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The effect of surfactant Tween 80 on the hydrophilicity, water vapor permeation, and the mechanical properties of cassava starch and poly(butylene adipate-co-terephthalate) (PBAT) blend films

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ABSTRACT

In this work, the affinity of water to cassava thermoplastic starch (TPS) and PBAT blend films with the addition of surfactant Tween 80 was investigated. The TPS and PBAT blend films were produced by extrusion with different starch concentrations added with 2% surfactant Tween 80, without surfactant Tween 80 or with 100% starch films (F100) as controls. The sorption isotherms, water vapor permeability (WVP), solubility coefficients, and diffusion coefficients of the films were evaluated. F100 films demonstrated the highest WVP and solubility coefficient values. Addition of the surfactant increased the diffusion coefficient and WVP. Films with the addition of surfactants had lower structural integrity and mechanical resistance than control films. The results indicated that the surfactant increased the free volume between the starch chains, thus, favoring the diffusion of water vapor. The combined effects of solubility coefficients and diffusion coefficients controlled the WVP of the films.

1. Introduction

The use of biodegradable packages is a trend due to the growing need to minimize the deposition of nondegradable solid residues in the environment. The high cost of biodegradable polymers when compared to the cost of conventional polymers, such as polyethylene and polypropylene, is an obstacle to their commercialization.

The compatibilization of starch with other biodegradable polymers, such as polyhydroxybutyrate (PHB), poly(lactic acid) (PLA), poly(€-caprolactone) (PCL), poly(butylene succinate co-adipate) (PBSA), polyvinyl alcohol (PVOH) and poly(butylene adipate-co-terephthalate) (PBAT) may reduce production cost that will make them more competitive (Alves, 2007; Averous & Boquillon, 2004; Godbole, Gote, Latkar, & Chakrabarti, 2003; Russo, Truss, & Halley, 2009; Sakanaka, 2006; Sin, Rahman, Rahmat, & Khan, 2010). Several researchers have studied biodegradable films composed of a mixture of TPS and biodegradable polymers (Fang et al., 2005; Jiang, Qiao, & Sun, 2006; Sakanaka, 2006; Sin et al., 2010).

In the presence of a plasticizer, granular starch gives rise to a fluid material called TPS that retains plastic characteristics after cooling, changed with recycling processes, in contrast of conventional thermoplastic (Chang, Jian, Zheng, Yu, & Ma, 2010). The extrusion of TPS in a similar way to the extrusion of polyethylene films and other plastic resins can result in biodegradable films. Glycerol is the most used plasticizer in the production of TPS, and 30 g glycerol/100 g starch or more of glycerol is necessary to produce starch films by extrusion (Alves, 2007; Rahman, Sin, Rahmat, & Samad, in press; Sin, Rahmat, Rahman, Sun, & Samad, in press; Thunwall, Kuthanová, Boldizar, & Rigdahl, 2007).Petersen et al. (1999) and Kester and Fennema (1986) reported the importance of developing films and packages that are capable of reducing the gas and water exchange between foods and the environment, which can retard the migration of oils, solutes, and volatile compounds as well as prevent the growth of microorganisms and inhibit photolytic reactions. The development of these materials will minimize the chemical and microbiological changes of foods during storage and extend their shelf life.

Starch containing films have higher WVP and poorer mechanical properties when compared to other synthetic resins films, such as low density polyethylene (LDPE) films and the characteristics of the starch containing films vary with the ERH (Bertuzzi, Vidaurre, Armada, & Gottifredi, 2006; Kester & Fennema, 1986; Krochta & De Mulder-Johnston, 1997; Mali, Sakanaka, Yamashita, & Grossmann, 2005; Petersen et al., 1999). Cassava starch/PBAT blends can produce films comparatively better than those obtained only with starch, with higher stability in different humidity conditions, better mechanical properties and better WVP (Averous, Moro L., Dole, & fringant, 2000; Krochta & De Mulder-Johnston, 1997; Sakanaka, 2006).

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The WVP of starch blend films is more complex than the WVP of films made from conventional thermoplastic because the diffusion and the interaction between starch and water sorption influence the WVP (Bertuzzi et al., 2006; Mali et al., 2005). The value of WVP increased with the amounts of starch and plasticizer in the blend. The interaction of starch and plasticizers with water increases the solubility coefficient of the films and promotes the saturation of the water binding sites resulting in the reduction of the sorption energy and permeation energy necessary for diffusion (Bertuzzi et al., 2006; Müller, Yamashita, & Laurindo, 2008).

The high WVP of starch blend films limits their application in the food industry (Bertuzzi et al., 2006; García, Martino, & Zaritzky, 2000). Several studies have shown that the addition of lipids and surfactants to starch films can reduce the film WVP because these molecules can act as barriers to water permeation and, thus, make the films more hydrophobic (HLB) (García et al., 2000; Han, Seo, Park, Kim, & Lee, 2006; Kester & Fennema, 1986; Kim & Ustunol, 2001; Liu, Kerry, & Kerry, 2006; Rodrígues, Osés, Ziani, & Maté, 2006; Villalobos, Hernández-Muñoz, & Chiralf, 2006).

