

## Effect of Oxidized Potato Starch on the Physicochemical Properties of Soy Protein Isolate-Based Edible Films

Sabina Galus<sup>1\*</sup>, Andrzej Lenart<sup>1</sup>, Andrée Voilley<sup>2</sup> and Frédéric Debeaufort<sup>2,3</sup>

<sup>1</sup>Department of Food Engineering and Process Management, Faculty of Food Sciences, Warsaw University of Life Sciences-SGGW (WULS-SGGW), 159c Nowoursynowska St., PL-02-776 Warsaw, Poland

<sup>2</sup>EA 581 EMMA, AgroSup Dijon, 1 esplanade Erasme, University of Burgundy, F-21000 Dijon, France

<sup>3</sup>IUT-Dijon Department of Biological Engineering, 7 Boulevard Dr. Petijean, B.P. 17867, F-21078 Dijon cedex, France

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### Summary

The influence of oxidized starch on the physicochemical properties of cast soy protein isolate films is determined in this study. Films were cast from heated (70 °C for 20 min) alkaline (pH=10) aqueous solutions of 7 % soy protein isolate containing 50 % (by mass) glycerol as a plasticizer and different levels of added oxidized starch (0, 5, 10, 15, and 20 %, by mass). For all types of films, opacity, contact angle, tensile strength, elongation at break, water vapour permeability, measured at 25 °C for four relative humidity differentials (30–53, 30–75, 30–84 and 30–100 %), differential scanning calorimetry and microstructure were determined after conditioning film specimens at 25 °C and 30 % relative humidity for 48 h. Oxidized starch content significantly affected ( $p < 0.05$ ) tensile strength, from 0.95 to 1.51 MPa, temperature at maximum degradation rate from 64.8 to 74.2 °C and water vapour permeability from  $1.08 \cdot 10^{-10}$  to  $3.89 \cdot 10^{-10}$  g/(m·Pa·s) at relative humidity differentials of 30–50 and 30–100 %, respectively. Various internal arrangements were observed as a function of film composition (percentage of oxidized starch).

*Key words:* soy protein, oxidized starch, edible films, mechanical properties, water vapour permeability

### Introduction

Development of alternative edible and/or biodegradable packaging material to partially or totally replace synthetic polymers may offer opportunities that would benefit both manufacturers and consumers. Various natural biodegradable polymers such as protein- and polysaccharide-based edible films can potentially serve as coating materials for environmentally friendly packaging. Edible films or coatings have been proved to have functional properties as a barrier to solutes and gases and to prolong food quality and shelf life (1–3). Food proteins have been widely applied. Soy protein

isolate is an abundant, inexpensive, biodegradable and nutritional raw material, but it can cause allergies and could impart earthy or ash taste to food. However, recent reports have described the use of soy protein isolate to develop edible and biodegradable films (4–6). Soy protein isolate is a complex mixture of proteins with widely different molecular properties. The major soybean proteins have molecular mass ranging from 200 to 600 kDa. Most soy proteins (approx. 90 %) are globulins, which can be fractionated in 2S, 7S, 11S and 15S according to their sedimentation coefficients. The 7S and 11S fractions, the main fractions making up about 37 and 31 % of the total extractable protein respectively, have the

\*Corresponding author; Phone: ++48 22 59 37 579, Fax: ++48 22 59 37 576; E-mail: sabina\_galus@sggw.pl

capability of polymerization (7,8). Soy protein isolate, plasticizer and water are the major components of soy protein isolate films. Glycerol is the most widely used plasticizer for soy protein films because of its small size and hydrophilic nature, which makes it compatible with soy films (9).

Unfortunately, soy protein isolate films do not show satisfactory mechanical or vapour barrier properties for practical applications, and these properties become even poorer under conditions of high humidity (10). One way to modify the physical properties of films is by inducing intermolecular and intramolecular chemical bonding through physical or chemical means (11). A lot of treatments, including physical, chemical and even enzymatic methods, have been tested to improve the mechanical properties of protein-based edible films, including the addition of chemical cross-linking agents (*e.g.* aldehydes), heat curing, transglutaminase-induced crosslinking treatment and ultraviolet C irradiation treatments (12–15).

