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Starch-vegetable fibre composites to protect food products

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ABSTRACT

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Keywords: Composites Starch-wheat bran Physicochemical characterization The influence of wheat bran content in biodegradable composites based on cassava starch and containing glycerol and potassium sorbate were studied. Films were produced by casting and three different fractions of wheat bran fibre were used: 1.5 mg, 13.5 mg and 27.1 mg/g of matrix.

It was observed that the addition of wheat bran, which contains 40 g of water insoluble fibre per 100 g of bran, shifted the glycerol-rich phase glass transition temperature toward higher temperatures, broadening and diminishing in intensity the peak associated with this relaxation. This effect suggests that the presence of fibre led to an enhancement in the glycerol dispersion.

At room temperature, an increase in fibre content did not affect density of the matrix but caused the increase of the storage modulus and the decrease of loss tangent, moisture content and water vapor permeability. Besides, the addition of fibres led to the increase of the yellow index.

The improvement in water vapor barrier properties jointly with the enhancement of mechanical properties when fibre was present, lead to the idea that the composite developed can be used to protect food and extend its shelf life.

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1. Introduction

In the field of the food industry, edible films are an emerging technology which produces increasing interest (García, Martino, & Zaritzky, 2000; Guilbert, Gontard, & Gorris, 1996; Tharanathan, 2003; Vermeiren, Devlieghere, Van Beest, de Kruijf, & Debevere, 1999). They can be used as food coatings with the objective of extending shelf life, minimizing changes in aroma, taste, texture, appearance or improving handling characteristics. One of the uses of edible films is as carriers of antimicrobials, antioxidants and other additives which are used for food preservation.

Starch is one of the polysaccharides frequently used to develop edible films because it is a natural polymer capable of forming a continuous matrix and it is a renewable and abundant resource (Bertuzzi, Armada, & Gottifredi, 2007; Lourdin, Valle, & Colonna, 1995; Romero-Bastida et al., 2005; Talja, Helén, Roos, & Jouppila, 2007). In particular, cassava is a good commercial cash crop and a major source of good quality starch (FAO, 2004), which is cheaper than other starches usually used by the food industry. Edible films formulated with cassava starch and glycerol have shown good mechanical properties expressed, for example, in strains higher than 70% when tensile tests were performed by Famá, Flores, Gerschenson, and Goyanes (2006) and Flores, Famá, Rojas, Goyanes, and Gerschenson (2007). However, this kind of films presented higher values of water vapor permeability (Flores et al., 2007), and smaller elastic modulus (Famá et al., 2006; Flores et al., 2007) than the ones of non-biodegradable packaging materials like polyethylene.

Over the last few years, a number of researchers investigated the use of natural fibres of vegetable origin as fillers in composite materials with the object of improving barrier (Alves et al, 2006) and mechanical properties of packaging (Curvelo, Carvalho, & Agnelli, 2001; Guan & Hanna, 2004; John & Thomas, 2008; Yang, Kim, Park, Lee, & Hwang, 2006). Lignocellulosic-based fibres have been used by (Avérous & Le Digabel, 2006) as fillers in a matrix constituted by a biodegradable and aromatic copolyester. Yang et al. (2006) used those fibres as reinforcing fillers in a polypropylene matrix. Moreover, Idicula, Malhotra, Joseph, and Thomas (2005) used fibres of banana/sisal and Mosiewicki (2005), sisal fibre, to reinforce polyester matrices.

According to Wollerdorfer and Bader (1998), when vegetal fibres are added to matrices of polysaccharides, the mechanical properties are notably improved. This fact has been attributed to the chemical similarity of polysaccharides and these fibres, providing good compatibility between them. In particular, Alemdar and Sain (2008) studied the use of cellulose fibres from wheat straw to reinforce starch based matrices not intended for food application. For the same purpose, Curvelo et al. (2001) used cellulose fibres isolated from eucalyptus pulp.

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The use of vegetable fibres to reinforce starch based matrices intended to be used as edible films has not yet been systematically studied. In particular, wheat bran has a high percentage of water-insoluble fibre constituted by cellulose, hemicellulose and lignin (National Public Heath Instituted of Finland, 2008), offering advantages as reinforcing material such as low density, non-abrasive nature, availability, low cost and renewability. In addition, the incorporation of bran into starch-based edible films, would contribute to the nutritional value of coated food products.

