



Agro-industrial residue from starch extraction of *Pachyrhizus ahipa* as filler of thermoplastic corn starch films



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ABSTRACT

Biocomposites films based on thermoplastic corn starch (TPS) containing 0.5% w/w fibrous residue from *Pachyrhizus ahipa* starch extraction (PASR) were obtained by melt-mixing and compression molding. PASR is mainly constituted by remaining cell walls and natural fibers, revealed by Scanning Electron Microscopy (SEM). Chemical composition of the residue indicated that fiber and starch were the principal components. Biocomposites thermo-stability was determined by Thermo-Gravimetric Analysis. A continuous PASR-TPS interface was observed by SEM, as a result of a good adhesion of the fibrous residue to starch matrix. Likewise, films containing PASR presented fewer superficial cracks than TPS ones, whereas their fracture surfaces were more irregular. Besides, the presence of PASR increased starch films roughness, due to fibers agglomerates. Films reinforced with PASR showed significantly lower water vapor permeability (WVP). In addition, PASR filler increased maximum tensile strength and Young's modulus of TPS films, thus leading to more resistant starch matrixes.

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1. Introduction

Growing environmental awareness and new legislation to reduce carbon emissions are encouraging industries to look for more ecologically friendly materials for their products (Oksman, Skrifvars, & Selin, 2003). Within this context, materials derived from renewable sources are essentially biodegradable, which makes them more compatible with the environment. Biodegradable materials are usually based on lipids, proteins and carbohydrates, such as cellulose, starch and their byproducts (Phattaraporn, Waranyou, & Thawien, 2011). By virtue of its low cost, in comparison to most synthetic polymers, and its worldwide availability, starch is a promising alternative material. Thermoplastic starch (TPS) is obtained after disruption and plasticization of native starch with water and plasticizers by applying thermo-mechanical energy (Averous & Boquillon, 2004). Unfortunately, compared to conventional thermoplastics materials, biodegradable products based on starch still have many disadvantages, such as low mechanical properties, deficient barrier against moisture and

an important post-processing variation of their properties (Averous & Boquillon, 2004; Phattaraporn et al., 2011).

In order to improve starch based films characteristics, results have been reported on the addition of natural fibers as a suitable reinforcing compound for these types of thermoplastic materials. As regards their reinforcing ability, natural fibers have many advantages compared to synthetic ones. Not only are these fillers available in a wide variety throughout the world, but they are also inexpensive, with low density, and reasonable strength and stiffness. In addition, they are innocuous, biodegradable and renewable (Kunanopparat, Menut, Morel, & Guilbert, 2008), and are easy to process due to their flexibility and non-abrasive nature in comparison to inorganic fillers (Habibi, El-Zawawy, Ibrahim, & Dufresne, 2009). Nonetheless, one of their most important advantages as reinforcing agent of starch based materials is their chemical compatibility, which allows a good interfacial filler–matrix adhesion. Fiber–starch composites have been previously discussed and reviewed by many authors reporting enhanced final properties of films (Curvelo, De Carvalho, & Agnelli, 2001; Müller, Laurindo, & Yamashita, 2009; Ma, Yu, & Kennedy, 2005).

Natural fibers can be obtained from agro-industrial or agricultural residues, providing added value to the corresponding raw materials. At industrial-scale starch extraction from roots and tubers three types of wastes are produced: outer skins, waste

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waters and fibrous residues (Ray, Mohapatra, Panda, & Kar, 2008). The outer skin and waste water could be used for biogas production (Sriroth, Piyachomkwan, Wanlapatit, & Nivitchanyong, 2010; Tung, Miyata, & Iwahori, 2004). Regarding the fibrous residue, even though it is employed as clarifying agent in the mining industry, an interesting approach would be to use it as filler of biodegradable films in order to improve materials functionality preserving their biodegradability.

In a previous work (López & García, 2012), cassava and ahipa starch films were developed by casting using the extracted starch obtained from the roots and tubers using a simple, low cost and optimized procedure (López et al., 2010). As a by-product from this procedure a solid residue, which could be used for livestock feed or fodder, is obtained. In this work an alternative use for this residue as natural reinforcing agent of TPS is proposed and a chemical and morphological characterization was conducted, in order to evaluate its effect on reinforced materials.

Thus, the aim of the present work was to develop biocomposites based on thermoplastic corn starch and residue obtained from *Pachyrhizus ahipa* (*P. ahipa*) starch extraction. Fibrous residue was quantified and physicochemically characterized by different techniques. In view of their application in food packaging, films appearance and microstructure as well as the influence of the residue addition on biocomposites final properties were studied.

2. Materials and methods

2.1. Materials

Native corn starch was provided by Misky–Arcor (Tucumán, Argentina) with an amylose content of $23.9 \pm 0.7\%$ (López, García, & Zaritzky, 2008).

P. ahipa starch residue (PASR) was obtained using a starch extraction optimized laboratory-scale method proposed by López et al. (2010). *P. ahipa* plants were grown at the INTA Montecarlo farm (Misiones, Argentina).

Fig. 1 shows the starch extraction procedure including the corresponding steps at which the principal residues (outer skins, waste waters and PASR) are produced. PASR was dried at 40 °C until constant weight and processed in a Commercial Laboratory Blender (Model 34BL99-8012) at 3000 rpm. Finally, the granulated solid residue was sieved with Standard 60US mesh to obtain a homogeneous fraction.

In order to determine PASR yield, approximately 5 g were dried at 105 °C until constant weight. Yield was calculated by weight difference and expressed as g PASR per 100 g roots (% w/w). The reported value corresponds to the mean of three determinations.