Surfactants are amphiphilic substances, and the balance between the hydrophilic and hydrophobic fractions can determine their application. Tween 80 has a high hydrophilic/lipophilic balance (HLB) value (>10) and it is used for oil-in-water-type applications (Rodrígues et al., 2006). Villalobos et al. (2006) observed a reduction in the water absorption capacity of methylcellulose films with increased HLB of mixture of surfactants. Surfactants with higher HLB allow a greater association of their hydrophilic fraction with the hydrophilic film matrix, which may reduce the amount of water binding sites while the hydrophobic fraction may act as a WVP barrier.

The objective of this work was to examine the effects of the Tween 80 surfactant on the hydrophilicity, WVP, and mechanical properties of TPS/PBAT blend films with high starch ratios under different ERH conditions.

2. Materials and methods

2.1. Materials

The starch of cassava (Manihot esculenta) was provided by Indemil (Diadema SP). This starch had 14.445 ± 0.55% moisture, 0.23 ± 0.07% ashes, 0.26 ± 0.07% lipids, 0.24 ± 0.006% proteins, and 22.5 ± 3.9% amylose as estimated by the method previously described (Landers, Gbur, & Sharp, 1991). The biodegradable polymer, PBAT, was purchased from Chemical Company BASF (Brazil) under the trade name of Ecoflex®-F. Commercial glycerol from Dinâmica was used as a plasticizer, and Tween 80 was used as a surfactant. Additionally, polyoxyethylene sorbitan monooleate was used (Synth, Brazil), and the HLB had a value of 15 and a density of 1.07 g/cm^3.

2.2. Production of starch/PBAT blends by blow extrusion

The films were processed in a pilot single screw extruder (BGM, model EL-25, Brazil) equipped with a 250 mm diameter screw and a 150–300 mm diameter film forming circular matrix with a cooling ring, reeler, and a granulator. The screw speed was set at 30 rpm. The three barrel zones and pellet die was operated at 120 °C and the balloon circular die at 130 °C.

Starch/PBAT films were processed in the amounts of 50, 65, and 80 g starch/100 g PBAT and 2 g of Tween 80 per 100 g starch/PBAT. The samples were labeled F50T, F65T, and F80T, respectively. Starch/PBAT films with amounts of 50, 65, and 80 g starch/100 g PBAT were labeled F50, F65, and F80, respectively. Starch films with 100 g starch/100 g starch/PBAT and PBAT films with 100 g PBAT/100 g de starch/PBAT were labeled F100 and F0, respectively. Both types of film without the addition of surfactant were used as controls. All formulations contained 30 g glycerol/100 g starch for starch plasticizing.

Starch, glycerol, and Tween 80 were homogenized and extruded for TPS pelleting. The TPS pellets were mixed with PBAT pellets according to the concentrations given above and extruded to produce homogenous TPS/PBAT pellets. The films were produced by the blow extrusion system, reeled, wrapped in foil, and stored until analysis. Starch films were produced by extruding the starch/glycerol mixture in three pelleting procedures to homogenize starch shearing.

2.3. Determination of thickness and density

Film thickness was determined using a manual micrometer (0.001 mm resolution, Mitutoyo). The final thickness was determined by the mean of 30 measurements from 5 random measurements of each of the 6 samples that were conditioned for 48 h at 64% ERH. Square samples (25 mm × 25 mm) were conditioned for 30 days in desiccators with calcium chloride, and the density was determined by weighing and calculating the mean of 18 measurements.

2.4. Water vapor permeability (WVP)

The permeability of the films was determined by the adapted gravimetric method according to standard ASTM E 96-95 (ASTM, 1995). WVP was determined by keeping the ERH gradient close to 30%. However, the absolute ERH was varied as previously described in the literature. ERH influences the permeability of hydrophilic films containing starch, whereas conventional films, such as polyethylene and polypropylene, are hydrophobic. The following ERH gradients were used: 2–32.8%, 32.8–64.5%, and 64.5–90%. The samples were conditioned at 64.5% relative humidity (RH) at 25 °C for 48 h and then placed in capsules partially filled with $CaCl_2$ (2% RH), saturated $MgCl_2$ (32.8% RH), or $NaNO_2$ (64.5% RH). The samples were set on the round opening of the capsule and sealed with silicone. The capsules were placed in the desiccator with 32%, 64.5%, or 90% ERH at 25 °C. The capsules were weighed in 12 h intervals for 5 days. WVP was calculated as g/m day Pa using Eq. (1), and the permeability was determined in duplicate.

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \cdot \delta}{A \cdot P_s((\mathrm{ERH}_1 - \mathrm{ERH}_2)/100)} \qquad (1)$$

WVPR is the water vapor permeability (g water/day), δ is the average film thickness (mm), A is the capsule permeation area (28.26×10^{-4} m^2), P_s is the water vapor saturation pressure at 25 °C (163,678.8 Pa), and ERH is the equilibrium relative humidity in the desiccators (subindex 1) and inside the capsule (subindex 2).

