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Effect of drying conditions and plasticizer type on some physical and mechanical properties of amaranth flour films

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ABSTRACT

In this work we studied the influence of the drying temperature and relative humidity on the solubility, mechanical properties, water vapor permeability (WVP), and drying time of amaranth flour films plasticized with glycerol or sorbitol. The effect of drying temperature and relative humidity on the mechanical properties of the film is a function of the plasticizer type. In the presence of glycerol, tougher flour films are obtained at a lower drying rate, but an inverse behavior is observed for the films plasticized with sorbitol. The drying conditions do not have a significant effect on WVP compared with sorbitol-plasticized samples, the water sorption isotherm shows that the glycerol-plasticized flour films are able to retain more water at equilibrium at all the studied temperatures. The lower moisture content, WVP and drying time achieved for these films in all the drying conditions indicate better interaction of sorbitol with the starch and protein macromolecules present in the amaranth flour. The optimized drying conditions are 50 °C and 76.2% RH, and 35 °C and 70.3% RH for the films plasticized with glycerol and sorbitol, respectively.

1. Introduction

Because of its high protein content and balanced amino acids composition, the amaranth is a pseudocereal recognized as a potential food source. Foods, such as flours, breakfast cereals, pasta, gluten-free biscuits, and tortillas can be produced from amaranth grains, in order to meet the requirements of special diets, enrich the protein content of bread, and increase the lysine content of foods (Breene, 1991; Tosi, Re, Masciarelli, Sanchez, & de la Torre, 2002). The amaranth flour was recently used as raw material for the production of edible films and coatings, still on a laboratory scale (Colla, Sobral, & Menegalli, 2006; Tapia-Blácido, Mauri, Menegalli, Sobral, & Añón, 2007; Tapia-Blácido, Sobral, & Menegalli, 2005a; Tapia-Blácido, Sobral, & Menegalli, 2011).

Edible films are usually obtained by the casting methodology. In the final stage of the process, the film-forming suspension of the polymer is dried on an appropriate support. In the literature, several researchers reported on the influence of drying conditions on the mechanical and barrier properties of alginate, gelatin, whey protein, chitosan, soy protein, amylose, and amylopectin films (Alcantara, Rumsey, & Krochta, 1998; Da Silva, Bierhalz, & Kieckbush, 2012; Denavi et al., 2009; Fernández-Pan, Ziani, Pedroza-Islas, & Maté, 2010; Jangchud & Chinnan, 1999; Mayachiew & Devahastin, 2008; Menegalli, Sobral, Roques, & Laurent, 1999; Rindlav-Wetsling, Standing, Hermansson, & Gatenholm, 1998; Soazo, Rubiolo, & Verdini, 2011; Stading, Rindlav-Westling, & Gatenholm, 2001; Thakhiew, Devahastin, & Soponronnarit, 2010). In the case of starch films, the drying conditions bring about changes in crystallinity and mechanical properties as a function of the amylose and amylopectin contents. Moreover, in the case of protein films, drying conditions must interfere in the final properties of the material. This is because the structures of proteins can be modified as a function of the processing parameters, as a consequence of proteins denaturation (Denavi et al., 2009). Working with alginate films, Da Silva et al. (2012) observed that films dried at 60 °C were significantly thinner, had lower moisture content, and were less flexible. In whey protein emulsion films, the decrease in drying temperature from 25 to 5 °C reduced the water vapor permeability (WVP) and increased the solubility of the films. Alcantara et al. (1998) verified that higher drying rates led to increased film strength and improved barrier properties in whey protein isolate films. Fernández-Pan et al. (2010) reported that the mechanical and barrier properties were much more influenced by the drying temperature than the drying relative humidity (RH) in the case of chitosan films. The drying of chestnut starch and hybrid carrageenan mixture under forced convection at

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50 °C reduced the drying times and resulted in biofilm with better mechanical properties (Moreira et al., 2011).

In a previous study (Tapia-Blácido et al., 2011), we described the preparation of amaranth flour films plasticized with glycerol or sorbitol and reported on the optimal formulation as a function of the plasticizer concentration and heating temperature, but we did not study the drying process. However, optimization of the drying conditions is paramount and must be taken into account when one considers the use of amaranth flour film as packaging material for fresh fruit and vegetable as well as dried food. Thus, the amaranth flour film should meet some requirements, regarding mechanical strength, flexibility, and permeability to water vapor and gases, in order to ensure food preservation during storage. Therefore, the aim of this work was to examine the effect of the drying conditions on the mechanical, solubility, barrier properties, and drying time of amaranth flour films plasticized with glycerol or sorbitol and optimize the drying process by using a response surface methodology and multi-response analyses, targeting the production of films with low solubility and good mechanical properties.

2. Materials and methods

2.1. Materials

The *Amaranthus cruentus BRS* Alegria seeds were grown in the state of Santa Catarina (Brazil) at 18.8–22 °C, soil pH of 5.5. The seeds were harvested in early October, transported to Campinas (Brazil), cleaned, and stored at 10 °C. The amaranth flour was obtained by using a modification to the alkaline wet milling method of Perez, Bahnassey, and Breene (1993), as proposed by Tapia-Blácido et al. (2005a). The composition of amaranth flour is: moisture content 8.3 ± 0.4 g/100 g, ashes 2.1 ± 0.0 g/100 g, lipids 7.9 ± 0.2 g/100 g, protein 14.1 ± 0.3 g/100 g, and starch 75.7 ± 0.3 g/100 g (11.9 ± 0.3 g amylose/100 g flour) (db). All the reagents were analytical grade. Sorbitol and NaOH were purchased from Synth (São Paulo, Brazil). All the solutions were prepared with deionized water.

2.2. Film formation

The films were produced by the casting method. Amaranth flour films were prepared by using the methodology proposed by Tapia-Blácido et al. (2005a). A suspension of flour in water (4 g/100 g) was homogenized in a mixer for 25 min, and the pH was regulated to 10.7 with 0.1 mol equi/L NaOH, to dissolve the protein. This suspension was then heated at 75 °C for 15 min, followed by addition of the plasticizer (29.6 g sorbitol/100 g flour or 20.02 g glycerol/100 g flour). For each film, 85 ± 3 g of the film-forming solution was poured onto acrylic plates (18 × 21 cm), in order to obtain a constant thickness of 80 ± 5 μm. The films were dried under different drying conditions by using an oven with air circulation and controlled temperature (model MA 415UR, Marconi, Piracicaba, Brazil). The studied drying conditions were 30 °C, 40% RH; 30 °C, 70% RH; 50 °C, 40% RH; 50 °C, 70% RH; 25.9 °C, 55% RH; 54.1 °C, 55% RH; 40 °C, 33.8% RH; 40 °C, 76.2% RH; and 40 °C, 55% RH, defined according to the experimental design that was being used (Tables 1 and 2). The drying kinetics curves of the amaranth flour films were determined for all the studied conditions. Prior to characterization, all the films were preconditioned for at least 48 h in desiccators containing a saturated NaBr solution (25 ± 3 °C, 58 ± 2% RH). The thickness of the films was measured with a digital micrometer Fowler (average of 8 measurements).

