Films of starch and poly(butylene adipate co-terephthalate) added of soybean oil (SO) and Tween 80

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ABSTRACT

Starch extruded in the presence of a plasticizer results in a material called thermoplastic starch (TPS). TPS mixed with poly(butylene adipate co-terephthalate) (PBAT), soybean oil (SO), and surfactant may result in films with improved mechanical properties due to greater hydrophobicity and compatibility among the polymers. This study characterized films produced from blends containing 65% TPS and 35% PBAT with SO added as compatibilizer. The Tween 80 was added to prevention of phase separation. The elongation and resistance were greater in the films with SO. The infrared spectra confirmed an increase in ester groups bonded to the PBAT and the presence of groups bonded to the starch ring, indicating TPS–SO and PBAT–SO interactions. The micrographs suggest that the films with SO were more homogenous. Thus, SO is considered to be a good compatibilizer for blends of TPS and PBAT.

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1. Introduction

The extrusion of starch in the presence of plasticizers, such as glycerol, results in a material known as thermoplastic starch (TPS). TPS may be used to produce low-cost biodegradable materials and to minimize environmental impact, as starch is biodegradable and a renewable resource (Thunwall, Kuthanová, Boldizar, & Rigdahl, 2008).

The addition of a plasticizer increases the flexibility of the films because its presence among the starch chains reduces their intermolecular interactions by separating them, thereby increasing their mobility (Mali, Sakanaka, Yamashita, & Grossmann, 2005). However, the plasticizers as glycerol or sorbitol are hydrophilic compounds, which increase sensibility of the films and their instability under different conditions of relative humidity (RH) (Müller, Yamashita, & Laurindo, 2008). According to Talja, Helén, Roos, and Jouppila (2008), at RH above 60%, there may be a substitution of the starch–starch and starch–glycerol interactions by starch–water and glycerol-water interactions, or there may be an increase in the crystallinity of the films, which may cause a decrease in their elongation.

The design of films from blends of starch with other biodegradable polymers has been studied as an option for obtaining starch films with better mechanical and barrier properties (Avérous & Boquillon, 2004; Avérous & Fringant, 2001; Brandelero, Grossmann, & Yamashita, 2011; Costa, Scapim, Brandelero, Grossmann, & Yamashita, 2008; Olivato, Grossmann, Yamashita, Eiras, & Pessan, 2011; Ren, Fu, Ren, & Yuan, 2009; Sarazin, Li, Orts, & Favis, 2008). PBAT is a biodegradable polyester that features mechanical properties similar to those of polyethylene films (BASF, 2009), and several authors have studied the formation of blends of this polymer with starch (Avérous & Fringant, 2001; Brandelero et al., 2011; Costa et al., 2008; Ren et al., 2009).

Ren et al. (2009) researched the properties of elongation and rupture resistance in TPS/PBAT films. The authors found that increasing the amount of polyester increased the elongation and decreased the resistance. The best results were obtained from films with high concentrations of maleic anhydride added as a compatibilizer, given that starch and PBAT are not very compatible.

According to Kalambur and Rizvi (2006), starch films with other, less polar biodegradable polymers display immiscibility among the polymeric phases, evidenced by the losses in the mechanical properties. The extrusion of starch in combination with substances that interact with the hydroxyls of the starch, resulting in covalent bonds among the polymers of the blend, may increase the interfacial adhesion between the polymer chains, in addition to increasing the elongation and rupture resistance of the films (Kalambur & Rizvi, 2006; Raquez et al., 2008; Ren et al., 2009).

The mechanical properties and water vapor impermeability of films prepared with TPS/PBAT blends are inferior to those of conventional films, with greater losses in these properties as the amount of starch increases. Additionally, the RH alters these parameters, which limits the applications of these films in the food industry (Avérous & Fringant, 2001; Costa et al., 2008; Ren et al.,

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Table 1
Formulations of the films prepared from blends of TPS + PBAT with the addition of soybean oil (SO) and/or Tween 80 (TW).

Formulations	Starch (g/100 g TPS + PBAT)	PBAT (g/100 g ATP + PBAT)	Glycerol (g/100 g starch)	Soybean oil (g/100 g starch)	Tween 80 (g/100 g starch)
FB (TPS/PBAT)	65	35	30	0	0
FBSO0.5	65	35	24.5	0.5	0
FBSO1.0	65	35	24.0	1.0	0
FBSO0.5TW0.5	65	35	24.0	0.5	0.5
FBSO1.0TW0.5	65	35	23.5	1.0	0.5
FBSO0.5TW1.0	65	35	23.5	0.5	1.0
FBSO1.0TW1.0	65	35	23	1.0	1.0
FTPS	100	0	30	0	0

2009). The addition of hydrophobic substances, such as oils and fatty acids, may decrease the hygroscopicity due to the increase in the hydrophobic portions in the film, thereby decreasing the water vapor permeability and generally causing a loss in tensile resistance and elongation (García, Martino, & Zaritzky, 2000; Kester & Fennema, 1986).