The incorporation of materials such as neutral lipids, fatty acids or waxes into carbohydrate or protein films has also been studied to improve moisture barrier properties of such films. Another approach to improve the physical properties of biopolymer films is to prepare composite films through combined use of compatible polysaccharide and protein materials. Film properties should be improved not only by the strength of one material compensating for the weakness of another, but also by any synergistic effect between the components (11). Very few scientific publications exist on the film-forming ability of such combinations of protein and polysaccharide components (16). Rhim *et al.* (17) demonstrated the potential use of dialdehyde starch as a cross-linking agent for protein films and coatings. Their study shows the potential of dialdehyde starch to substantially reduce the solubility of soy protein films in water and to increase their mechanical strength. However, the effect of oxidized starch on the properties of soy protein films has not been comprehensively tested. The incorporation of oxidized starch into protein-based film-forming solution is expected to affect the structure and properties of cast protein films.

The present study has been undertaken to understand the effect of oxidized potato starch mass fraction on the opacity, contact angle, mechanical and thermal properties, water vapour permeability and structure of soy protein isolate-based edible films.

## Materials and Methods

### Materials

Soy protein isolate (SPI) (Supro 670, approx. 90 g per 100 g of protein) was obtained from The Solae Company (Solae LLC, St. Louis, MO, USA). Oxidized potato starch was purchased from WPPZ S.A. (Lubon, Poland). It is labelled E1404 and classified as a food additive and not as a hazardous substance (18). Anhydrous glycerol was purchased from Fluka (purity of 98 g per 100 g, Fluka Chemical, Seelze, Germany) and used as a plasticizer in order to improve the mechanical properties of soy protein films. Sodium hydroxide (NaOH) was purchased

from POCH S.A. (Gliwice, Poland). Three saturated salt solutions (Prolabo, Fontenay-sous-Bois, France) of magnesium nitrate, sodium chloride and potassium chloride were used to control the water humidity at 53, 75 and 84 % respectively, at 25 °C.

### Film formation

Film-forming solutions were prepared by slowly dispersing 7 g of SPI and 0, 0.35, 0.7, 1.05 or 1.4 g of oxidized starch in water on a magnetic plate stirrer, adding 3.5 g of glycerol, adjusting the pH to 10±0.1 with 1 M sodium hydroxide and making the solution up to a final mass of 100 g with water. The value of pH=10 was chosen due to the good solubility in water (19) and good miscibility with polysaccharides (*i.e.* covalent bond), and was also widely presented in the literature in preparation of soy films and coatings (20). Film-forming solutions were heated on a magnetic plate at 70 °C for 20 min, then cooled down to room temperature, and finally poured onto a series of Petri dishes (diameter of 14 cm). To control the film thickness, the quantity of each film-forming solution poured onto a plate was the same (14 mL). The solutions were dried for 10 h at (25±1) °C and (30±2) % relative humidity (RH) in a ventilated chamber (KBF 240 Binder, ODIL, Dijon, France). After that, the dried solutions became easily detachable films. The dried films were peeled-off and conditioned again at 30 % RH and (25±1) °C for 48 h prior to testing. The compositions of the film-forming solutions are given in Table 1. Before testing, the thickness of the film samples was measured with an electronic gauge (Multi Check FE, SODEXIM, Tourcoing, France) with a precision of 1 µm, which was calibrated at 25, 51, 127 or 260 µm using standards, prior to film thickness measurements. Mean thickness was calculated from five measurements taken at different locations on each film sample (one at the centre and four near the perimeter).