The goal of this paper is the study of the influence of wheat bran on physicochemical characteristics of cassava starch biocomposites intended to be used as edible films, with the objective of improving the quality of food products.

2. Experimental

2.1. Materials

The composite investigated in this study consists of wheat bran employed as natural fibre in a cassava starch matrix.

Cassava starch was provided by *Industrias del Maíz S.A.* (Argentina). Glycerol (Mallickrodt, Argentina) and potassium sorbate (Sigma, St. Louis, Missouri) used were of analytical grade. Wheat bran was provided by *Dietética Científica S.A.C.I.F.I.* (Argentina). It was milled and sieved through mesh N° 200-120 obtaining a product with a size between 75 µm and 125 µm and before use, it was dried. Wheat bran contains, approximately, 40 g of water insoluble fibre per 100 g of bran (Danish Food Composition Databank, 2007) constituted by 28 g of hemicellulose, 9 g of cellulose and 3 g of lignin (Anderson & Clydesdale, 1980).

2.2. Film formation

The Matrix film was constituted according to the procedure described by Famá et al. (2006). A mixture of 50 mg/g of cassava starch, 25 mg/g of glycerol (plasticizer), 2 mg/g of potassium sorbate (antimicrobial) and 923 mg/g of distilled water was brought to gelatinization by heating the suspension at ~1.7 °C/min till the sample achieved 82 °C. After gelatinization, the gel was degassed during 30 minutes with a vacuum mechanical pump. Then, it was distributed in glass dishes and dried at 52 °C during two hours. Drying was finished in a chamber with a temperature of 25 °C; the procedure lasted 4 days.

In the case of the composites, a suitable amount of bran (1.5 mg, Composite A; 13.5 mg, Composite B and 27.1 mg, Composite C, per g of matrix), was hydrated at room temperature (25 °C), 24 h in half of the water used in the matrix fabrication. Then, it was incorporated into the mixture described for Matrix film but containing only the other half of the water, and the gelatinization process was performed as previously described, till a temperature 5% higher than the temperature of gelatinization was achieved ($T_{\text{gelatinization}}$ was between 74 °C and 89 °C). In the composite preparation, it was necessary to maintain the system agitation during the degasifi-

cation using an orbital agitator (150 rpm) to assure system homogeneity.

After film casting, samples were separated from glass dishes and conditioned over NaBr (water activity, $a_w \cong 0.575$ at 25 °C) before characterization. As a consequence, samples were characterized 2 weeks after performing the gelatinization process. The thickness of the films, before their characterization, was \cong 400 µm.

Dehydration involved in the casting process determined \cong 90% of mass loss. Table 1 shows the mass of the conformed starchwheat bran composite films, on the basis of 100 g of the gel, and the percentages (mass of component in g present in 100 g of dry solids) of different components: starch, glycerol, sorbate and wheat bran (Φ_{starch} , $\Phi_{glycerol}$, $\Phi_{sorbate}$ and Φ_{wheat} bran, respectively).

2.3. Density determination

The density (ρ) of matrix film, composite film and wheat bran was determined using the "Archimedes principle", measuring the weight of the samples in air and in alcohol ($\rho_{alc} = 0.8 \text{ g/cm}^3$). It was used a Denver balance (Denver Instruments, USA) equipped with a density determination kit.

The time employed in each measurement was less than one minute and, as a consequence no dissolution of material was observed in the solvent used.

The reported results represent the average of, at least, 10 samples.

2.4. Microscopic observation

Composite C surface was studied by means of an optical microscope (Olympus BX60M), with a magnification of $50\times$, to determine distribution of the fibre and to observe possible agglomeration of the particules.

2.5. Moisture determination

Moisture content of the starch, sorbate and films (AOAC, 1990) was determined drying samples (\sim 0.5 g) in a vacuum oven at 70 °C, over calcium chloride, till constant weight.

Moisture content of glycerol was determined in an Ohaus IR gravimetric moisture analyzer (Model MB45, New Jersey) at 75 °C. The reported results represent the average of three samples.

The reported results represent the average of three sample

2.6. X-ray diffraction analyses

A Philips X-ray diffractometer with vertical goniometer (40 kV, 30 mA and Cu K α radiation λ = 1.542 Å), was used to obtain the X-ray spectrums in a scattering angle (2 θ) range of 3–33, at 1°/min. Distances between the planes of the crystals *d* (Å) were calculated from the diffraction angles (°) according to Bragg's law (Janot, 1997).