2.3. Mechanical properties

The mechanical tests were performed using a texture analyzer TA.XT2i (SMS, Surrey, England). The tensile strength (TS) and elongation at break (*E*) were obtained according to the ASTM D882-95 method (ASTM, 1995). Films were cut into strips with a width of 0.6 cm and a length of 10 cm. The initial grip spacing and cross-head speed were 8 cm and 1.0 mm/s, respectively. The tensile strength (TS) was calculated as the maximum force at break divided by the initial cross-sectional area (thickness of film × 0.6 cm) of the initial film. Elongation at break (*E*) was calculated as the percentile of the change in the length of the specimen with respect to the original distance between the grips (8 cm). Young's modulus (YM) was calculated from the initial slope of the stress–strain curve using Texture Expert version 1.22 (SMS).

2.4. Solubility in water and moisture content

The solubility in water was computed as the percentage of dry matter of the solubilized film after immersion in water at 25 ± 2 °C for 24 h (Gontard, Guilbert, & Cuq, 1992). Film discs (diameter = 2 cm) were cut, weighed, immersed in 50 mL of distilled water, and slowly and periodically agitated. The moisture content of the films was determined gravimetrically by placing the samples in an oven at 105 °C for 24 h.

2.5. Water vapor permeability (WVP)

The water vapor permeability (WVP) test was conducted by using a modified ASTM E96-95 (ASTM, 1995) method at 25 ± 2 °C. Film samples were sealed over the circular opening of a permeation

Table 1
Properties mechanical, solubility, moisture content, WVP and drying time of amaranth flour film plasticized with sorbitol.

T (X_1)[a]	RH (X_2)	TS[b] (MPa)	E (%)	YM (MPa)	S (%)	MC (g H_2O/100 g)	WVP (g mm h^{-1} m^2 kPa)	Drying time (h)
30(−1)	40(−1)	2.9 ± 0.3	30.0 ± 6.3	108.2 ± 7.1	53.8 ± 0.4	11.9 ± 0.1	0.48 ± 0.03	10.0 ± 0.2
30(−1)	70(+1)	5.0 ± 0.2	14.2 ± 1.1	233.0 ± 8.8	42.5 ± 0.3	12.7 ± 0.4	0.42 ± 0.05	14.6 ± 0.1
50(+1)	40(−1)	3.9 ± 0.2	23.6 ± 2.6	200.0 ± 11.4	56.2 ± 4.3	13.9 ± 0.2	0.48 ± 0.01	4.2 ± 0.2
50(+1)	70(+1)	3.3 ± 0.1	35.4 ± 3.9	112.1 ± 5.2	27.6 ± 2.2	12.3 ± 0.3	0.40 ± 0.02	8.7 ± 0.2
25.9(−1.414)	55(0)	1.9 ± 0.3	47.3 ± 2.2	90.1 ± 3.1	50.8 ± 4.1	13.0 ± 0.4	0.51 ± 0.02	9.8 ± 0.4
54.1(+1.414)	55(0)	3.1 ± 0.3	38.9 ± 0.7	105.1 ± 3.1	42.2 ± 3.1	13.4 ± 0.1	0.48 ± 0.01	5.5 ± 0.3
40(0)	33.8(−1.414)	5.4 ± 0.8	10.5 ± 1.3	292.7 ± 7.2	38.3 ± 3.9	12.5 ± 0.8	0.50 ± 0.03	4.6 ± 0.2
40(0)	76.2(+1.414)	4.8 ± 0.5	18.2 ± 2.6	181.2 ± 5.9	30.2 ± 2.9	12.5 ± 0.1	0.46 ± 0.03	12.8 ± 0.2
40(0)	55(0)	4.5 ± 0.6	28.2 ± 1.7	215.6 ± 10.1	57.0 ± 1.6	13.8 ± 0.5	0.43 ± 0.02	7.6 ± 0.3
40(0)	55(0)	4.4 ± 0.4	26.1 ± 1.1	225.2 ± 7.4	55.9 ± 2.5	12.3 ± 0.4	0.42 ± 0.04	7.6 ± 0.2
40(0)	55(0)	4.4 ± 0.3	25.1 ± 0.9	228.2 ± 5.9	55.0 ± 1.0	12.8 ± 0.3	0.43 ± 0.05	7.6 ± 0.3

Values reported are measurement replication means ± standard deviation (n = 03 replicates).
[a] Independent variables values (the values between brackets are the coded variables). *T*, temperature (°C) and RH, relative humidity (%).
[b] Tensile strength (TS), elongation at break (*E*), Young's modulus (YM), solubility (*S*), moisture content (MC), and water vapor permeability (WVP), drying time (*h*) to reach moisture content of 3.04 g H_2O/g db.

Table 2
Properties mechanical, solubility, moisture content, WVP and drying time of amaranth flour film plasticized with sorbitol.

T (X_1)[a]	RH (X_2)	TS[b] (MPa)	E (%)	YM (MPa)	S (%)	MC (g H_2O/100 g)	WVP (g mm h^{-1} m^2 kPa)	Drying time (h)
30(−1)	40(−1)	5.0 ± 0.2	18.5 ± 4.4	296.4 ± 3.8	60.7 ± 4.0	11.9 ± 0.1	0.266 ± 0.06	9.5 ± 0.2
30(−1)	70(+1)	7.5 ± 0.9	13.1 ± 1.5	401.9 ± 5.0	50.3 ± 2.6	12.7 ± 0.4	0.250 ± 0.04	13.1 ± 0.2
50(+1)	40(−1)	8.5 ± 0.5	10.6 ± 2.0	465.2 ± 8.8	44.1 ± 2.3	13.9 ± 0.2	0.287 ± 0.03	4.2 ± 0.2
50(+1)	70(+1)	5.0 ± 0.1	19.1 ± 2.4	248.0 ± 7.0	35.0 ± 1.5	12.3 ± 0.3	0.217 ± 0.04	8.0 ± 0.2
25.9(−1.414)	55(0)	6.2 ± 0.1	17.7 ± 1.8	358.2 ± 4.8	58.2 ± 4.3	13.0 ± 0.4	0.204 ± 0.00	10.1 ± 0.3
54.1(+1.414)	55(0)	8.0 ± 0.6	11.3 ± 1.5	480.2 ± 7.5	50.0 ± 2.0	13.4 ± 0.1	0.262 ± 0.01	5.1 ± 0.2
40(0)	33.8(−1.414)	8.0 ± 1.4	8.9 ± 1.2	405.9 ± 5.9	39.4 ± 1.7	12.5 ± 0.8	0.233 ± 0.03	4.5 ± 0.3
40(0)	76.2(+1.414)	5.8 ± 0.3	16.3 ± 2.2	279.2 ± 3.1	30.4 ± 2.9	12.5 ± 0.1	0.264 ± 0.03	12.4 ± 0.2
40(0)	55(0)	6.2 ± 0.5	20.1 ± 2.5	302.2 ± 3.3	47.5 ± 2.5	13.8 ± 0.5	0.240 ± 0.02	6.9 ± 0.2
40(0)	55(0)	6.0 ± 0.3	21.1 ± 0.9	306.9 ± 3.5	47.1 ± 1.2	12.3 ± 0.4	0.243 ± 0.02	6.9 ± 0.2
40(0)	55(0)	6.2 ± 0.3	20.1 ± 1.1	310.6 ± 2.8	48.2 ± 2.0	12.8 ± 0.3	0.240 ± 0.03	6.9 ± 0.2