2.5. Sorption isotherms

The sorption isotherms of the films were determined in different RH conditions (11.8%, 32.8%, 43.2%, 52.9%, 64.5%, and 90%) at 25 °C. The samples (25 mm × 25 mm) were conditioned for 30 days in NaCl and then placed in closed containers with saturated saline solutions until the desired ERH was obtained. The films were weighed in regular intervals until three equal weight measurements were obtained (equilibrium condition). The absolute humidity (dry base) was determined by the oven method (105 °C for 24 h). All the tests were conducted in triplicate. The isotherms were modeled using the Guggenhein–Anderson–de Boer (GAB) model according to Eq. (2). The Statistica 6.0 software was used in modeling, and the parameters were converged by the Quasi-Newton method.

$$X_w = \frac{Ckm_0a_w}{[(1-ka_w)(1-ka_w+Cka_w)]} \tag{2}$$

The model parameters are as follows: C is the monolayer sorption heat, k is the multilayer sorption heat, and m_0 is the monolayer (g water/g solids). X_w is the dry base humidity (g water/g solids) and a_w is ERH/100.

2.6. Determination of the solubility ($\boldsymbol{\beta}$) and diffusion (D^w) coefficients

The method used to calculate the solubility coefficient (β) was proposed by Larotonda, Matsui, Sobral, and Laurindo (2005) based on the first order derivative of the GAB model. This model correlates humidity to the water activity divided by the water vapor pressure (P_s) at 25 °C according to Eq. (3).

$$\beta = \frac{Ckm_0}{P_s}\left[\frac{1}{(1-ka_w)(1-ka_w+Cka_w)} - \frac{a_w}{[(1-ka_w)(1-ka_w+Cka_w)]^2}[-k(1-ka_w+Cka_w)+(1-ka_w)(-k+Ck)]\right] \tag{3}$$

β is the solubility coefficient; C, K, and m_0 are the GAB model parameters; and P_s is the water vapor pressure at 25 °C. The a_w value used was the mean of the ERH/100 gradient described in Section 2.4.

The water vapor diffusion coefficient (D^w) was determined from the solubility coefficient and WVP values determined for the films in the humidity conditions described in Section 2.4 using Eq. (4) with ρ as the density of the films:

$$\text{WVP} = \rho D^w \beta \tag{4}$$

2.7. Mechanical properties

The mechanical properties were evaluated according to ASTM D 882-88 (ASTM, 1996). The tensile strength (MPa), elongation at break (%), and Young modulus (MPa) were evaluated. The tensile strength properties were determined using a Stable Micro System texturometer (model TA.TX2i, England). The test samples were cut (100 mm long and 10 mm wide) and conditioned in desiccators containing saturated saline solutions at ERH of 32.8%, 52.9%, and 90% until equilibrium was reached as determined from the isotherms. The samples were fixed to pneumatic grips (A/TG tensile grips), and the tensions (MPa) and deformations (% elongation) were measured. The distance between the grips was 50 mm, and the traction extension speed was 8.3 mm/min. The pre-test speed was 2.0 mm/s and post-test speed was of 8.0 mm/s. The time to determination was fixed in 5.00 s.The tests were performed at 25 °C and five measurements were performed for each sample.

2.8. Scanning electron microscopy

The micrographs were obtained by a JEOL-LSMP 100 (Japan) scanning electron microscope of the microscopy laboratory of Universidade Estadual de Londrina. The films were kept in desiccators with phosphorous oxide (P_2O_5) for 15 days, frozen in liquid nitrogen, fractured, and set onto aluminum supports. The stubs were gold coated (SPUTTER COATER BALZERS_SCD 050, Baltec, Austria) (40–50 nm) at 25 °C under 2.6 × 10^7 Pa for 180 s. The gold-coated samples were analyzed at 15 kV and 600× magnification.

3. Results and discussion

Films were obtained by extruding the starch/PBAT blends with either 50% or 80% starch with (F50T and F80T) and without (F50 and F80) surfactant. It was not possible to produce TPS pellets with 65% starch and surfactant (F65T) because the material flowed back from the barrel into the feeder. For this reason, the characterization results of blend films with 65% starch with and without surfactant (F65T and F65) are not presented.

Table 1
GAB modeling parameters fitted to the isotherms of films made from TPS/PBAT with 2% Tween 80 (F50T and F80T), films without surfactants (F50 and F80), and starch films (F100).

Film	Model parameter			R^2
	C	k[a]	m_0[a]	
F50	138 ± (706)	0.791 ± (0.04)	0.103 ± (0.013)	0.83
F50T	17 ± (28)	0.765 ± (0.074)	0.109 ± (0.028)	0.85
F80	386 ± (209)	0.954 ± (0.002)	0.092 ± (0.002)	0.99
F80T	67 ± (1145)	0.895 ± (0.003)	0.133 ± (0.005)	0.96
F100	7 ± (2)	0.967 ± (0.001)	0.090 ± (0.001)	0.99

[a] Significant parameters (p < 0.5); m_0 is the monolayer value of g water/g solids.

3.1. Sorption isotherms

The sorption isotherms of the films are shown in Fig. 1. The lines between the experimental points do not represent the modeling. The GAB model fit well with the experimental data, and similar modeling was considered satisfactory according to others who investigated biofilms (Costa, 2008; Larotonda et al., 2005; Mali et al., 2005; Martelli, Moore, Paes, Gandolfo, & Laurindo, 2006). Table 1 shows the model parameters and the respective coefficient of determination (R^2).