Samples used were constituted over a special glass attaining a final thickness of 200 μ m.

Table 1

Mass of the conformed films on the basis of 100 g of gel, and percentages of the components in the films

Systems	Mass of the films (%) ^a	Initial wheat bran added (%) ^b	$arPsi_{ m wheat\ bran}$ of the films (%) ^c	$arPhi_{ m starch}$ of the films (%) ^c	$\Phi_{ m glycerol}$ of the films (%) ^c	$\Phi_{ m sorbate}$ of the films (%) ^c
Matrix	10.8 ± 0.1	0	0	40.7 ± 0.1	22.2 ± 0.1	1.9 ± 0.1
Composite A	10.0 ± 0.1	0.15 ± 0.01	1.5 ± 0.1	43.8 ± 0.1	23.9 ± 0.1	2.0 ± 0.1
Composite B	11.0 ± 0.1	1.35 ± 0.01	12.3 ± 0.1	39.9 ± 0.1	21.7 ± 0.1	1.8 ± 0.1
Composite C	12.3 ± 0.1	2.71 ± 0.01	22.1 ± 0.1	35.7 ± 0.1	19.5 ± 0.1	1.6 ± 0.1

^a Gram of film/100 g gel.

^b Gram of wheat bran added/100 g gel.

 $^{\rm C}\,$ Gram of component/100 g of dry solids present in the films.

From the scattering spectrum, the effective percent crystallinity of films was determined, according to Hermans & Weidinger (1961), as the ratio of the integrated crystalline intensity to the total intensity. Crystalline area was evaluated on the basis of the area of the main peaks (main d-spacing).

The tests were carried out in duplicate.

2.7. Color determination

A Minolta CM-508d colorimeter (Japan) was used to evaluate the color parameters in the Hunter and CIE scale. The color differences (ΔC) and the yellow index (YI) of the films were used for comparison of different films.

Color difference is the magnitude of the resultant vector of three component differences: lightness difference, ΔL ; red-green chromaticity difference, Δa ; and yellow-blue chromaticity difference, Δb .

Yellow index was calculated according to ASTM D-1925 (1936). This parameter evaluates the degree of yellowness for certain nearly colorless transparent plastics.

Samples were cut in circles of 2 cm diameter for these tests. Three samples of each type of films were analyzed, performing 10 measurements at different points of each one. The results reported are the average of all measurements, for each type of film.

2.8. Water vapor permeability (WVP)

Water vapor permeability of films was determined gravimetrically at 25 °C, according to a modification of ASTM E96-00 (2000). Circular acrylic cups with an external diameter (ED) of 8.4 cm and an internal diameter (ID) of 4.4 cm (exposed area: 15.205 cm²) and with a depth of 3.5 cm, were used. The film was placed between the cell and its acrylic ring shaped cover. The cell was located in a temperature (25 °C) and relative humidity (68%) controlled chamber (Ibertest, Spain). Water vapor permeability values were calculated using the WVP Correction Method described by Gennadios, Weller, and Gooding (1994).

The results reported are the average of four samples.

2.9. Mechanical characterization

Dynamic and quasi static tests were performed using a Dynamic Mechanical Thermal Analyzer (DMTA IV Rheometric Scientific) in the rectangular tension mode at 1 Hz.

Dynamics tests were carried out from $-90 \,^{\circ}$ C to $20 \,^{\circ}$ C at $2 \,^{\circ}$ C/ min and using a fix deformation of 0.04%, to assure working in the lineal viscoelastic range (Famá et al., 2006). Loss tangent (Tan δ), and storage modulus (*E*') were obtained, as a function of temperature.

Quasi static tests were performed at a constant rate of $5 \times 10^{-3} \text{ seg}^{-1}$ and the stress (σ)-strain (ε) curves were obtained.

All the tests were carried out at room temperature in, at least, seven samples of dimensions 5.0 mm \times 5.1 mm \times 0.35 mm.

Microscopic examination of specimens used was performed to assure the use of free flaw samples.

2.10. Mathematical data treatment and statistical analyses

Data were analyzed through one-way ANOVA. Tukey test was the post-hoc test applied. Results are quoted on the basis of their average and confidence interval (α : 0.05) (Sokal & Rohlf, 1969).

