

Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibers obtained by a baking process

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Abstract

Biodegradable food packaging trays made from cassava starch, sunflower proteins and cellulose fibers were obtained by a foam baking process. The effect of varying the proportions of these three components on physico-chemical and mechanical properties of the trays was studied, as was the relationship between these properties and the trays' microstructure. All trays presented thicknesses between 1.55 and 1.76 mm, and densities between 0.46 and 0.59 g/cm³. The increment of fiber concentration from 10% to 20% w/w improved the mechanical properties and slightly reduced the post-pressing moisture content, but increased the water absorption capacity of the material in at least 15%. The addition of sunflower proteins till 20% w/w reduced significantly the post-pressing moisture content (ca. 5.7%), the water absorption capacity (till 43%) and the relative deformation of the trays (till 21%). The formulation presenting the best properties contained 20% fiber and 10% protein isolate, and had a maximal resistance of 6.57 MPa and a 38% reduction in water absorption capacity, corresponding to a more compact, homogeneous and dense microstructure.

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1. Introduction

The extensive use of oil-derived synthetic plastics and the difficulty for recycling them have promoted the development of biodegradable materials, made from agro-industrial polymers obtained from renewable, abundant and low cost sources (Davis & Song, 2006; Gáspár, Benkó, Dogossy, Réczey, & Czigány, 2005). Since about 41% of plastics production is used for packaging industry, and 47% of this is used for food packaging (Fomin & Guzeev, 2001), the use of biopolymers within this field appears as an excellent alternative for reducing current environmental problems.

Some previous studies have shown that it is possible to obtain food containers from mixtures of starch, fibers and water by processes such as vacuum filtration (Matsui et al., 2004) or thermopressing (Glenn & Orts, 2001; Glenn, Orts, & Nobes, 2001; Schmidt, 2006; Shey, Imam, Glenn, & Orts, 2006; Shogren, Lawton, Doane, & Tiefenbacher, 1998; Shogren, Lawton, & Tiefenbacher, 2002; Soykeabkaew, Supaphol, & Rujiravanit, 2004), that can be an alternative to the extensively used expanded polystyrene foams. When applied to starch suspensions, the process known as foam baking includes two steps. The first one includes starch gelatinization and water evaporation, expanding the mixture and forming foam; and in the second step the foam is dried up to a final moisture content of 2–4% (Shogren et al., 1998).

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The disadvantage of the resulting materials is their fragility and their high affinity for water (Glenn et al., 2001). To improve these properties, the generation of these materials from modified starches or after addition of plasticizers, polymers, fibers and other additives has been reported. Shogren et al. (1998) showed that starch foam tensile strength and density increased while foam flexibility decreased with increasing starch concentration, molecular weight and amylose content. They reported that tuber starches, such as potato, produce trays with lower densities and higher flexibilities than those from cereals such as corn. Others reported that foams made from chemically modified starches presented lower baking times, lower weight and higher deformability than unmodified starches, while foams made from genetically modified (waxy) starches added with polyvinyl alcohol had higher elongations at break (Shogren et al., 2002). The tensile strength of baked starch foams, and occasionally the deformation at break, were also improved by the addition of different types of fibers, such as softwood, aspen, jute and flax fibers (Glenn et al., 2001; Lawton, Shogren, & Tiefenbacher, 2004; Shogren et al., 2002; Soykeabkaew et al., 2004). Furthermore, the resistance of starch trays to direct contact with water was improved by the addition of a high proportion of corn fibers and polyvinyl alcohol, the addition of natural rubber latex, and by preparation of starch foams laminated with foil, tissue paper, weighting paper, polyvinyl alcohol and polyvinyl chloride films (Cinelli, Chiellini, Lawton, & Iman, 2006; Glenn et al., 2001). After studying the effect of adding other polysaccharides and proteins, such as cellulose, hemicellulose and corn zeins to the formulation, Gáspár et al. (2005) concluded that hemicellulose and zeins conferred the best mechanical properties to the resulting materials. Other authors also reported that combining starches with other biopolymers, such as proteins or cellulose, results in the formation of biodegradable materials with improved properties (Arvanitoyannis, Psomiadou, & Nakayama, 1996; Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Coughlan, Shaw, Kerry, & Kerry, 2004; Jagannath, Nanjappa, Das Gupta, & Bawa, 2003; Psomiadou, Arvanitoyannis, & Yamamoto, 1996; Wongsasulak et al., 2006; Wongsasulak, Yoovidhya, Bhumiratana, & Hongprabhas, 2007).