Bourtoom and Chinnan (2009) and Han, Seo, Park, Kim, and Lee (2006) studied the addition of lipids to starch films and found that the films became less resistant and less flexible as the amount of lipids increased. According to the authors, the presence of these substances caused phase separation, decreasing the structural integrity of the films. Debeaufort and Voilley (1995) and Perez-Gago and Krochta (2001) showed that the addition of lipids along with surfactants improves the mechanical properties and water vapor impermeability of the films due to the decrease in the size of the fat globules, resulting in the more compact structure, prevention of phase separation and increase in hydrophobicity.

Soybean oil (SO) is an abundant and renewable raw material that features a mixture of triglycerides in its chemical composition, containing saturated, monounsaturated, and polyunsaturated fatty acids. Oleic acid (22.98%), linolenic acid (7.23%), and linoleic acid (54.51%) are the major components (Hammond, Johnson, Wang, Su, & White, 2005). Ethoxylated sorbitan monooleate, called Tween 80 (TW), is a non-ionic surfactant that displays a high hydrophilic/lipophilic balance (>10) and is applied as a surfactant in oil-in-water systems (Rodrígues, Osés, Ziani, & Maté, 2006).

The objective of this study was to characterize films produced from blends of TPS and PBAT with added SO and Tween 80 and to test the effect of these substances on the microstructure, mechanical properties and water absorption capacity of these films under different moisture conditions.

2. Materials and methods

2.1. Materials

Starch from cassava (*Manihot esculenta*) was provided by Indemil Ind. Com. Ltda. (Brazil). The polymer poly(butylene adipate co-terephthalate) (PBAT) was provided by the company BASF (Brazil) under the commercial name of Ecoflex® F BX 7011. Commercial glycerol (Dinâmica, Brazil) was used as a plasticizer, and ethoxylated sorbitan monooleate (Synth, Brazil) under the commercial name Tween 80 (TW) was used as a surfactant. Tween 80 has a hydrophilic/lipophilic balance (HLB) of 15.0 and a density of 1.07 g/cm³. Refined commercial SO from the Bunge Alimentos S.A. refinery was acquired at the local market.

2.2. Preparation of the films by extrusion blow molding

The films were processed in a single-screw pilot extruder (BGM, model EL-25, Brazil) by a balloon-blowing system that was equipped with a 250-mm-diameter screw, a circular array with a cooling ring for the formation of 150–300-mm-diameter films,

a winder, and a granulator. The screw speed was maintained at 30 rpm, and the temperature program used was 120 °C for the three cannon areas, 120 °C for the pellet-forming array, and 125 °C in zone 1 and 130 °C in zone 2 of the circular array of the balloon.

TPS/PBAT films were processed that contained SO and Tween 80 in the amounts described in Table 1. Films with 100% TPS (FTPS) and films with 65% TPS + 35% PBAT without surfactant and/or SO (FB-TPS/PBAT) were prepared as controls. The amount of glycerol added varied according to processability criteria.

The starch, glycerol, Tween 80, and SO were homogenized and extruded for the production of TPS pellets. The TPS pellets were mixed with the PBAT pellets and were extruded, producing TPS/PBAT pellets that were again extruded to obtain a more homogenous material. The films were produced by the balloon-blowing extrusion system, wound, and stored in laminated paper packages until the time of analysis. The starch films were produced from the mixture of the starch and the glycerol, and three cycles of pelleting were performed to standardize the shear suffered by the starch.

2.3. Determination of the density and the thickness

The thickness of the films was determined using a manual micrometer (0.001-mm resolution, Mitutoyo, Brazil). The final thickness was determined by the arithmetic mean of 18 random measurements covering the area of the film. The density was determined in 2.5 cm × 2.5 cm square specimens that were first conditioned for 30 days in a desiccator with calcium chloride; after this period, the specimens were weighed to calculate the density, which was the arithmetic mean of 18 measurements.

2.4. Mechanical properties

The mechanical properties that were evaluated followed the D 882–88 of the ASTM standard (ASTM, 1996). The maximum tensile strength and the elongation at rupture were analyzed. The tensile strength properties were determined using a Stable Micro Systems texture analyzer, model TA.TX2i (England). The specimens were cut to dimensions of 100 mm in length and 10 mm in width and were conditioned in desiccators containing saturated saline solutions that provided RH levels of 32.8%, 52.9%, and 90% until equilibrium was reached. The distance between the clamps was 50 mm, and the traction speed was 8.3 mm/min. The tests were performed in a room maintained at 25 °C, with five replicates.

2.5. Fourier transform infrared analysis (FT-IR)

The infrared analysis was performed on a Bomen FT-100 FT-IR spectrophotometer (Canada) with an attachment to read the total reflectance and equipped with a diamond/ZnSe crystal with triple reflection; the apparatus belonged to the Chemical Laboratory of the State University of Maringá. The spectral region investigated was 4000–400 cm⁻¹, with a spectral resolution of 4 cm⁻¹. The

Table 2
Thickness, density, and moisture of the films under different relative humidity (RH) equilibrium conditions.