Starch films (F100) were more hydrophilic than the starch/PBAT blend films resulting in greater equilibrium humidity over 11.8 ERH. Films with 80% starch and no added surfactant had isotherms similar to the films with 50% starch for less than 75% ERH. F50 films were the least hydrophilic in high ERH (90%) conditions with values two-fold lower than those of F100 films. The bigger hydrophilic of F100 film was due to the numerous hydroxyl groups available for binding hydrogen to water, which effectively occurred in high

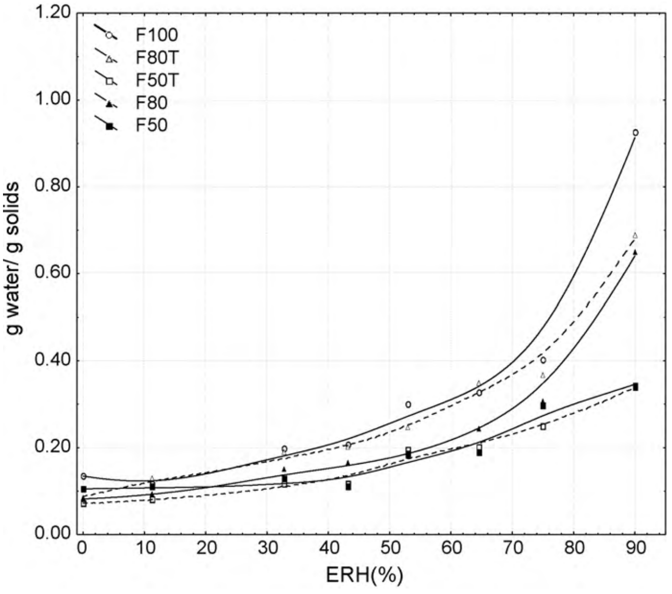

Fig. 1. Sorption isotherms of films made from starch/PBAT blends with 2% Tween 80 (F50T and F80T), films without surfactant (F50 and F80), and starch films (F100) as control. (○) F100, (△) F80T, (□) F50T, (▲) F80, (■) F50.

Table 2
Water vapor permeability (WVP), solubility coefficient (β), and diffusion coefficient (D^w) of cassava starch + PBAT blend films added with 2% tween (F80T and F50T), films without surfactant (F80 and F50), and PBAT (F0) and starch (F100) films as control.

Film	ΔERH (%)	WVP (10^{-7} g day^{-1} Pa^{-1} m^{-1})[a]	Density, ρ (g/cm^3)	Thickness (μm)	β (10^{-6} g/g Pa)	D^w (10^{-7} m^2/day)
F0	2.00–32.8	0.82 ± 0.006 a A	1.5 ± 0.15 b	152 ± 2 a b	–	–
	32.8–64.5	0.80 ± 0.003 a A			–	–
	64.5–90.0	1.06 ± 0.07 a B			–	–
F50	2.00–32.8	0.57 ± 0.024 a A	1.18 ± 0.63 abc	147 ± 58 a	0.84	0.57
	32.8–64.5	2.51 ± 0.23 a B			1.33	1.60
	64.5–90.0	2.42 ± 0.24 a B			3.30	0.62
F50T	2.00–32.8	5.35 ± 0.31 c B	0.5 ± 0.08 c	1206 ± 200 d	1.51	0.71
	32.8–64.5	7.27 ± 1.63 b B			1.47	0.99
	64.5–90.0	22.0 ± 5.9 b B			3.22	1.36
F80	2.00–32.8	1.09 ± 0.091 a A	1.44 ± 0.42 b	218 ± 42 a b	0.82	0.93
	32.8–64.5	0.95 ± 0.299 a A			1.86	0.36
	64.5–90.0	3.94 ± 0.025 a B			7.74	0.36
F80T	2.00–32.8	1.14 ± 0.06 a A	0.99 ± 0.25 c	228 ± 50 b	1.40	0.82
	32.8–64.5	3.58 ± 0.01 a B			2.33	0.70
	64.5–90.0	3.68 ± 0.80 a B			7.61	0.50
F100	2.00–32.8	2.84 ± 0.31 b A	2.24 ± 0.58 a	344 ± 142 c	1.49	0.85
	32.8–64.5	7.52 ± 1.16 b A			2.10	1.61
	64.5–90.0	20.5 ± 3.75 b B			8.30	1.10

[a] Upper case letters compare treatments in relation to WVP in the different humidity conditions , lower case letters compare WVP for treatments in the same humidity condition, equal letters mean significantly similar at $p < 0.05$.

equilibrium humidity (>75%). The addition of PBAT resulted in films with lower humidity under high ERH because of the reduction in the number of sites active for binding to water due to the hydrophobic character of PBAT.

