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Development of films based on blends of *Amaranthus cruentus* flour and poly(vinyl alcohol)

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ABSTRACT

The aim of this work was to develop biodegradable films based on blends of *Amaranthus cruentus* flour and poly(vinyl alcohol). Five different PVA types were tested. Blends with higher hydrolysis (HD) degree PVA were more resistant, showing greater tensile strength (TS) and puncture force (PF). However, the films with PVA with lower HD showed more flexibility, greater elongation at break (ELO) and greater puncture deformation (PD), with the exception of PVA 325. The latter was chosen due to it superior mechanical performance (TS = 10.2 MPa, ELO = 89.8%, PF = 9.4 N and PD = 16.3%). When films based on blends of amaranth flour and PVA 325 (10–50%) were evaluated, all mechanical properties were enhanced with increase in PVA 325 content. The solubility in water of the films made with PVA and amaranth flour decreased with increasing PVA content, reaching 44% of soluble matter for the 50% PVA film. The formation of hydrogen bonds between the blend components was confirmed by the FTIR spectra analysis.

1. Introduction

The use of biodegradable polymers for packaging offers an alternative form of packaging and also a partial solution to the problem of the accumulation of solid waste composed of synthetic inert polymers (Jayasekara, Harding, Bowater, Christie, & Lonergan 2004). Recently, the interest in using biodegradable materials for food packaging has increased because of consumer awareness of the environmental damage caused by non-biodegradable packaging (Oh, Wang, Field, & Aglan, 2004).

Also interest in the use of raw materials such as carbohydrates, proteins and lipids from renewable resources has increased. The use of natural blends of protein, polysaccharides and lipids directly obtained from agricultural sources, takes advantage of each component in the original system and appears to be a new opportunity for materials in the area of biodegradable films (Tapia-Blácido, Mauri, Menegalli, Sobral, & Añon, 2007). Thus amaranth flour is an interesting source of such raw materials for biodegradable film production (Colla, Sobral, & Menegalli, 2006a, 2006b; Tapia-Blácido, Sobral, & Menegalli, 2005a, 2005b).

Amaranth is a pseudo cereal showing rapid growth, with high tolerance to arid conditions and poor soils where traditional cereals cannot be grown. The main cultivars used are *Amaranthus hipochondriacus*, *Amaranthus cruentus* and *Amaranthus caudatus*. Amaranth seeds contain a significant proportion of starch (62%), protein (14–17%) and fat (5–9%) which make the flour a promising material for film production (Colla et al., 2006a; Tapia-Blácido et al., 2005a).

Tapia-Blácido et al. (2005a) developed films based on *A. caudatus* flour that were slightly yellowish with moderate opacity, good flexibility and good barrier properties, although the mechanical resistance was relatively low. Colla et al. (2006a) also produced films based on *A. cruentus* flour with stearic acid. The incorporation of stearic acid into the polymeric matrix provided an additional water vapor barrier in comparison to films without added lipids (Tapia-Blácido et al., 2005b).

Attempts to improve the properties of biopolymer films have been made in several ways. One strategy is the preparation of blended films via the combined use of compatible polymers to enhance the mechanical properties of biopolymers. Starch based polymers are frequently blended with high-performance polymers (e.g. aliphatic polyesters) to achieve the necessary performance properties for various applications (Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006). Nevertheless, these materials remain non-biodegradable (Tharanathan, 2003). Thus a better alternative may be the use of a biodegradable synthetic polymer (Abd El-Kader, Abdel Hamied, Mansour, El-Lawindy, & El-Tantaway, 2002; Jayasekara et al., 2004; Sreedhar et al., 2006), such as poly(vinyl alcohol) (Matsumura, Tomizawa, Toki, Nishikawa, & Toshima, 1999).

Poly(vinyl alcohol) (PVA) is a water-soluble, partially crystalline polymer, with technological potential as a biodegradable material (Abd El-Kader et al., 2002). The incorporation of PVA into starch changes the thermomechanical properties of the material and thus

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modifies the polymer structure at both the molecular and morphological levels, allowing for greater flexibility and more functional properties (Sreedhar, Sairam, Chattopadhyay, Syamala Rathnam, & Mohan Rao, 2005).