Agro-industrial proteins also constitute an interesting source for economic biopolymers suitable for packaging. In particular, sunflower proteins have shown to possess adequate properties for use in the preparation of films by casting (Ayhllon-Meixueiro, Vaca-García, & Silvestre, 2000) and by thermopressing (Orliac, Rouilly, Silvestre, & Rigal, 2003), and also for the production of materials by injection molding (Rouilly, Orliac, Silvestre, & Rigal, 2006).

The goal of the present work was to investigate the use of a thermopressing process to prepare composite trays based on cassava starch, sunflower proteins and cellulose fibers. It was also aimed to assess the effect of varying the proportion of these three components on the physico-chemical and mechanical properties of trays, and the relationship between these properties and tray microstructure.

2. Materials and methods

2.1. Materials

Cassava starch containing 17% amylose (Molinari S.A., Brazil) was used. A sunflower protein isolate – containing 88% w/w proteins dry basis – was obtained at a pilot plant (ITA-UNL, Santa Fe, Argentina) from sunflower flour kindly provided by Aceitera Santa Clara (Molinos Río de la Plata, Rosario, Argentina). Eucalypt cellulose pulps were softwood short fibers with 1.2 mm and obtained from Klabin S.A. (Brazil). Magnesium stearate (Quimidro Ltda., Brazil), glycerol (Nuclear Casa da Química Ind e Com. Ltda., Brazil), and guar gum (Nicrom Química Ltda., Brazil) were also used as additives.

2.2. Experimental design

A factorial experimental design with two factors (fiber percentage and protein content) and three levels (3^2) in one block and without centerpoint was used to study the effect of formulation on the properties of the obtained materials, resulting in a total of 9 experiments (Statistica 6.0, StatSoft, Inc, USA) (Montgomery, 1993). On the basis of previous results, fiber percentages from 10% to 20% and protein concentrations from 0% to 20% were assessed. The initial formulations of the studied materials are shown in Table 1.

2.3. Tray manufacturing by thermopressing

To prepare each formulation (Table 1), the indicated cellulose fibers and water quantities were mixed for 5 min with a mechanic stirrer (Fisaton model 713D, Brazil), and were added with cassava starch, protein isolate and additives (4% w/w magnesium stearate, 1.5% w/w guar gum and 4% w/w glycerol). After further stirring for 5 min, 42–45 g of each formulation were homogeneously layered on a Teflon[®] plate of 16 cm by 11 cm, with a metallic guide 1.5 mm thick. A Teflon[®] lid was placed over the mixture and thermopressing was applied with a hydraulic press equipped with an electric heating system, Pt100 temperature sensor-and-register and PID controller. A pre-pressing was initially performed at 150–155 °C for 4 min in order to eliminate water by evaporation and to expand the mixture, followed by a pressing step of 3 min at 0.36 MPa at the same temperature. Finally, trays were removed from the press, cooled for 3 min at room temperature and unmolded. Trays were stored for 4 days at 25 °C and 75% relative humidity before characterization of their physico-chemical and mechanical properties.

2.4. Tray analyses

Foam tray thickness: Before testing, material thickness was measured by a digital micrometer (Digimatic, Mitutoyo, Japan). For each formulation, the reported value is

Table 1
Experimental factorial design

Samples	Cassava starch (g)	Cellulose fibers (g)	Sunflower protein isolate (g)	Water (g)
10F–0P	90	10	0	170
10F–10P	81	10	9	170
10F–20P	72	10	18	170
15F–0P	85	15	0	190
15F–10P	76.5	15	8.5	190
15F–20P	68	15	17	190
20F–0P	80	20	0	210
20F–10P	72	20	8	210
20F–20P	64	20	16	210

Initial formulation of materials under study.

the average of three measurements from every 10 tested samples.

Density: Density was calculated as the relationship between weight and volume (Shogren et al., 1998). Reported values are averages of five determinations for each formulation.

Moisture Content (MC): Samples MC was determined after drying in an oven at 105 °C for 24 h. Tray specimens (12.5 cm²) were placed on Petri dishes and were weighed before and after oven drying. MC values were calculated as the percentage of weight loss based on the original weight (ASTM D644-94, 1994), and they were the mean of ten measurements for each formulation.

Water absorption of samples during immersion: Samples measuring 2.5 cm by 5 cm were weighted and soaked in distilled water for 60 s. After removing the water excess using tissue paper, samples were weighted again. The quantity of adsorbed water was calculated as the weight difference and expressed as mass of absorbed water per mass of original sample (ABNT NBR NM ISO 535, 1999). Reported values were the mean of five determinations for each formulation.