Film	Thickness (μm)	Density (g/cm^3)	RH (%)	Moisture (g water/g solids)
FTPS	334[a]	2.24[a]	33	0.10 ± 0.001[ab]
			53	0.22 ± 0.073[a]
			90	0.67 ± 0.005[a]
FB(TPS/PBAT)	200[b]	1.34[bc]	33	0.16 ± 0.002[a]
			53	0.21 ± 0.010[ab]
			90	0.59 ± 0.020[b]
FBSO0.5	221[b]	0.91[d]	33	0.09 ± 0.010[b]
			53	0.14 ± 0.005[ab]
			90	0.37 ± 0.010[e]
FBSO1.0	237[b]	1.26[c]	33	0.10 ± 0.010[ab]
			53	0.12 ± 0.050[b]
			90	0.41 ± 0.005[cde]
FBSO0.5TW0.5	119[b]	1.18[cd]	33	0.08 ± 0.050[b]
			53	0.13 ± 0.010[ab]
			90	0.46 ± 0.010[c]
FBSO1.0TW0.5	145[b]	1.20[cd]	33	0.12 ± 0.009[ab]
			53	0.17 ± 0.002[ab]
			90	0.45 ± 0.008[cd]
FBSO0.5TW1.0	173[b]	1.12[cd]	33	0.09 ± 0.010[b]
			53	0.13 ± 0.010[ab]
			90	0.41 ± 0.030[cde]
FBSO1.0TW1.0	118[b]	1.56[b]	33	0.10 ± 0.004[ab]
			53	0.14 ± 0.008[ab]
			59	0.42 ± 0.010[cde]

[a,b,c,d,e] Means with different letters under same relative humidity (RH) to moisture and in the same column in the same column indicate a difference at 0.05 level by Tukey's test.

samples were conditioned for 15 days in a desiccator containing P_2O_5. The spectra were obtained in triplicate.

2.6. Determination of the water sorption

Film specimens were produced measuring 25 mm × 25 mm and stored in a desiccator containing calcium chloride for 30 days. Subsequently, the specimens were weighed and conditioned in a sealed container containing saturated saline solutions at RH values of 32.8%, 52.4%, and 90%. The specimens were weighed until three equal consecutive values were obtained, and the moisture was determined in a stove at 105 °C.

2.7. Scanning electronic microscopy

The micrographs were obtained on a JEOS-LSMP 100 scanning electronic microscope (Japan) of the Microscopy Laboratory of the State University of Londrina. The films were kept in desiccators with P_2O_5 for 15 days and were frozen in liquid nitrogen, fragmented, and fixed on aluminum stubs. The stubs were covered with a layer of gold (Sputter Coater Balzers – SCD-50, Baltec Austria) (40–50 nm) at 25 °C under a pressure of 2.6 × 10^7 Pa for 180 s. The covered samples were analyzed at 15 kV. The magnification of the observation was 600×.

3. Results and discussion

The blends of TPS/PBAT were able to produce films by blow extrusion. Blends of TPS/PBAT added with OS or OS + TW showed good processability, unlike the blends of TPS and PBAT added only with TW do not flowed continuously through the extruder barrel, and it was not possible to produce the film.

3.1. Moisture, thickness, and density

The values of the moisture of the films under the RH conditions studied are presented in Table 2. The films with PBAT in the mixture displayed the lowest moisture at 53% and 90% RH and differed significantly ($p < 0.05$) from the films with 100% starch (F100) (Table 2). All of the films exhibited increased moisture with increasing RH, and the greatest values were obtained for the films with 100% starch.

The films containing SO or SO + TW displayed lower moisture under high RH conditions (90%) in comparison to the films without SO, indicating that the oil reduced the hygroscopicity of the films. There was no difference between the moisture levels of the films with SO and those with SO + TW, indicating that the observed effect is due to the presence of the lipid.

The films containing SO and/or TW displayed lower thickness and density values than the control films (FTPS and FBTPS/PBAT), with the exception of the FBSO1.0TW1.0 formulation, which displayed a higher density than FB (TPS/PBAT). The addition of SO and/or TW led to a lower density and thickness of the films, likely due to the increase in interfacial adhesion among the polymers of the blend, resulting in more compact films.

