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EFFECTS OF DRYING TEMPERATURE AND RELATIVE HUMIDITY ON THE COLOR, SOLUBILITY AND MECHANICAL PROPERTIES OF TWO TYPES OF SOY PROTEIN FILMS

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Abstract: The influence of drying conditions (air temperature and relative humidity) on mechanical properties, solubility in water, and colour of soy protein films was studied. Two kinds of soy protein isolate were used: a commercial one (CSPI) and other obtained at laboratorial conditions (LSPI). It was verified that film properties of the LSPI and CSPI are influenced in a very different way by the drying conditions. DSC studies verified that the very different behaviour in relation of drying conditions must be due to a diverse initial protein conformation in both materials.

Keywords: soy protein isolates, edible films, drying conditions, mechanical properties, solubility

INTRODUCTION

Edible films are usually obtained by the casting methodology. In the final stage of the process, the filmogenic suspension of polymer is dried on an appropriate support.

Film properties depend of conditions of processing but also on the initial structure of raw material.

In the case of protein films, drying conditions must interfere on final properties of material as proteins can change their structure as a function of the parameters of processing (Tapia-Blácido et al., 2005). In that sense, temperature is a strong denaturing agent for proteins. But the thermal stability and conformation of each protein depend on the amino acid composition.

During the drying period, when water is progressively eliminated, proteins conformation change and the degree of protein unfolding determines the type and proportion of covalent (S-S bonds) or non-covalent (hydrophobic interactions, ionic and hydrogen bonds) interactions that can be establish among protein chains. It is known that

being denatured protein chains can interact strongly and easier, especially by disulphide bonds (Darby and Creighton, 1995). So the cohesion of the final network would be a function of these bonds and determines the properties of the films obtained.

Gennadios et al. (1996a) showed that it was possible to improve the moisture barrier properties of soy protein films by heat curing. Perez-Gago et al. (1999) reported that heat-denatured whey protein films had higher tensile properties than native ones. Others studies showed that heat curing improved the toughness and moisture resistance of cast protein films made with various proteins, inclusive soy protein (Gennadios et al., 1996b; Rangavajhyala et al., 1997; Rhim et al., 2000).

The aim of this paper was to compare the influence of drying conditions on mechanical properties, solubility in water, and film colour of soy films, prepared from two types of soy protein isolates: one obtained at the laboratory containing native proteins and a commercial one with totally denatured proteins.

MATERIALS AND METHODS

Two kinds of soy protein isolate were used as raw materials: a commercial one (CSPI) and other that was obtained at laboratorial conditions (LSPI). LSPI was prepared from defatted low-heat soybean meal produced by Bunge-Ceval S.A. (Brazil, PDI: 83.82% $\pm$ 0.143 %). Soy flour was dispersed in distilled water (1:10 w/w). The dispersion was adjusted to pH 8.0 with 2N NaOH, stirred at room temperature for 2 hours, and centrifuged at 10,000 xg for 30 minutes at 15°C. The supernatant was then adjusted to pH 4.5 with 2N HCl and centrifuged at 3,300 xg for 20 minutes at 4°C. The pellet was washed with an aqueous solution at pH 4.6 and centrifuged as above. The pellet was suspended in distilled water and adjusted to pH 8.0. Finally SPI was frozen at -80 °C and freeze-dried (Petrucelli and Añón, 1995).

Commercial isolate, vCSPI (SUPRO 500E BATCH: E330001704), was supplied by The Solae Company, Brazil.

Film Formation

Films were prepared by casting, dispersing SPI (5 % w/v) and glycerol (2.5 % w/v) in distilled water. SPI solutions were magnetically stirred for 20 minutes at room temperature. The pH was adjusted to pH 10.5 with 2M NaOH and stirred for additional period of 10 minutes.

Films were dried in a chamber with air circulation under controlled condition of relative humidity (24, 30, 45, 60, 66 %) and air temperature (34, 40, 55, 70, 76 °C) up to constant moisture content of ~25 % (w.b). Water content was determined by drying in an oven at 105°C for 24 hours in triplicate and calculated according to ASTM D644-94 (ASTM, 1994). Films were conditioned for 48 hours at 58 % of RH prior to measure film mechanical properties, colour and solubility.

Mechanical properties

The tensile tests were performed according to the standard method D882-95 (ASTM, 1995), using a TA XT2 (SMS) texturometer.