2.1.1. Characterization of PASR

Residue microstructure was studied by SEM in a JEOL JSM-35CF electron microscope (Japan), with a secondary electron detector. Samples, mounted on bronze stubs using a double-sided tape and metalized with gold layer (40–50 nm), were analyzed under high vacuum mode.

Dry matter, ash, lipid fraction, crude protein and total dietary fiber were determined following standard methods, as thoroughly described by Versino and García (2014). Total starch content was determined by Megazine Total Starch kit, K-TSTA 05/06 (Megazyme International Ireland Ltd., Co., Wicklow, Ireland) based on the amyloglucosidase/ α -amylase method (AOAC 996.11). Results are expressed as percentages and reported values correspond to the mean value of three determinations.

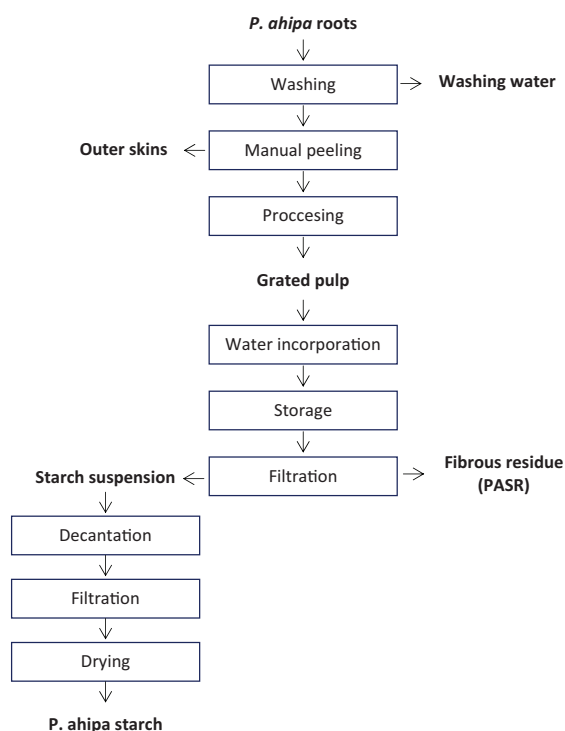


Fig. 1. Process scheme of starch extraction from *P. ahipa* roots.

2.2. Biocomposites preparation

Mixtures of native corn starch, glycerol (30% w/w), distilled water (45% w/w) and PASR (0.5% w/w) were prepared. Composition was expressed as g per 100 g of starch. PASR were premixed with starch to achieve good filler distribution. Then, glycerol and distilled water were added and samples were mixed and conditioned at 25 °C during 24 h. Mixtures were processed by melt mixing in a Brabender Plastograph (Brabender, Germany) at 140 °C and 50 rpm for 15 min. Biocomposites based on TPS and PASR were ground and conditioned at 25 °C and 60% relative humidity (RH). Correspondingly a formulation without PASR was prepared to be used as control sample.

Films were obtained by compression molding. For this purpose a hydraulic press was heated for 6 min at 140 °C under controlled pressure (150 kg cm⁻²). Before pressure release, the material was cooled under pressure up to approximately 50 °C.

2.3. Thermo gravimetric analysis (TGA)

Biocomposites thermo-stability was determined using a PerkinElmer Thermogravimetric Analyzer (TGA-2, USA), employing the dynamic method. Samples (approximately 10 mg) were placed in the equipment and heated in nitrogen atmosphere (40 mL/min) from 30 to 700 °C at 10 °C/min heating rate. Assays were performed at least by duplicate for each formulation. Thermograms, corresponding to the percentage weight loss evolution as a function of heating temperature, were recorded. First derivative of weight loss curves were obtained, which represent the decomposition rate of each compound and can be used to determine their contribution to the total weight loss and their proportion in the blends.

2.4. Film characterization

Before film characterization samples were conditioned during 7 days at 20 °C and 72% relative humidity.

2.4.1. Scanning electronic microscopy

Homogeneity and appearance of the films were examined by visual observation and by SEM with a JEOLJSM 6360 electron microscope (Japan). Film samples were cryofractured by immersion in liquid nitrogen. Film pieces were mounted on bronze stubs using a double-sided tape and coated with a layer of gold (40–50 nm), allowing surface and cross-section observations. All samples were examined using an accelerating voltage of 10 kV.

2.4.2. Atomic force microscopy (AFM)

Topography and roughness surfaces of the starch films were evaluated using a multimode atomic force microscope Nanoscope V (Veeco Instruments). Images were obtained in tapping mode using a silicon nitride tip model NP20 (Veeco Instrument Inc., NY, USA). Images of the film surface were randomly taken at different locations of the specimens to obtain reliable and reproducible data. The 2D and 3D images were analyzed with Scanning Probe Microscopy WSxM 3.1 Software (Horcas et al., 2007). To assess the films surface roughness, the following statistics parameters were computed: ironed surface (three-dimensional image area, corresponding to the sum of all formed triangles areas by three adjacent points, nm²) and RMS (height standard deviation, nm).

2.4.3. Moisture content

According to the method proposed by Avérous, Fringant, and Moro (2001) TPS and TPS-PASR films were ground under cryogenic conditions and then stored at 54% RH and 23 °C, during 8 days. The resulted powder was then heated at low temperature (40 °C) using a vacuum oven for 3 h. Moisture content was determined gravimetrically and the reported values correspond to the mean value of three determinations.