Values reported are measurement replication means ± standard deviation (n = 03 replicates).
[a] Independent variables values (the values between brackets are the coded variables). T, temperature (°C) and RH, relative humidity (%).
[b] Tensile strength (TS), elongation at break (E), Young's modulus (YM), solubility (S), moisture content (MC), and water vapor permeability (WVP), drying time (h) to reach moisture content of 3.04 g H_2O/g db.

cell containing silica gel. The cells were then placed in desiccators containing distilled water. The weight gain of the cells was monitored every 24 h, for 7 days.

2.6. Water sorption isotherms

Initially, the film samples were placed in chambers containing silica gel, which allowed for determination of the water vapor absorption isotherms. Film specimens (approximately 500 mg), in triplicate, were placed in hermetic chambers containing oversaturated salt solutions of LiCl (a_w 0.111), $MgCl_2 \cdot 6H_2O$ (a_w 0.328), K_2CO_3 (a_w 0.432), NaBr (a_w 0.577), $NaNO_2$ (a_w 0.642), NaCl (a_w 0.757), KCl (a_w 0.843), and $BaCl_2$ (a_w 0.904) at 25 ± 2 °C for 3 weeks, which was the time period required for equilibrium to be reached. The equilibrium moisture content was determined by drying the samples to constant weight in a vacuum oven at 70 °C. The Guggenheim–Anderson–De Boer (GAB) model was used to represent the experimental equilibrium data. The GAB model follows the formula (Bizot, 1984)

$$M = \frac{m_o \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C \cdot K \cdot a_w)}, \quad (1)$$

where M is the equilibrium moisture content (g water/g db) at a water activity (a_w), m_o is the monolayer value (g water/g db), and C and K are the GAB constants.

2.7. Experimental design

The surface response methodology was employed for evaluation of the effect of the drying temperature (T) and relative humidity (RH) on the mechanical properties, solubility, water vapor permeability, moisture content, and drying time of the films. The levels of the independent variables were defined according to a 2^2 full-factorial central composite design (star configuration) with four axial and three central points (triplicate only at the central point), which resulted in 11 experiments (Tables 1 and 2). The experimental range of drying temperature and relative humidity was defined on the basis of previous studies on amaranth flour films of the species *A. caudatus* (Tapia-Blácido, Sobral, & Menegalli, 2005b). An analysis of variance (ANOVA), a multiple comparison test, and all the statistical analyses were performed using the Statistica 6.0 software. The data were fitted to a second order equation (equation (2)) as a function of the independent variables.

$$Y_i = b_0 + b_1 X_1 + b_2 X_2 + b_{12} X_1 X_2 + b_{11} X_1^1 + b_{22} X_2^2, \quad (2)$$

where b_n are constant regression coefficients, Y_i are dependent responses (tensile strength (TS), elongation at break (E), Young's modulus (YM), solubility (S), water vapor permeability (WVP), and drying time (t)). X_1 and X_2 are the coded independent variables (drying temperature and relative humidity, respectively).

After the surface-response results were obtained, optimization of the process conditions was carried out by multi-response analysis (Derringer & Suich, 1980). This method involves the transformation of response variables (Y_i) to an individual function of dimensionless desirability (g_i) (equation (4)) ranging from 0 (undesirable response) to 1 (desired response). From the geometric means of individual desires, the overall desirability function (G) (equation (3)) is achieved. G is later maximized by using the software Mathematic 5.0.

$$G = \left(g_1^{n_1}, g_2^{n_2}, \ldots\ldots, g_k^{n_k}\right)^{1/k}, \quad (3)$$

where:

$$g_i = \frac{Y_i - Y_{min}}{Y_{max} - Y_{min}}, \quad (4)$$

and where Y_{min} is the response minimum value, Y_{max} is the response maximum value, k is the number of considered responses, and n_i is the weight of each response.

In the case of solubility, equation (4) had to be redesigned, so that the minimum values for these responses could be obtained (equation (5)).

$$g_i = \frac{Y_{max} - Y_i}{Y_{max} - Y_{min}} \quad (5)$$

3. Results and discussion

3.1. Drying kinetics of amaranth flour films

Fig. 1(a, b) illustrates the curves obtained for the drying kinetics of the amaranth flour film plasticized with glycerol or sorbitol. The drying temperature and relative humidity conditions correspond to the values considered in the experimental design 2^2 presented in Tables 1 and 2.

The drying curves reveal that a long period with a constant drying rate is predominant in all the studied conditions. This trend was also observed by Tapia-Blácido et al. (2005b), Denavi et al. (2009), Thakhiew et al. (2010) and Da Silva et al. (2012) in the case of amaranth flour (*A. caudatus*), soy protein, chitosan, and alginate films. According to Da Silva et al. (2012), the absence of