3. Results and discussion

Density, color parameters, moisture content, crystalline fraction and water vapor permeability of the films are reported in Table 2.

Moisture contents of starch and glycerol were 11.4 and 3.8% (w/w), respectively.

Density of wheat bran, obtained applying Archimedes principle, resulted equal to (1.39 ± 0.01) g/cm³, which is similar to the value obtained for the matrix and composite density (Table 2).

Color parameters suffered an important increase with wheat bran fraction. This trend was observed for both, ΔC and YI, whose values were more than 100% higher in composites with the minimum amount of wheat bran added (Composite A). This behavior is consistent, taking into account the color of the bran. The change in the color with the addition of fibre limits the application of this kind of coatings to food products not affected by the change (cereal bars, cookies, wafers).

Moisture content and WVP of the composites diminished with the increase of wheat bran content as can be seen in Table 2. Results reported in that table also show that composites had lower WVP than matrix: however, no significant differences could be observed between B and C composites. It is important to remark that, during the permeability tests, the films remained intact. The general reduction of WVP with increasing fibre content results in an improvement of the characteristics of these biocomposites, considering the hydrophilic characteristics of the matrix. The decrease of water vapor permeability with fibre content is in agreement with results usually reported for composites studied for packaging applications (Matthews & Rawlings, 1994, chap. 2; Pinnavaia & Beal I, 2000). As it is known, water vapor permeability for hydrophilic films is linked to water adsorption and water diffusion rate (Kester & Fennema, 1986). Taking into account the theory of tortuous pathway of composite materials (Nielsen, 1962; Pinnavaia & Beall, 2000), it is highly expectable that diffusivity rate decrease in the presence of fibre, explaining the decrease in WVP obtained for Composites A and B (Table 2).

As it is shown in Table 2, the composite with 27.1 mg of wheat bran per g of matrix did not show additional modifications of the water vapor permeability. It is known that the changes in WVP due to the effect of the filler added are highly dependent on the

Tab	ole 2
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Density, color parameters, moisture content, crystalline fraction and water vapor permeability of the films

Systems	Density (g/cm ³) ^a	Color paramet	ers ^a	Moisture content (%) ^a	Crystalline fraction (%)	WVP (ng/smPa) ^a
		ΔC	YI			
Matrix	1.380 ± 0.004^{a}	7.2 ± 0.1	11.4 ± 0.2	35.2 ± 1.2	7.8 ± 0.8	0.64 ± 0.01
Composite A	1.379 ± 0.007^{a}	14.3 ± 0.3	26.7 ± 0.8	28.8 ± 0.6	11.0 ± 1.1^{b}	0.55 ± 0.01
Composite B	1.38 ± 0.01^{a}	33.8 ± 0.3	69.0 ± 0.5	24.3 ± 1.7	12.9 ± 1.3 ^b	0.22 ± 0.01 ^c
Composite C	1.384 ± 0.003^{a}	44.3 ± 0.7	85.8 ± 1.7	21.1 ± 1.1	13.3 ± 1.3 ^b	$0.20 \pm 0.01^{\circ}$

Samples were equilibrated at a water activity ($a_W = p/p_0$) of 0.575 at 25 °C, and characterized 2 weeks after gelatinization. p is the water vapor pressure in the sample and p_0 is the vapor pressure of water at the same temperature.

Systems with the same letter are not significantly (α : 0.05) different.

n is equivalent to 10^{-9}

^a Data is informed as $x \pm \varepsilon$, being x, the average and $\varepsilon = t_{(N-1)} s/N^{1/2}$. t is the Student parameter (α : 0.05); s is the standard deviation and N is the number of samples assayed.

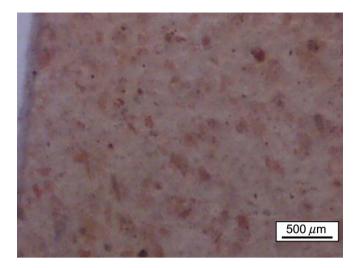


Fig. 1. Optical micrography of Composites C ($\Phi_{\text{wheat bran}} = 22.1\%$) at magnification of 50×.

size and aspect ratio (width-to-height) of the filler (Pinnavaia & Beall, 2000). As can be seen in Fig. 1, Composite C was agglomerated and, probably, this fact diminished the effectiveness of fibre for WVP decrease.