2.4.4. Color, opacity and transparency evaluation

Colorimetric analysis was performed with a Minolta colorimeter (CR 200, Osaka, Japan), according to CIELab scale. The parameters: L^* , a^* and b^* were recorded in at least ten randomly selected positions for each film sample. Color parameters range from $L=0$ (black) to $L=100$ (Park, Scott Whiteside, & Cho, 2008), $-a$ (greenness) to $+a$ (redness) and $-b$ (blueness) to $+b$ (yellowness). Standard values considered were those of the white background. In addition, absorbance spectra (400–800 nm) were recorded using a U-1900 spectrophotometer (HITACHI, Japan). Film opacity (AU nm) was determined by integration of absorbance curves according to the standard test method for haze and luminous transmittance of transparent plastics recommendations (American Society for Testing and Materials, 2000). Film transparency was defined as the ratio between absorbance at 600 nm (A_{600}) and film thickness and was expressed as A_{600}/mm in accordance with Piermaria et al. (2011).

2.4.5. Water vapor permeability

The ASTM method E96 with several modifications was used. Samples previously conditioned at 25 °C and 60% RH were sealed over a circular opening of 38.48 cm² in a permeation cell stored at 25 °C in a permeation camera. The driving force, expressed as partial pressure of water vapor, was 1584 Pa. In order to maintain this driving force (corresponding to 50% RH) distilled water (100% RH) was placed inside the cell and a 50% RH was set in the permeation camera. After steady state conditions were reached eight weight measurements were made. Samples were analyzed at least in duplicate.

2.4.6. Mechanical properties

Mechanical performance of biocomposites films were carried out by tensile tests using an Instron 3369 universal machine (Instron, USA) through tensile tests. Ten probes of 13 × 100 mm were assayed for each sample and stress–strain curves were

recorded. Maximum tensile strength (σ_m), elongation at break (ϵ_b) and elastic modulus (E) were calculated according to the ASTM D882-00 (1996). Reported results corresponded to the mean values of each mechanical parameter.

2.5. Statistical analysis

A completely randomized experimental design was used to characterize the composite films. Analysis of variance (ANOVA) was used to compare mean differences of samples properties. Besides, comparison of mean values was performed by Fisher's least significant difference test conducted at a significance level $p=0.05$.

3. Results and discussion

3.1. Characterization of PASR

Processing of *P. ahipa* roots to obtain starch generates two types of residues: liquids and solids (Fig. 1). On the one hand, liquid waste corresponds to residual water from roots washing and centrifugation. On the other hand, solid waste is mainly constituted by the outer skins and the fibrous residue (*P ahipa* starch residue–PASR). Following starch extraction method proposed by López et al. (2010), a $36.13 \pm 1.07\%$ w/w PASR material yield was achieved.

Chemical composition of PASR is shown in Table 1. The moisture content of the solid ahipa residue (13%), as well as, the ash content were similar to those corresponding to fiber-rich compounds derived from pumpkin (*Cucurbita moschata*) reported by De Escalada Pla, Ponce, Stortz, Gerschenson, and Rojas (2007). Bodros, Pillin, Montrelay, and Baley (2007) stressed that fiber water content influences their performances, small variations in absorbed water leads to great variations in section size (swelling and shrinkage).

PASR consists mainly of carbohydrates, quantified as fiber (45%) and starch (38%), all hydrophilic in nature, which affects their functional properties. The residue protein content, which can be estimated by multiplying the total nitrogen content by the conversion factor 6.25, was $4.83 \pm 0.09\%$. This value was lower than those corresponding to pumpkin pulp (De Escalada Pla et al., 2007).

SEM micrographs corresponding to PASR are shown in Fig. 2. This residual material was essentially constituted by agglomerates of fibrous compounds, which were possibly linked together by remained starch granules (Fig. 2A). Such compounds are found in the plant anatomic structures, mainly remaining cell walls of reserve parenchymal tissue and conduction tissue, mainly xylem vessels. During roots processing, cell walls are damaged revealing the corresponding xylem vessels (Fig. 2B). This tissue includes parenchyma cells, fibers, and two cell types specialized in water and mineral transport from tracheids and vessel members. Besides, natural fibers were composed by crystalline cellulose nanofibrils embedded in an amorphous matrix of cross-linked lignin and hemicelluloses and appeared as bundles of individual fibers as can be observed in Fig. 2C (MacDougall & Selvendran, 2001).

3.2. Thermogravimetric analysis (TGA)

Fig. 3A shows TGA curves of TPS and TPS reinforced with PASR. TPS thermal decomposition occurred in three main steps. First stage corresponded to sample water loss, the second one to glycerol decomposition and the third to matrix starch degradation. On the contrary, only two thermal decomposition stages were observed for TPS-PASR samples, which were attributed to water loss and starch degradation.

In Fig. 3B, TGA first derivative curves are presented while Table 2 shows the obtained data from peaks integration. For both formulations, the area corresponding to the first peak was correlated with

Table 1
Chemical composition of *Pachyrhizus ahipa* starch residue (PASR).

Dry matter (%)	Total lipid content (% dry basis)	Total ash content (% dry basis)	Total nitrogen content (% dry basis)	Total dietary fiber (% dry basis)	Total starch content (% dry basis)
87.0 ± 2.0	0.30 ± 0.04	2.15 ± 0.01	0.77 ± 0.02	45.0 ± 2.0	38.0 ± 2.0

Reported values correspond to the mean ± standard deviation.