Table 1. Composition of soy protein isolate films with various levels of oxidized starch film-forming suspensions before drying

| $\frac{m(\text{OS})}{m(\text{SPI})} \cdot 100$ | $\frac{m(\text{OS})}{\text{g}}$ | $\frac{m(\text{SPI})}{\text{g}}$ | $\frac{m(\text{glycerol})}{\text{g}}$ | $\frac{m(\text{water})}{\text{g}}$ |
|--|---------------------------------|----------------------------------|---------------------------------------|------------------------------------|
| 0  | 0                               | 7                                | 3.5                                   | 89.50                              |
| 5  | 0.35                            | 7                                | 3.5                                   | 89.15                              |
| 10   | 0.70                            | 7                                | 3.5                                   | 88.80                              |
| 15   | 1.05                            | 7                                | 3.5                                   | 88.45                              |
| 20   | 1.40                            | 7                                | 3.5                                   | 88.10                              |

OS=oxidized starch, SPI=soy protein isolate

### Opacity

The films were cut into rectangular pieces and directly placed in a spectrophotometer test cell, using an empty test cell as reference. The opacity index of the films was calculated by the following equation (21):

$$O = \frac{A_{600\text{nm}}}{x} \quad /1/$$

where  $A_{600\text{ nm}}$  is the value of absorbance at 600 nm and  $x$  is the film thickness (mm). Measurements were made using a UV-1650 spectrophotometer (Shimadzu, Kyoto, Japan).

### Contact angle

Contact angle of water on film surfaces was measured using a contact angle meter (GBX, Romans-sur-Isere, France), equipped with the DIGIDROP image analysis software (Digidrop, GBX). The sessile drop technique is basically an optical contact angle method, which is the most frequently used method to estimate the wetting properties of a solid surface (22). A droplet of distilled water (approx. 1  $\mu\text{L}$ ) was deposited on the film surface with a precision syringe. Then, the method is based on image processing and curve fitting for contact angle measurement from a theoretical meridian drop profile, measuring the contact angle between the baseline of the drop and the tangent at the drop boundary. The video acquisition of a magnified image of the drop profile is conveyed to a computer *via* a charge-coupled device (CCD) camera which enables one to quantify the changes in the droplet shape recorded as digital images over time. The contact angle was measured on the air-sides of the drop and averaged. All the films were preconditioned in a chamber under the same environmental conditions to avoid interference due to concurrent moisture exchange at the surface around the droplet. Four measurements were independently replicated for film samples and duplicated for film making. All the measurements were made on the air-side of the films (face in contact with the air during casting and drying).

### Mechanical properties

The tensile strength and elongation at break of the films (100 $\times$ 25 mm), as the average of 10 determinations, were measured using a TA-XT2i Texture Analyzer (Stable Microsystems, Godalming, UK) according to the ASTM D882-95 method (23). The initial distance of separation and velocity were adjusted to 50 mm and 1 mm/s, respectively, considering conditioned samples with the load cell of 5 kg.

### Differential scanning calorimetry

The differential scanning calorimetry (DSC) analysis was performed using a PerkinElmer DSC-7 calorimeter, and data were recorded and analyzed using PYRIS software (PerkinElmer, Courtaboeuf, France). Prior to analysis, the DSC equipment was calibrated with indium, the phase transitions of which are well known. The reference inert material during sample analysis and indium calibration was an airtight empty capsule. All film samples and capsules were equilibrated at 30 % RH and 25  $^{\circ}\text{C}$  before DSC analyses. The heating and cooling rates were fixed at 10  $^{\circ}\text{C}/\text{min}$ . The temperature program was: heating from 25 to 110  $^{\circ}\text{C}$  (first run), cooling down to 25  $^{\circ}\text{C}$ , heating again to 110  $^{\circ}\text{C}$  (second run), and finally cooling down to 25  $^{\circ}\text{C}$ . The initial temperature of degradation (or denaturation) corresponding to the peak onset,

$t_d$ , temperature at maximum degradation (maximum peak value),  $t_{\text{max}}$ , and apparent enthalpy of fusion,  $\Delta H_f$ , were computed from the thermal curve of the first heating according to Ryan *et al.* (24). Two independent measurements per film sample were made on each film preparation.