Several researchers (Follain, Joly, Dole, & Bliard, 2005b; Guohua et al, 2006; Imam, Cinelli, Gordon, & Chiellini, 2005; Jayasekara et al., 2004; Khan, Bhattacharia, Kader, & Bahari, 2006; Kim, Na, Park, Yoon, & Ihm, 2002; Lawton, 1996; Lee, Youn, Yun, & Yoon, 2007; Park, Chough, Yun, & Yoon, 2005; Raj, Raj, Madan, & Siddaramaiah, 2003; Siddaramaiah, Raj, & Somashekar, 2004; Sreedhar et al., 2005, 2006; Yin, Li, Liu, & Li 2005; Yoon, Chough, & Park, 2006a, 2006b) have reported the characterization of starch–PVA blended films. Amongst these trials, several authors studied the properties of films formulated with equal parts of starch–PVA (Lawton, 1996; Lee et al., 2007; Park et al., 2005; Sreedhar et al., 2005; Yoon et al., 2006a, 2006b), and many have used chemical or physical cross-linking to increase the compatibility of both polymers (Follain et al., 2005b; Guohua et al., 2006; Imam et al., 2005; Kim et al., 2002; Lee et al., 2007; Sreedhar et al., 2005, 2006; Yin et al., 2005). However, no previous work on biodegradable films based on blends of natural flours with PVA was found in the specialized literature.

Thus, the aim of this work was to develop biodegradable films based on blends of *A. cruentus* flour and poly(vinyl alcohol), and to study the effect of the PVA content in the blends on its mechanical properties and solubility. Firstly, 6 PVA types with different hydrolysis degrees were blended with amaranth flour and tested for film production. PVA 325 with 98–99% hydrolysis degree and a molecular weight in the range of 85,000–124,000, presented films with better mechanical properties and was chosen for the next study. Films were produced varying the PVA content from 10% to 50% (w/w) of the dry matter, and the mechanical properties and solubility measured. All the films were plasticized with glycerol.

2. Materials and methods

2.1. Materials

The amaranth flour was obtained from *A. cruentus* seeds (cultivar BRS Alegria provided by Embrapa Cerrados, a Brazilian Company for Agricultural Research, Federal District, Brazil) using the alkaline wet milling method described elsewhere (Colla et al., 2006a), obtaining a yield of 57%. This flour was analyzed according to standard AOAC methods (1997) and the results reported on a dry basis. The amylose content was determined using a colorimetric method (Juliano, 1971) with the modifications proposed by (Martínez & Cuevas, 1989). The *A. cruentus* flour contained 72.5% starch (7.8 ± 0.2% amylose), 11.9 ± 0.3% protein, 7.7 ± 0.8% lipids, 2.2 ± 0.6% ash and 5.6 ± 0.2% moisture.

The poly(vinyl alcohol) polymers with different molecular weights and hydrolysis degrees (Table 1) were from Celanese Chemicals and donated by Dermet Agekem (São Paulo, Brazil). The glycerol, NaOH and other chemicals were of analytical reagent grade, purchased from Synth (São Paulo, Brazil) and used without further purification.

Table 1
Characteristics of selected poly(vinyl alcohol) types

PVA grade[a]	Hydrolysis degree (%)	Molecular weight range
Celvol® 107	98.0–98.8	13,000–23,000
Celvol® 325	98.0–98.8	85,000–124,000
Celvol® 350	98.0–98.8	146,000–186,000
Celvol® 205	87.0–89.0	13,000–23,000
Celvol® 523	87.0–89.0	85,000–124,000
Celvol® 540	87.0–89.0	146,000–186,000

[a] *Source:* Celanese (2005).

2.2. Film preparation and conditioning

Amaranth flour/PVA blended films were made by the casting technique. The two solutions were first prepared separately. The amaranth flour solution was prepared according to Tapia-Blácido et al. (2005a) with 4 g of amaranth flour/100 g solution. The amaranth flour and deionized water were firstly mixed for at least 2 h with a magnetic stirrer with the pH adjusted to (10.7) for protein dissolution. The amaranth flour dispersion was then heated to 70 °C, and glycerol (20 g glycerol/100 g of polymers) was added. The temperature was then increased to allow the starch gelatinization, at 80 °C for 15 mins with constant magnetic stirring in a jacketed beaker connected to a water bath (Tecnalise, Brazil).

The poly(vinyl alcohol) solution was prepared with PVA (4 g/100 g solution) and deionized water. Six types of PVA were used, from partially hydrolyzed PVA (87–89% hydrolysis degree) to a fully hydrolyzed PVA (98–99% hydrolysis degree) (Table 1). Firstly, the PVA was dispersed in water by stirring for at least 4 h at room temperature, and then heated at 85 or 90 °C depending of the PVA type, until the PVA was completely dissolved.

Blends of amaranth flour and PVA solutions were prepared by mixing these two solutions. In the first study, six different types of poly(vinyl alcohol) were tested in the formulation of blended films, using equal proportions of amaranth flour–PVA. In the second one, the solutions described above were mixed to produce blends with different poly(vinyl alcohol) proportions, from 10% to 50%. These blends were homogenized using an Ultra-Turrax emulsifier (model T18-Basic, IKA Works Brazil) for 2 min at 6000 rpm, since PVA and starch are not very compatible when one or the other is added at high concentration (Lawton, 1996). The blends were heated at 75 °C for 30 min for increase the interaction between the components, and then kept under vacuum (Tecnal, TE-058) for 30–60 min for de-foaming.