3.2. Mechanical properties

Films with 100% TPS showed relative low elongation at break (32%) and low tensile strength (0.55 MPa) (Figs. 1 and 2) and these values are similar to those found by Pelissari, Grossmann, Yamashita, and Pineda (2009) that worked with of cassava starch films with 18% (w/w) of glycerol produced by blow extrusion. Mali, Grossmann, García, Martion, and Zaritzky (2006) reported strain at break of corn, cassava and yam films (28%, 46% and 25%, respectively) produced by casting with 40% of glycerol. The source starch influences the mechanical properties due the different amounts
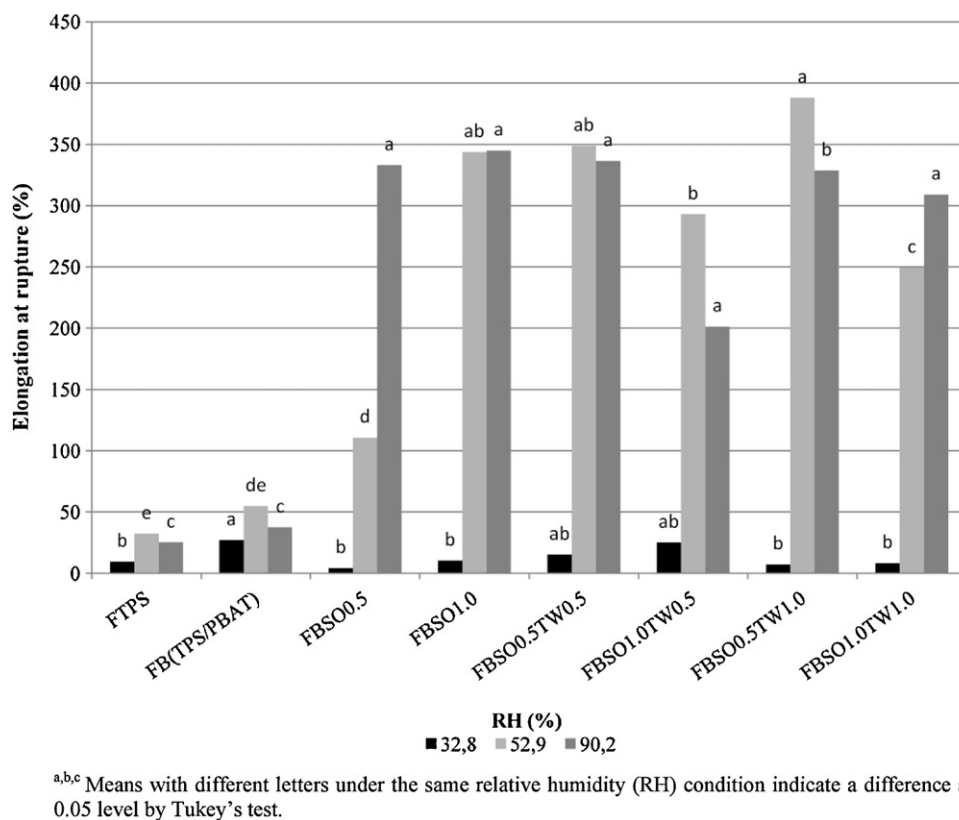
Fig. 1. The elongation (%) of starch films (F100) and starch + PBAT films without (F0) and with the addition of SO (F1 and F2) or with SO + TW (F3, F4, F5, and F6). Films followed by the same letter under the same RH condition displayed similar behavior (Tukey's test at 5%).
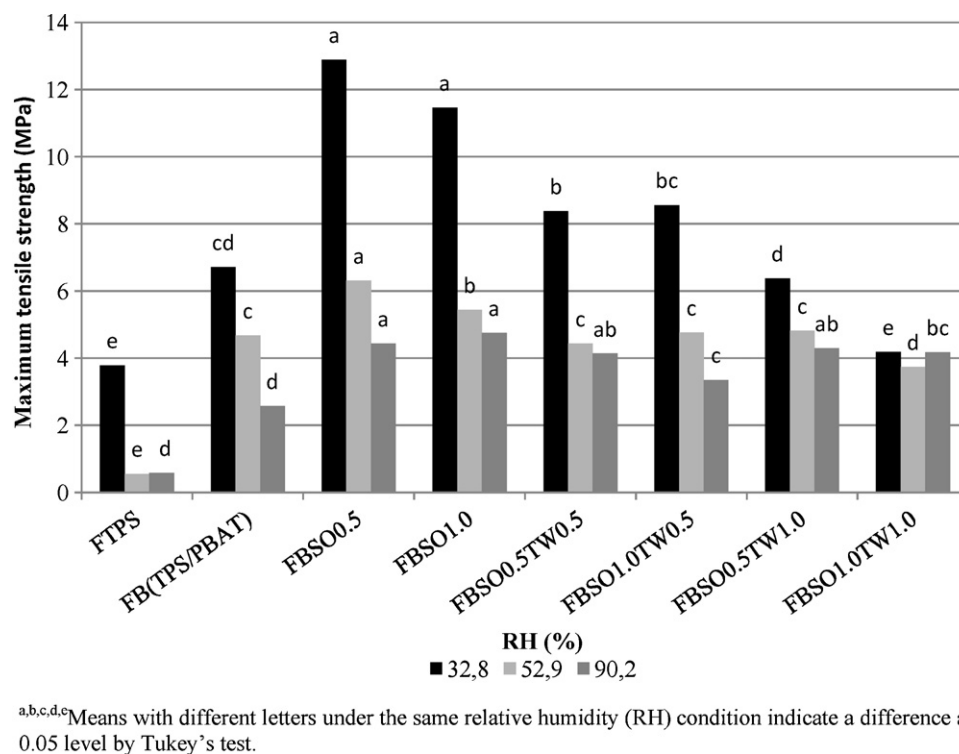
Fig. 2. The maximum rupture resistance of starch films (F100) and starch + PBAT films without (F0) and with the addition of SO (F1 and F2) or with SO + TW (F3, F4, F5, and F6). Films followed by the same letter under the same RH condition displayed similar behavior (Tukey's test at 5%).

amylase and amylopectin. The films produced in this work showed good elasticity due the higher amylopectin content in cassava starch than others starches.

Films with 35% of PBAT presented higher tensile strength and similar elongation than100% TPS films (Figs. 1 and 2). According to Avérous and Fringant (2001) the mechanical properties of films produced from TPS/PBAT blends are depend of the polyester concentration, and according to Ren et al. (2009) the higher the starch content in the blend, the higher the amount of starch not compatible with PBAT, which produces starch agglomerates in the film microstructure and reduces the strength and elongation.