### Water vapour permeability

The water vapour permeability (WVP) of the films was measured gravimetrically according to the ASTM E96-00 standard method (25) modified and adapted to edible and bio-packaging films by Debeaufort *et al.* (26). The method is based on the mass variation of the permeation cells over time. Prior to WVP measurements, all film samples were equilibrated at 25  $^{\circ}\text{C}$  and 30 % RH for 48 h. Film samples were then placed between two rubber-based rings on the top of the glass cell containing the saturated salt solutions of  $\text{Mg}(\text{NO}_3)_2$ , NaCl, KCl or distilled water, which allowed the internal RH of the permeation cells to be kept constant at 53, 75, 84 and 100 %, respectively. These permeation cells were introduced into a ventilated chamber (the same one as for film drying) maintained at 30 % and 25  $^{\circ}\text{C}$ . The RH gradients in film or differentials between film sides were 30–53, 30–75, 30–84 and 30–100 %. These RH gradient values were selected because they correspond to the most common gradients observed within composite foods or between packaged foods and surrounding media. WVP ( $\mu$ ) was calculated using the following equation:

$$\mu = \frac{\Delta m \cdot e}{A \cdot \Delta t \cdot \Delta p} \quad /2/$$

where  $\Delta m/\Delta t$  is the mass of moisture loss per unit of time (g/s),  $A$  is the film area exposed to moisture transfer (8.55 $\cdot 10^{-4}$   $\text{m}^2$ ),  $e$  is the film thickness (m), and  $\Delta p$  is the water vapour pressure difference between the two sides of the film (Pa). Linear regression was used to estimate the slope of the g/s plot.  $\Delta p$  was calculated according to Eq. 3:

$$\Delta p = \frac{\Delta \text{RH}}{100} \cdot p_{\text{vap.sat}} \quad /3/$$

where  $p_{\text{vap.sat}}$  is the saturated vapour pressure of pure water and equals 3160 Pa at 25  $^{\circ}\text{C}$ .

At least three replicates per film sample were performed.

### Film microstructure

Film microstructure was observed by scanning electron microscope (Quanta 200, FEI, Brno, Czech Republic). A 5 $\times$ 5 mm film was fixed on the support using silver paste, at an angle of 90 $^{\circ}$  to the surface, which allowed observation of the film surface. No particular film preparation was necessary. Films were observed at a magnification of 1600 $\times$  and an intensity of 30 kV.

### Statistical analysis

Statistical analysis was performed with the program Statgraphics Plus v. 5.1 (Manugistics Corp., Rockville, MD, USA). The mass fraction of oxidized starch was the studied factor and the variables were: opacity, contact angle, mechanical and thermal properties, and water vapour permeability. The analysis of variance and Fisher's

LSD multiple comparison test were performed to detect significant differences in film properties. The significance level used was 0.05.

## Results and Discussion

Opacity is an important element to control the light incidence on a food, which is a relevant property since it has a direct impact on the appearance of the coated product. The analyzed films were yellowish, optically clear to the naked eye and transparent. Control and protein-starch films showed low opacity values (Table 2). The opacity varied with starch mass fraction, but a significant increase was observed only when 15 % of starch was added. The interaction with oxidized starch and water molecules modifies the refractive index of soy protein isolate, thus affecting the film transparency. The increase of light barrier properties of edible soy films as a consequence of the addition of different agents had been reported previously. The opacity of soy protein isolate and gelatine films was evaluated by Cao *et al.* (6), who found a significant opacity change. Also Su *et al.* (27) showed that an increasing level of poly(vinyl alcohol) (PVA) increases the opacity (decreases the transparency) of soy films by the dilution effect and the interaction between protein and PVA molecules. Brandenburg *et al.* (28) pointed out that soy protein isolate films were clear in appearance. However, insoluble particles may be present. Commercial processing methods for soy protein isolate may have caused this insolubilization. Cho *et al.* (29) mentioned that soy protein isolate was produced from a defatted soy meal by alkali extraction followed by acid precipitation (pH=4.5). Due to the fact that acid precipitation decreases the nitrogen solubility of soy proteins by their denaturation and aggregation, soy protein isolates had limited solubility.