Films with greater starch contents had larger k (multilayer sorption heat) values and an increase in humidity greater than 75% ERH indicating the need to reduce the interaction between the multilayers by increasing starch content. Costa (2008) observed the same correlation between the k value and increase in the starch contents in TPS/PBAT blend films. This behavior was correlated to the larger mass transfer for greater than 75% ERH. When k is equal to one, it is considered that no interactions occur between the water molecules sorbed in the multilayers and the isotherm model is equal to the Brunauer–Emmett–Teller (BET) model. The increase in equilibrium humidity may result in the saturation of the active water binding sites with the consequent decrease in the sorption energy. The films with surfactant had k values lower than those of the control films indicating that the surfactant increased the interaction between the multilayers.

The addition of surfactant affected the isotherms of films with 80% starch (F80T) and increased their affinity for water when compared with control films (F80) that had a high m_0. Films with 50% starch and surfactant (F50T) had m_0 values and isotherms that were similar to those of control films (F50). Furthermore, the m_0 values did not vary with the increase in the starch content of films without surfactant. A similar behavior was observed by Villalobos et al. (2006). They found that m_0 increased when the hydrocolloid/surfactant ratio (H/S) increased suggesting that films with surfactants become more hydrophilic with the increase in the hydrocolloid content. A similar result was reported by Rodrígues et al. (2006) when they demonstrated that the humidity of potato starch films increased with the addition of Tween 80. They correlated the effect to the interaction of water with the hydrophilic portion of the surfactant.

3.2. *Water vapor permeability (WVP), solubility coefficient **(β)**, diffusion coefficient (D^w), thickness, and density*

The thickness and density values of the films are shown in Table 2. PBAT films (F0) had lower densities and thickness than the starch films because polyester results in more flexible films and starch makes the films more rigid. The thickness of blend films were proportionally higher for higher starch contents.

Standardizing the thickness and density of films is important for comparing films and their characteristics. In blow extrusion, thickness is mainly controlled by the reeler speed. As the starch/PBAT films have different resistances to reeling speed, we used the fastest speed that allowed film reeling without breaking the film blowing of TPS/PBAT. This condition was used to produce the study material. Therefore, the variations of thickness resulted from the differences in the formulations and machinability of the material obtained. Adjusting thickness to a single value for all films was not feasible.

The F50T films were thicker than the F80T films suggesting that the addition of surfactant changed the density and thickness values of control films. This behavior strengthens the possibility of interaction between the surfactant and film polymers, which reduces the flexibility of the polymer chains during film formation and may lead to thicker films.

The values of WVP, solubility coefficient (β), and diffusion coefficient (D^w) of the films are shown in Table 2. The solubility coefficient expresses the affinity of the film matrix for water, and the diffusion coefficient measures the capacity of the movement of water molecules through the film matrix (Larotonda et al., 2005).

The starch/PBAT blend films had lower WVP than starch films (F100) in the humidity ranges studied with the exception of F50T, which had similar WVP values. The F50, F80, F80T, and PBAT (F0) films had similar WVP values. Films with a greater starch content demonstrated higher solubility coefficient values under high ERH (64.5–90%) and lower diffusion coefficient values in all humidity ranges. The similarity of WVP values in the F50 and F80 films may be attributed to the combined effects of the solubility coefficients and diffusion coefficients. This result indicated an increase in the affinity for water (higher solubility coefficient values) and compatibility between starch and PBAT (lower diffusion coefficient values) with the increase in starch content and ERH value. The F50, F80, and F80T films had WVP values lower than the values reported by Costa (2008) for the same conditions. They determined the WVP values for TPS/PBAT films as a function of the ERH range between 2.96×10^{-6} and 12.4×10^{-6} (g/m day Pa) for films with 50% starch and between 1.45×10^{-6} and 17.5×10^{-6} (g/m day Pa) for films with 80% starch.

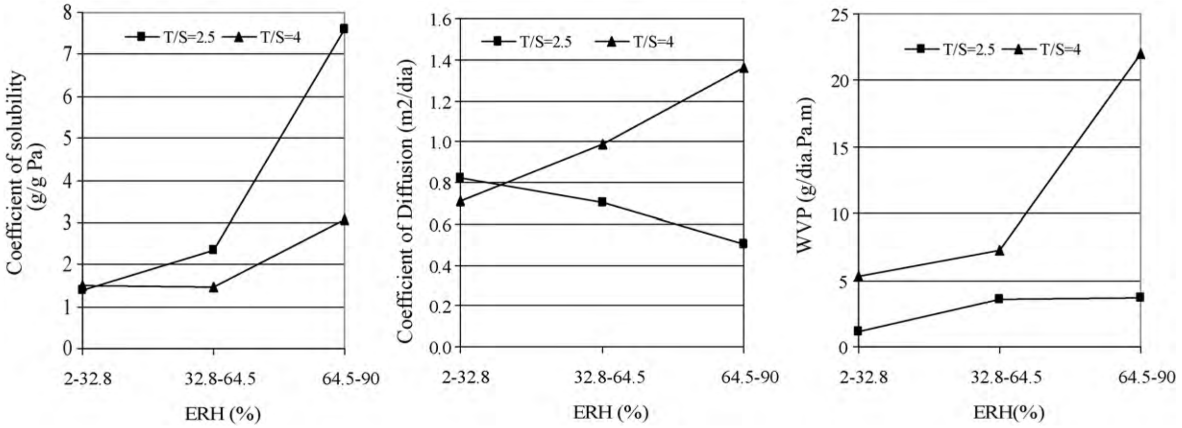

Fig. 2. Behavior of the solubility coefficient (β), diffusion coefficient (D^w), and WVP as a function of the surfactant/starch ratio (T/S) for different ERH ranges (■) $T/S = 2.5$, (▲) $T/S = 4$.