Films of TPS/PBAT with 65% of TPS added with 1% SO (FBSO1.0) showed higher elongation (Fig. 1) and higher tensile strength (Fig. 2) than films without SO. The mechanical properties of FBSO1.0 film (65% TPS) were similar to the films with 50% TPS obtained in a previous work (Brandelero, Yamashita, & Grossmann, 2010), so the SO permitted to incorporate more TPS in the blend without changing their mechanical characteristics. Comparing films with SO (FBSO0.5 and FBSO1.0) and films with SO + TW, the addition of TW does not cause significant changes in the mechanical properties of the films. Films containing 0.5% SO showed higher elongation values at 53% RH when a surfactant was added. Similar results were obtained by Rodrígues et al. (2006) in starch films with Tween surfactant. According to the authors, the surfactant may facilitate the presence of glycerol between the starch chains, increasing their mobility, being the effect verified only when the minor amounts of SO was used.

The effect of the soy oil on the mechanical properties of the films was probably due to the interaction of the carboxylic groups of the fatty acids present in the oil with the rings of the PBAT and starch, as is indicated in the infrared spectra (Fig. 3).

The films with 100% TPS (FTPS) and the films with 65% TPS (FBTPS/PBAT) displayed increases in elongation with increasing RH. The maximum values were obtained under 53% RH, and the values decreased under conditions of high RH (>90% RH). The films with SO and SO + TW displayed similar elongation values under the conditions of 53% RH and 90% RH, as shown in Fig. 1. Talja et al. (2008) found a similar behavior in starch films. According to these authors, the increase in elongation reaches its maximum at 60% RH, and the values subsequently decrease with increasing RH due to the substitution of starch–starch and plasticizer–starch bonds for weaker bonds, such as starch–water, or due to the increase in the crystalline zones of the films, which would decrease the mobility of the starch chains.

The films with added SO or SO + TW displayed a notable increase in the elongation with humidity values greater than 33% (Fig. 1), displayed elongation values between 200% and 350%, and there was no significant difference between the values obtained at 53% RH and 90% RH, indicating that the high RH associated with the presence of SO favored the elongation of the films.

Under humidity conditions greater than 33% RH, the films formulated with SO displayed an increase in elongation of at least seven-fold compared with the films with 100% starch (FTPS) and the films with 65% starch without the addition of SO or TW (FB-TPS/PBAT), as shown in Fig. 1. These results suggest that SO acted as a plasticizer, increasing the mobility of polymers chains and that there was synergy between the presence of SO and the increase in RH. The increase in the elongation of the films with the addition of SO cannot be related to only with the effect of the water, as there was no difference in moisture between the conditions of 33% RH and 53% RH (Table 2), and the films with 100% or 65% starch without the addition of SO or SO + TW displayed the highest moisture levels and lowest elongation values.

Bourtoom and Chinnan (2009) observed an effect contrary to that observed in this study. These authors found a decrease in the elongation of starch films with added lipids. According to the authors, the films displayed reduced structural integrity due to phase separation. In contrast, Pelissari et al. (2009) observed an increase in elongation with the presence of oregano oil in starch films. According to the authors, the effect is related to the plasticizing action of the oil.

The maximum rupture resistance varied with the RH and with the formulation (Fig. 2). Comparing films with 100% TPS and 65% TPS under 53% RH, it is evident the increase of tensile strength in the films with addition of PBAT, from 0.55 MPa (FTPS) to 4.58 MPa (FB-TPS/PBAT). The PBAT is a hydrophobic polymer and the PBAT films show good mechanical properties, explain the better mechanical properties of the films elaborated with TPS/PBAT blends under all RH conditions tested.

The films with 100% (FTPS) and 65% (FB-TPS/PBAT0) of TPS without the addition of SO or SO + TW displayed less resistance than the films that contained these substances for all of the RH conditions that were evaluated. The results for the resistance displayed in Fig. 2 indicate that the presence of SO reinforced the structure of the films.

Under conditions of low RH (33% RH) the films containing SO displayed high tensile strength and high rigidity. These films displayed moderate resistance and high flexibility at RH higher than 33%, and the most resistant films under these conditions were those with 65% or 100% starch without the addition of SO or SO + TW. At 53% RH, the films containing SO with and without surfactant were the most resistant, of which the films with 0.5% SO (FBSO0.5) were the most resistant (6.41 MPa). At higher RH levels, the values of the maximum rupture resistance decreased for all of the films (Fig. 2). That effect is due to the plasticizing action of the water on the starch chains; other authors have shown this behavior in starch films (Mali et al., 2006; Talja et al., 2008).

The reduction in resistance with the addition of TW may be related to interactions between the starch and the surfactant. Chen, Kuo, and Lai (2009) and Brandelero et al. (2010) showed a reduction in the resistance and elongation of starch films with the addition of surfactants. According to the authors, surfactants are amphiphilic molecules and their hydrophilic groups may form complexes or may interact with the starch, decreasing the amylose–amylose interactions, whereas the hydrophobic portion (groups with high molecular mass) of the surfactant may form aggregates between the starch chains, impeding the structural formation of the film.

