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Effect of the method of production of the blends on mechanical and structural properties of biodegradable starch films produced by blown extrusion

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ABSTRACT

Biodegradable starch films can be produced by blown extrusion, but it is necessary to add a plasticizer, e.g., glycerol, to decrease the rigidity and blend with other biodegradable polymers, such as poly (butylene adipate co-terephthalate) (PBAT) because films with only starch and glycerol are fragile. A method for producing these films is to produce pellets of thermoplastic starch (starch + glycerol) and extrude them again along with PBAT pellets (M1) or extrude the starch granules with PBAT and glycerol pellets (M2), reducing the processing cost. The objective of this work was to evaluate the effect of the method of producing PBAT + starch blends (M1 and M2) on the mechanical, structural, and micro-structural barrier to water vapor of biodegradable films produced by blown extrusion. Films with a higher amount of starch had characteristics similar to those of films with lower concentrations when the blends were prepared by the method M2, probably due to the increased contact area of the starch granules compared to pellets of TPS, allowing greater interaction between starch and PBAT. The method M1 resulted in films with better mechanical properties when the concentration of PBAT was equal to 50%. With increasing concentration of starch (>50%), blends can be prepared with the method M2 (starch granules) in a single extrusion phase without loss of mechanical properties, which can result in lower production cost.

1. Introduction

The process of blown extrusion can be used to produce biodegradable starch films. During the extrusion, the disruption of starch granules (fusion) occurs, yielding a homogeneous and fluid material known as a thermoplastic starch (TPS). TPS, when expanded by blowing into a tubular matrix or form, produces rigid films, which then require the addition of plasticizers, e.g., glycerol, to decrease the melting temperature of the starch and increase flexibility. However, the resulting films are fragile (Brandelero, Yamashita, & Grossmann, 2010; Zullo & Iannace, 2009).

From blends of starch and other biodegradable polymers, e.g., polycaprolactone (PCL) and poly (butylene adipate co-terephthalate) (PBAT), it is possible to obtain biodegradable films with better mechanical and processability properties than those prepared only with TPS (Bilck, Grossmann, & Yamashita, 2010; Ren, Fu, Ren, & Yuan, 2009; Sarazin, Li, Orts, & Favis, 2008). A method for producing these films is to produce TPS pellets and extrude them again along with pellets of other polymers (Alves, Mali, Beléia, & Grossmann, 2007; Brandelero et al., 2010; Godbole, Gote, Latkar, & Chakrabarti, 2003; Sarazin et al., 2008). Another method is to extrude the granular starch with pellets of other polymers in addition to the plasticizer, eliminating the step of TPS pellet production and reducing the processing cost (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Mani & Bhattacharya, 1998). However, changes in the blend formulation may alter the parameters of the extrusion process, such as the specific mechanical energy and residence time, resulting in differences in the characteristics of the film (Brümmer, Meuser, Lengerich, & Niemann, 2002).

There are few studies evaluating the effect of the method of production of the blends, whether from the granular starch or TPS, on the characteristics of the films. Noomhorm and Tokiwa (2006) investigated the effect of the granular starch and previously gelatinized starch on the properties of films of blends of cassava and polycaprolactone starch produced by extrusion. The authors found that there was an increase in the tensile strength at break when the films were prepared with gelatinized starch due to the improved structural integrity of the films because of the reduction of the size of the starch aggregates.

The mass transfer through an initially dried hydrophilic film, submitted to different relative humidities, takes place in three steps: (i) adsorption of water molecules on the film surfaces; (ii) movement of the water molecules from higher to lower moisture; (iii) desorption of water molecules from the film surface with the lower moisture. Therefore, this mass transfer depends on the

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Table 1
Composition of starch + PBAT biodegradable films.

Film	Starch (g amido/100 g amido + PBAT)	PBAT (g PBAT/100 g de amido + PBAT)	Glycerol (g glicerol/100 g amido)
FATP30G	100	0	30
F80A30G	80	20	30
F65A30G	65	35	30
F50A30G	50	50	30
FPBAT	0	100	0

resistance of water to move through the matrix polymers (porosity) in terms of coefficient of diffusion and of affinity between the film material and water represented by the solubility coefficient. According to Larotonda, Matsui, Sobral, and Laurindo (2005), at the linear zone of the isotherms the solubility coefficient (β) is correlated with water activity (a_w) by Eq. (1).

$$\beta = \tan(\theta) = \frac{X}{a_w} \tag{1}$$

where β (kg water/kg dry solid) is the solubility coefficient, X is the moisture content on dry basis (kg water/kg dry solid), and a_w is the water activity.

The objective of this paper was to evaluate the effect of the production method of starch blends, granular or thermoplastic, and poly (butylene adipate co-terephthalate) on the mechanical and structural properties and the micro-structural barrier to water vapor of biodegradable films produced by blown extrusion.

2. Materials and methods

2.1. Materials

Native starch from cassava (Indemil, Brazil) and commercial grade glycerol (Dinamica, Brazil) were used to produce thermoplastic starch. The biodegradable polymer used was poly (butylene adipate co-terephthalate) (PBAT), manufactured by BASF (Germany) under the commercial name of Ecoflex® 7011.