Solubility in water and barrier properties

Solubility was measured by immersing 2.0 cm diameter film disks, in water at 25 $\pm$ 2°C, for 24 hours (Gontard et al 1992). A water vapour permeability test was also performed using a modified protocol of the E 96-80 ASTM Standard method (ASTM, 1995). Oxygen transmission was measured using the ASTM F 1927 method (ASTM, 1995) with a Mocon 2/20 Oxtran.

Colour

The colour, represented as difference of colour, was determined according Gennadios et al. (1996b) with a Miniscan XE Colorimeter HunterLab.

Differential Scanning Calorimetry (DSC)

The thermal properties of the films were determined by differential scanning calorimetry, using a DSC TA 2010 controlled by a TA 5000 module (TA Instruments, New Castle, DE, USA), with a quench-cooling accessory. The temperature range studied was -150 to 150°C. The heating/cooling rate was 10°C/min.

Scanning electron microscopy (SEM)

Small strips of film (4mm long x 4mm wide) were cut and were fixed in a solution of 2 % v/v glutaraldehyde and 0.1M sodium cacodylate buffer (pH 7.2) for 2 hours. The samples were washed with 0.1M sodium cacodylate buffer (3 times for 10 minutes) and post-fixed in 2 %, w/v, OsO₄ and 0.2M sodium cacodylate buffer (pH 7.2) for 2 hours. After washing in 0.1M sodium cacodylate buffer (3 times for 10 minutes), samples were dehydrated for 15 minutes through a graded ethanol series: 30, 50, 70, 90 % v/v, three times for 15 minutes at 99.5 % v/v, and dried at the critical point. Then, dried samples were mounted on aluminium stubs and coated with gold. The samples were observed with a JEOL Model JSM-5800LV scanning electron microscope, at an acceleration voltage of 10 kV.

Experimental Design

A central composite rotatable design with two replicates at the central point was performed. The studied variables were the drying conditions: temperature (T) and relative humidity (RH). The statistical design considered and the values of the independent and coded variables are shown in Table 1.

An analysis of variance (ANOVA), a multiple comparison test and all statistical analysis were performed using Statistica 6.0 software. The data were fitted to a second order equation (Equation 1) as a function of the dependent variables.

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

where b_i are constant regression coefficients, Y_i dependent variables (mechanical properties, solubility, colour and drying time) and X_1 and X_2 are the coded independent variables (temperature and relative humidity).

Table 1. Full factorial design 2²

Test	T(X ₁)*	RH(X ₂)
1	40(-1)	30(-1)
2	40(-1)	60(+1)
3	70(+1)	30(-1)
4	70(+1)	60(+1)
5	33.8(-1.414)	45(0)
6	76.2(+1.414)	45(0)
7	55(0)	23.8(-1.414)
8	55(0)	66.2(+1.414)
9	55(0)	45(0)
10	55(0)	45(0)

*Independent variables values (the values between brackets are the coded variables).

RESULTS

The two soy protein isolates used has the following protein content: the commercial one contained 94 $\pm$ 2 % of protein and the other obtained in the laboratory, 91.5 $\pm$ 2 % of protein, both based on a dry basis (N x 6.25) and measured by Kjeldahl method.

Both isolates are mainly formed by β -conglycinin and glycinin globulins, as was observed by SDS-PAGE electrophoresis (data not shown). DSC thermograms of LSPI solutions showed the two typical endotherms of soybean proteins, the first at 78.2 $\pm$ 0.2°C, corresponding to β -conglycinin denaturation, and the second at 92.4 $\pm$ 0.1 °C, corresponding to glycinin. LSPI preparation method did not affect the native nature of soy globulins, as it is a mild process without any thermal treatment of the raw material. The isolates prepared at industrial level suffer different process in order to obtain distinctive functional properties in the final product. Thermal treatment is the most usual process used for the industry to modify proteins behaviour provoking the unfolding of the macromolecules.

Full Experimental Design

The results of the full experimental design are shown in Table 2, for the two raw materials. Data were fitted to a second order equation (Equation 1) as a function of the dependent variables. The significant effects at 90% (p $\leq$ 0.1) and 95% confidence level (p $\leq$ 0.05) were considered.