In contrast to control films, films with surfactant had WVP values that were inversely proportional to the starch content. The correlation between WVP, solubility coefficients, diffusion coefficients and T/S ratios indicated that the effect resulted from the increased diffusion, as shows Fig. 2. Films with a T/S ratio equal to 4.0×10^{-2} (F50T) had higher WVP and diffusion coefficient values and lower solubility coefficient values in all ERH ranges when compared with film with a T/S ratio equal to 2.5×10^{-2} (F80T). The F80T film had similar WVP and higher diffusion coefficients when compared to control values, and this film demonstrated the highest hygroscopicity. These results suggested that the differences in the WVP in films with surfactants cannot be explained by the water sorption effect and that the diffusion coefficient values increased with the T/S ratio, which is an increase in the surfactant content.

Surfactant Tween 80 did not reduce the WVP of the films because it behaved as a plasticizer in the amounts used increasing the free volume between the adjacent starch chains. The effect was stronger in films with higher T/S ratios due to the higher values of diffusion coefficients indicating that the structure of these films was less compact and more permeable to water. According to Villalobos et al. (2006) and García et al. (2000), WVP increases when the surfactant/hydrocolloid ratio is not sufficient to overcome the effect of the increase in the water sorption capacity due to the presence of the surfactant polar region and in the case of excess surfactant, the films may become more permeable to water due to the increase in the free volume between the hydrocolloid adjacent chains. This behavior may explain the WVP observed in films with different starch contents.

The concentration of surfactant was kept equal for all films to ensure an equal dispersion of Tween 80 in the continuous matrix formed by starch/PBAT. However, the results indicated that the behavior of WVP depended mainly on the starch/surfactant ratio. Furthermore, the results suggested that the proportions used increased the free volume between the starch chains, thus, favoring the permeation of water vapor. According to Villalobos et al. (2006), films with surfactant added had a critical concentration that allowed the formation of a continuous polymer network with dispersed surfactant particles. In such conditions, the surfactant would act as a barrier to water, thus, decreasing the WVP. García et al. (2000) reported similar results for starch films containing 0–10% soybean oil with a decrease in WVP only for films with 2% soybean oil.

F50T films were thicker and more permeable to water than similar films without surfactant presenting higher diffusion coefficients and similar humidity values when compared to control films (F50) (Fig. 1). Bertuzzi et al. (2006) and Mali, Grossmann, García, Martion, & Zaritzky (2004) observed a linear increase in WVP with thickness and humidity. Thicker films had higher humidity resulting in saturation of water binding sites and reduction of sorption energy. Our results for the F50T film indicate that although the films were thicker, the equilibrium humidity was similar to that of the control film suggesting that permeability was mainly controlled by the diffusion processes.

The WVP and solubility coefficients of the films increased with the increase in ERH and the diffusion coefficient values did not vary with the increase in ERH. Müller et al. (2008) and Bertuzzi et al. (2006) observed a similar behavior for starch films and demonstrated that it was related to the saturation of water binding sites. The saturation occurred more effectively with the increase in the

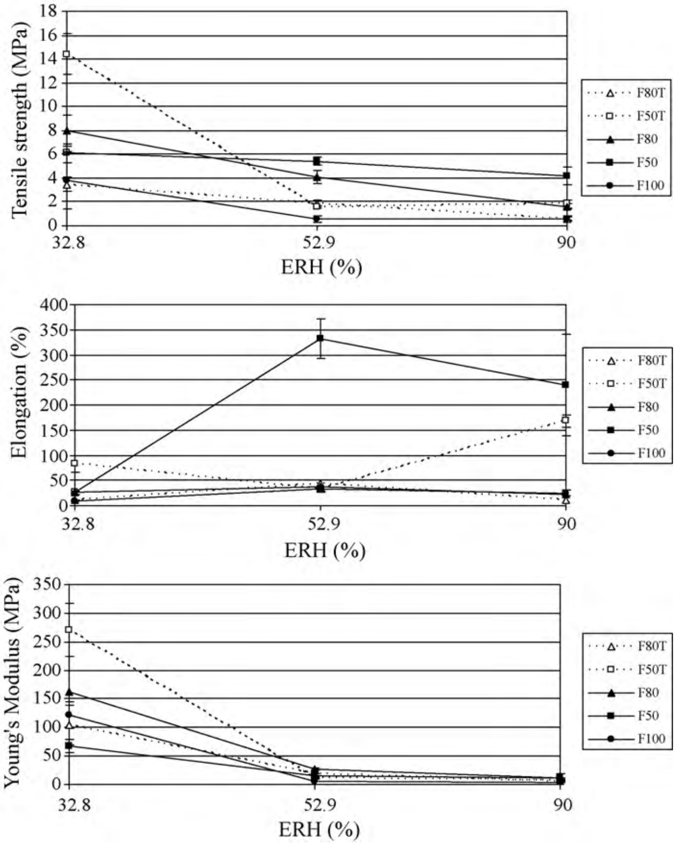

Fig. 3. Mechanical properties of films made from cassava starch/PBAT blends with 2% Tween 80 (F50T and F80T), films without surfactant (F50 and F80), and starch films (F100) as control. (△) F80T, (□) F50T, (▲) F80, (■) F50, (●) F100.