Water sorption of samples at high relative humidities: Samples of starch foam trays containing 20% of fibers and no protein, and those with 20% fibers and 10% protein (20F–0P and 20F–10P) were placed in desiccators at 75% and 90% of relative humidities (RH), until the equilibrium was reached. Afterwards the samples equilibrium moistures were determined by the gravimetric method.

Color: Foams color was determined using a colorimeter (CR 300, Minolta Chroma Co., Osaka, Japan). A CIE Lab color scale was used to measure the degree of lightness (L), redness ($+a$) or greenness ($-a$), and yellowness ($+b$) or blueness ($-b$) of the foams. The instrument was calibrated using a set of three Minolta calibration plates. Foams were measured on the surface of the white standard plate with color coordinates of $L = 97.3$, $a = 0.14$ and $b = 1.71$. Total color difference (ΔE) was calculated from Eq. (1):

$$\Delta E = [(L_{\text{foam}} - L_{\text{standard}})^2 + (a_{\text{foam}} - a_{\text{standard}})^2 + (b_{\text{foam}} - b_{\text{standard}})^2]^{0.5}. \quad (1)$$

Values were expressed as the mean of five measurements for each sample, using five samples for each formulation.

Mechanical properties: A texture analyser model TA.XT2i (SMS, Surrey, UK), with a 25 N load cell was used to determine the mechanical properties of foam samples by means of tension and puncture tests. Tensile Tests were performed using foam strips measuring 100 mm by 25 mm, an initial grip separation of 80 mm and a crosshead speed set at 2 mm/s. Stress–strain curves were recorded during extension, and tensile strength at break (σ_{break}) was determined. Each formulation was assayed 10 times, reported values being an average of such assays. Puncture tests were performed using material samples of 10 cm by 10 cm. Force vs. distance were recorded during tests using a spherical probe with a diameter of 21 mm. Samples were broken at a speed rate of 1 mm/s with a 0.5 N load. Relative deformation (δ) was calculated as the ratio between the vertical distance traveled by the probe from sample contact until rupture and the sample diameter that coincides with the hole of the measuring device (80 mm).

Values of tensile strength at break (σ_{break}) and relative deformation (δ), named as Y_i , were fitted with a second order equation (Eq. (2)) with the Statistica 6.0 software (StatSoft, Inc, USA.) as a function of the independent variables fiber content (F) and protein percentage (P), b_n being the fit constants

$$Y_i = b_0 + b_1F + b_2P + b_{12}FP + b_{11}F^2 + b_{22}P^2 \quad (2)$$

Scanning electron microscopy: Samples were covered with a thin gold layer using a metallizer (SCD 005, BAL–TEC, Switzerland). Images were taken with a scanning electron microscope (XL-30, Philips, Netherlands) using an acceleration voltage of 10 kV in all cases.

2.5. Statistical analysis

Statistical analysis was carried out using SigmaStat 2.0 (Jandel Corporation, USA). Tukey's test ($P < 0.05$) was used to detect significant differences in the physico-chemical and mechanical properties of trays obtained with different formulations.

3. Results and discussion

3.1. Process variables

Limit concentrations for each component (starch, proteins, fibers) (Table 1) were chosen on the basis of previous results. To improve the mechanical properties of trays, 10–20% cellulose fiber was added. Schmidt (2006) reported that cassava starch trays containing higher than 30% cellulose fiber presented cavities that affected their mechanical properties. Shogren et al. (2002) also founded that the addition of low aspen fiber contents (5–10%) improved the mechanical properties of cornstarch foams. Cinelli et al. (2006) reported that increasing corn fibers content of the potato starch batters increased batter viscosity and diminished foaming.

The volume of water added to each formulation was directly related to the fiber content (Schmidt, 2006). Values presented in Table 1 correspond to the minimal water volumes that improved the addition of fiber to the mixture and allowed to obtain homogeneous dispersions. Sunflower protein isolates were added up to 20%, since at higher protein concentrations the trays presented superficial defects that affected not only their mechanical properties but also their aspect. Magnesium stearate, a hydrophobic compound that helps to unmold the trays, was added to all formulations. Guar gum was added to increase the viscosity of the suspension and to prevent solids separation, and glycerol was added as plasticizer (Shogren et al., 1998).