Data were fitted to a second order equation (Equation 1) as a function of the dependent variables. The significant effects at 90% (p $\leq$ 0.1) and 95% confidence level (p $\leq$ 0.05) were considered.

Table 2. Results of full factorial design 2²

Test	Film	Tensile test		S (%)	C(ΔE)	t(h)
		TS (MPa)	E (%)			
1	LSPI	0.3	54.5	86.4	13.8	2.5
	CSPI	1.4	26.8	42.8	17.4	3.3
2	LSPI	0.3	96.9	58.1	15.3	3.7
	CSPI	1.9	51.5	39.4	15.7	3.9
3	LSPI	0.7	45.1	71.5	20.8	0.8
	CSPI	4.1	61.2	41.1	14.4	0.9
4	LSPI	0.9	69.7	59.6	15.5	1.0
	CSPI	2.9	44.8	37.0	15.1	1.0
5	LSPI	0.3	111.8	95.5	15.7	4.2
	CSPI	1.9	38.5	44.8	15.7	5.4
6	LSPI	1.0	57.9	72.9	13.0	0.7
	CSPI	2.9	38.7	38.9	18.5	0.5
7	LSPI	0.7	45.2	80.5	13.4	1.2
	CSPI	2.7	53.3	39.9	14.9	1.5
8	LSPI	1.2	97.3	56.7	13.7	3.6
	CSPI	2.5	43.8	40.9	15.3	3.2
9	LSPI	0.8	81.4	68.2	13.2	2.1
	CSPI	1.8	64.5	41.8	15.9	2.2
10	LSPI	0.8	85.9	68.0	14.1	2.2
	CSPI	1.8	61.7	39.2	19.3	2.3

Equations 2 to 8, show the coded models for the tensile strength (TS), tensile elongation (E), solubility (S) and time of drying (t) up to 2.0 (d.b.) (~65% w.b) for the two materials: laboratory soy protein isolate (LSPI) and the commercial product (CSPI).

According to the analysis of variance (ANOVA) the coded models for tensile elongation, solubility and drying time were significant at 5% of significance (p $\leq$ 0.05) and for tensile strength at 10% of significance (p $\leq$ 0.1), for LSPI film. However, for CSPI film, the models for tensile strength and drying time were significant at 5% of significance (p $\leq$ 0.05) and for tensile elongation at 10% (p $\leq$ 0.1).

The solubility data for the commercial protein film (CSPI) and colour for both materials were not significant correlated (p $>$ 0.05).

LSPI

$$TS = 0.805 + 0.238X_1 - 0.145X_1^2 + 0.117X_2 \quad (R^2 = 0.82) \quad (2)$$

$$E = 74.58 - 14.12X_1 + 17.58X_2 \quad (R^2 = 0.81) \quad (3)$$

$$S = 66.68 - 5.66X_1 + 6.60X_1^2 - 9.76X_2 \quad (R^2 = 0.83) \quad (4)$$

$$\text{Time} = 2.19 - 1.20X_1 + 0.60X_2 - 0.24X_1X_2 \quad (R^2 = 0.94) \quad (5)$$

CSPI

$$TS = 1.775 + 0.632X_1 - 0.331X_1^2 + 0.428X_2^2 - 0.42X_1X_2 \quad (R^2 = 0.85) \quad (6)$$

$$E = 63.16 - 11.65X_1^2 - 6.68X_2^2 - 10.30X_1X_2 \quad (R^2 = 0.80) \quad (7)$$

$$\text{Time} = 2.22 - 1.53X_1 + 0.37X_2 \quad (R^2 = 0.95) \quad (8)$$

The responses surfaces generate using eqs.2-8 are given in Figures 1-4.

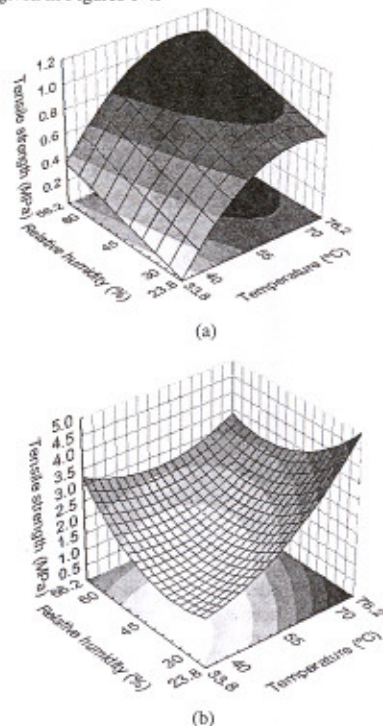


Fig. 1. Tensile strength of SPI films as a function of temperature and relative humidity. (a) LSPI, (b) CSPI

The general tendencies for tensile strength as a function of drying conditions for the two materials showed different behaviours, although some general trends are maintained (Fig. 1).