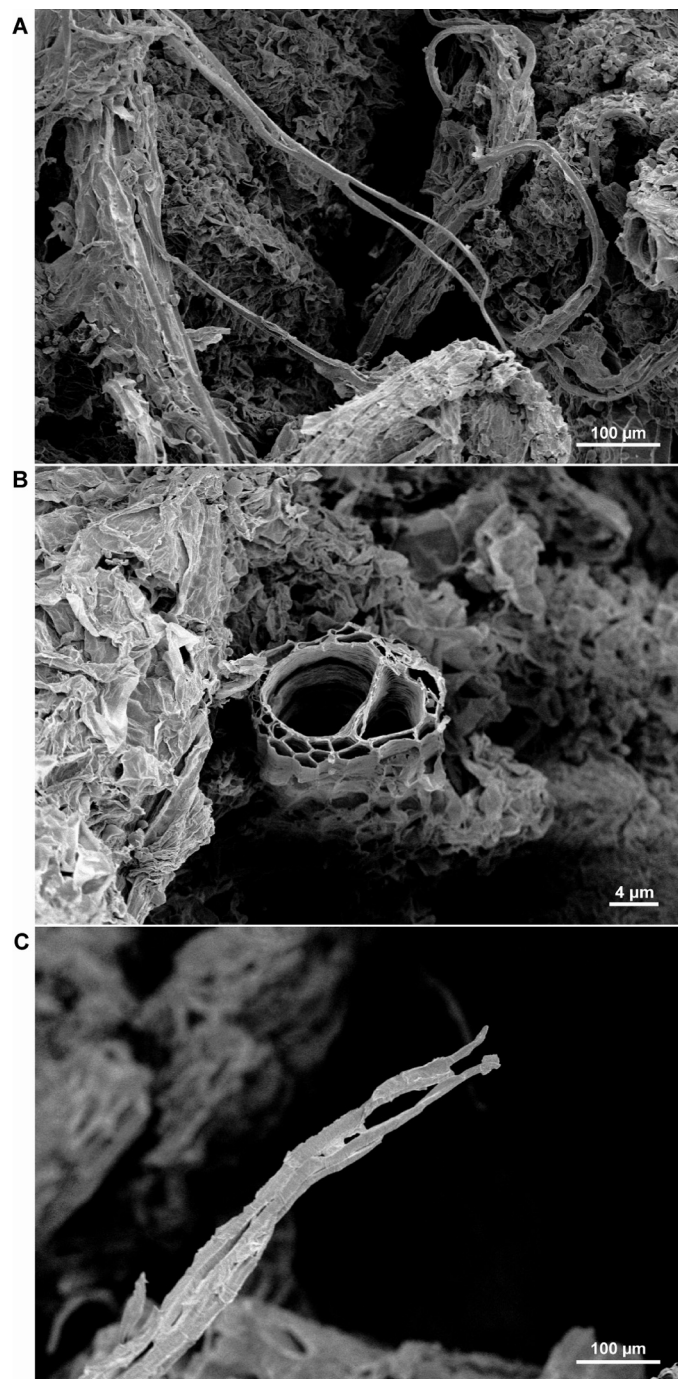


Fig. 2. SEM micrographs of *P. ahipa* starch residue: (A) agglomerates of fibrous components, (B) xylem vessels and (C) bundles of individual fibers.

sample water content being 26.8 and 4.1% w/w for TPS and reinforced TPS, respectively. First peak temperature increase 6.9% with fiber addition (Table 2).

A similar trend was found by Narkchamnan and Sakdaronnarong (2013) working on thermo-molded biocom-

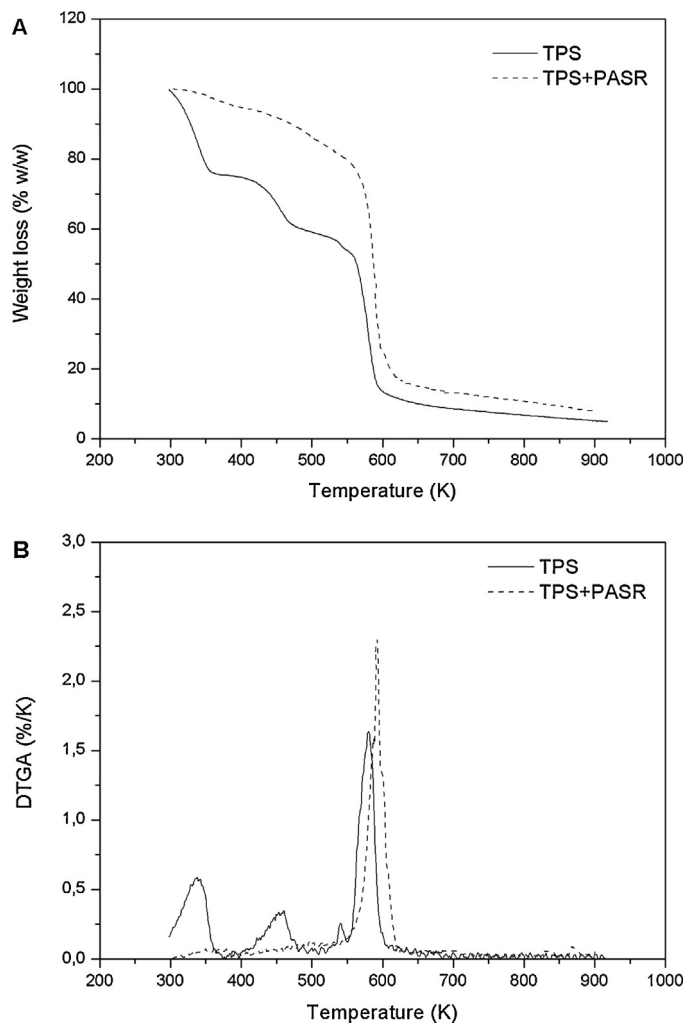


Fig. 3. TGA curves of films based on thermoplastic corn starch (TPS) and TPS with 0.5% w/w *P. ahipa* starch residue (PASR): (A) weight loss as function of temperature and (B) first derivative TGA curves (DTGA).

posites from cassava starch with natural fibers. For TPS samples, the second peak, which appeared at 460 K, was attributed to free glycerol which was not interacting with starch molecules. In this case starch decomposition occurred in two steps at 542 and 580 K (Fig. 3B), which could be attributed to the different

Table 2

Peaks integration of TGA first derivative curves of thermoplastic corn starch (TPS) and TPS with *P. ahipa* starch residue (TPS-PASR).