Trays containing proteins presented a “burned” aspect when pressed at temperatures between 180 and 200 °C even for times shorter than those used by Glenn et al. (2001), Lawton et al. (2004) and Schmidt (2006), for making trays with starch and fibers. Therefore, trays were processed for 7 min at 150–155 °C, which is similar to the procedure used by Gáspár et al. (2005) to obtain baked foams based on corn starch, cellulose and zeins.

3.2. Physico-chemical and mechanical properties of the trays

Thickness and densities of the obtained materials are shown in Table 2. All trays had average thickness values

ranging from 1.5 and 1.76 mm, and average densities ranging from 0.46 and 0.59 g/cm³. Variations in fiber content did not affect the thickness or density of starch trays. Only for a 10% protein concentration, an increase in fiber content resulted in a reduction of tray thickness accompanied by an increase of density. For trays with 10% fiber content, thickness increased as protein content increased, without a significant change in density. For higher fiber contents, however, thickness was minimal and density was maximal for trays containing 10% proteins. The highest density corresponded to trays containing 10% proteins and 15% fiber. Glenn et al. (2001) reported a reduction of foam density with the addition of corn fibers. The same tendency was described by Schmidt (2006) for trays made from cassava starch, cellulose fibers and CaCO₃. Density values registered in the present study were higher than those of expanded polystyrene – close to 0.06 g/cm³ according to Shey et al. (2006) and Glenn et al. (2001), paperboard – 0.18 g/cm³ (Glenn et al., 2001), and also higher than those reported by other authors for foams made of wheat, corn, tapioca, potato and cassava starch – 0.07–0.41 g/cm³ (Carr, Parra, Ponce, Lugão, & Buchl, 2006; Cinelli et al., 2006; Glenn et al., 2001; Shogren et al., 1998). Schmidt (2006) reported density values higher than those found in the present study – 0.63–1.3 g/cm³ – for trays made from the same starch and the same fibers, but added with CaCO₃.

Although at the moment of unmolding the moisture of trays ranged from 2% to 4%, they adsorbed water during storage (4 days at 25 °C and 75% RH). The MC values for each formulation are shown in Table 2. A slight diminution of water content was observed with the addition of proteins and fibers, which corresponds to a reduction in the starch content of the formulation. No significant reduction was detected when protein content was increased from 10% to 20%.

Results obtained for each formulation in the water absorption assay during immersion are shown in Fig. 1. For starch trays, an increase in fiber content from 10% to 20% resulted in a 18% increase in water absorption, whereas the addition of sunflower proteins reduces water absorption in up to 44%, the most significant variation

Table 2
Thickness, density, and moisture content of composite trays based on cassava starch, sunflower proteins and cellulose fibers

Samples	Thickness (mm)	Density (g cm ⁻³)	Moisture content (%)
10F-0P	1.6298 ± 0.0987 ^{a,b}	0.482 ± 0.043 ^{a,b,c}	10.81 ± 0.01 ^c
10F-10P	1.7216 ± 0.0853 ^{b,c}	0.474 ± 0.038 ^{a,b,c}	10.32 ± 0.14 ^{c,d}
10F-20P	1.7623 ± 0.0910 ^c	0.511 ± 0.049 ^{b,c}	10.18 ± 0.05 ^{b,c}
15F-0P	1.6197 ± 0.0650 ^{a,b}	0.518 ± 0.042 ^c	10.58 ± 0.04 ^{d,e}
15F-10P	1.5509 ± 0.0750 ^a	0.587 ± 0.044 ^d	10.14 ± 0.19 ^{b,c}
15F-20P	1.7207 ± 0.0873 ^{b,c}	0.463 ± 0.028 ^{a,b}	10.00 ± 0.13 ^{a,b}
20F-0P	1.6932 ± 0.1480 ^{b,c}	0.476 ± 0.044 ^{a,b,c}	10.35 ± 0.12 ^{c,d}
20F-10P	1.5490 ± 0.0587 ^a	0.522 ± 0.034 ^c	10.00 ± 0.18 ^{a,b}
20F-20P	1.6866 ± 0.0691 ^{b,c}	0.456 ± 0.013 ^a	9.74 ± 0.12 ^a

Average ± standard deviation. Different letters (a–e) denote significant difference ($p < 0.05$) between averages obtained by Tukey's test.