Fig. 2 shows the X-ray diffraction pattern for matrix material and different composites studied. In the matrix material, it can

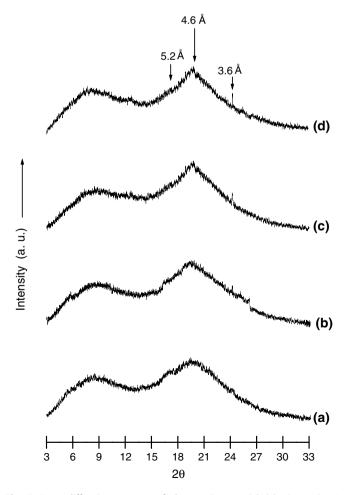


Fig. 2. X-ray diffraction patterns of the matrix material (a), Composite A ($\Phi_{\text{wheat bran}} = 1.5\%$) (b), Composite B ($\Phi_{\text{wheat bran}} = 12.3\%$) (c) and Composite C ($\Phi_{\text{wheat bran}} = 22.1\%$) (d).

be observed peaks which diffracted in the planes $d \cong 3.6$, 4.6 and 5.2 Å, as it was previously reported by Famá et al. (2006). Composite diffractograms showed similar patterns but with peaks slightly more intense (Fig. 2). Results concerning crystalline fraction indicate that fibre incorporation on starch films increased very slightly the crystalline fraction, but no differences are observed for different fibre contents. Probably, bran addition produced the modification of film crystallinity due to the contribution of cellulose crystallinity (John & Thomas, 2008) and/or to changes in the interphase. The agglomeration of fibres (see Fig. 1) occurred for high wheat bran content might have precluded the occurrence of additional changes in the interphase and, as a consequence, in the crystallinity.

The incorporation of wheat bran in the films produced a decrease in the moisture content of samples (Table 2). It is known that the increase in the crystalline phase of a semi-crystalline material is highly linked with the decrease in its moisture content (Chang, Chea, & Seow, 2000). As a consequence, the decrease in moisture content can be linked, at least partially, to the increase in crystalline fraction with fibre in some of the composites and/ or to the formation of composite structures with different water sorption characteristics than those of the matrix.

Fig. 3 shows the loss tangent, Tan δ (a), and storage modulus, *E'* (b), as a function of the temperature, for all contents of fibre studied. In this figure, it is possible to appreciate two peaks: one around -60 °C and other, wide and with low intensity, between -30 °C and room temperature. According to the literature (Jiang, Qiao, & Sun, 2006; Wilhelm, Sierakowski, Souza, & Wypych, 2003), the sys-

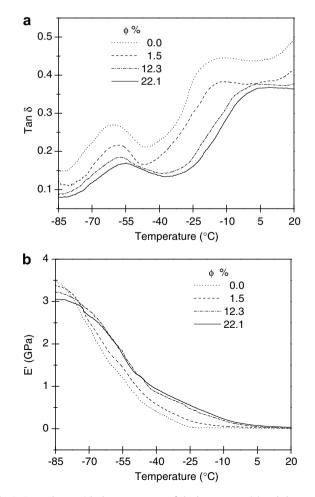


Fig. 3. Dependence with the temperature of the loss tangent (a) and the storage modulus (b); for the matrix and the different composites studied.

tem starch-glycerol is partially miscible and two phases can be observed: one, rich in glycerol, with a peak around -60 °C; and the other, rich in starch, at higher temperatures. Mathew & Dufresne (2002) showed a relaxation peak around 0°C, and they associated this peak with a rearrangement of amorphous starch chains in the presence of moisture; this phenomenon, known as retrogradation, is favored by the plasticizing effect of water. It is interesting to note in Fig. 3 (a) that both relaxation peaks shifted slightly to higher temperatures, broadened and diminished their intensity with the increase in wheat bran fibre content, trends that are usually observed in particulated composites (Goyanes, Konig, & Marconi, 2003; Nielsen & Landel, 1994, chap. 4). As it is well-know, the shift of one relaxation to higher temperatures is associated with the decreased mobility of the polymer chain. Then, the results showed in Fig. 3(a) are expected due to the addition of wheat bran fibre. The effect on the low temperature peak suggests that the presence of fibre led to an enhancement in the glycerol dispersion. Besides, this behavior is congruent with the decrease in moisture content with fibre fraction increase observed in Table 2; as it is well known, water is a plasticizer and, as a consequence, its decrease reduced plasticizing effect, modifying Tan δ .