Film formulation	Peaks	Area	Temperature (K)		
			$T_{initial}$	T_{final}	T_{centre}
TPS	1	26.8	298.0	421.6	337.7
	2	12.6	421.6	476.1	460.0
	3	3.5	530.4	551.6	541.7
	4	43.5	551.6	622.4	580.4
TPS + PASR	1	4.1	303.4	394.1	360.9
	2	57.9	536.9	642.9	592.8

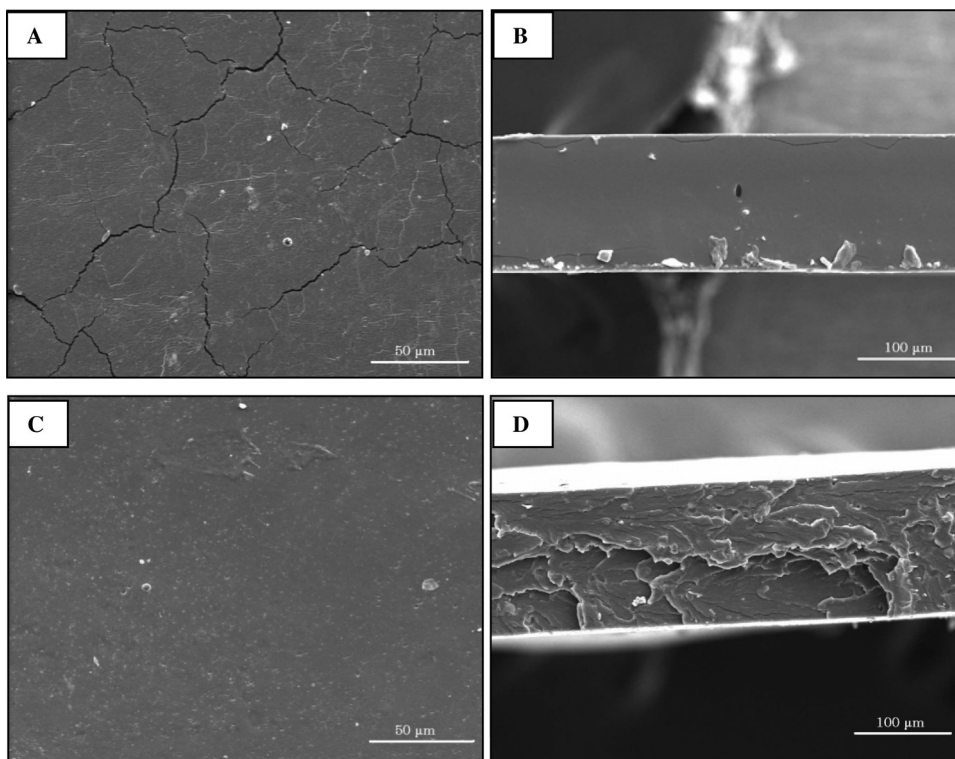


Fig. 4. SEM micrographs of: (A) and (B) surface and cross-section of thermoplastic corn starch (TPS) films, respectively, (C) and (D) surface and cross-section of TPS films with 0.5% w/w *P. ahipa* starch residue, respectively.

degradation rate of the amylose and amylopectin due to the structural characteristics of both macromolecules. Amylose structural configuration is linear which allows a higher OH groups exposition and accessibility for degradation, while amylopectin is branched polymer making more difficult the access to these functional groups. Reinforced TPS revealed a simple step for starch decomposition with the maximum rate was recorded at 592.8 K. The absence of the peak at 460 K, corresponding to the free glycerol could indicate that in composite materials the plasticizer is strongly retained in the matrix, mainly by H-bonding interactions. Dias, Müller, Larotonda, and Laurindo (2011) and Kunanopparat et al. (2008) reported that lignin, considered a highly reactive thermoplastic polymer, is essentially located at the fibers surface by covalent bond with cellulose molecules. The hydroxyl groups of lignin can interact with glycerol and starch, acting as an interfacial compatibility agent between fibers and starch.

3.3. Film characterization

Films based on TPS and TPS reinforced with PASR produced by compression molding had a homogeneous visual appearance and uniform thickness which varied between 125 and 136 μm .

3.3.1. Scanning electron microscopy (SEM)

Scanning electron microscopy of TPS films surfaces and fractures are presented in Fig. 4. Surfaces micrographs of TPS films revealed the presence of some non-molten starch granules and micro-pores, as well as numerous superficial micro-cracks (Fig. 4A). Fracture micrographs show that TPS films presented a homogeneous and continuous structure, which is indicative of their structural integrity, hence good mechanical properties would be expected (Fig. 4B).

Likewise Fig. 4C shows SEM micrographs of TPS films reinforced with PASR. Despite biocomposites surface micrographs exhibited a similar appearance than those of the control samples;

filler presence decreased considerably material cracking as well as the amount of non-molten starch granules. In this respect, Luna, Villada, and Velasco (2009) and Ma et al. (2005) stressed that starch granular fusion was affected by fibers presence during the thermoplastic processing of TPS. Similarly, Martins et al. (2009) reported that bacterial cellulose had an effect on corn starch plasticization, since no residual starch granular structures were observed after composite processing. As it has been previously mentioned, the surface hydroxyl groups of lignin can interact with glycerol and starch, increasing the fibers-starch compatibility. Likewise, in a previous work the torque–mixing time curves were studied for cassava TPS reinforced with cassava bagasse and peels; the plasticization energy involved was calculated as the area under the curve (Versino, López, & García, 2015). The addition of natural fillers resulted in a reduction in the steady torque reached at the end of processing and it could be related to a decrease of TPS melt viscosity. These results are indicative that the presence of the filler during the thermomechanical processing led to a better melting of the starch granules.