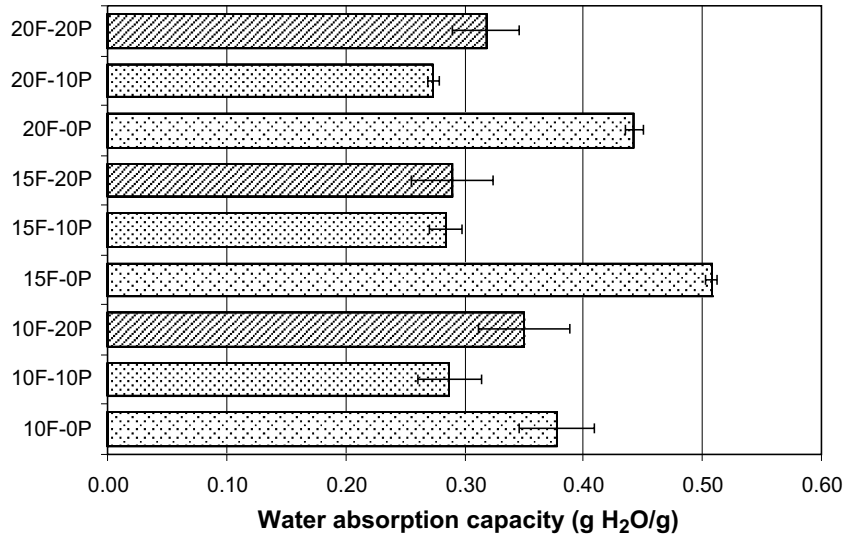


Fig. 1. Water absorption capacity of trays prepared with cassava starch, sunflower proteins and cellulose fibers.

occurring with 10% protein. In the presence of proteins, this parameter did not increase with the addition of fibers. From these results, it is evident that the presence of proteins reduces the sensitivity of trays to water and changes the effect of fibers.

Although the water absorption values of these materials were higher than those of trays obtained in other studies by impregnation processes or using starch acetate or PVOH (Cinelli et al., 2006), the reduction achieved is important in magnitude and broadens the possibilities of these materials.

As the water sorption during storage of these packaging materials would also determine their real commercial use, the equilibrium moistures of trays were determined at high relative humidities conditions. Equilibrium moistures of both samples (20F-0P and 20F-10P) conditioned at RH = 75% varied between 0.078 and 0.082 g water/g dry solid, i.e., no considerable difference was observed for this parameter. The same behaviour was observed for RH = 90%, when both sample trays showed equilibrium moisture very close to 0.105 g water/g dry solid. These moisture levels did not change the trays characteristics, indicating that the composites are stable at high air RH.

The effect of proteins was also observed by Gáspár et al. (2005) when corn zeins were added to corn starch foams. They carried out water uptake studies at different relative humidities on corn starch foams and its composites with cellulose, hemicellulose, zein and polycaprolactone. Instead composites presented better water resistance, after 14 days of conditioning, zein composites proved to be the best ones, having significantly lower water uptake than the others.

The effect of the addition of fibers and proteins on the tensile strength at break and relative deformation – obtained in puncture tests – of samples was studied, since these two properties are the most important mechanical properties for

assessing the usefulness of trays. For tensile strength at break, protein concentration (*P*) was significant in linear and quadratic terms, while fiber concentration (*F*) was significant only for the lineal term. Fiber–protein and fiber–fiber interactions were not significant ($p \geq 0.05$). The polynomial equation (3) fitted experimental data with $r^2 = 0.945$.

$$\sigma_{\text{break}} = 4.035 + 0.198F + 0.028P + 0.006FP - 0.005F^2 - 0.009P^2. \quad (3)$$

The response surface generated by Eq. (3) is shown in Fig. 2. It can be observed that for starch trays, the strength at break did not vary significantly when fiber percentage was increased from 10% to 20%. For trays containing sunflower proteins, in contrast, it increased with fiber addition,

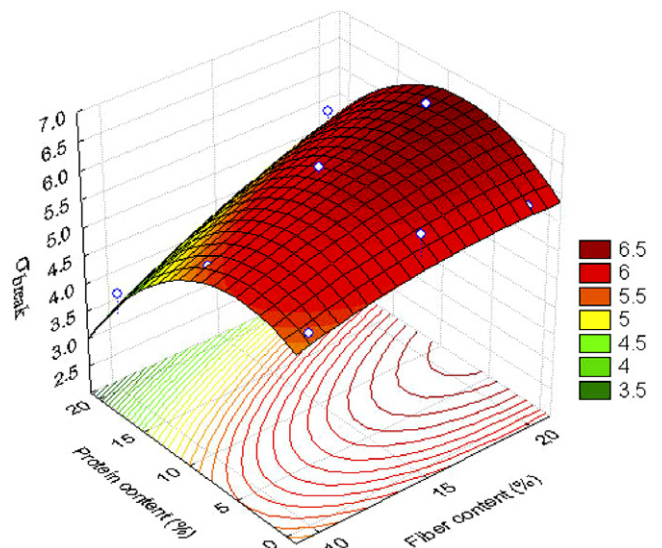


Fig. 2. Tensile strength at break (σ_{break}) (measured by tensile tests) as a function of fibers and protein content.