Many authors have shown a reduction in the mechanical resistance of the films when lipids are added (Bourtoom & Chinnan, 2009; Han et al., 2006; Liu, Kerry, & Kerry, 2006; Pelissari et al., 2009; Shellhammer & Krochta, 1997). In the present study, the resistance increased in the presence of SO, which is contrary to the behavior observed in films with 100% starch with lipids added.

Comparing the results for the mechanical resistance of the films analyzed in this study with those obtained by Ren et al. (2009), who found an increase in resistance when a compatibilizer was added to the starch/PBAT blends, it can be suggested that SO acted as a compatibilizer between the starch and the PBAT. According to these authors, the increase in resistance is due to the increase in the interfacial adhesion among the polymers in the presence of a compatibilizer. The compatibilizing action of SO may be confirmed by the micrographs (Fig. 4), which showed greater structural integrity in the films with the lipids added when compared with the films without SO (FBTPS/PBAT).

3.3. Infrared spectra

The spectra obtained for the films prepared with 100% TPS (FTPS), with 100% PBAT, and with SO are shown in Fig. 3B, and the spectra of the films prepared with TPS/PBAT blends are shown in Fig. 3A.
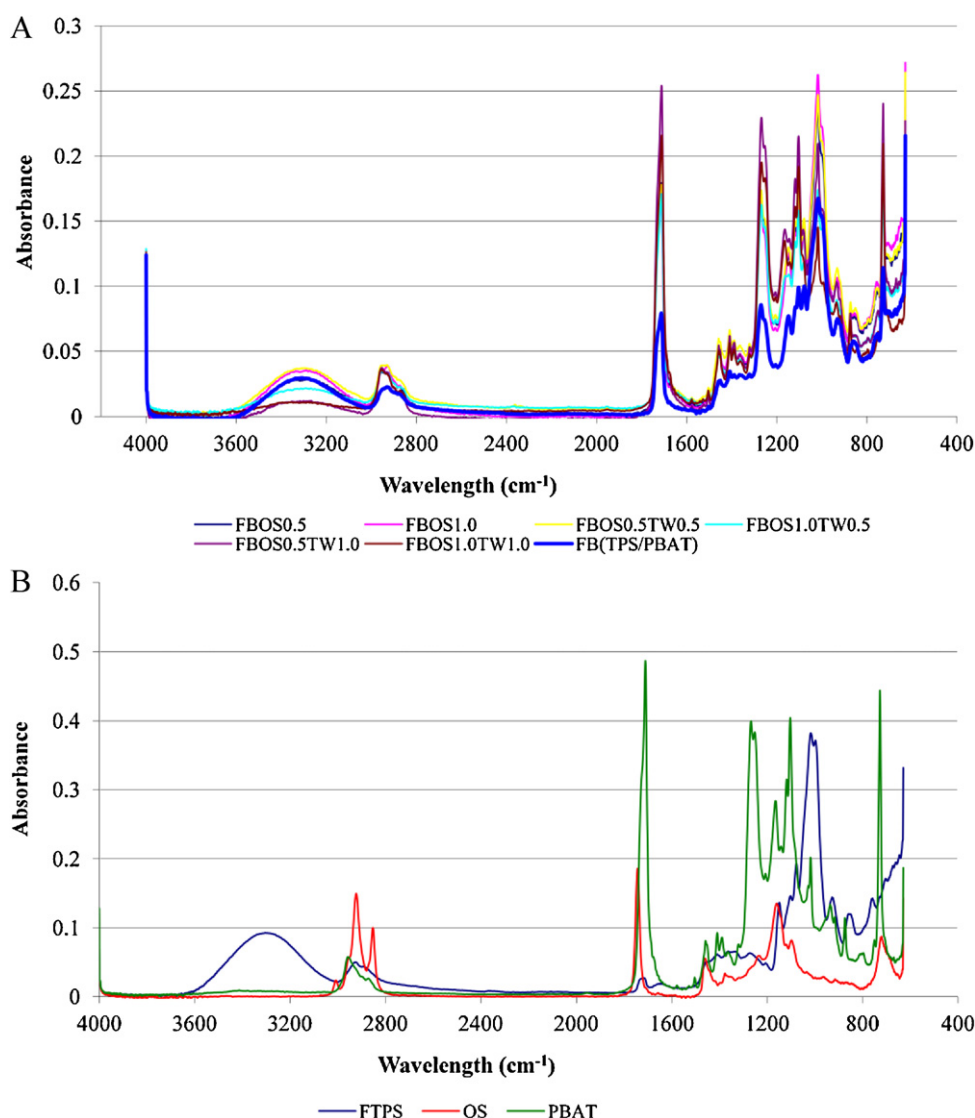
Fig. 3. The infrared spectra obtained for starch + PBAT films without (F0) and with the addition of SO and/or TW (A) and for the films with 100% starch or PBAT and SO (B).

Kijchavengkul, Auras, and Rubino (2008) characterized the infrared spectra for PBAT films. Furthermore, Fang, Fowler, Tomkinson, and Hill (2002) and Zullo and Iannace (2009) obtained the spectra for potato starch and cornstarch films. The spectra obtained by these authors were similar to those presented in Fig. 3B, which were obtained in this study.