At lower temperature, an increase of relative humidity provokes an increase of tensile strength for both materials. However, this effect is more notorious in CSPI films than for LSPI ones. A zone of minimum tensile strength is verified at lower temperatures and RHs.

At high RH, the behaviour of materials is quite different: meanwhile the tensile strength is practically maintained constant with the increase of temperature for CSPI films; those made with LSPI suffer a steep elevation of this property with air temperature.

At high temperature the behaviour is also very different: the range of higher tensions are localise at high RH for LSPI film and at the lowest RH for the commercial one. It would be mentioned that absolute values of tensile strength of CSPI films are higher than those of the laboratory protein ones.

Elongation tendencies are very different for both materials (Fig. 2). For the LSPI films, maximum values of elongation are verified at high RH and low temperature while in CSPI films, the maximum values are measured at medium temperature, nearly 60°C at a range of RH of 35-55%.

Moreover, for the CSPI films, values of E, ranges for nearly all condition in a range of 45-60% (Table 2). Meanwhile, for the LSPI, more extreme changes are verified (45-112%) (Table 2 and Fig. 2a).

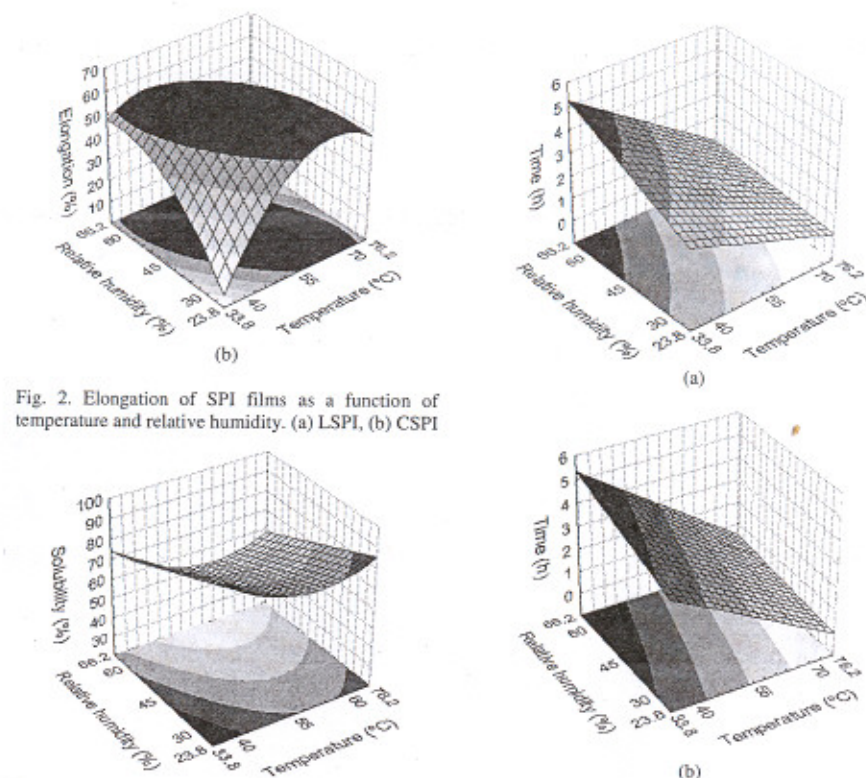
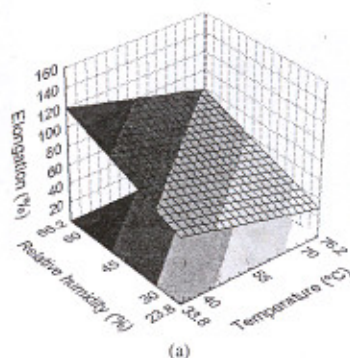


Fig. 2. Elongation of SPI films as a function of temperature and relative humidity. (a) LSPI, (b) CSPI

Fig. 3. Solubility of LSPI film as a function of temperature and relative humidity

The solubility data for LSPI films was adequately correlated as a function of drying conditions (eq. 4 and Fig. 3) but no correlation was obtained for the commercial one. Thus, solubility does not depend of drying process for this material and it maintains nearly constant (~40%).