Biocomposite films cross-sections showed a more irregular structure than TPS ones, since PASR addition modified material fracture manner because of the rigidity of the filler (Fig. 4D). Voids absence could be indicative that PASR' pulling-out was scarce due to good adhesion between filler and TPS matrix. This observation was also reported by Curvelo et al. (2001) for corn starch films reinforced with cellulose fibers.

It should be clarified that higher magnification levels could not be used for TPS films because samples suffer degradation during the assays.

3.3.2. Atomic force microscopy (AFM)

Filler presence effect on TPS films topography and roughness was evaluated through AFM. This technique provides information in respect to the material surface morphology and homogeneity with nanometric resolution.

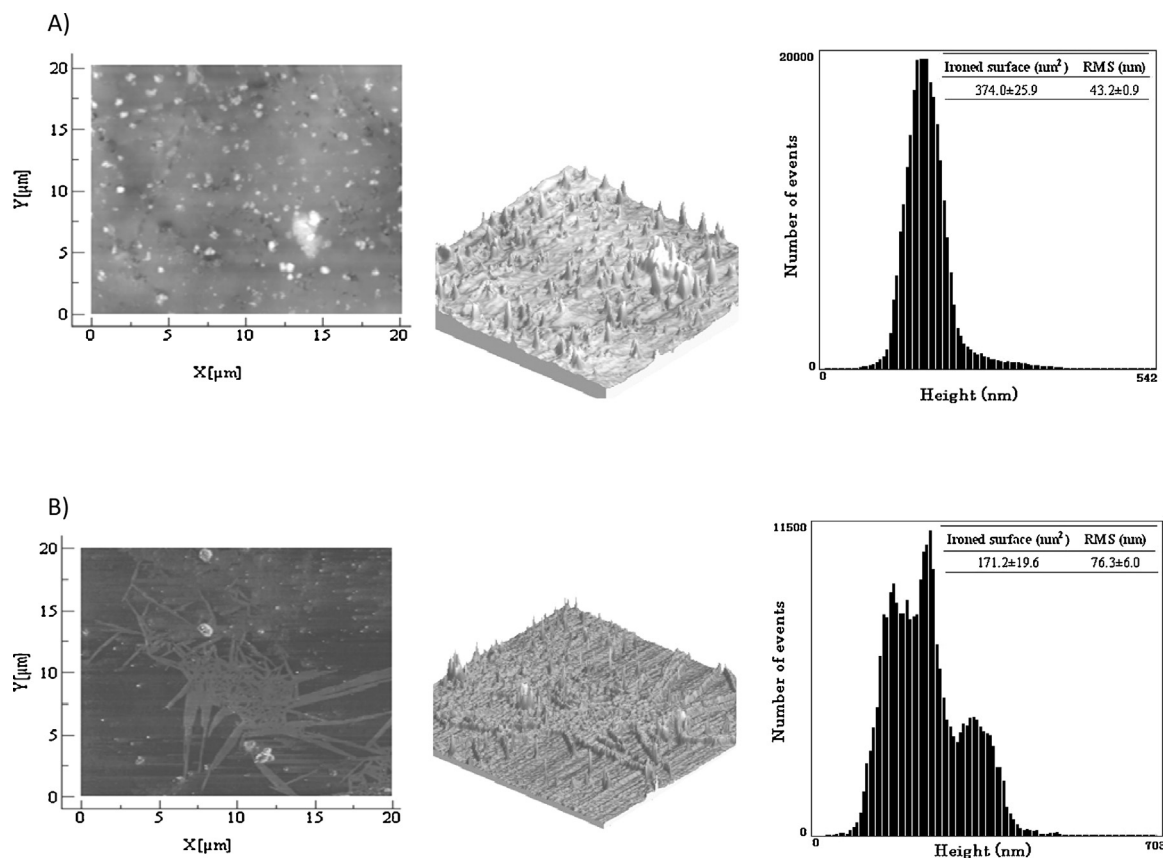


Fig. 5. AFM images (2- and 3-D), height profiles and roughness parameters of (A) thermoplastic corn starch (TPS) films and (B) TPS films with 0.5% w/w *P. ahipa* starch residue.

Fig. 5 shows bi and tri-dimensional images, height profiles and roughness parameters of the films under study. AFM images of TPS films revealed the presence of non-molten starch granules randomly distributed along their surface (Fig. 5A). This observation is in accordance with SEM micrographs discussed previously (Fig. 4A). It could be observed that, at nanometric scale, these starch granules provide certain roughness to TPS films surfaces.

On the contrary, Fig. 5B corresponds to reinforced TPS films AFM images showing a scarce presence of starch granules without melting, which is again in agreement with SEM micrographs suggesting that PASR affected starch melting and plasticization during TPS processing (Fig. 4B). Biocomposites AFM images showed the occurrence of several fibers which seemed to be erratically oriented forming nano-scale agglomerates. Similarly, Kunanopparat et al. (2008) and Lu, Weng, & Cao (2005) reported the presence of filler agglomeration in wheat gluten/glycerol-based materials with natural fiber and soy based composite containing pineapple leaf fiber, respectively.

Height profiles corresponding to TPS films surfaces are also shown in Fig. 5. As it could be observed, PASR incorporation increased significantly ($p < 0.05$) materials roughness. Addition of 0.5% w/w PASR to TPS formulations caused a 76% increment in RMS values.

