 50 °C, and maintained at this temperature for a further 45 min, with gentle magnetic stirring. The quinoa starch dispersion was gelatinized at 97 °C for 30 min with constant stirring in a water bath (TECNAL, TE184, Brazil). The glycerol was then added and stirring continued for another 15 min in order to completely homogenize the FFS. The FFS was then poured evenly onto polycarbonate plates (≈12 × 12 cm), and the weight controlled (±0.001) using a semi-analytical balance (SCIENTECH, model AS 210, 210 g, ±0.0001 g) so as to obtain a constant film thickness of 80 ± 2 μm. The films were dehydrated in an oven with air renewal and circulation and controlled temperature and relative humidity (MARCONI, model MA037, São Paulo, Brazil), using the different drying conditions determined by the experimental design (Table 1) and 55% relative humidity (RH). The dried quinoa starch films (QSF) were peeled off the casting surface, cut into adequate samples and conditioned at 25 °C and 58% RH in desiccators with saturated solutions of NaBr for 72 h prior to characterization. The thickness of the conditioned films was measured with a digital micrometer (±0.001 mm, probe diameter of 6.4 mm, Mitutoyo, Suzano, Brazil), and the value reported was the average of 15 measurements made at ten different locations. All the tests were carried out in air-conditioned rooms (T = 25 °C and relative humidity between 55 and 65 °C).

2.4. Experimental design

A 2^3 full-factorial central composite design (star configuration) with 6 axial and 3 central points, resulting in 17 experiments, was used to obtain a second-order model for prediction of mechanical properties such as tensile strength (Y_1), elongation at break (Y_2), Young's modulus (Y_3), puncture force (Y_4), puncture deformation (Y_5), as well as solubility (Y_6), which were denoted as dependent variables, as a function of three variables (independent variables): glycerol content (X_1), pH levels (X_2) and drying conditions (X_3). The dependent variables were expressed individually as a function of the aforementioned independent variables using the following polynomial equation (1):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

The statistical design and the coded and real values of these variables are given in Table 1. All experiments were performed randomly, and data were treated with the aid of STATISTICA 5.0 from Statsoft Inc (Colla et al., 2006; Khuri & Cornell, 1996).