The minimum solubility of the LSPI films (50%) was verified at high RH and temperature range from 45 up to 76°C. In almost conditions de LSPI was more soluble than the CSPI films.

Figure 4 shows the drying time of films up to moisture content of 2 (d.b.) (~65% w.b). The general tendencies are very similar in both cases. However, at low temperatures a deeper influence of RH is detected for the LSPI films.

Fig. 4. Drying time of SPI films as a function of temperature and relative humidity. (a) LSPI, (b) CSPI

Drying Kinetic of Soy Protein Films

Figures 5 and 6 show the films behaviour for the whole period of drying (up to final moisture content)

A constant rate period is found for both materials from the initial moisture content up to 3 d.b. Then a decreasing period is obtained up to the final water content. The total time of drying ranges from 8 hours at mild conditions (34°C, 45% RH) to 1 hour at severe conditions (76°C, 45% RH). Thus, the choice of the drying process conditions may result an economy in time of processing if the quality of film is not damaged.

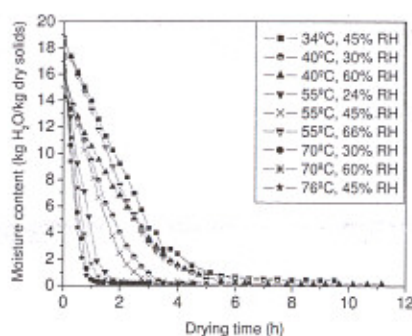


Fig. 5. Moisture content of LPSI films as a function of drying time, temperature and relative humidity

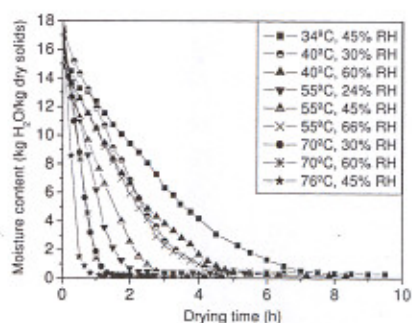


Fig. 6. Moisture content of CSPI films as a function of drying time, temperature and relative humidity

Barrier and optical properties of films

Films dried at the optimal conditions: 60°C and 60% RH for the LPSI and 70°C and 30% for the CSPI (Table 3) were also characterized by their optical, barrier and thermal properties and microstructure.

Barrier properties (water and oxygen) were higher in the commercial protein film, which means lower permeabilities. Specially, oxygen permeability of CSPI film was half of the LPSI one. Though, the CSPI film was thinner than the LPSI one. Figure 7 shows the films thermograms obtained by DSC. Both materials have similar T_g values ($-78.8 \pm 0.75^\circ\text{C}$ for CSPI and $-82.36 \pm 0.58^\circ\text{C}$ for LPSI), which must be related with the plasticizer. For LPSI film two endotherms were observed at $105.46 \pm 0.2^\circ\text{C}$ and $124.46 \pm 0.4^\circ\text{C}$ corresponding to the β -conglycinin and glycinin denaturation, respectively. Consequently, despite of some denaturation occurs by the alkaline pH of the filmogenic solution and the drying process, some protein structure is preserved in the film of LPSI, whereas, CSPI proteins are totally

denatured. Its thermogram did not show any endotherms.

Table 3. Barrier and optical properties of optimised films

Properties*	LPSI	CSPI
Moisture content (%d.b.)	25.96 ± 1.21	24.46 ± 0.30
WVP ($\text{g m}^{-1}\text{s}^{-1} \text{ Pa}^{-1}$)	$(1.54 \pm 0.19) \cdot 10^{-10}$	$(1.25 \pm 0.08) \cdot 10^{-10}$
Oxygen permeability ($\text{cm}^3 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ kPa}^{-1}$)	47.62 ± 9.52	18.23 ± 9.54
$a^*(a_0^* = -1.90)$	-5.56 ± 0.29	-3.21 ± 0.07
$b^*(b_0^* = 2.50)$	16.65 ± 1.65	16.20 ± 1.15
$L^*(L_0^* = 95.1)$	90.05 ± 1.49	87.12 ± 0.93
ΔE^*	15.50 ± 1.67	15.90 ± 1.45
Opacity	9.48 ± 3.06	12.57 ± 1.02
Thickness (mm)	0.076	0.060

* Films were conditioned at 25°C and 58% of relative humidity for 48 h

The LPSI films were a little more yellowish and also presented a lower opacity than CSPI films.