The film forming solutions were then poured and spread evenly over a Teflon surface (18 × 21 cm). The weight of the film forming solutions was controlled to obtain a constant thickness (0.080 ± 0.002 mm). These solutions were dried in a controlled temperature and relative humidity oven (model MA 415UR, Marconi, Brazil) at 37 °C and 55% relative humidity (RH) for 12–14 h.

Prior to characterization, the films were conditioned at 25 °C and 58% RH for 72 h in desiccators with a saturated solution of NaBr for the mechanical tests, at 0% RH for 48 h in desiccators with silica gel for the solubility tests, and for 1 week for the FTIR analysis. Films of *A. cruentus* flour with no PVA and films PVA without flour were also prepared and analyzed.

2.3. Film characterization

Thickness was measured using a micrometer (model FOW72-229-001, Fowler) with a 0–25 mm range and accuracy of 0.0025 mm. The film thickness was determined from an average of 15 measurements made at five different locations.

Moisture content of the films was determined by the AOAC Official Methods of Analysis (1997) method, drying the sample (0.200 ± 0.001 g) at 105 °C for 24 h in an air oven, in triplicate.

Mechanical properties were determined using the puncture test (puncture force, PF, and puncture deformation, PD) and tensile test (tensile strength, TS, and elongation at break, ELO) using a TA-XT2i Stable Micro Systems texture analyzer (SMS).

For the puncture test, circular sample films were fixed in a 34mm diameter cell and perforated using a 3 mm diameter cylindrical probe moving at 1 mm/s (Gontard, Guilbert, & Cuq, 1992), in triplicate. The puncture force was determined with the software

Texture Expert V.1.15 (SMS) directly from the force × displacement curves. The puncture deformation was calculated using Eq. (1):

$$PD = \Delta l/l_0 = [(D^2 + l_0^2)^{1/2} - l_0]/l_0 \qquad (1)$$

where l_o is the initial disc radius (17 mm) and D the distance penetrated at the break point.

The tensile test was performed according to the ASTM standard method D882-97 (ASTM, 1997). Dumb bell shaped samples were cut for each film with 115 mm in length and 6 mm in width at the middle. The initial grip separation was set at 80 mm and the crosshead speed at 1.0 mm/s. At least four samples from each film were evaluated. The tensile strength (force/initial cross-sectional area) and elongation at break ($\Delta l/l_o$) were determined with the software Texture Expert V.1.15 (SMS) directly from the stress × strain curves. Elongation at break was obtained using Eq. (2):

$$\mathrm{ELO} = (\Delta L/L_0)100 \qquad (2)$$

where ΔL is the elongated distance at break and L_o the initial distance between the grips (80 mm).

Solubility in water was determined according to the method described by Gontard et al. (1992), with modifications. Three dried film discs (2 cm diameter) were weighed (w_i) and immersed in 50 mL of deionized water (with sodium azide, 0.02%) at 25 °C for 24 h, with constant agitation (50 rpm) in a shaker (Tecnal, TE-420). The films were then recovered by vacuum filtration on a filter paper of known weight, dried at 105 °C for 24 h and weighed (w_f). The solubility (S) was calculated as the percentage of dissolved dry matter in the film using Eq. (3):

$$S = [(w_i - w_f)/w_i]100 \qquad (3)$$

2.3.1. Fourier transformed IR spectroscopy (FTIR)

Fourier transformed IR spectroscopy (FTIR). Infrared spectra of dry films were recorded between 4000 and 600 $\mathrm{cm^{-1}}$ at 4 $\mathrm{cm^{-1}}$ of resolution with a Spectrum One (Perkin Elmer, USA) spectrometer, supplied with a universal attenuated total reflectance (UATR) accessory according to Vicentini, Dupuy, Leitzelman, Cereda, and Sobral (2005). For each spectrum, 16 scans were co-added.

2.3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) analyses were performed using a Leica (Cambridge, England) model LEO440i scanning electron microscope operating at 10 kV. Film samples were maintained in a desiccator with silica gel for 7 days and then randomly broken up to investigate the cross-section of the samples (Tapia-Blácido et al., 2007). A cylindrical aluminum stub cut like a straight-backed chair, on which the film was fixed using a double-sided cupper tape, was used in a specific way to observe the morphology of the cross-section and of the surfaces. The stubs holding the films were then coated with gold in a VG Microtech (Cambridge, England) model SC7620 sputter coater for 180 s at 4 mA.

2.3.3. Statistical analysis

For the statistical analysis, mean values of the mechanical properties and solubility were analyzed by the Tukey honest significant difference (HSD) test, performed using Statistica 5.0 software (Statsoft Inc., USA).