the increase being more significant for those containing 20% proteins. It can be also observed that the addition of 10% protein to the formulation led to an increase of tensile strength values as compared with those of cassava starch trays with the same fiber content, but these values were reduced when proteins were increased to 20%, specially for materials containing 10% and 15% fiber. The highest tension values (6.57 ± 1.16 MPa) corresponded to samples with 20% fiber and 10% protein. There was a close relationship between trays tensile strength and density. Trays with the highest densities presented the highest resistance. The same conclusion was reached by other authors. Shogren et al. (1998) observed that the strength and rigidity of starch foams were highly correlated with density and hence amylose content. According to these authors, this is an expected result since higher densities mean a higher content of starch, the load-bearing component.

Relative deformation, as measured with the puncture test, was significantly affected only by the protein content. The polynomial equation (4) fitted experimental data with $r^2 = 0.891$.

$$\delta = 0.07304 + 0.00018F - 0.00112P - 0.00004FP + 0.00002F^2 + 0.00006P^2. \quad (4)$$

Only the protein linear term had a significant effect on relative deformation, while no effect of fibers or protein–fiber interactions were observed. The response surface yielded by (4) is shown in Fig. 3. Fiber addition to starch trays increased the deformation at break of trays, but this change was less significant as the protein concentration increased. While Fig. 3 reveals a marked tendency to a reduction in relative deformation with the addition of proteins, differences only reached statistical signification for samples containing 20% fiber. These results are similar to those reported by Schmidt (2006) for trays prepared with

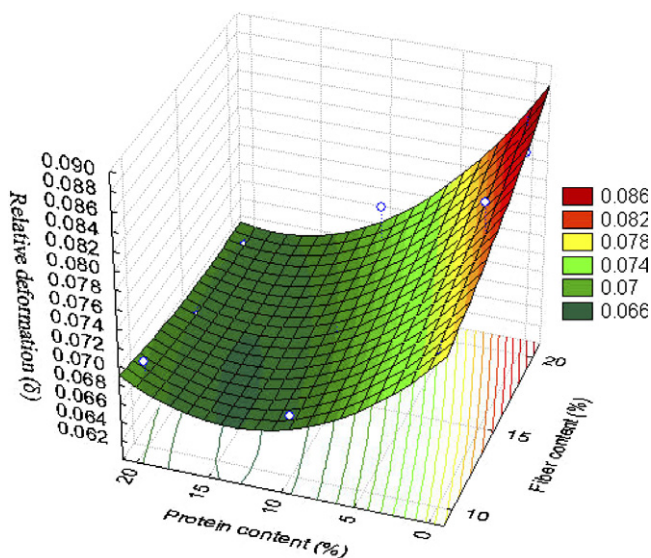


Fig. 3. Relative deformation (δ) (measured by puncture tests) as a function of fibers and protein content.

cassava starch, cellulose fibers and CaCO_3 . Lawton, Shogren, and Tiefenbacher (1999) reported that using high amilopectin starches resulted in lighter foams with low strength. Notably, the trays produced in the current study that presented higher densities than those reported in the literature had an increased resistance. But these values were still lower than those reported for Gáspár et al. (2005) for corn starch trays. Other authors showed that when the content of aspen fibers was increased up to about 15%, the tray tensile strength increased because the fibers adhered well to the starch matrix, reinforcing it. They found that trays resistance did not improve for fiber contents higher than 15%, but it began to diminish for fiber contents higher than 30% because of an uneven distribution of fibers in the starch matrix (Lawton et al., 2004; Shogren et al., 2002). Gáspár et al. (2005) also observed an improvement in tensile strength of corn starch trays when corn zeins were added at 10% to the formulation. They attributed this effect and the lower water uptake to the compatibility between both polymers, which allowed a more compact structure. Even though water is a strong plasticizer of materials based on polysaccharides and proteins (Gontard, Guilbert, & Cuq, 1993; Wongsasulak et al., 2006), no correlations among mechanical properties and moisture content were observed in this work.