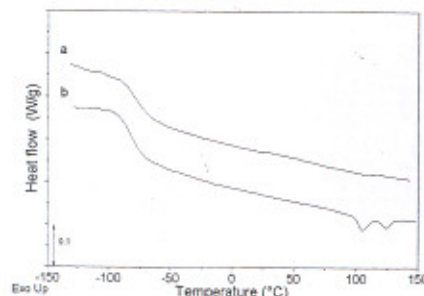


Fig. 7. DSC thermograms of SPI films conditioned in NaBr (58% RH) for three weeks. (a) CSPI, (b) LPSI

The previous data may be clarified if the SEM micrographs are examined (Fig. 8 and 9). It can be observed that LPSI film structure is dense with a fibrous formation parallel to film surface but some porous formation is also detected (Fig. 8), although these cavities seem to be closed porous. Characteristics quite different if compared with the commercial protein film (Fig. 9). The structure of CSPI reveals a denser network of protein chains without any porous macrostructure.

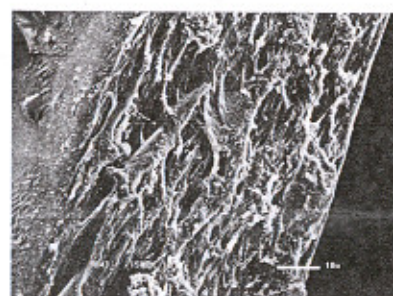


Fig. 8. SEM of the LPSI films - cross-section at 1500x magnification

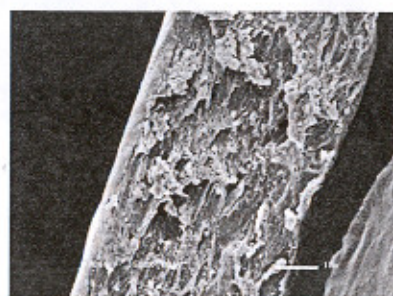


Fig. 9. SEM of the CSPI films - cross-section at 1500x magnification

The optimal drying conditions for CSPI were found in the highest drying rates that provoke higher shrinkage of the protein network. This can be seen by the thinner films obtained with CSPI (60 μm) than with LPSI (75 μm), although the same methodology was used for both films preparation. As both films were prepared with the same dried mass per unit area.

CONCLUSIONS

The main differences between the two raw materials are the initial structure of their proteins that result from the method of preparation. In the case of LPSI, a milder process than the commercial one was used. Thus, it allows maintain the globular conformation of soybean proteins. It must remember that no thermal treatment was performed prior drying on the casting suspension.

The commercial protein suffers a more severe treatment during the industrial process so develops a more denatured structure. Heating modifies the structure of proteins. They are probably partially

unfolded and can interact easily and strongly among adjacent polypeptide chains through covalent (disulphide bonds) and non-covalent (hydrophobic interactions and hydrogen and electrostatic bonds) interactions producing cohesive films. Disulphide bond enhances the formation of a resistant gel (Mauri and Añón, 2006).

However, during drying, these reactions will proceed in a very different way depending on the previous degree of unfolding of the raw material.

CSPI proteins present a greater degree of unfolding than LPSI proteins, so during drying, their chains can easier interact each other through a higher number of interactions mainly covalent (S-S links) ones. These facts can explain why CSPI films were tougher, and presented a lower solubility, and water and oxygen permeability than LPSI ones. The protein is completely denatured at the end of drying as DSC thermograms showed.

When the films are prepared from the laboratory soy protein isolate, the drying process acts like a thermal treatment for the protein where the unfolding of the molecule must proceed. The best properties of drying are obtained at higher RH and temperature, which allowed higher temperatures and a little longer time of process that allowed the required thermal treatment of protein. However, LPSI proteins are still partially denatured at the end of drying (Figure 7).