The water contact angle of films is one of the indicators for direct determination of the hydrophilicity of films. The final state of the water drop on the film surface is taken as an indication of the wettability of the surface by water. The initial contact angle (at time 0 s) of soy protein isolate films with different levels of oxidized starch was measured to analyze surface properties (Table 2). The values ranged from (28.16±2.83) to (33.70±5.75)°, but they were not significantly different (p<0.05). Protein films having the highest contact angle values exhibit higher surface hydrophobicity, thus having better potential to overcome the limitation of hygroscopic property (14). The water contact angle increases with the increase of

surface hydrophobicity. Similar surface differences were previously described for chitosan-soy protein (30) and chitosan-whey protein (31) blend films and may be related to the affinity of the protein to the air-liquid interface.

The effect of oxidized starch on tensile strength and elongation at break of soy protein isolate films is reported in Table 2. The results showed that tensile strength of the composite films significantly increased as the oxidized starch content increased. The increase of tensile strength suggested the occurrence of cross-linking between soy proteins and oxidized starch. Increases in tensile strength had previously been reported for soy films prepared with sodium dodecyl sulphate (32), montmorillonite (33) or transglutaminase (34). Elongation at break increased significantly only in films containing 5 and 10 % starch (p<0.05). Values ranged from (19.45±2.94) to (26.73±1.89) %. When higher amounts of starch were added, elongation at break remained constant. In this case, more extensive phase separation may contribute to increased polymer-polymer interaction in each phase domain. Similar results were obtained by Rhim *et al.* (32) and by Tang *et al.* (34) for composite films. Rhim *et al.* (17) studied soy protein isolate films with different levels of dialdehyde starch and pointed out that in films with the addition of 5 % of starch, the tensile strength increased. However, they noted a decrease at a higher mass fraction of the agent. Moreover, the increase of tensile strength and elongation at break was observed by Cao *et al.* (6) for gelatine-soy protein films and Ou *et al.* (35) for soy protein films modified with the addition of ferulic acid.

Compared with pure soy protein film and blend films of soy protein, oxidized starch has considerably enhanced mechanical properties in the dry state because of the hydrogen bonding between soy proteins and oxidized starch. Better mechanical properties of the blend films make them more promising than pure soy protein films used in food packaging and renewable applications.

The thermal properties of soy protein isolate films with various levels of oxidized starch were investigated using DSC (Table 3). The initial and maximum temperatures of degradation and the enthalpy of fusion of the films were analyzed according to Ryan *et al.* (24). Oxidized starch affects the initial temperature of degradation when films contain from 5 to 20 % of oxidized starch. The values of the initial temperature of film degradation

Table 2. Opacity, contact angle, tensile strength and elongation at break of soy protein isolate films with various levels of oxidized starch