It should be noticed that the relaxation associated to the glycerol rich phase, observed in the loss tangent curves, is in good agreement with the abrupt fall in the storage modulus (Fig. 3 (b)). The fibre addition produced a decrease in the intensity of the main relaxation $\Delta E'$ (difference between the E' value in the glassy zone and the E' value in the rubbery zone). For example, in the Composite C, $\Delta E'$ took a value of (2.7 ± 0.1) GPa, while in the matrix it was (3.2 ± 0.1) GPa.

In Fig. 4 it can be observed the dependence of E' and Tan δ with the fibre content at room temperature. These values were obtained from Fig. 3 at 20 °C. As can be seen, a fibre increase led to an increment in E' and a decrease in Tan δ . It is important to state that fibre addition can exert different effects on Tan δ : it can increase the interfacial area, producing an increase in Tan δ and, on the other hand, while producing a decrease in moisture content (Table 2), it tends to reduce the internal friction. According to our results, this last effect, are the one that prevailed. The increase in E' as a consequence of a decrease in moisture content could be also influenced by the high value of storage modulus of the wheat bran due to its important insoluble fibre content, producing a reinforcing effect on the material.

The decrease in WVP and the increase of *E*' observed for starch films with edible filler, are similar to those reported in literature

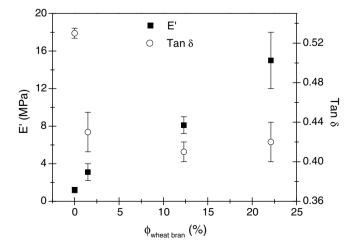


Fig. 4. Dependence with the wheat bran fraction ($\Phi_{wheat bran}$) of the storage modulus (*E*') and the loss tangent (Tan δ), at room temperature.

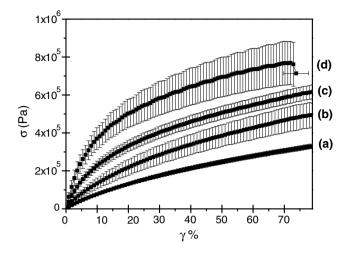


Fig. 5. Curves stress (σ)-strain (ε) of the matrix material (a), Composites A ($\Phi_{\text{wheat bran}} = 1.5\%$) (b), Composites B ($\Phi_{\text{wheat bran}} = 12.3\%$) (c), and Composites C ($\Phi_{\text{wheat bran}} = 22.1\%$) (d).

for composites with non-edible fibres like sisal (Mosiewicki, 2005), jute or flax (Wollerdorfer & Bader, 1998).

Quasi static behavior of the composites is shown in Fig. 5. As can be observed, all stress (σ)-strain (ε) curves present a small strain range where the stress increased linearly with the strain (less than 5%); then, a non linear behavior started without arriving to plastic deformation region. Flores et al. (2007), previously, reported a similar behavior for cassava starch films casted by other techniques than the ones herein used.

The curves reported in Fig. 5 show an increase of the hardening (defined as the tension to achieve the same deformation) with the increase of fibre content. This effect correlates with a smaller deformation to rupture in the sample that had the highest filler content, as can be seen in Fig. 5 (line d). The change in the hardening shown in the curves σ - ε with fibre content, might be linked to: (i) the contribution of fibre. The stiffness of the filler used in this research is expected to be higher than that of the matrix due to its high water-insoluble fibre content and/or (ii) the decrease in moisture content with fibre increment, as previously reported (Table 2). Marcovich, Aranguren, and Reboredo (2001) observed that the incorporation of wood flour to an unsaturated polyester/styrene resin increased the compression modulus and the yield stress but decreased the ultimate deformation and the toughness.

4. Conclusions

The use of wheat bran, which contains 40 g of water insoluble fibre per 100 g of bran, as a filler for edible films based on cassava starch was studied with the object of providing systematic information concerning the production and properties of these biocomposites. Films were plasticized with glycerol and contained potassium sorbate.

The presence of the filler did not affect the density of the matrix. Color parameters suffered an important increase with wheat bran fraction. The change in the color with the addition of fibre limits the application of this kind of coating to food products not affected by the change.