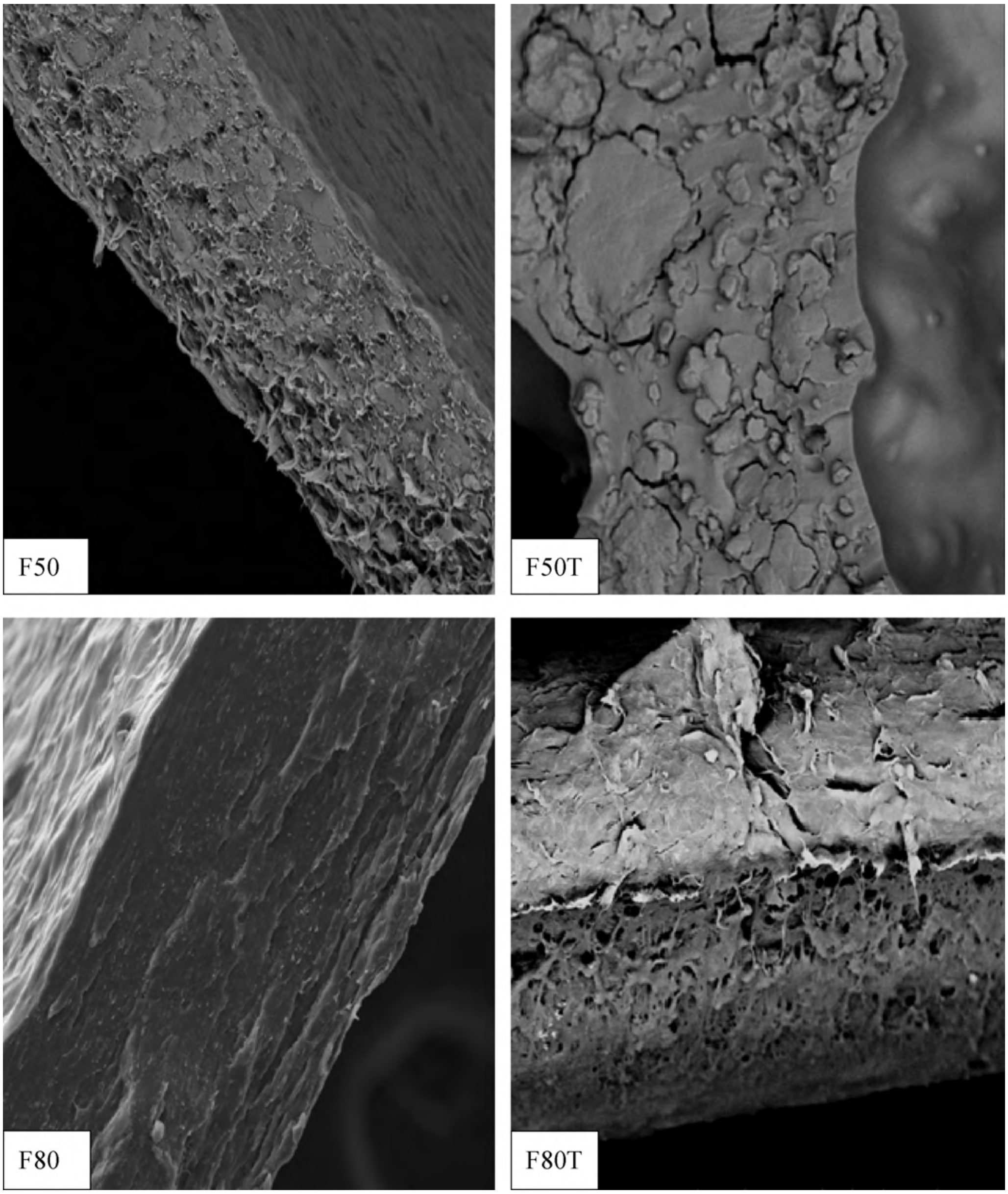

Fig. 4. Fracture micrographs of films with 50% and 80% starch with (F50T and F80T) and without (F50 and F80) surfactant, 600× magnification.

ERH, which energetically favored the permeation of water vapor through the film matrix.

3.3. *Mechanical properties*

The starch/PBAT blend films demonstrated higher tensile strength and elongation than the starch film (F100), as shows Fig. 3, probably because PBAT has properties similar to PE-LD because of its high molecular weight and its long chain branched molecular structure and its good compatibility with starch (BASF, 2009). This biodegradable polyester reinforced the structure of starch films, which was confirmed by the increase in the tensile strength and elongation with the increase in the PBAT concentration in the blend (Fig. 3). Costa (2008) and Alves (2007) reported similar behaviors for starch/PBAT blend films.