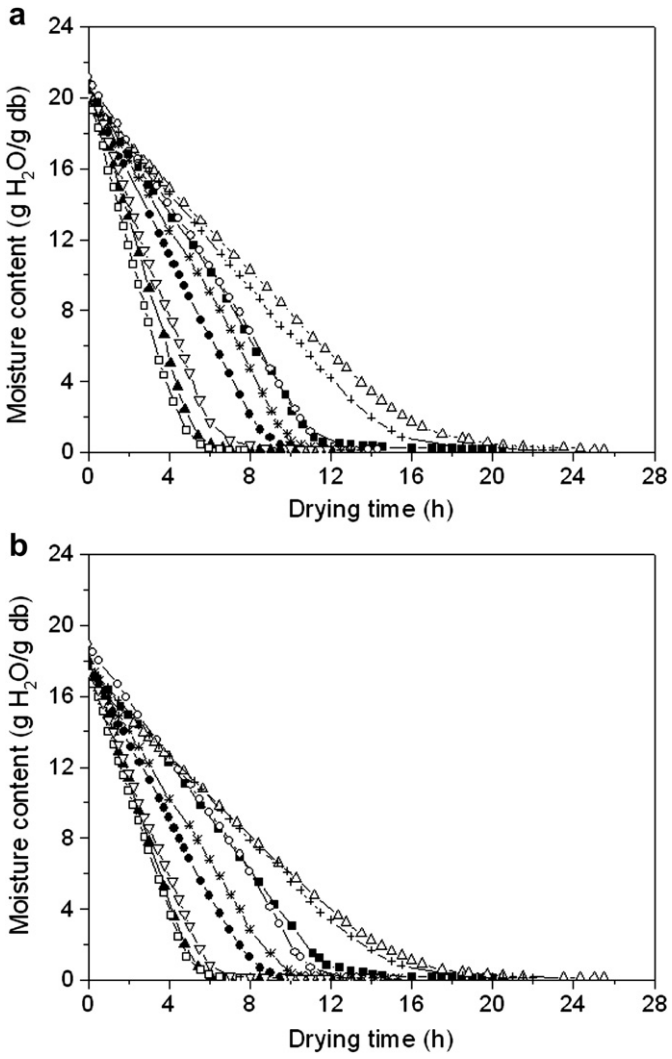

Fig. 1. Drying curves of amaranth flour films at (■) 25.9 °C, 55% RH; (○) 30 °C, 55% RH; (△) 30 °C, 70% RH; (▲) 40 °C, 33.8% RH; (●) 40 °C, 55% RH; (+) 40 °C, 76.2% RH; (□) 50 °C, 40% RH; (*) 50 °C, 70% RH; (▽) 54.1 °C, 55% RH. (a) Glycerol, (b) Sorbitol.

a falling rate period indicates that no internal resistance is imposed by the film/gel structure. Fig. 1(a, b) also evidences that the drying rate drops with lower *T* and RH values. Thus, a higher drying rate is obtained when the amaranth flour film is dried at 50 °C and 40% RH. In this drying condition, the time necessary for a moisture content of 3.04 kg/kg db to be reached is 4.2 h for the amaranth flour films plasticized with glycerol or sorbitol (Tables 1 and 2). The flour films dried at 30 °C and 70% RH reach the same moisture content more slowly (14.6 h for glycerol and 13.1 h for sorbitol). The films plasticized with glycerol (Fig. 1a) require longer drying time than the films plasticized with sorbitol (Fig. 1b), for the same drying conditions. This is because glycerol acts as a water holding agent, while sorbitol functions as plasticizer with minimum contribution from water molecules (Tapia-Blácido et al., 2011).

3.2. Mechanical properties

According to the variance analysis (ANOVA), the models calculated for the tensile strength (TS), elongation at break (*E*), and Young's modulus (YM) of flour films plasticized with glycerol (equations (6)–(8)) and sorbitol (equations (9)–(11)) are statistically significant ($p < 0.05$) and predictive ($F_{cal} > F_{list}$).

For glycerol:

$$\mathrm{TS} = 4.47 + 0.14X_1 - 0.98X_1^2 + 0.30X_2^2 - 0.68X_1X_2 \quad \left(R^2 = 0.90\right) \tag{6}$$

$$E = 26.47 + 7.58X_1^2 - 6.78X_2^2 + 6.89X_1X_2 \quad \left(R^2 = 0.87\right) \tag{7}$$

$$\mathrm{YM} = 228.66 - 65.45X_1^2 - 15.09X_2 - 53.19X_1X_2 \quad \left(R^2 = 0.88\right) \tag{8}$$

For sorbitol:

$$\mathrm{TS} = 6.59 - 0.52X_2 - 1.49X_1X_2 \quad \left(R^2 = 0.90\right) \tag{9}$$

$$E = 20.48 - 2.53X_1^2 - 3.49X_2^2 + 3.50X_1X_2 \quad \left(R^2 = 0.88\right) \tag{10}$$

$$\mathrm{YM} = 306.61 + 23.44X_1 - 36.35X_2 + 49.30X_1^2 - 10.98X_2^2 - 80.68X_1X_2 \quad \left(R^2 = 0.91\right) \tag{11}$$

Fig. 2 corresponds to the response surface of TS of the films plasticized with glycerol or sorbitol as a function of *T* (X_1) and RH (X_2). Fig. 2a shows that higher TS values are achieved at lower drying rate (30 °C, 76% RH). Moreover, lower TS values had been attained at an intermediate drying rate (26 °C, 34% RH or 54 °C, 76% RH). These results contrast with data obtained for flour films from the species *A. caudatus* plasticized with glycerol because the latter films, which were dried at 50 °C and 70% RH, were more resistant to strain (Tapia-Blácido et al., 2005b).

Concerning the film plasticized with sorbitol, the effect of *T* on the TS values is only evident at low RH (Fig. 2b). In these films, the TS values are mainly affected by the RH. In addition, the films plasticized with sorbitol and dried at higher drying rate (54 °C, 34% RH) furnish a larger TS value (~10 MPa).

The effect of *T* and RH on the elongation at break (*E*) has inverse behavior compared with the TS (Fig. 3). As usual, more resistant films are less ductile. The *E* response surface of flour films plasticized with sorbitol display a maximum region defined at intermediate *T* and RH values (Fig. 3b). Hence, flour films dried at *T* between 30 and 45 °C and RH ranging from 45 to 60% result in more flexible films ($E \sim 21\%$). On the other hand, the flour films plasticized with glycerol give higher *E* values when they are dried at higher *T* (54 °C) and RH (70–76% RH), compared with the flour film plasticized with sorbitol. In the case of the flour film from the species *A. caudatus* plasticized with glycerol (Tapia-Blácido et al., 2005b), larger *E* values have been reported for films dried at lower drying rate (30 °C and 70% RH).

Other authors also observed that high drying rates lead to films with larger TS and *E* for peanut and whey protein films (Alcantara et al., 1998; Jangchud & Chinnan, 1999). However, soy protein films became more resistant as the air temperature was increased up to 70 °C, when using higher RH (Denavi et al., 2009). Here, the flour films plasticized with sorbitol exhibit larger TS values and lower *E* values than the films plasticized with glycerol, for all the drying conditions (Tables 1 and 2). Tapia-Blácido et al. (2011) also verified that the flour film plasticized with sorbitol is more resistant to break and less flexible than the film plasticized with glycerol. According to these authors, compared with sorbitol, glycerol is a more powerful plasticizer. This is because glycerol has smaller