3. Results and discussion

3.1. Poly(vinyl alcohol) (PVA) grade selection

Six different types of poly(vinyl alcohol) were tested in the formulation of blended films with equal proportions of amaranth flour–PVA (Table 1). Phase separation occurred during the drying of the films produced using PVA 205, suggesting a reduced compatibility between this partially hydrolyzed and low molecular weight PVA and the amaranth flour. Mixing in high proportions resulted in stable suspensions of both polymers for the other PVA types and homogeneous dried films.

Excepted that produced using the PVA 205, all films were homogeneous and easily peelable from the support. Moreover, subjectively, they could be considered as transparent and almost colorless.

Mechanical properties of the blended films such as puncture force and deformation, tensile strength and elongation at break, were analyzed. Fig. 1 shows the variation and significant differences ($p < 0.05$) in the mechanical properties due to the addition of poly(vinyl alcohol) with different hydrolysis degrees (HD) and molecular weights. High HD PVA (107, 325 and 350) blended films were more resistant ($p < 0.05$), with greater tensile strength (Fig. 1a) and puncture force (Fig. 1b) than low HD PVA (523 and 540). The higher hydrolysis degree increased the amount of hydroxyl groups present in the PVA molecule, allowing for the formation of hydrogen interactions between the –OH groups of the PVA and –OH groups of the starch and/or with other polar groups of the amaranth flour proteins, reinforcing the film structure (Siddaramaiah et al., 2004). On the other hand, contrary to the behavior observed by Abd El-Kader et al. (2002), who reported that the tensile strength of PVA films decreased as the molecular weight of the PVA increased, no effect of the molecular weight of the PVA was

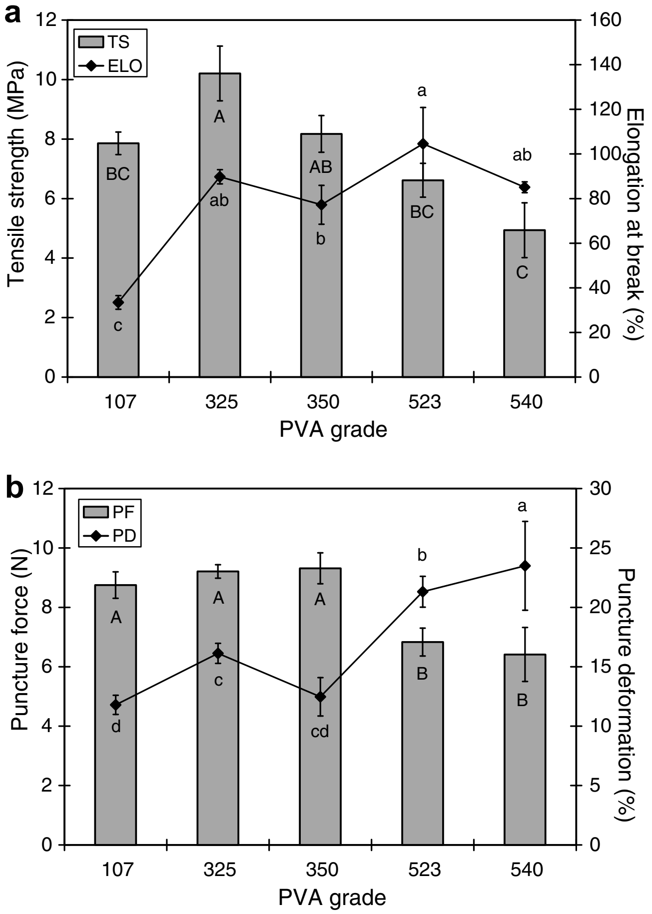

Fig. 1. Mechanical properties of *A. cruentus* flour–poly(vinyl alcohol) blended (50:50) films made with different PVA types: (a) tensile strength (MPa) and elongation at break (%), (b) puncture force (*N*) and deformation (%). Bars indicate standard deviations. Different letters means significant difference ($P < 0.05$) between values on the same plot (a or A).

evident in the present study. No significant difference ($p > 0.05$) was observed between the tensile strength of samples with the same HD and different molecular weights, for example when comparing films with PVA 325 and 350, or with 523 and 540.

The values obtained for elongation at break (Fig. 1a) and puncture deformation (Fig. 1b) reveal the flexibility of the polymer structure and generally increase as the resistance decreases (Follain, Joly, Dole, & Bliard 2005a). However, in the present work, PVA 325, which showed greater resistance (TS and PF), also presented considerably greater elongation at break, just like the PVA 523 and 540 films.