3.3.3. Color, opacity and transparency evaluation

The filler addition effect on plasticized TPS films optical properties were informed in Table 3. Color measurements were expressed in accordance with CIELab system and the rectangular coordinates (L^* , a^* and b^*).

Albeit PASR incorporation did not significantly modify ($p > 0.05$) TPS films luminosity, it significantly affected TPS films color. As regards chromatic parameters: the b^* parameter increased 20.4% with PASR incorporation while a^* values decreased 23.9%. The yellowish color of the used filler could be responsible for the increment in b^* values of TPS biocomposites. Phattaraporn et al. (2011) reported similar results for rice starch films reinforced with different concentration of palm pressed fibers. Moreover, color development of biocomposite films could be related with thermal degradation of PASR during TPS processing. Xu (2008) attributed the darker color of nylon fiber composites to the cellulose fibers degradation during extrusion–injection/compression molding processing.

No significant differences were observed on opacity and transparency of corn-TPS films with PASR addition ($p > 0.05$). However, corn starch based materials resulted more transparent than cassava TPS materials previously studied (Versino et al., 2015). Moreover, films opacity was slightly higher than that reported for LDPE (28.8 ± 3.3 AU nm) by Park et al. (2008).

Table 3

Optical properties of films based on thermoplastic corn starch (TPS) and TPS with *P. ahipa* starch residue (TPS-PASR).

Film formulation	L^* (luminosity)	a^* (red–green)	b^* (yellow–blue)	Transparency (A_{600}/mm)	Opacity (AU nm)
TPS	95.2 ± 0.1^a	-0.71 ± 0.03^a	5.4 ± 0.2^a	0.52 ± 0.14^a	36.16 ± 2.84^a
TPS + PASR	94.9 ± 0.2^a	-0.88 ± 0.06^b	6.5 ± 0.4^b	0.39 ± 0.016^a	32.34 ± 2.67^a

Reported values correspond to the mean \pm standard deviation. Values within each column followed by different letters indicate significant differences ($p < 0.05$).

3.3.4. Moisture content

Since water acts as a plasticizer for TPS films, moisture content is an important factor that depends on storage conditions such as humidity and temperature among others (Avérous et al., 2001). Special care must be taken into water content measurement because of the tendency of TPS to absorb or desorb water. Moisture content of TPS films and reinforced TPS films were 16.25 ± 0.27 and $9.24 \pm 0.37\%$ w/w, respectively. This reduction was in agreement with the low moisture of PASR, compared with the TPS matrix. Comparable results were reported by Avérous et al. (2001) for the addition of leafwood cellulose fibers to a matrix obtained from water/glycerol plasticization of wheat starch.

3.3.5. Water vapor permeability (WVP)

As food packaging films are often required to avoid or at least to decrease moisture transfer between the food and the surrounding atmosphere, thus water vapor permeability should be as low as possible (Ma et al., 2005). WVP of TPS films and reinforced TPS films were 1.28 ± 0.08 and $0.86 \pm 0.06 \times 10^{-9}$ g/s m Pa, respectively. PASR addition decreased 33% WVP values of TPS films. Analogous WVP reduction was reported by Müller et al. (2009) for cassava starch films reinforced with fibers (0.30 g fiber/g dry starch) with 0.3 g glycerol/g dry starch.

Several authors informed that WVP depends on the simultaneous effect of diffusivity and solubility coefficient of water in the polymeric matrix (Larotonda, Matsui, Sobral, & Laurindo, 2005; Müller & Krochta, 1997; Müller et al., 2009). Dias et al. (2011) stressed that water solubility coefficient in starch films decreased with cellulose fibers addition, while diffusion coefficient increased with filler incorporation. Müller et al. (2009) also found that solubility coefficient values decreased with increase of cellulose fibers in cassava starch films. This behavior was associated with the stronger hydrophilic character of starch when compared with the cellulose fibers, also described by other authors (Avérous et al., 2001; Curvelo et al., 2001). WVP reduction was in agreement with SEM observations (Fig. 4A and C), since PASR addition reduced considerably cracks occurrence.

3.3.6. Mechanical properties

Fig. 6 shows stress–strain curves of TPS and reinforced films assayed at room temperature. Both formulations presented a mechanical behavior typical of ductile materials. TPS films exhibit two characteristic regions of deformation behavior: at low strains, the stress increases rapidly with an increase in strain, while at higher ones these materials show a slow increase in stress with increasing strain until failure occurs. No necking phenomenon can be seen in the stress–strain curves, which evidences the relatively good dispersion of the fillers and the relatively homogeneous morphology of the resulting biocomposites. Ma et al. (2005) have reported a similar behavior for thermoplastic starch composites reinforced with natural fibers.

PASR addition effect on mechanical properties of TPS films are shown in Fig. 6. Reinforced films presented higher values of maximum tensile strength and Young's modulus and lower elongation at break, if compared with TPS films without filler addition (Table 4).

Reported values correspond to mean value \pm standard deviation. Values within each column followed by different letters indicate significant differences ($p < 0.05$).

Table 4

Mechanical properties of films based on thermoplastic corn starch (TPS) and TPS with *P. ahipa* starch residue (TPS-PASR).

Formulation	Elastic modulus (E, MPa)	Maximum tensile strength (σ_m , MPa)	Elongation at break (ϵ_B , %)
TPS	24.9 ± 3.7^a	1.8 ± 0.4^a	66.2 ± 3.3^a
TPS-PASR	180.0 ± 13.8^b	4.3 ± 0.2^b	29.9 ± 1.5^b

Reported values correspond to mean value \pm standard deviation. Values within each column followed by different letters indicate significant differences ($p < 0.05$).