| $\frac{m(\text{OS})}{m(\text{SPI})} \cdot 100$ | Opacity<br>( $A_{600 \text{ nm}}/\text{mm}$ ) | Contact angle/°           | Tensile strength<br>MPa   | Elongation at break<br>%  |
|--|---|---------------------------|---------------------------|---------------------------|
| 0  | (2.47±0.36) <sup>a</sup>                      | (30.79±2.47) <sup>a</sup> | (0.95±0.14) <sup>a</sup>  | (19.45±2.94) <sup>a</sup> |
| 5  | (2.84±0.42) <sup>ab</sup>                     | (30.30±3.32) <sup>a</sup> | (1.22±0.21) <sup>b</sup>  | (26.56±2.52) <sup>b</sup> |
| 10   | (2.45±0.12) <sup>a</sup>                      | (30.03±2.90) <sup>a</sup> | (1.23±0.11) <sup>b</sup>  | (26.73±1.89) <sup>b</sup> |
| 15   | (3.32±0.39) <sup>b</sup>                      | (28.16±2.83) <sup>a</sup> | (1.37±0.14) <sup>bc</sup> | (21.58±0.34) <sup>a</sup> |
| 20   | (2.90±0.27) <sup>ab</sup>                     | (33.70±5.75) <sup>a</sup> | (1.51±0.10) <sup>c</sup>  | (21.44±0.37) <sup>a</sup> |

Values with the same superscripts within a column are not significantly different (p<0.05). OS=oxidized starch, SPI=soy protein isolate

Table 3. Differential scanning calorimetry (DSC) measurement results of soy protein isolate films with various levels of oxidized starch.

| $\frac{m(OS)}{m(SPI)}$ | $t_d/^\circ C$ | $t_{max}/^\circ C$       | $\Delta H_f/(J/g)$ |
|------------------------|----------------|--------------------------|--------------------|
| 0                      | (57.6±3.5)     | (64.9±0.8) <sup>a</sup>  | (0.17±0.05)        |
| 5                      | (64.0±4.9)     | (75.0±0.4) <sup>c</sup>  | (0.42±0.21)        |
| 10                     | (72.4±0.7)     | (71.5±2.6) <sup>bc</sup> | (0.42±0.13)        |
| 15                     | (59.7±8.6)     | (66.3±4.9) <sup>ab</sup> | (0.42±0.11)        |
| 20                     | (67.9±6.9)     | (74.2±0.9) <sup>c</sup>  | (0.44±0.14)        |

Values with different superscripts are significantly different ( $p < 0.05$ ).  $t_d$ =initial temperature of degradation,  $t_{max}$ =temperature at maximum degradation rate,  $\Delta H_f$ =apparent enthalpy of fusion. OS=oxidized starch, SPI=soy protein isolate

with different oxidized starch content ranged from (59.7±8.6) to (72.4±0.7) °C, and were higher than of the control film. The values of maximum temperature of degradation of soy protein isolate containing 15 % oxidized starch ranged between (66.3±4.9) and (75.0±0.4) °C. There was no significant influence of oxidized starch addition on the apparent enthalpy of fusion ( $p < 0.05$ ). The values were from (0.42±0.11) to (0.44±0.14) J/g and these values were higher than of control film, (0.17±0.05) J/g. No glass transition was observed due to the temperature range studied (25–100 °C). With the increase of oxidized starch content in the blend films, higher initial and maximum temperatures of degradation or enthalpy of fusion shifted in an obvious manner to a higher thermal stability, which indicates the strong interaction between the two kinds of molecules.

Results of WVP shown in Fig. 1 were used to determine the behaviour of films at four different RH gradients. The values for soy protein isolate films at various oxidized starch content ranged between  $1.08 \cdot 10^{-10}$  and  $2.22 \cdot 10^{-10}$  g/(m·s·Pa) at 30–53 % RH gradient, and between  $2.86 \cdot 10^{-10}$  and  $3.86 \cdot 10^{-10}$  g/(m·s·Pa) for films at 30–100 % RH gradients. When the oxidized starch content increased, WVP values increased too, except at 5