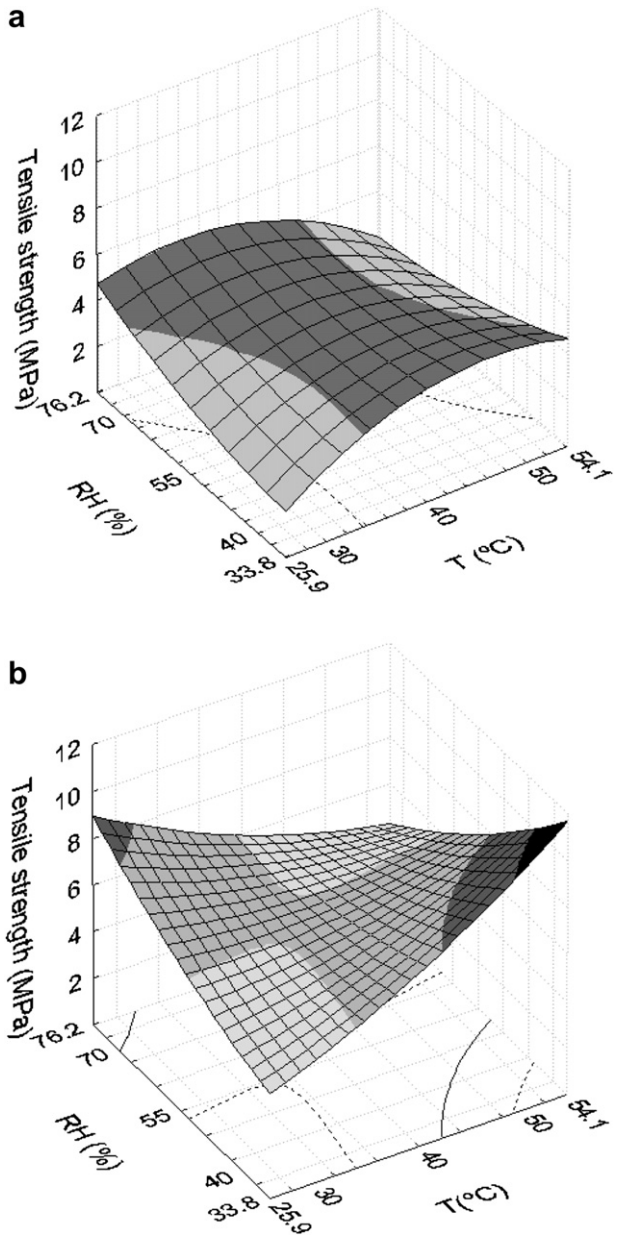

Fig. 2. Tensile strength of amaranth flour films as a function of the temperature and relative humidity. (a) Glycerol, (b) Sorbitol.

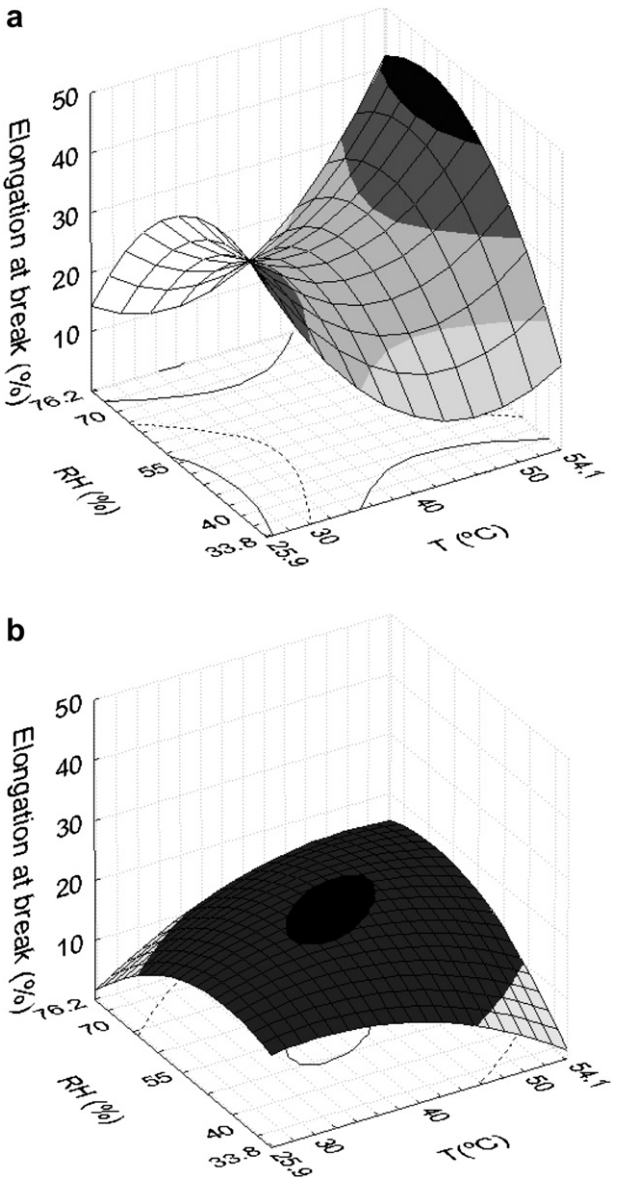

Fig. 3. Elongation at break of amaranth flour films as a function of the temperature and relative humidity. (a) Glycerol, (b) Sorbitol.

molecular mass (glycerol 92 mol g^{-1} and sorbitol 182 mol g^{-1}), which makes it a more effective plasticizer for many edible films.

Young's modulus exhibits the same behavior as the TS as a function of *T* and RH (figure not shown). The larger YM values for films plasticized with sorbitol are obtained at higher drying rates, so a different behavior is detected for the films plasticized with glycerol. In the latter case, intermediate temperatures and a wide range of relative humidity give higher YM values.

3.3. Film solubility and moisture content

According to the analysis of variance (ANOVA), the linear, quadratic, and interaction parameters are statistically significant ($p < 0.05$). Therefore, these parameters were considered in the second-order model for the solubility (equations (12) and (13)). Because the *F* values were greater than the listed values, the models can be considered predictive.

For glycerol:

$$S = 55.99 - 3.07X_1 - 3.59X_1^2 - 6.41X_2 - 9.69X_2^2 - 4.35X_1X_2 \quad \left(R^2 = 0.87\right) \tag{12}$$

For sorbitol:

$$S = 47.35 - 7.59X_2 + 2.16X_1^2 - 7.33X_2^2 + 5.10X_1X_2 \quad \left(R^2 = 0.90\right) \tag{13}$$

The solubility (*S*) response surface obtained for flour films plasticized with glycerol contains a maximum region (Fig. 4a), which does not occur for the films plasticized with sorbitol (Fig. 4b). The maximum solubility of the flour film plasticized with glycerol can be verified at *T* ranging from 30 to 40 °C and RH from 45 to 60%, so intermediate drying rates yield more soluble flour films. On the other hand, the solubility of flour films plasticized with sorbitol increases almost in the full range of the RH when the films are dried