Color parameters of the trays are shown in Table 3. Sunflower protein isolates exhibited a greenish aspect (L : 42.33 ± 0.15 ; a : -1.71 ± 0.06 ; b : 6.80 ± 0.08 ; ΔE : 55.24 ± 0.16) due to oxidation of phenolic compounds of sunflower flour during the alkaline treatment step of protein isolation (Shamanthaka Sastry & Narasinga Rao, 1997). Since cassava starch and cellulose fibers were white, trays lacking proteins presented a slight yellowish aspect (weakly positive for b), probably due to the high temperatures used in their preparation. In such trays, changes in the concentration of cellulose fiber did not result in significant differences of color. An increase in the protein content of the formulation resulted in an intensification of the greenish aspect ($a -$ and $b +$) and a reduction of L values, leading to an increase of ΔE .

3.3. Trays morphology

Fig. 4 depicts the surface (a) and transversal (b) microstructures of trays obtained with: (1) starch + 20% fiber (20F–0P), (2) starch + 20% fiber + 10% protein (20F–10P), and (3) starch + 10% fiber + 20% protein (10F–20P). As described previously by Shogren et al. (1998), starch trays present, because of their manufacturing process, a denser surface skin (shell), since contact with the hot mold leads to a rapid gelling and drying of the starch paste and prevents an extensive expansion. In addition, such trays present several cavities or holes in their surface, probably caused by air or vapour bubbles, which contract and break during the drying step (Fig. 4a). Usually, the inner structure of this type of trays is less dense, similar to foam, with open cells formed by leakage of water to

Table 3

Color parameters (L , a , b) and total color difference (ΔE) of trays composed by different proportions of cassava starch, sunflower proteins and cellulose fibers

Samples	L	a	b	ΔE
10F–0P	$88.68 \pm 0.42^{f,g}$	0.03 ± 0.07^c	6.77 ± 0.27^a	$9.99 \pm 0.47^{a,b}$
10F–10P	51.82 ± 1.58^d	-2.99 ± 0.41^a	9.15 ± 0.18^c	46.19 ± 1.58^d
10F–20P	41.54 ± 0.65^c	-2.58 ± 0.17^a	8.01 ± 0.29^c	56.18 ± 0.64^c
15F–0P	87.57 ± 0.71^f	0.10 ± 0.14^c	7.48 ± 0.32^b	11.32 ± 0.63^b
15F–10P	53.62 ± 1.08^c	-2.84 ± 0.12^a	9.69 ± 0.28^c	44.51 ± 1.07^c
15F–20P	44.85 ± 1.20^a	$-2.65 \pm 0.41^{a,b}$	9.29 ± 0.34^b	53.07 ± 1.13^c
20F–0P	89.43 ± 0.33^g	-0.20 ± 0.07^c	7.49 ± 0.35^b	9.78 ± 0.40^a
20F–10P	54.63 ± 1.08^b	$-2.90 \pm 0.34^{a,b}$	9.36 ± 0.66^c	43.47 ± 1.09^f
20F–20P	46.86 ± 0.61^c	-2.33 ± 0.36^b	9.75 ± 0.76^c	51.14 ± 0.52^g

Average \pm standard deviation. Different letters (a–g) denote significant difference ($p < 0.05$) between averages obtained by Tukey's test.