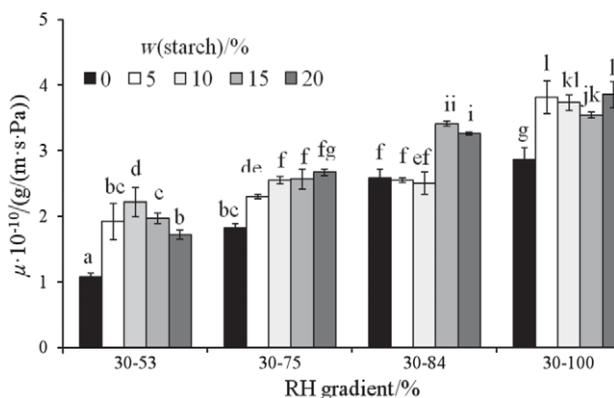


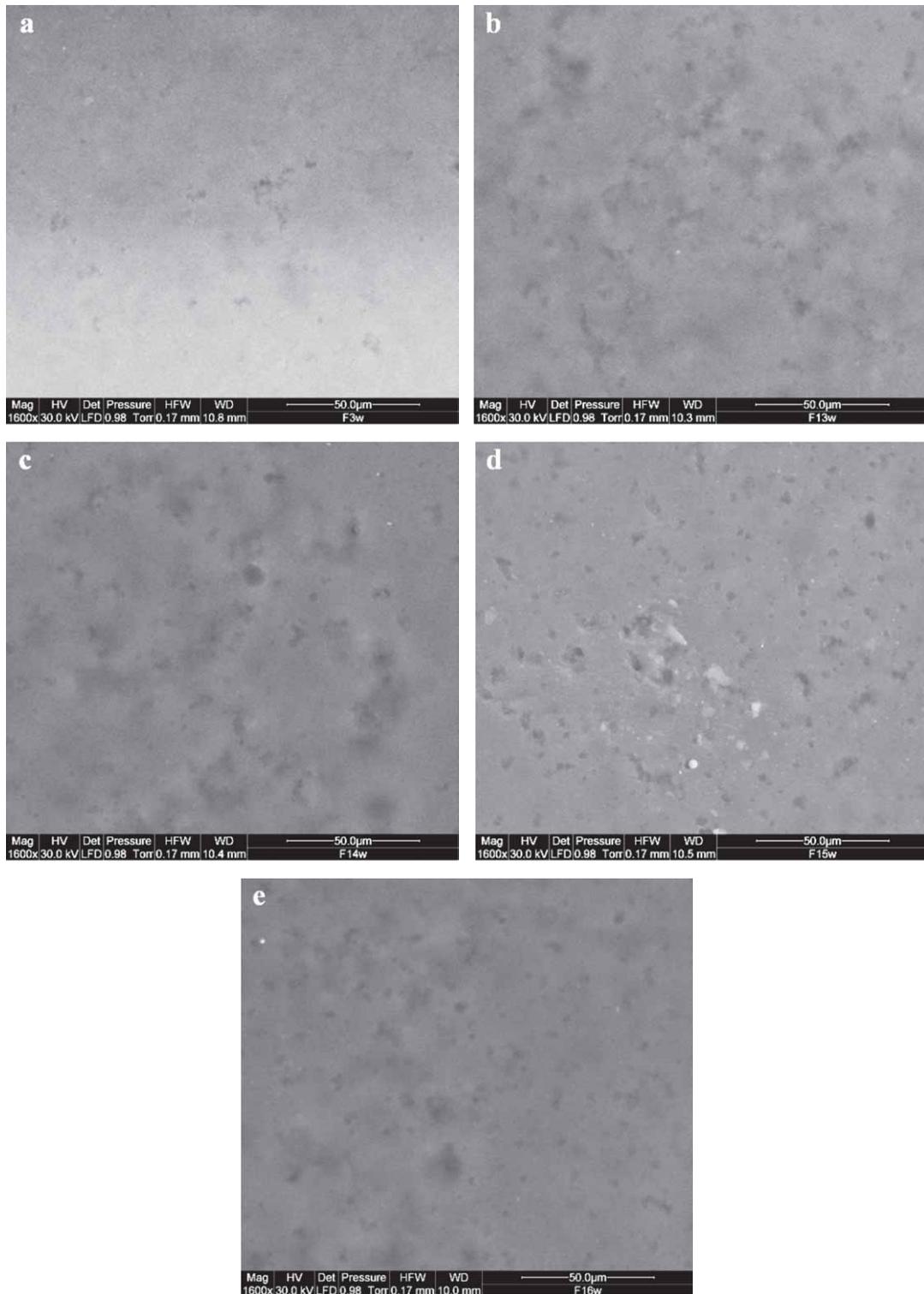
Fig. 1. Water vapour permeability ( $\mu$ ) of soy protein isolate films with various levels of oxidized starch at four different relative humidity (RH) gradients at 25 °C. Values with different letters are significantly different ( $p < 0.05$ )