Ren, Fu, Ren, & Yuan (2009) determined for films of starch/PBAT with 50% of starch values of tensile strength (5 MPa) and elongation (17.5%) similarly to the values determined for F80 films. Sarazin, Li, Orts, and Favis (2008) determined values strain at break of 5% for films with 50% TPS (24% glycerol) and 50% PLA, indicating that they were more rigid than the films elaborated in this work, similar behavior was verified in films elaborated with TPS/PLA/PCL blends. Shi et al. (2008) manufactured films with of starch/PVOH (1:3) blends added with 30% of citric acid and determined values of tensile strength (42 MPa) and elongation at break (207.8%) higher than ours films. Although some authors claimed that blends with hydrophobic polymers, as the PBAT, and hydrocolloids, as starch, are thermodynamically incompatible (Kalambur & Rizvi, 2006, Rahmat, Rahman, Sin, & Yussuf, 2009), others authors (Alves, 2007; Ren et al., 2009) obtained films with good mechanical properties adding compatibilizers.

Lee, Youn, Yun, and Yoon (2007) verified that starch/POHV films with 30% glycerol presented tensile strength of 10 MPa and elongation of 60% when conditioned at 55% ERH and 4 MPa and 120%, respectively, at 80% ERH. These films were more sensible to the equilibrium relative humidity that the F50 films. Imam, Cinelli, Gordon, and Chiellini (2005) and Zhao et al. (2006) verified the same behavior of starch films with POHV. According to the authors, the higher water vapor permeability was due to the hydrophilic characteristic of the polymers, i.e., the water sorption affected the mechanical properties of the films.

The tensile strength of F50 films showed little variation and higher elongation with the ERH increase. The other treatments presented lower mechanical resistance and Young modulus and higher elongation for ERH greater than 52.9% and this effect was more pronounced in the films with higher starch content (Fig. 3). According to Mali et al. (2005) and Lee et al. (2007), this behavior was associated to the water plasticizer effect. The PBAT is more hydrophobic than the starch and its presence decreased the water sorption capacity of the films (Fig. 1).

Films with surfactant presented lower resistance and elongation values than the films without surfactant. The F50T films had similar moisture values for all ERH conditions and higher diffusion coefficients compared with F50 films. This result indicated that the effect of the surfactant on the free volume only might explain the decrease in resistance for the F50T film. Films with 80% starch and surfactant (F80T) showed mechanical properties similar to those of starch films (F100) probably due to the combined effect of the surfactant and the high amount of starch. Rodrígues et al. (2006) observed that potato TPS films with Tween 80 presented a reduction in the mechanical resistance values due to the plasticizing effect of the surfactant increasing the free volume between the adjacent chains of starch and making the structure more fragile.

3.4. Scanning electron microscopy

Fig. 4 shows the fracture micrographs of films with 50% and 80% starch with and without surfactant. Films without surfactant presented a compact internal structure without cracks and pores while the films with surfactants presented a discontinuous and porous structure.

Films with higher starch content (F80) presented a more compact structure, the increase of the structural integrity with the reduction of the PBAT content probably occurred due to the non-complete compatibility between the starch and the PBAT. Rahmat et al. (2009) verified by SEM micrographs that starch films when added of PVOH (polyvinyl alcohol) presented better structural integrity than the only starch film and according to the authors due to the hydrophilic characteristic of the PVOH that increased the hydrogen linking and the adhesion between the starch chains.

The films with 50 or 80% starch and surfactant showed aggregates surrounded by micro-cracks resulting in a less compact structure and the behavior of WVP and diffusion coefficients of the F50T and F80T films can be correlated with these structures since the water could migrate thought these cracks increasing both WVP and diffusion coefficient. According to Chen, Kuo, and Lai (2009) the tensile strength reduction of the films with surfactant can be related with the starch–surfactant interactions. These authors verified the reduction in both tensile strength and strain at break of films when added of 10% sucrose ester surfactant. According to them, the surfactants can form complexes or interactions with the starch, decreasing the amylose–amylose interactions, while the hydrophobic functional groups (groups with high molecular mass) of the surfactant can form aggregates between the starch chains that difficult the film structural formation.

4. Conclusions

The hydrophilicity of the films obtained depended on the starch content of the blend. Films with and without surfactant became more hydrophilic as the starch content increased. The increase in starch content resulted in more hydrophilic and compact films, therefore, less susceptible to diffusion processes. The films obtained demonstrated lower tensile strength with increases in ERH due to the plasticizing effect of the sorbed water.

The addition of surfactant did not result in the desired increase in the water vapor barrier. The relation between the solubility coefficient and diffusion coefficient was important to understand the variations in WVP with the film formulations. Films with a higher surfactant/starch ratio (T/S) had a higher WVP and water vapor diffusion indicating that the surfactant increased the free volume between the adjacent chains of starch. The micrographs confirmed that the films with surfactant had less structural integrity. The reduced maximum tensile strength of films with surfactant may be related to the increase in the free volume between the adjacent chains of starch. The results indicate that the variation in the T/S ratio minimizes the variation of the diffusion coefficient value and reduces the solubility coefficient value that produces a decrease in the WVP of starch/PBAT blend films.

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