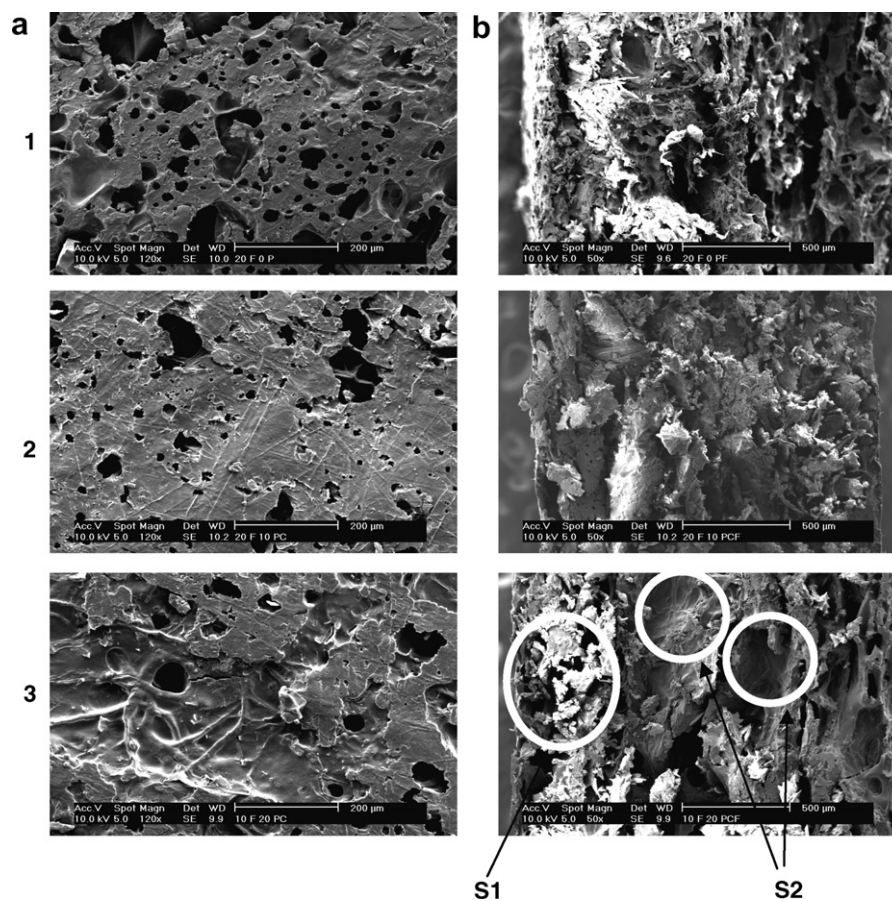


Fig. 4. SEM micrographs of (a) surfaces at 120 \times magnification and (b) cross-section at 50 \times magnification of trays. The numbers 1–3 represent the 20F–0P, 20F–10P and 10F–20P trays, respectively.

the mold and the consequent rupture of cells (Cinelli et al., 2006; Glenn et al., 2001; Shogren et al., 2002).

The micrography of the transversal section of a tray prepared with starch and fibers (Fig. 4b1) shows cells of moderate size, with fibers homogeneously spread throughout the whole material. As Lawton et al. (2004) reported for cornstarch foams reinforced by aspen fibers, no orientation of the fibers in the foam occurs, due to the nature of the baking process. In the present case there is no flow in the

baking machine, leading to not-aligned fibers in the baked foam.

The micrography of the transversal section of a tray prepared with the same proportion of fiber but with 10% proteins (Fig. 4b2) shows a greater homogeneity and density than in trays obtained without proteins. The same difference can be also observed in the surface of the same trays (Fig. 4a1 and a2). Trays that included proteins were virtually devoid of inner open cells, and zones attributable to

each component can not be identified. This material presented the best mechanical properties, lower water absorption, a lower thickness and a higher density.

When protein concentration was increased to 20%, the aspect of the inner structure of trays changed again (Fig. 4b3), resembling that of the 20F–0P trays, albeit with larger cells. The inner structure was not homogeneous, since the S1 region near the surface presented a foamy aspect, while in more deep structures (S2 region) the walls of larger cells had smoother appearance. Based on the knowledge about the microstructure of protein and starch films obtained by casting (Mauri & Añón, 2006; Tapia Blacido, Mauri, Menegalli, Amaral Sobral, & Añón, 2007), S2 zones can be attributed to a protein-rich phase. In such phase, fibers are well fixed and impregnated, and surely contribute to reinforce the matrix. An increase in protein concentration probably leads to an interference of proteins with the establishment of a starch network, which is reflected in a reduction of density and an impairment of mechanical properties. It is known that protein–polysaccharide systems are characterized by limited compatibility between their components, occasionally resulting in phase separation (Arvanitoyannis et al., 1996; Arvanitoyannis et al., 1997; Donald, Durrani, Jones, Rennie, & Tromp, 1995; Grinberg & Tolstoguzov, 1997). But for this system, when cellulose fibers are added, they would impregnate mainly in the protein matrix, improving the mechanical properties without affecting water absorption.

4. Conclusions

In this study, biodegradable packaging trays were prepared from raw materials from crops economically important in South America, such as cassava starch and sunflower proteins. The addition of proteins to trays made of starch and cellulose fibers led to a significant reduction in water absorption and water content of trays, without affecting other properties. The formulation containing starch, 20% cellulose fiber and 10% sunflower protein isolate exhibited the best properties, including maximal resistance and a notably reduced water absorption. Such characteristics correlated with denser materials that exhibited a more compact and homogenous microstructure.

Results reported in this work showed that these materials represent an alternative to the EPS trays, although their use still requires a detailed analysis, considering the specific needs of each case and safety needs of each food.

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