and 10 % mass fraction of starch and 30–75 % RH gradient, when there was not any significant difference ( $p < 0.05$ ). WVP increased with RH gradient, which can be explained by the plasticizing effect of water and by the increasing driving force of the mass transfer. The mean values of WVP at 30–100 % RH gradient were much higher than at 30–84 % RH, which was also higher than at 30–75 % RH, and the lowest WVP values were obtained at 30–53 % RH gradient. However, the effect of oxidized starch on WVP of soy protein isolate films is greater at a lower RH gradient. It is worth noting that the addition of oxidized starch was not found to improve their water resistance. As suggested from the measurements of mechanical properties, the oxidized starch content affects the structure and organization of the soy protein isolate network. Olivas and Barbosa-Canovas (36) found that the change in physicochemical properties occurs at RH higher than 80 %. Rhim *et al.* (32) observed decreased WVP of soy protein isolate films after adding sodium dodecyl sulphate (50–10 % RH gradient). Similar results were obtained by Ou *et al.* (35) for soy protein isolate films with ferulic acid, and by Kokoszka *et al.* (37) for whey protein isolate films with rapeseed oil.

Figs. 2a–e show scanning electron micrographs of the surface of the soy protein films containing 0 (control), 5, 10, 15 and 20 % oxidized starch, respectively. A different internal arrangement was observed visually as a function of film composition. While the control film containing only soy protein isolate and glycerol showed a rough and homogeneous microstructure (Fig. 2a), the films prepared with oxidized starch showed structural discontinuities (Figs. 2b–e) due to the lack of miscibility of components. Surfaces of modified soy films were rough and uneven in comparison with those of control films. That means that blending with oxidized starch cannot eliminate structural defects of soy protein films. This phenomenon could be closely related to the differences of water-holding ability of soy protein isolate and oxidized starch. However, the surface of blend films becomes more coarse probably because starch agglomerates and causes phase separation. These structural differences could also be attributed to a different mass transfer of water and different drying rate. Similar results were reported by Tang *et al.* (34) for soy protein films prepared in the presence of transglutaminase, where the surface of modified films was rougher than that of control films. They analyzed this phenomenon in relation to the surface hydrophobicity and the rate of moisture loss of film-forming solutions, and suggested that it was dependent on the aggregation of exposed hydrophobic groups of soy proteins induced by transglutaminase. A different internal arrangement was also presented for other biopolymeric composite films, *i.e.* chitosan-whey protein films (31) or cellulose-chitosan films (38).

### Conclusions

A series of transparent films was prepared by blending soy protein isolates with various levels of oxidized starch in water solution. Differential scanning calorimetry results imply that the thermostability of the blend



**Fig. 2.** Scanning electron micrographs of soy protein isolate films with various levels of oxidized starch ( $(m(OS)/m(SPI)) \cdot 100$ ): a) 0, b) 5, c) 10, d) 15 and e) 20 %

films is obviously enhanced due to the hydrogen bonding between soy proteins and oxidized starch molecules. The high tensile strength in the dry state and the good miscibility between soy protein isolates and oxidized starch were confirmed by observing the microstructure. Composite films based on soy protein isolate and oxidized starch represent promising packaging materials

and provide a niche and a value-added industrial outlet for two abundant agricultural feedstocks.

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