PVA 325, which is a fully hydrolyzed (HD = 98%) and medium molecular weight poly(vinyl alcohol), allowed for the best mechanical characteristics in the blended films, with TS = 10.2 MPa, ELO = 89.8%, PF = 9.4 N and PD = 16.3%. These values are comparable to those reported by some researchers for starch–poly(vinyl alcohol) films blended in equal proportions (Table 2). Thus, the PVA Celvol® 325 was chosen for the next study.

3.2. *Amarantus cruentus flour–poly(vinyl alcohol) (PVA 325) blended films*

3.2.1. *Mechanical properties*

Both the tensile strength and elongation at break of *A. cruentus* flour–PVA 325 blended films varied linearly and showing a parabolic trend, respectively, as a function of the PVA concentration in the blends (Fig. 2a). These properties varied between those of *A. cruentus* flour films (TS = 5.8 MPa and ELO = 13.8%), and of PVA films (TS = 44.8 MPa and ELO = 84.4%, data not shown in Fig. 2a).

Similar behavior was observed for the puncture force (PF) and deformation (PD) of the *A. cruentus* flour–PVA 325 blended films (Fig. 2b). These properties varied between PF = 4.7 N and PD = 2.4% for *A. cruentus* flour films (plasticized with 20% glycerol), and PF = 43.4 N and PD = 23.9% (data not shown in Fig. 2b) for PVA films (plasticized with 20% glycerol). These results demonstrated that it was possible to overcome the incompatibility between *A. cruentus* flour and PVA by homogenization and heating of the blends.

This improvement in the mechanical properties of films based on biopolymers by adding PVA, was also reported for hydrolyzed starch-g-PAN (HSPAN) and PVA blended films (Kim et al., 2002), and for methylated corn starch and PVA blended films cross-linked with formaldehyde (Guohua et al., 2006). Ke and Sun (2003) also observed similar results for films based on blends of cornstarch and poly(lactic acid) with different PVA concentrations. These authors observed that this tensile behavior is typical of homogeneous and thermodynamically miscible systems. However, Chiellini, Cinelli, Fernandes, Kenawy, and Lazzeri (2001) observed a minimum resistance for films blended at 50:50 gelatin:PVA, plasticized with glycerol.

Table 2
Mechanical properties of starch–poly(vinyl alcohol) blended films reported in the literature

Formulation and conditions	TS (MPa)	ELO (%)	Reference
Starch (21% amylose)–PVA (NH-17R), 15 wt% glycerol	12.1	59.2	Sreedhar et al. (2005)
Waxy cornstarch (41%), PVA 325 (41%), glycerol (15%) and EAA (3%) at 50% RH	~16	144	Lawton (1996)
Cornstarch (5%), PVA (5%) and glycerol (20 wt%), mixed at 1500 rpm for 40 min. At 22 °C and 52% RH	~10	~75	Park et al. (2005)
Starch-g-PAN (HSPAN)–PVA, without plasticizer	~27	~10	Kim et al. (2002)
Methylated-cornstarch–PVA, 10 wt% glycerol, crosslinked with formaldehyde (1 wt%)	~15	~175	Guohua et al. (2006)
Amaranth flour (4%), PVA 325 (4%) and glycerol (20 wt%), homogenized at 6000 rpm for 2 min, at 58% RH	10.2	89.8	This work

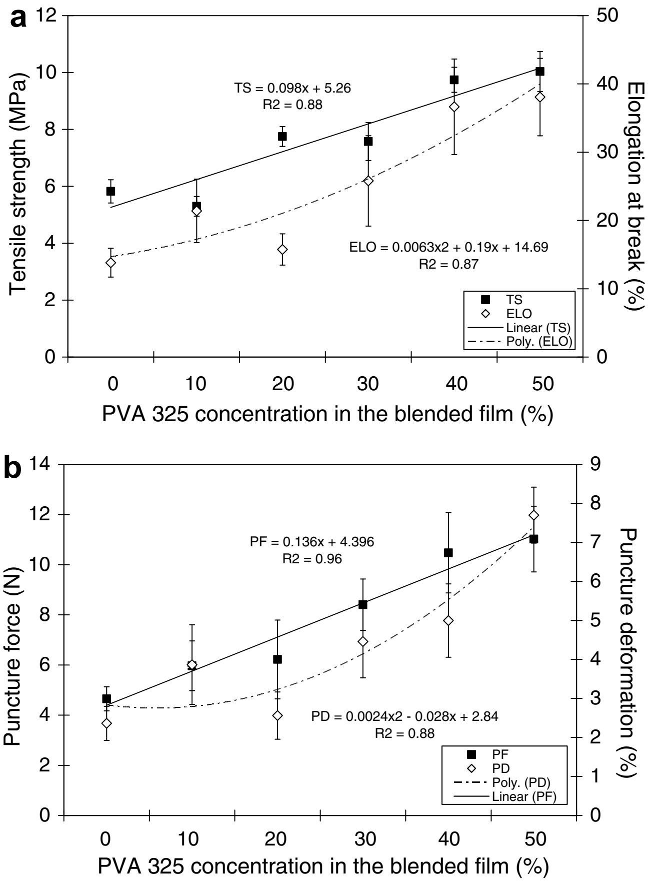

Fig. 2. Mechanical properties of poly(vinyl alcohol) (PVA 325)–*A. cruentus* flour blended films as a function of the PVA concentration in the blends: (a) tensile strength (MPa) and elongation at break (%), (b) puncture force (*N*) and deformation (%). Bars indicate standard deviations.