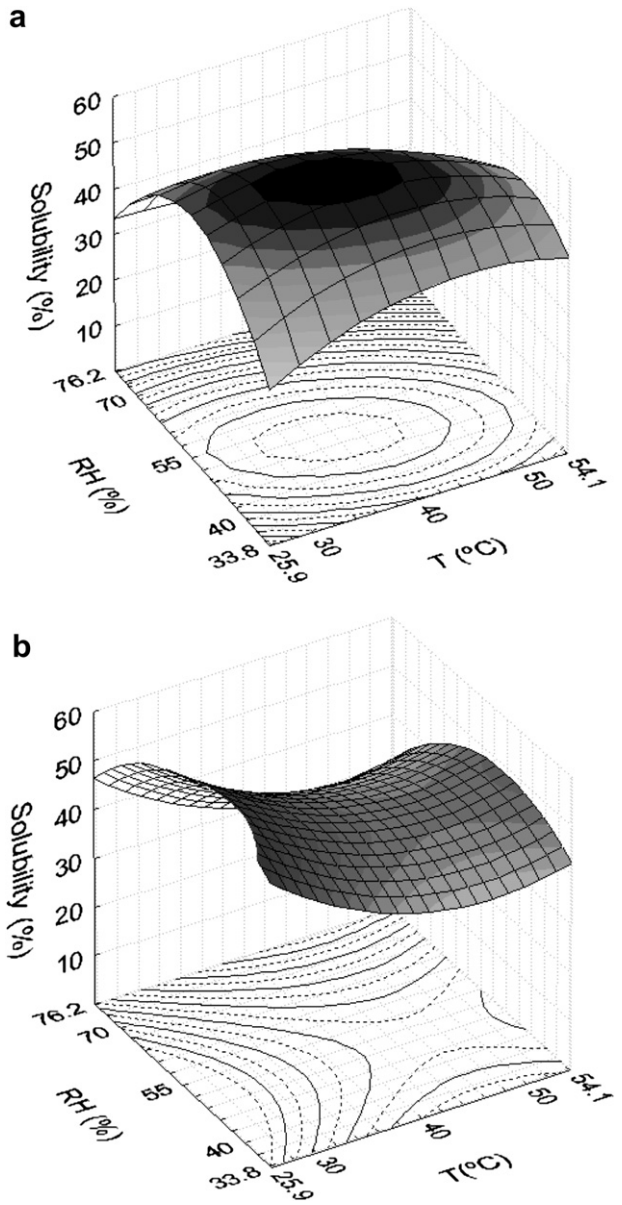

Fig. 4. Solubility of amaranth flour films as a function of the temperature and relative humidity. (a) Glycerol, (b) Sorbitol.

at temperatures below 30 °C. However, at high T values (>40 °C), the solubility decreases when the RH values range from 33.8 to 40%, and from 70 to 76.2%. Thus, high drying rates as well as intermediate drying rates allow for the formation of films with low solubility. It can be assumed that these drying conditions promote hydrophobic interactions between lipid and proteins, as well as protein–protein and starch–starch interactions, with homogenous distribution of these interactions within the film matrix. All these interactions can culminate in lower solubility of the amaranth flour film.

Comparison of the solubility values achieved for the flour films plasticized with glycerol and sorbitol reveals that, in the presence of glycerol, the flour film is less soluble (Tables 1 and 2).

As for the moisture content data, there is no correlation was observed between the plasticizer and the studied drying conditions, because the data variation is small: between 12 and 13.9 for the films plasticized with glycerol (Table 1) and 9.2 and 10.7 for the films plasticized with sorbitol (Table 2).

3.4. Water vapor permeability (WVP)

According to the statistical analysis of the WVP experimental values listed in Tables 1 and 2, the linear, quadratic, and interaction parameters of drying temperature (X_1) and relative humidity (X_2) are not statistically significant ($p > 0.05$). Therefore, the WVP of amaranth flour films plasticized with glycerol and sorbitol does not depend on the drying process.

On the other hand, the WVP of flour films prepared with sorbitol is lower than that of glycerol-containing films (Tables 1 and 2). The better water vapor barrier properties of edible films containing sorbitol as plasticizer compared with those of the films containing glycerol might be due to the fact that sorbitol is less hygroscopic (Kowalczyk & Baraniak, 2011). The difference between both plasticizers in terms of WVP values was also reported by several authors in the case of protein films (Gennadios, Weller, Hanna, & Froning, 1996; Kowalczyk & Baraniak, 2011; McHugh, Aujard, & Krochta, 1994; Wan, Kim, & Lee, 2005).

3.5. Drying time

According to the analysis of variance (ANOVA), the second-order models obtained for the drying time, represented as equations (14) and (15), are statistically significant ($p < 0.05$) and predictive ($F_{calculated} > F_{listed}$). Therefore, the drying time data (Tables 1 and 2) are adequately correlated with T (X_1) and RH (X_2).

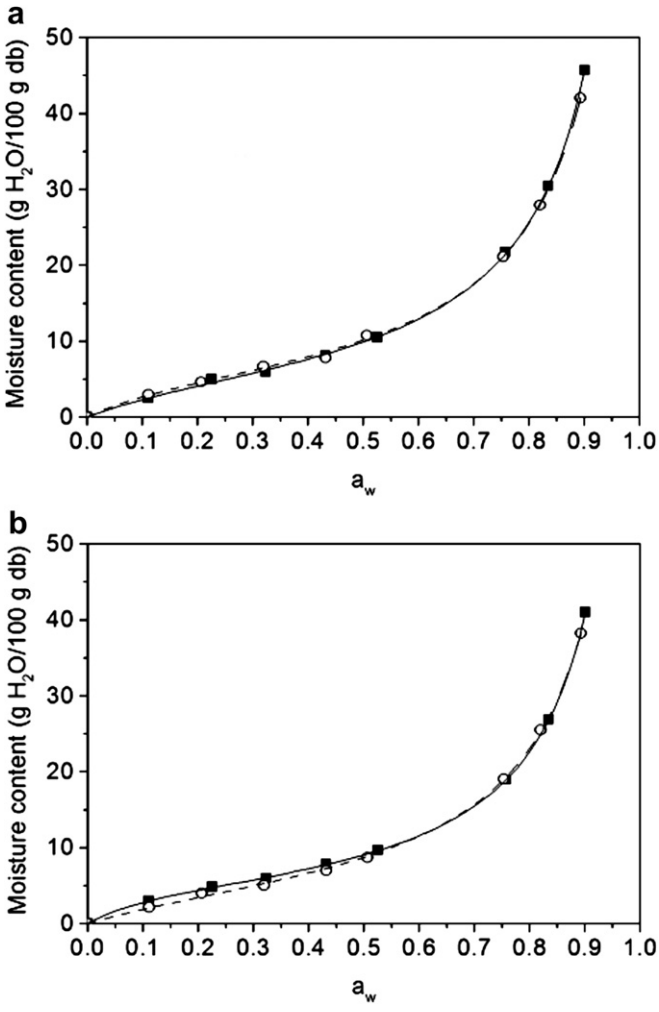

Fig. 5. Water sorption isotherms of amaranth flour films at (■) 30 and (○) 40 °C. (a) Glycerol, (b) Sorbitol. (—) GAB 30 °C, (–) GAB 40 °C.

Table 3
Parameters of the Guggenheim–Anderson–de Boer (GAB) model for sorption isotherms of amaranth flour film plasticized with glycerol or sorbitol.

Plasticizer	Temperature (°C)	m_o (g H_2O/100 g db)	C	K	RMSE (%)
Glycerol	30	6.3	4.5	0.960	3.6
	40	6.3	5.7	0.957	4.2
Sorbitol	30	5.2	3.1	0.970	1.0
	40	5.7	3.9	0.962	3.7

m_o = moisture content of the monolayer, C and K are constants, RSME = Root mean square error.