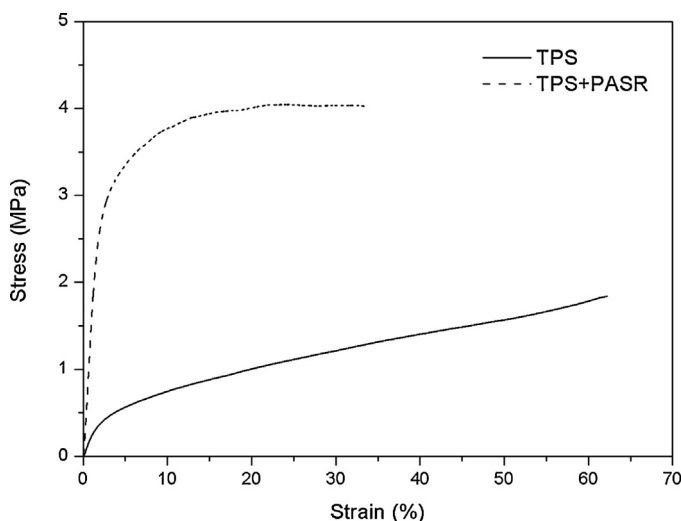


Fig. 6. Stress–strain curves of thermoplastic corn starch (TPS) films and TPS films with 0.5% w/w *P. ahipa* starch residue (PASR).

The maximum tensile strength and Young's modulus increased 2.3 and 7.2 times, respectively. These results indicated that TPS was suitable as matrix for this natural filler due to intrinsic interfacial adhesion caused by chemical similarity between starch and fibers presents in the PASR. Intermolecular interactions between starch molecules and fibers through hydrogen bonds form a tridimensional network, reducing starch chains mobility and increasing material rigidity (Lu et al., 2005). Yu, Dean, and Li (2006) stressed that mechanical performance of biocomposites based on TPS and natural fibers is strongly influenced by several factors such as starch botanical origin, plasticizer (type and concentration), fibers characteristics (origin, aspect ratio, dispersion and orientation within matrix, and degradation), processing method as well as ambient conditions (temperature and humidity).

3.4. Films properties in relation to potential food packaging applications

Nowadays, food packaging materials need to have tailored mechanical, optical, and barrier properties in order to assure integral product quality and prolonged shelf-life. Materials must be tough and flexible enough to guarantee their manipulation without any food product damage and meet specific barrier requirements depending on food characteristics and intended end-use applications (Siracusa, 2012). In addition such materials must be completely innocuous. Therefore, synthetic polymers have been the worldwide prime packaging material since they offer versatile solutions for several needs (Puthusseray, Prasad, Gorazda, & Roy, 2015). Nonetheless, environmental issues raised due to conventional packaging polymers have triggered the study of new bio-based materials for food packaging in order to replace their non-degradable counterparts (Azeredo, 2009). As was previously mentioned, owing to its availability, biodegradability, and low cost, starch is one of the most studied natural polymers for packaging applications. Unfortunately, TPS films have two main disadvantages in comparison to synthetic polymers: moisture absorption

susceptibility and poor mechanical performance. The addition of PASR filler aimed to improve TPS both barrier and mechanical properties of the polymeric material.

On one hand, water vapor permeability of TPS films was reduced in a 33% with PASR incorporation. Reinforced films WVP values were of $8.6 \pm 0.06 \times 10^{-10}$ g/s mPa, comparably similar to other TPS materials reported WVP values (Abreu et al., 2015; Müller, Laurindo, & Yamashita, 2012), other bio-based materials such as chitosan or wheat gluten films (El-Wakil, Hassan, Abou-Zeid, & Dufresne, 2015; Rivero, García, & Pinotti, 2009) and slightly higher than that of cellophane films (Shellhammer & Krochta, 1997). However, such values are yet significantly higher than those reported for LDPE and HDPE (Smith, 1986).

On the other hand, tensile strength of PASR TPS reinforced films was increased in an 58.1%, though this values are 50% lower than those reported for LDPE (Prasad, 1999), a common synthetic polymers used in food packaging. Furthermore, unlike other bio-based materials TPS films can be thermo-sealed, which is an important characteristic in packaging design.

Similarly, the optical properties of a material ultimately determine wrapped product acceptability by consumers. Material opacity is a critical property to consider if the film is useful to develop packaging in which the product is intended to be seen while in the package. In this regard, the fact that TPS films opacity resulted similar to LDPE films make them suitable for transparent packaging applications.

4. Conclusions

The remaining residue of the starch extraction from ahipa roots was morphologically characterized by SEM. This byproduct was constituted mainly by remaining cell walls and natural fibers. PASR chemical composition was determined, indicating that fiber and starch were the major compounds.

Biodegradable films based on thermoplastic corn starch (TPS) and residues of *P. ahipa* starch extraction (PASR) were satisfactorily obtained. Films produced by compression molding were easy to handle and had acceptable appearance and uniform thickness. Besides, SEM observations evidenced a good adhesion between the filler and the TPS matrix.

Additionally, TPS films surface cracking decreased with PASR addition, whereas the cross-sections increased its irregular appearance. Biocomposites AFM images showed the occurrence of several fibers which seemed to be oriented randomly forming agglomerates, increasing the TPS films roughness.

Furthermore, PASR addition decreased 33% WVP values of TPS films and reinforced the film matrix increasing maximum tensile strength and Young's modulus. The improvement in film properties with natural filler addition broaden the potential applications of TPS-based materials in food packaging.

The use of an agro-industrial residue as biocomposite filler offers a good alternative to improve barrier and mechanical properties of thermoplastic corn starch based films, preserving the biodegradability of these materials and providing added value to raw materials.

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