The observed enhancement in the mechanical properties observed in this work could be due to interaction of the components by way of hydrogen bond formation between the –OH groups of the PVA and polar groups of the amaranth starch and protein.

3.2.2. *Solubility in water and moisture content*

Due to the lower hydrophilicity of the PVA, the solubility in water of the blended films was considerably reduced for films blended with more than 10% of PVA (Fig. 3). The 50% PVA films (MC = 7.6%) were less hygroscopic than the films based on pure amaranth flour (MC = 13%), but the moisture content of the blended films was only reduced for films with more than 20% of PVA in the blend (Fig. 3).

The water resistance of PVA and also the film moisture content after conditioning under a determined relative humidity are related to the hydrolysis degree and molecular weight of the polymer, amongst other physical properties of the polymer. An increase in the HD provokes greater water resistance (Celanese., 2005), which could explain the lower values for the moisture content of the pure and blended PVA films.

According to Finch (1983), the solubility in water of PVA depends on the crystallinity degree and the structures in the amorphous regions of the polymer. Thus it can be suggested that PVA Celvol® 325 possesses a partially crystalline structure and its crystals have a dense arrangement, giving more resistance to water and

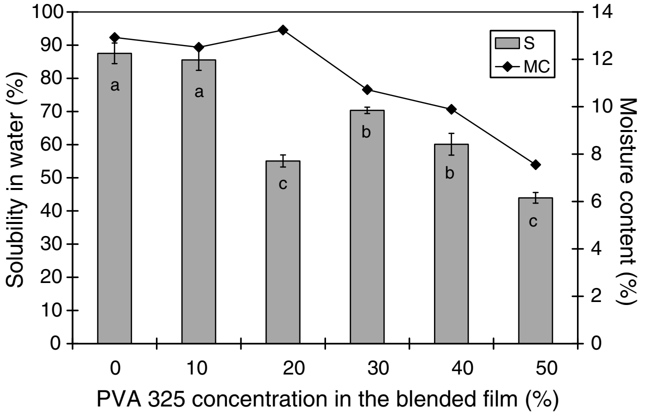

Fig. 3. Solubility in water (%) and moisture content (%) of poly(vinyl alcohol) (PVA 325)–*A. cruentus* flour blended films as a function of the PVA concentration in the blend. Bars indicate standard deviations. Different letters means significant difference ($P<0.05$) between values on the same plot (a or A).

explaining the lower solubility of the PVA film as compared to the solubility of films based only on the flour (87.5%).

The reduction in solubility in water (Fig. 3) of the blended films could be attributed to the formation of hydrogen bonds between the two polymers, which reduce its capacity to absorb water (Follain et al., 2005b). These strong interactions between the amaranth flour and the PVA, which contributed to the reduction in solubility of the films, were probably due to the homogenization (1–2 min at 6000 rpm) of the blends. Park et al. (2005), working with cornstarch–PVA (99% hydrolyzed and MW: 89,000–98,000) blended films, observed that an increase in the mixing time decreased the solubility of the films. This phenomenon was explained by the effect of homogenization on the free volume of the polymers, which decreased, in combination with hydrogen bond formation between the starch and poly(vinyl alcohol).

3.2.3. Fourier transformed infrared (FTIR) spectroscopy

Fig. 4 shows the FTIR spectra obtained for the *A. cruentus* flour–PVA blended films at different concentrations. It can be observed that an increase in the PVA concentration provoked a decrease in the spectra intensity. This trend could be explained by the crystallinity of the films (the PVA and also the starch could present a certain crystallinity), which generally provokes a loss of intensity due to excessive dispersion of the light (Silverstein & Webster, 2000).