For glycerol:

$$t = 7.59 - 2.23X_1 + 0.31X_1^2 + 2.63X_2 + 0.90X_2^2 \quad \left(R^2 = 0.90\right) \tag{14}$$

For sorbitol:

$$t = 6.88 - 1.92X_1 + 0.37X_1^2 + 2.60X_2 + 0.81X_2^2 - 0.50X_1X_2 \quad \left(R^2 = 0.99\right) \tag{15}$$

The drying time corresponds to the time required for the films plasticized with glycerol or sorbitol to reach a moisture content of 3.04 g H_2O/g db (Tables 1 and 2). As drying to those final moisture contents virtually takes place during the constant rate period, the drying rate is controlled by heat and mass transfer in the external gas phase. Hence, the drying time is almost a linear function of the T and is inversely related to the RH (figure not shown).

3.6. Water sorption isotherms

The water sorption isotherms of flour films plasticized with glycerol or sorbitol as plasticizer are presented in Fig. 5. The experimental data obtained for these films at 30 and 40 °C fit by the GAB model well. The parameters for the GAB equation are summarized in Table 3. All the water sorption curves of the films are sigmoid in shape, revealing a slower increase in the equilibrium moisture content until a_w 0.6; thereafter, there is a dramatic increase in the slope of the isotherm, indicating the presence of non-bound or free-state water associated with enhanced solubilization (Hernández-Muñoz, Kanavouras, Ng, & Gavara, 2003; Su et al., 2010). For the films containing sorbitol, at lower a_w (<0.5) there is clear reduction in the equilibrium moisture content of the films with rising temperature. However, this behavior is less evident for films plasticized with glycerol. At the same a_w, the equilibrium moisture content is higher for amaranth flour films in the presence of glycerol (Fig. 5a), compared with films containing sorbitol (Fig. 5b). Therefore, the glycerol-plasticized flour films are able to retain more water at equilibrium, compared with the sorbitol-plasticized samples. In the other words, films prepared with glycerol are more hygroscopic than films prepared with sorbitol, even at high temperatures. This observation confirms the higher affinity of glycerol for water, which generates a more pronounced plasticizing effect. Chaudhary, Adhikari, and Kasapi (2011) listed several reasons for this behavior, such as the lower molecular weight of glycerol (92.09 g mol^{-1}) compared with sorbitol (182 g mol^{-1}) and the better interaction of sorbitol with starch macromolecules. Furthermore, glycerol is highly hydrophilic and a strong humectant; at 25 °C and 50% RH, its hygroscopicity is 25 g H_2O/100 g, while the hygroscopicity of sorbitol is 1 g H_2O/100 g (Takahashi, Yamada, & Machida, 1984). Because sorbitol crystallizes at room temperature and high RH, the edible films plasticized with this compound are less hygroscopic than those plasticized with glycerol (Talja, Helén, Roos, & Jouppila, 2007).

Table 3 shows that glycerol increases the value of the monolayer water content (m_o) and the value of constant C, related to the water–substrate interaction energy, at all the studied temperatures. This result suggests that the hydrophilic groups of the starch and protein present in the amaranth flour are less available for interaction with water molecules in the presence of sorbitol; and that stronger water association might occur in the presence of glycerol. In other words, sorbitol is more compatible with the polymers existing in the flour, thereby strongly interacting with these macromolecules. Moreover, the m_o values found in this study agree with values reported for soy protein isolate/poly(vinyl alcohol)/glycerol blend, methylcellulose/glycerol, cassava starch/sorbitol, and pea protein/sorbitol films (Kowalczyk & Baraniak, 2011; Mali, Sakanaka, Yamashita, & Grossmann, 2005; Müller, Yamashita, & Borges-Laurindo, 2008; Su et al., 2010; Vargas, Albors, Chiralt, & González-Martínez, 2011). The k values obtained for the films plasticized with glycerol or sorbitol are <1. These values do not appear to be affected by the temperature or plasticizer type.

3.7. Determination of the optimal drying conditions

The desirability function (G) was formulated from the models calculated for the tensile strength (TS), elongation at break (E), and solubility (S) of the flour films plasticized with glycerol (equations (6), (7) and (12)) and sorbitol (equations (9), (10) and (13)). The minimum and maximum values of each response variable were extracted from the experimental results obtained in the experimental design (Tables 1 and 2). The g_i function was achieved by considering these minimum and maximum values. The optimization was performed in order to attain films with good mechanical properties and lower solubility. Thus, the g_i functions for TS, E, and S were assigned weights 3, 3, and 6, respectively (equations (16) and (17)). Parameter k was assigned the value of 3, because three were the responses variables (TS, E, and S) considered in the desirability function (G).

For glycerol films:

$$G = \left[\left(\frac{2.59 + 0.14X_1 - 0.98X_1^2 + 0.30X_2^2 - 0.68X_1X_2}{3.52}\right)^3 * \left(\frac{16.00 + 7.58X_1^2 - 6.78X_2^2 + 6.89X_1X_2}{36.82}\right) * \left(\frac{1.04 + 3.07X_1 + 3.59X_1^2 + 6.41X_2 + 9.69X_2^2 + 4.35X_1X_2}{29.42}\right)^6\right]^{1/3} \tag{16}$$

For sorbitol films:

$$G = \left[\left(\frac{1.59 - 0.52X_2 - 1.49X_1X_2}{3.5}\right)^3 * \left(\frac{11.61 - 2.53X_1^2 - 3.49X_2^2 + 3.50X_1X_2}{12.3}\right)^3 * \left(\frac{16.98 + 7.59X_2 - 2.16X_1^2 + 7.33X_2^2 - 5.10X_1X_2}{30.4}\right)^6\right]^{1/3} \quad (17)$$

The optimization of the desirability function (G) showed that amaranth flour films with good mechanical properties and lower solubility can be obtained at T and RH values of 50 °C and 76.2%, and 35 °C and 70.3% for the films plasticized with glycerol and sorbitol, respectively.

4. Conclusion

We have verified that the drying rate affects the mechanical properties and the solubility of amaranth flour films plasticized with glycerol or sorbitol in a different way. The drying conditions to which the amaranth flour films are submitted do not have a significant effect on WVP. The water sorption isotherm showed that the hydrophilic groups of the starch and protein present in the amaranth flour are less available for interaction with water molecules in the presence of sorbitol. However, there might be stronger association with water molecules in the presence of glycerol. Thus, the flour films plasticized with glycerol are more soluble, more permeable to water vapor, and more elongable in all the drying conditions, mainly at higher relative humidity. The optimized drying conditions were 50 °C and 76.2% RH, and 35 °C and 70.3% RH for the films plasticized with glycerol and sorbitol, respectively.

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References

Alcantara, C. R., Rumsey, T. R., & Krochta, J. M. (1998). Drying rate effect on the properties of whey protein films. *Journal of Food Process Engineering, 21*, 387–405.

ASTM. (1995). *Annual book of ASTM standards*. Philadelphia: American Society for Testing and Materials.

Bizot, H. (1984). Using the GAB model to construct sorption isotherms. In *Physical properties of foods* (pp. 43–61). London: Applied Science Publishers.

Breene, W. M. (1991). Food uses of grain amaranth. *Cereal Food World, 36*, 426–429.