The spectrum determined for the PBAT film was characterized by the presence of a peak in the region of 1708 cm^{-1} due to the stretching of the carbonyl groups (C=O), a peak in the region of 1269 cm^{-1} due to stretching of the C—O groups that represented the ester bonds, and stretching between 1020 and 880 cm^{-1} due to the presence of the substituted benzene ring. The starch films (FTPS) were characterized by the presence of a long band in the region of 3300 cm^{-1} due to the vibrational stretching of the inter- and intra-chain bonded hydroxyls; in the 2968 cm^{-1} region, a band was present due to stretching in the C—H groups bonded to the ring, along with a peak in the 1151–931 cm^{-1} region due to the vibrational stretching of the C—O groups, with peaks at 1080 and 1020 cm^{-1} that are characteristic of the stretching of the C—O group bonded to the glucose ring.

In the spectra for SO (Fig. 3B), a low-intensity peak was observed at 3012 cm^{-1} due to the stretching of the CH present in alkene;

peaks in the 2925 cm^{-1} and 2856 cm^{-1} regions were related to the stretching of the CH$_2$ of alkane groups; peaks in the 1742 cm^{-1} region were related to C=O and those in the 1110 cm^{-1} region were related to the C—O group, both of which were related to ester bonds; peaks in the 1467 cm^{-1} region were related to the deformation of the CH$_2$ group of alkane; and a peak in the 720 cm^{-1} region was related to the asymmetric angular deformation of CH$_2$ groups, which is characteristic of long-chain hydrocarbons (Fig. 3B). The spectrum of Tween 80 displayed a long band in the 2914 cm^{-1} region related to the CH groups, along with peaks in the 1795 cm^{-1} and 1095 cm^{-1} regions that were related to C=O and C—O ester bonds, respectively, and peaks in the 904 cm^{-1} region that were related to the —CO group.

Observing Fig. 3A, it is evident that the spectra of the films containing 65% starch with or without the addition of SO and/or TW were similar with respect to the peaks and bands. However, when SO or SO + TW was added, the films displayed more intense bands and peaks in the 1740–1710 cm^{-1}, 1270 cm^{-1}, and 1020 cm^{-1} regions, and the FOS0.5 films displayed the greatest intensity of peaks and bands in these spectral regions (Fig. 3A). Films with a greater amount of TW (FBSO0.5TW1.0 and FBSO1.0TW1.0) compared with the other films did not display a band at 3340 cm^{-1},
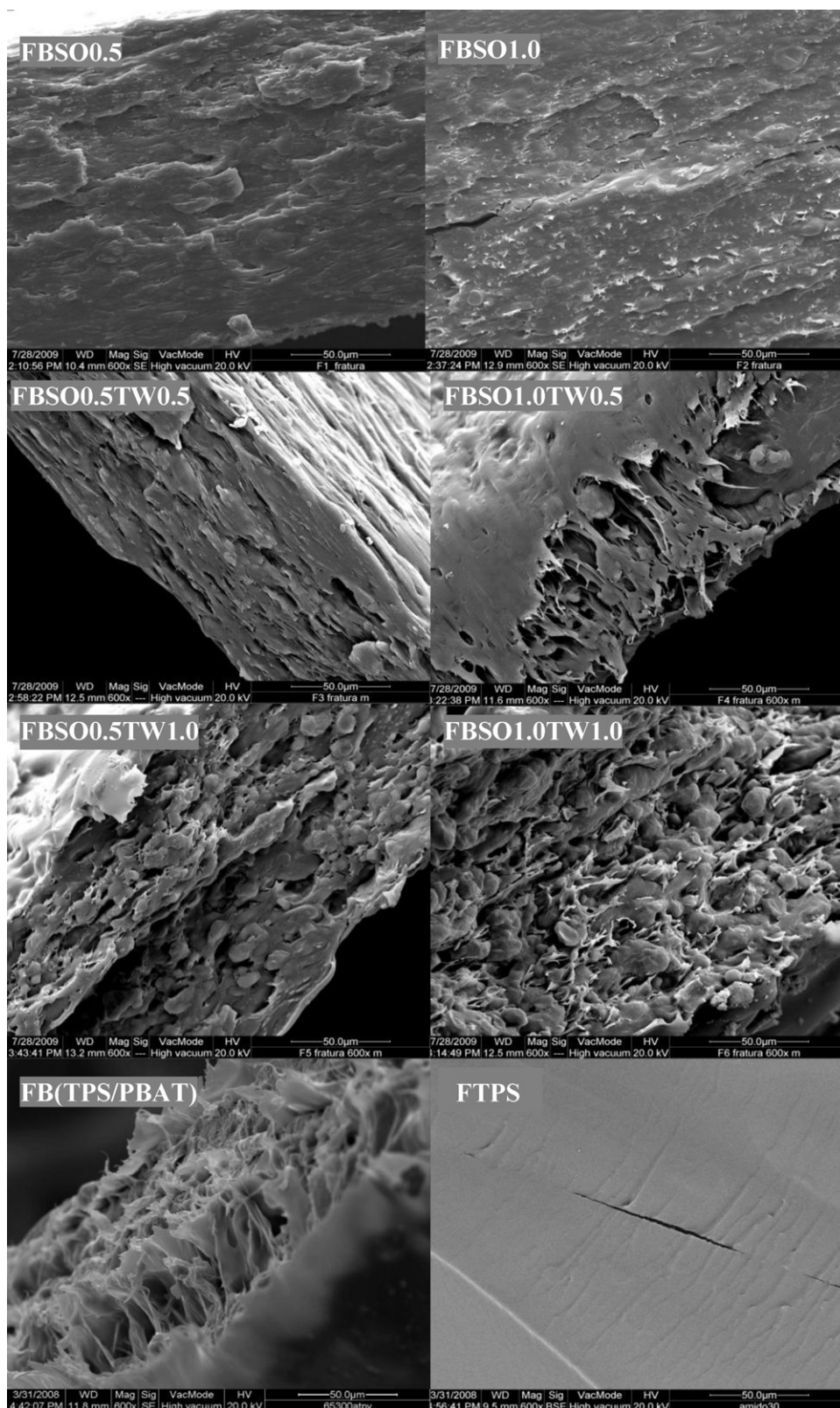
Fig. 4. Micrographs of the starch films (F100) and starch + PBAT films, without the addition of SO or TW (F0), with the addition of SO (F1 and F2), and with the addition of SO and TW (F3, F4, F5, and F6) at 600× magnification.