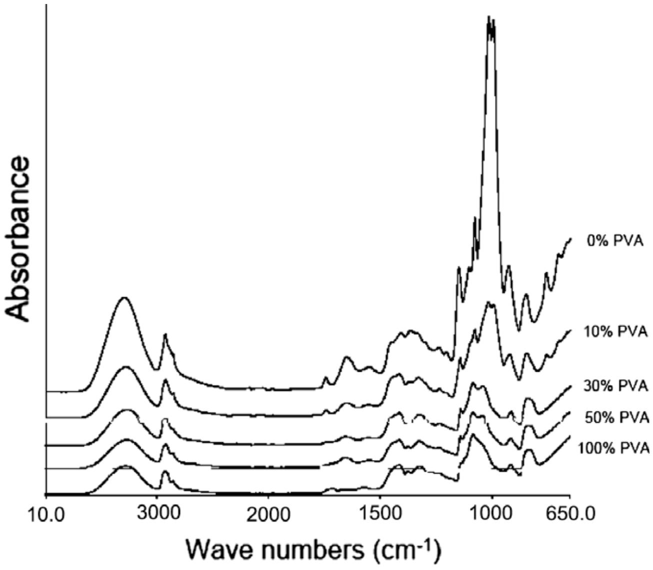

Fig. 4. FTIR spectra of poly(vinyl alcohol) (PVA 325)–*A. cruentus* flour blended films (0%, 10%, 30% and 50% of PVA in the blends).

The main IR bands observed in the film spectra and their assignments are summarized in Table 3. The *A. cruentus* flour film (0% PVA) spectrum displayed the typical profile of a polysaccharide in the 1200- to 930-cm^{-1} range (characteristic peaks attributed to COC bond stretching), since the amaranth flour has a high starch content (72.5%). The strong peaks observed at 996, 1016 and 1078 cm^{-1} are characteristic of the anhydroglucose ring such as found in starch, although these signals could also be associated with the presence of glycerol molecules. The peak at 1078 cm^{-1} shifted to higher frequencies as the PVA concentration increased. However, only the 10% PVA blended film presented peaks at 995 and at 1019 cm^{-1}. The band at 1016 cm^{-1} is characteristic of amorphous starch (Vicentini et al., 2005), so the increase in PVA concentration in the blends allowed for retrogradation of the amaranth flour starch in the films.

The broad band at 3293 cm^{-1} was due to hydrogen-bonded hydroxyl groups (O–H). This band is of great importance since it indicates the presence of hydrogen bonding in the polymer. There was a shift to lower frequencies as the PVA concentration increased (3272–3278 cm^{-1}), which could mean an increase in hydrogen bonding between the PVA and *A. cruentus* flour hydroxyl groups, provoking an improvement in the mechanical properties and a reduction water solubility of the blended films.

This fact was explained by Silverstein and Webster (2000), as follows. The formation of hydrogen bonds modifies the force constants of both the groups involved in the bond, thus altering the frequencies of axial and angular deformation. The "free" hydroxyl groups absorb strongly between 3650 and 3584 cm^{-1}, but when intermolecular hydrogen bonding becomes important, the bands start to appear at lower frequencies, typically between 3550 and 3200 cm^{-1}. Silverstein and Webster (2000) observed a considerable absorption at 3333 cm^{-1} for polymeric structures.

In addition, the bands situated at 3288 cm^{-1} may be associated with amide III, which corresponds to vibrations in the C–N plane (Prystupa & Donald, 1996), and this group is present in the amaranth flour proteins. Thus, the reduction in intensity of these peaks may be explained by the effect of protein dilution provoked by the PVA. Other signals typical of proteins may be observed at 1632 and 1548 cm^{-1} and are associated with the amides I and II, respectively. Amide I arises from C=O stretching of the amide proteins; amide II arises from the vibrational groups N–H and stretching vibrations of the C–N groups.

3.2.4. Scanning electron microscopy (SEM)

Fig. 5 shows the results of the scanning electronic microscopy of the *A. cruentus* flour–PVA 325 blended films and also of films based on pure *A. cruentus* flour. It can be seen that the upper surface of the blended film (Fig. 5a) was dense and showed some roughness distributed along the surface, but without the cracked aspect observed for the *A. cruentus* film surface (Fig. 5c). These results are in agreement with Sreedhar et al. (2005), who considered that the incorporation of PVA into starch provoked changes in the biopolymer structure at both the molecular and morphological levels, reducing its rigidity. These observations were confirmed by the results of the mechanical properties (Section 3.2.1).

Moreover, Fig. 5b shows that the cross-section of the blended film presented a considerable amount of well-distributed micro pores, such as in an emulsion, probably due to the homogenization process used to improve the miscibility between the PVA and the amaranth flour starch and proteins. On the other hand, the microstructure of the films without PVA (Fig. 5d) was denser and more compact, typical of starch and protein films. This type of structure

Table 3
Assignment of the main bands of the FTIR spectra for the *A. cruentus* flour–poly(vinyl alcohol) blended film