These results agree with those determined by Kim et al. (2002) working with SPI films plasticized with glycerol and dried in mild conditions. The authors demonstrated that still after the drying of the films, a heat treatment improved film properties. Using vacuum and temperatures ranging from 60 up to 85°C , they obtained films with higher tensile strengths and lower elongations at break, solubilities and water permeabilities.

It also notorious that the different conditions of drying and of raw material structure also influenced the final macro-structure, as was demonstrated by SEM micrographs.

It can be concluded that the optimal condition to film drying to obtain the best film properties for both materials depends on RH and temperature. That is not clearly understood at bibliography, yet. Generally, biofilms, prepared by casting process, are usually dried at ambient temperature without controlling RH and final moisture content and without any consideration to the different chemical nature of biopolymer.

More over, the optimal conditions of drying will depend on the kind of raw material (protein, starch, lipids) but also on the previous method of preparation of biopolymer that modifies the chemical and structural nature of raw material.

NOMENCLATURE

E	tensile elongation	%
S	solubility	%
t	drying time	h
RH	relative humidity	%
T	drying temperature	°C
TS	tensile strength	MPa
WVP	water vapour permeability	$\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$
d.b	drying basis	$\text{g H}_2\text{O/g dry solids}$
w.b	wet basis	$\text{g H}_2\text{O/100 g solids}$

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CHARACTERIZATION OF *SPIRULINA* SHRINKAGE FOR DIFFERENT INITIAL FORMS DURING DRYING

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Abstract *Spirulina* is a photosynthetic prokaryotic oxygen producing micro organism. After filtration and before drying, the fresh product has homogeneous structure. During convective drying at 40°C or 60°C, a crust appears on the air-product surface, making the product inhomogeneous and involving Shrinkage and the creation of pores are also involved in the drying process. The shrinkage of different initial sizes and forms by free convective drying at 45°C is studied. 1 to 6 mm initial diameter cylinders and thin layers (with a thickness that varies from 1 to 4 mm) of *Spirulina* are dried. The shrinkage is characterised by the variation of each dimension (length, width, height) in according to drying time and is represented in function of water content ratio. For *Spirulina* cylinders, shrinkage is very important in the direction perpendicular to its support. The shrinkage curves are not linear and depend on the initial dimensions and forms. The drying rates are corrected taking into account the variation of the exchange surface. That allows for the low critical moisture content to be determined.

Keywords: Shrinkage, critical moisture content, initial form, *Spirulina*, *Arthrospira*, convective drying.

INTRODUCTION

Spirulina (often called *Arthrospira*) is a photosynthetic prokaryotic oxygen producing micro organism. Due to its rich composition of essential elements such as amino acids, B12 vitamin, β -carotene, phycocyanine, exopolysaccharides and digestible proteins (from 60 to 74% in dry weight Belay, 1997), it has therapeutic, dietetic and nutritional applications.

If, after harvest, *Spirulina* is not dried or frozen, it will quickly ferment and be attacked by bacteria. Drying which facilitates variety in food consumption is the most convenient technological method for processing *Spirulina*.

The small cultures use convective drying (Desmorieux and Decaen, 2005) or solar drying rather than spray drying. The biomass is then extruded into cylinders of a few millimeters in diameter (from 2 to 4 mm). Product shrinkage and colour modification is noted. In drying of thin layers or cylinders of *Spirulina*, the surface become hard and thus cracks appear. The consequence of this phenomenon is water flux limitation from the core of the cylinder or layer into the air.

Shrinkage phenomenon particularly affects the material diffusion coefficient, which is one of the main parameters governing the drying process; it also has an influence on the drying rate (Queiroz and Nebra, 1996).

Shrinkage and porosity are important properties that have to be taken into account for modelling and characterization of the drying process; this is especially true for products (May and Perré, 2002) with high initial moisture content like *Spirulina*. The initial moisture content of *Spirulina* varies from 3 to 7 kgw/kgdm. Then, during drying *Spirulina* shrinks and cracks. Since shrinkage is not regular it has to be characterized in order to obtain a better understanding of pore formation. As the work of May (May and Perré, 2002) shows, taking the shrinkage into account will allow for water flux correction and the appearance of a constant drying rate period. The objective of this work is to measure the macroscopic changes due to shrinkage during convective drying of *Spirulina*.

We studied the influence of the different initial sizes and forms of *Spirulina* on its shrinkage under free convection at 45°C. One kinetic drying curve is corrected using the real calculated exchange surface.