Chaudhary, D. S., Adhikari, B. P., & Kasapis, S. (2011). Glass-transition behaviour of plasticized starch biopolymer system – a modified Gordone–Taylor approach. *Food Hydrocolloids, 25*, 114–121.

Colla, E., Sobral, P. J. A., & Menegalli, F. C. (2006). *Amaranthus cruentus* flour edible films: Influence of stearic acid addition, plasticizer concentration, and emulsion stirring speed on water vapor permeability and mechanical properties. *Journal of Agriculture and Food Chemistry, 54*, 6645–6653.

Da Silva, M. A., Bierhalz, A. C. K., & Kieckbush, T. G. (2012). Influence of drying conditions on physical properties of alginate films. *Drying Technology, 30*, 72–79.

Denavi, G., Tapia-Blácido, D. R., Añón, M. C., Sobral, P. J. A., Mauri, A. N., & Menegalli, F. C. (2009). Effects of drying conditions on some physical properties of soy protein films. *Journal of Food Engineering, 90*, 341–349.

Derringer, G., & Suich, R. (1980). Simultaneous optimization of several response variables. *Journal of Quality Technology, 12*, 214–219.

Fernández-Pan, I., Ziani, K., Pedroza-Islas, R., & Maté, J. I. (2010). Effect of drying conditions on the mechanical and barrier properties of films based on chitosan. *Drying Technology, 28*, 1350–1358.

Gennadios, A., Weller, C. L., Hanna, M. A., & Froning, G. W. (1996). Mechanical and barrier properties of egg albumen films. *Journal of Food Science, 61*, 585–589.

Gontard, N., Guilbert, S., & Cuq, J. (1992). Edible wheat gluten films: influence of the main process variables on films properties using response surface methodology. *Journal of Food Science, 57*, 190–195.

Hernández-Muñoz, P., Kanavouras, A., Ng, P. K. W., & Gavara, R. (2003). Development and characterization of biodegradable films made from wheat gluten protein fractions. *Journal of Agriculture and Food Chemistry, 51*, 7647–7654.

Jangchud, A., & Chinnan, M. S. (1999). Peanut protein film as affected by drying temperature and pH of film forming solution. *Journal of Food Science, 64*, 153–157.

Kowalczyk, D., & Baraniak, B. (2011). Effects of plasticizers, pH and heating of film-forming solution on the properties of pea protein isolate films. *Journal of Food Engineering, 105*, 295–305.

Mali, S., Sakanaka, L. S., Yamashita, F., & Grossmann, M. V. E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymers, 60*, 283–289.

Mayachiew, P., & Devahastin, S. (2008). Comparative evaluation of physical properties of edible chitosan films prepared by different drying methods. *Drying Technology, 26*(2), 176–185.

McHugh, T. H., Aujard, J. F., & Krochta, J. M. (1994). Plasticized whey protein edible films: water vapor permeability properties. *Journal of Food Science, 59*, 416–419.

Menegalli, F. C., Sobral, P. J. A., Roques, M. A., & Laurent, S. (1999). Characteristics of gelatin biofilms in relation to drying process conditions near melting. *Drying Technology, 17*, 1697–1706.

Moreira, R., Chenlo, F., Torres, M. D., Silva, C., Prieto, D. M., Sousa, A. M. M., et al. (2011). Drying kinetics of biofilms obtained from chestnut starch and carrageenan with and without glycerol. *Drying Technology, 29*, 1058–1065.

Müller, C. M. O., Yamashita, F., & Borges-Laurindo, J. (2008). Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach. *Carbohydrate Polymers, 72*, 82–87.

Perez, E., Bahnassey, Y. A., & Breene, W. M. (1993). A simple laboratory scale method for isolation of amaranth starch. *Starch/Stärke, 45*, 211–214.

Rindlav-Wetsling, A., Standing, M., Hermansson, A., & Gatenholm, P. (1998). Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydrate Polymers, 36*, 217–224.

Soazo, M., Rubiolo, A. C., & Verdini, R. A. (2011). Effect of drying temperature and beewax content on physical properties of whey protein emulsion films. *Food Hydrocolloids, 25*, 1251–1255.

Stading, M., Rindlav-Westling, A., & Gatenholm, P. (2001). Humidity-induced structural transitions in amylose and amylopectin films. *Carbohydrate Polymer, 45*, 209–217.

Su, J. F., Huang, Z., Zhao, Y. H., Yuan, X. Y., Wang, X. Y., & Li, M. (2010). Moisture sorption and water vapor permeability of soy protein isolate/poly(vinyl alcohol)/glycerol blend films. *Industrial Crops and Products, 31*, 266–276.

Takahashi, M., Yamada, M., & Machida, Y. (1984). A new method to evaluate the softening effect of cosmetic ingredients on the skin. *Journal of the Society of Cosmetic Chemists, 35*, 171–181.

Talja, R. A., Helén, H., Roos, Y. H., & Jouppila, K. (2007). Effect of various polyols and polyol contents on physical properties of potato starch-based films. *Carbohydrate Polymers, 67*(3), 288–295.

Tapia-Blácido, D., Mauri, A. N., Menegalli, F. C., Sobral, P. J. A., & Añón, M. C. (2007). Contribution of protein and lipid fraction in the physical, thermal and structure properties of amaranth flour films (*Amaranthus caudatus*). *Journal of Food Science, 72*(5), 293–300.

Tapia-Blácido, D., Sobral, P. J. A., & Menegalli, F. C. (2005a). Development and characterization of biofilms based on amaranth flour (*Amaranthus caudatus*). *Journal of Food Engineering, 67*, 215–223.

Tapia-Blácido, D., Sobral, P. J. A., & Menegalli, F. C. (2005b). Effect of drying temperature and relative humidity on the mechanical properties of amaranth flour films plasticized with glycerol. *Brazilian Journal of Chemical Engineering, 212*, 249–256.

Tapia-Blácido, D., Sobral, P. J. A., & Menegalli, F. C. (2011). Optimization of amaranth flour films plasticized with glycerol and sorbitol by multi-response analysis. *LWT-Food Science and Technology, 44*(8), 1731–1738.

Thakhiew, W., Devahastin, S., & Soponronnarit, S. (2010). Effects of drying methods and plasticizer concentration on some physical and mechanical properties of edible chitosan films. *Journal of Food Engineering, 99*, 216–224.

Tosi, E. A., Re, E. D., Masciarelli, R., Sanchez, O. C., & de la Torre, M. A. (2002). Whole and defatted hyperproteic amaranth flours tested as wheat flour supplementation in mold breads. *LWT – Food Science and Technology, 35*, 472–475.

Vargas, M., Albors, A., Chiralt, A., & González-Martínez, C. (2011). Water interactions and microestructure of chitosan-methylcellulose composite films as affected by ionic concentration. *LWT – Food Science and Technology, 44*, 2290–2295.

Wan, V. C. H., Kim, M. S., & Lee, S. Y. (2005). Water vapor permeability and mechanical properties of soy protein isolate edible films composed of different plasticizer combinations. *Journal of Food Science, 70*, 387–391.