A. cruentus flour film			*A. cruentus* flour–PVA blended film	
Wavenumber (cm^{-1})	PI	Assignment	Wavenumber (cm^{-1})	Assignment
3293	M	OH stretching (H bonded)	3272–3278[c]	OH stretching (H bonded)
2925	M	CH stretching (asym, sym)	2919–2921[c]	CH stretching (asym, sym)
1650	W	OH bending (water)	1650–1657[b]	OH bending (water)
1409	M	CH bending (CH_2)	1417[d]	CH bending (CH_2)
1239	W	CH_2–OH mode	1237[a]	CH_2–OH mode
1150	M	C–O stretching glycosidic bond, C–O stretching/OH bending	1142–1144[c]	C–O stretching glycosidic bond, C–O stretching/OH bending
1078	M	CH bending	1079–1086[d]	CH bending
1016	S	C–O/C–C stretching	1019[a,d]	C–O/C–C stretching
996	S	COH bending vibration	995[a]	COH bending vibration

PI, peak intensity; W, weak; M, medium; S, strong peak intensity.
[a] Only present in 10% PVA.
[b] Not present in 100% PVA.
[c] Shift to lower frequency.
[d] Shift to higher frequency.

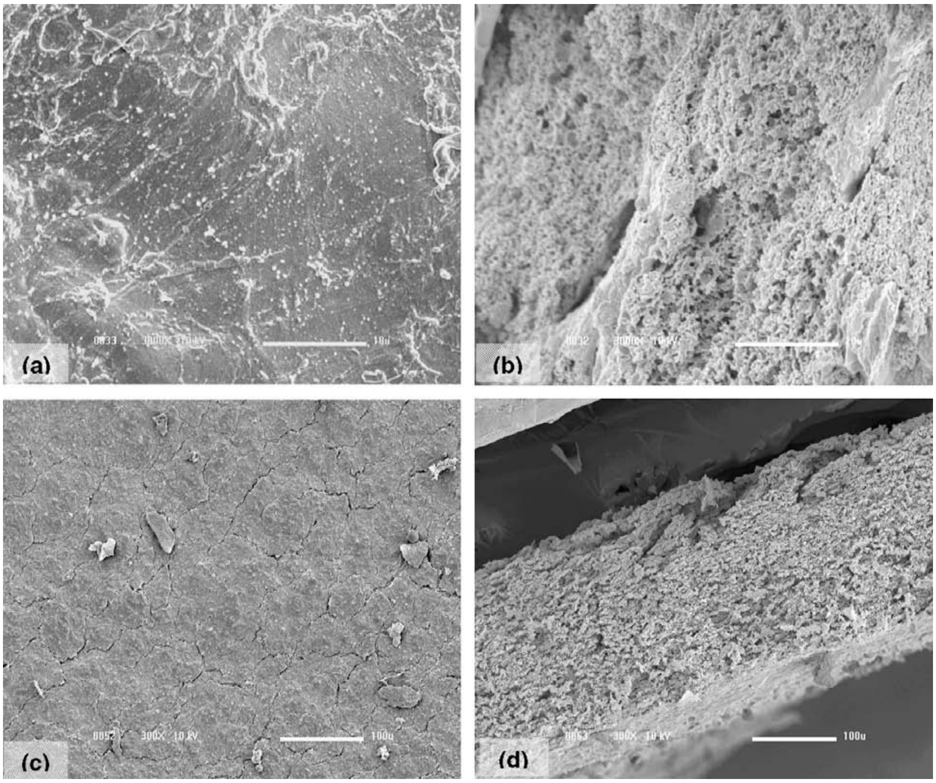

Fig. 5. Scanning electron micrographs of the surface (a) and the cross-section (b) of *A. cruentus* flour–poly(vinyl alcohol) (PVA 325) films (3000×) blended in equal proportions, and of the surface (c) and cross-section (d) of a pure *Amaranthus cruentus* flour film (300×).

was reported for *A. cruentus* flour–stearic acid emulsified films (Colla et al., 2006a).

4. Conclusions

The mechanical properties of the amaranth (*A. cruentus*) flour films were improved by the addition of poly(vinyl alcohol) (PVA). For blends made with different grades of poly(vinyl alcohol), the fully hydrolyzed PVA (107, 325 and 350) blended films were more resistant with respect to tensile strength and puncture than the partially hydrolyzed PVA (523 and 540) films. In addition the films made with partially hydrolyzed PVA showed greater elongation at break (ELO) and puncture deformation (PD).

PVA 325, which showed greater resistance (TS and PF), also presented considerable elongation at break like the PVA 523 and 540 films. PVA 325, which is a fully hydrolyzed (98%) and medium molecular weight poly(vinyl alcohol), was chosen for further studies because it presented the best mechanical performance as compared to the other grades evaluated.

All the mechanical properties (TS, ELO, PF and PD) were enhanced as the PVA 325 content was increased (up to 50%) in the blended film. The water solubility of the blended films decreased as the PVA content increased. The formation of hydrogen bonds between the components of the blend was confirmed by the FTIR analysis.

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