The mechanical properties of starch-wheat bran composites were improved when the content of the fibre was increased. The storage modulus and hardening of the films increased but maintained high deformation to rupture (beyond 70%). This reinforcing effect might be attributed, to the high storage modulus of wheat bran due to its water-insoluble fibre content. On the other hand, the composites showed a decrease in the moisture content, with bran content increase, which can also contribute to the increase in storage modulus and hardening.

Two relaxations were observed for thermoplastic cassava starch, one around -60 °C and the other between -30 °C and room temperature. It was observed that the relaxation at lower temperature, corresponding to glycerol rich domains, was influenced by the filler content. With the increase in wheat bran content, the relaxation peak around -60 °C shifted slightly to higher temperatures, broadened and diminished its intensity. This effect suggests that the presence of fibre led to an increase in the glycerol dispersion.

It has been shown that an increase in the wheat bran content produces an improvement in water vapor barrier properties. This in conjunction with the improved mechanical properties, lead to the idea that the composite developed can be used to protect food and extend their shelf life.

Acknowledgments

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References

- Alemdar, A., & Sain, M. (2008). Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Composites Science and Technology*, 68, 557–565.
- Alves, V., Costa, N., Hilliou, L., Larotonda, F., Goncalves, M., Sereno, A., et al. (2006). Design of biodegradable composite films for food packaging. *Desalination*, 199(1), 331–333.
- Anderson, N. E., & Clydesdale, F. M. (1980). An analysis of the dietary fiber content of a standard wheat bran. Journal of Food Science, 45, 336–340.
- AOAC (1990). Official methods of analysis. 13th ed. Washington, DC: Association of Official Analytical Chemists.
- ASTM D-1925 (1936). MacFarlane, Darby, S., David, K., Billmeyer & Fred, W. Method and instrument for selecting personal compatible colors. US Patent office, Pat. No. 5313267.
- ASTM E96-00 (2000). Standard test method for water vapor transmission of materials. Philadelphia: American Society for Testing and Materials.
- Avérous, L, & Le Digabel, F. (2006). Properties of biocomposites based on lignocellulosic fillers. Carbohydrate Polymers, 66, 480–493.
- Bertuzzi, M. A., Armada, M., & Gottifredi, J. C. (2007). Physicochemical characterization of starch based films. Journal of Food Engineering, 82, 17–25.
- Chang, P., Chea, P. B., & Seow, C. C. (2000). Plasticizing-antiplasticizing effects of water on physical properties of cassava starch films in the glassy state. *Journal* of Food Science, 65(3), 445–451.
- Curvelo, A. A. S., Carvalho, A. J. F., & Agnelli, J. a. M. (2001). Thermoplastic starchcellulosic fibrecomposites: Preliminary results. *Carbohydrate Polymers*, 45, 183–188.
- Danish Food Composition Databank (2007). http://www.foodcomp.dk. Accessed 01/ 01/2008.
- Famá, L., Flores, S., Gerschenson, L., & Goyanes, S. (2006). Physical characterization of cassava starch biofilms with special reference to dynamic mechanical properties at low temperatures. *Carbohydrate Polymers*, 66(1), 8–15.
- FAO (2004). Food and Agriculture Organization. Proceedings of the validation forum on the global cassava development strategy (Vol. 6). Rome: International Fund for Agricultural Development.
- Flores, S. K., Famá, L., Rojas, A. M., Goyanes, S., & Gerschenson, L. (2007). Physical properties of cassava-starch edible films: Influence of filmmaking and potassium sorbate. *Food Research International*, 4(2), 257–265.