and the peaks in the region of 1740–1710 cm^{-1} were less intense.

The films with SO displayed more intense peaks in the region that indicates the presence of C—O and C=O groups of ester bonds in the PBAT (1710 and 1270) and in the region that shows the presence of C—O groups bonded to the starch ring (1020). Thus, the presence of SO in the films led to an increase in these bonds. The carbonyl groups of the ester bonds may interact with hydroxyl starch groups

through weak interactions known as hydrogen bridges; hydrophobic interactions may also occur between the oil and the polyester due to the similarity in polarity, and the results indicate that there was an increase in C—O groups bonded to the glucose ring. Therefore, under these conditions, a greater interfacial adhesion between the polymers of the blend was obtained, likely due to the summation of the effects of various weak interactions.

Substances capable of increasing the adhesion between the polymer chains and thus to promote an improvement in the properties of the films are known as compatibilizers (Kalambur & Rizvi, 2006; Ren et al., 2009). These substances are added to allow a reaction of the starch with other chemical groups through a process known as reactive extrusion. Raquez et al. (2008) showed that TPS films extruded in the presence of maleic anhydride displayed a peak in the infrared spectrum at $1720\,cm^{-1}$, which is characteristic of the C=O group. According to the authors, this finding indicates the presence of an ester bond between the starch and the compatibilizer. Under the temperature and pressure conditions at the extrusion process, it is unlikely that a covalent bond occurred between SO and the polymers of the blend. The observed effect on the mechanical properties was likely due to the presence of weak interactions between SO and the starch and between SO and the PBAT.

3.4. Scanning electronic microscopy

The micrographs of the films are shown in Fig. 4. It was evident that the films with 100% starch have a compact and homogenous structure. With the addition of PBAT, there was damage to the microstructure, and the films were considered to be less homogenous (Fig. 4F BTPS/PBAT), possibly due to the incompatibility between the starch (hydrophilic phase) and the PBAT (hydrophobic phase). The films with only SO added (FBSO0.5 and FBSO1.0) displayed more compact structures (Fig. 4), which is reminiscent of the starch films (FTPS), but without the presence of microfissures (FBSO0.5). These results suggest that the effect of SO is related not only to the increase in the hydrophobic portions of the film array but also to the improved compatibility among the polymers in the presence of oil, as shown in the infrared spectra.

A loss of structural integrity was observed with the addition of TW in the films with 0.5% SO (FBSO0.5TW0.5, FBSO1.0TW0.5, FBSO0.5TW1.0, and FBSO1.0TW1.0) due to the presence of agglomerations, especially in film F4. Similar to this study, Chen et al. (2009) observed the presence of agglomerations in micrographs of cassava starch films with the addition of sucrose esters. The structure became less compact after increasing the amount of TW to 1% (FBSO0.5TW1.0 and FBSO1.0TW1.0) due to the increase in the amount of agglomerations that are dispersed in the film array.

Brandelero et al. (2010) found agglomerations in TPS/PBAT films with the addition of 2% Tween. More agglomerations were present in films with a higher surfactant/starch ratio (T/S). Comparing these results with those found in this study, it can be confirmed that the size of the agglomerations depends on the ratio between the concentrations of starch and surfactant and that the agglomerations will be smaller and more dispersed as the T/S ratio decreases.

4. Conclusions

Starch + PBAT films containing a large amount of starch with added soybean oil exhibit good mechanical properties, and increasing humidity improves the performance of the films. Films with oil exhibit less moisture. The micrographs and infrared spectroscopy revealed an increase in the compatibility among the polymers. The presence of lipids improves processability by extrusion and allows for a reduction in the amount of glycerol, resulting in a marked expansion of the balloon and films that can be wound. The soybean oil acted as a good compatibilizer between TPS and PBAT, which improved the other characteristics of the film. The compatibilizing effect of soybean oil between starch and PBAT is related to the increase in groups that are characteristic of ester bonds and groups that are bonded to the glucose ring. Therefore, lipids are chemically associated with the polymers of the blends, increasing the interactions among the polymeric fractions and improving the polymeric mixture by increasing the interfacial adhesion of the polymers.

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