- García, M., Martino, M., & Zaritzky, N. (2000). Lipid addition to improve barrier properties of edible starch-based films and coatings. *Journal of Food Science*, 65(6), 941–947.
- Gennadios, A., Weller, C. L., & Gooding, C. H. (1994). Measurement errors in water vapor permeability of highly permeable, hydrophilic edible. *Journal of Food Engineering*, 21, 395–409.
- Goyanes, S. N., Konig, P. G., & Marconi, J. D. (2003). Dynamic mechanical analysis of particulate-filled epoxy resin. *Journal Applied Polymer Science*, 88, 883–892.
- Guan, J., & Hanna, M. A. (2004). Functional properties of extruded foam composites of starch acetate and corn cob fibre. *Industrial Crops and Products*, 19, 255–269.
- Guilbert, S., Gontard, N., & Gorris, L. G. M. (1996). Prolongation of the shelf-life of perishable food products using biodegradable films and coatings. *Labensm.– Wiss. U.–Technology*, 29, 10–17.
- Hermans, P. H., & Weidinger, A. (1961). On the determination of the crystalline fraction of polyethylenes from X-ray diffraction. *Macromolecular Chemistry*, 24–36.
- Idicula, M., Malhotra, S. K., Joseph, K., & Thomas, S. (2005). Dynamic mechanical analysis of randomly oriented intimately mixed short banana/sisal hybrid fibre reinforced polyester composites. *Composites Science and Technology*, 65, 1077–1087.
- Janot, C. (1997). Quasicrystals a primer. Monographs on the physics and chemistry of materials. Oxford Science Publications. pp. 9.
- Jiang, W., Qiao, W., & Sun, K. (2006). Mechanical and thermal properties of thermoplastic acetylated starch/poly(ethylene–co–vinyl alcohol) blends. *Carbohydrate Polymers*, 65(2), 139–143.
- John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, 71, 343–364.
- Kester, J. J., & Fennema, O. R. (1986). Edible films and coatings. A review. Food Technology, 40, 47–59.
- Lourdin, D., Valle, G. D., & Colonna, P. (1995). Influence of amylose content on starch films and foams. *Carbohydrate Polymers*, 27(4), 261–270.
- Marcovich, N., Aranguren, M., & Reboredo, M. (2001). Modified woodflour as thermoset fillers. Part I. Effect of the chemical modification and percentage of filler on the mechanical properties. *Polymer*, 42, 815–825.
- Mathew, A. P., & Dufresne, A. (2002). Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromolecules*, 3(5), 1101–1108.
- Matthews, F. L., & Rawlings, R. D. (1994). Composite materials: Engineering and science. London: Chapmen & Hall (ldt.).
- Mosiewicki, M.A. (2005). Materiales compuestos con refuerzos y matrices poliméricas de origen vegetal. Tesis de Doctorado en Ciencias de Materiales. Universidad Nacional de Mar del Plata. INTEMA. Argentina.
- Nielsen, L. E. (1962). *Mechanical properties of polymers*. New York: Van Nostrand Reinhold.
- Pinnavaia, T. J., & Beall, G. W. (Eds.). (2000). Polymer clay nanocomposites. England: Wiley, J. & Sons (ltd.).
- Nielsen, L. E., & Landel, R. F. (1994). In S. Ochiai (Ed.), Mechanical properties of polymers and composites. New York: Marcel Dekker.
- Romero-Bastida, C. A., Bello-Pérez, L. A., García, M. A., Martino, M. N., Solorza-Feria, J., & Zarintzky, N. E. (2005). Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from non-conventional sources of starches. *Carbohvdrate Polvmers*, 60, 235–244.
- Sokal, R. R., & Rohlf, J. B. (1969). Biometry. The principles and practice of statistics in biological research. San Francisco, California: W.H. Freeman and Company.
- Talja, R. A., Helén, H., Roos, Y. H., & Jouppila, K. (2007). Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. *Carbohydrate Polymers*, 67, 288–295.
- Tharanathan, R. N. (2003). Biodegradable films and composite coatings: Past, present and future. *Trends in Food Science and Technology*, 14, 71–78.
- Vermeiren, L., Devlieghere, F., Van Beest, M., de Kruijf, N., & Debevere, J. (1999). Developments in the active packaging of foods. *Trend of Food Science Technology*, 10, 77–86.
- Wilhelm, H. M., Sierakowski, M. R., Souza, G. P., & Wypych, F. (2003). Starch films reinforced with mineral clay. Carbohydrate Polymers, 52, 101–110.
- Wollerdorfer, M., & Bader, H. (1998). Influence of natural fibres on the mechanical properties of biodegradable polymers. *Industrial Crops and Products*, 8(2), 105–112.
- Yang, H.-S., Kim, H.-J., Park, H.-J., Lee, B.-J., & Hwang, T.-S. (2006). Water absorption behavior and mechanical properties of lignocellulosic filler-polyolefin biocomposites. *Composite Structures*, 72, 429–437.