Films were prepared according to Table 1, including films with 100% starch plasticized with 30% glycerol (FTPS) and PBAT (FPBAT) films without the addition of starch, which were used as the control.

The blends were obtained by two different methods, M1 and M2. In method M1, starch granules were mixed with glycerol in the quantities described in Table 1 and extruded to produce pellets of thermoplastic starch (TPS). For the production of blends, pellets of TPS and PBAT were extruded, and the material was pelletized and re-pelleted to improve homogeneity. The PBAT + TPS pellets were extruded to produce the films by blown extrusion. The winding speed and airflow in the matrix forming the balloon was adjusted to allow for the formation of the balloon without tearing or cracking and with adequate thickness.

In method M2, the blend was obtained by mixing granular starch, glycerol, and PBAT and extruded pellets, obtaining the starch + PBAT pellets. This material was extruded twice under the same conditions to standardize the shear process experienced by the starch. The films were produced in the same manner as in method M1.

2.2. Determination of thickness and density

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

2.3. Water vapor permeability (WVP)

To determine the WVP of the films, the gravimetric method adapted from the standard E 96-95 of ASTM (ASTM, 1995) was used. Three relative humidity gradients were used: (2–32.8%), (32.8–64.5%), and (64.5–90%).

2.4. Sorption isotherms

The sorption isotherms of the films were determined according to the method described in Brandelero et al. (2010). The isotherms were modeled using the GAB (Guggenheim–Anderson–de Boer) model (Eq. (2)), and Statistica 6.0 software was used to calculate the model parameters.

$$X_w = \frac{C \cdot k \cdot m_0 \cdot a_w}{[(1 - k \cdot a_w)(1 - k \cdot a_w + C \cdot k \cdot a_w)]} \tag{2}$$

where C (heat of sorption of the monolayer), k (heat of sorption of the multilayer) and m_0 (monolayer given as g water/g solid) are the parameters of the model, X_w is the moisture in dry basis (g water/g solid) and a_w is the RH/100.

2.5. Determination of the solubility (β) and diffusion (D^w) coefficients

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

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

The water vapor diffusion coefficient (D^w) was determined from the β and WVP values determined for the films in the humidity conditions described in Section 2.3 using Eq. (4).

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

2.6. Mechanical properties

The maximum tensile strength and elongation at break were determined according to norm D 882-88 of ASTM (ASTM, 1996), using a texture analyzer (Stable Micro System, Model TA.TX2i, England) with a traction speed of 8.3 mm/min. The specimens, conditioned to 52.9% RH, were cut in the longitudinal direction and transversal to processing. The tests were performed at 25 °C, and five determinations were made for each sample.

2.7. Analysis of Fourier transform infrared (FT-IR) spectroscopy

The infrared analysis was performed on a FT-IR spectrophotometer (Bomen, model FT-100, Canada) coupled with a device for attenuated total reflectance reading equipped with diamond crystal/ZnSe with triple reflection. The spectral region investigated was 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1}. The samples were conditioned for 15 days in a desiccator containing P_2O_5. The spectra were obtained in triplicate.

Table 2
Parameters of the GAB isotherms of starch + PBAT films.

Film	Parameters of the GAB			R^2
	C	k^*	m_0[a]	
F50A30G-M1	138	0.79	0.103	0.83
F50A30G-M2	100	0.78	0.105	0.80
F65A30G-M1	21	0.90	0.112	0.98
F65A30G-M2	400	0.95	0.090	0.97
F80A30G-M1	386	0.95	0.092	0.99
F80A30G-M2	38	0.84	0.104	0.82
FATP30G	7	0.97	0.090	0.99

[a] g water/g solids dry.

2.8. Scanning electron microscopy

The micrographs were obtained in a scanning electron microscope (JEOL, model LSMP-100, Japan) of the Microscopy Laboratory of the Universidade Estadual de Londrina. The films were frozen in liquid nitrogen, fragmented, and kept in desiccators with P_2O_5 for 15 days. Subsequently, they were fixed in stubs and coated with a layer of gold (40–50 nm) (Sputter Coater SCD-050, Bal-Tec, Balzers, Liechtenstein) at 25 °C under a pressure of 2.6×10^7 Pa for 180 s. The coated samples were analyzed at 15 kV. The magnitude of the observation was 600×.

3. Results and discussion

3.1. Sorption isotherms

The parameters of the GAB model are shown in Table 2, and, according to the coefficients of determination (R^2), the model represented the experimental data of sorption isotherms of biodegradable films satisfactorily, ranging from 0.80 to 0.99.

The values of the parameter k of the films increased with increasing starch content in the blends due to the higher affinity of water to starch than to PBAT (Table 2). Thus, there was saturation of binding sites and reduction of multilayer interactions, and therefore also an increased in the value of the k parameter because this parameter is related to the sorption heat of water vapor in the multilayer. 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.

Comparing the methods of extrusion of films containing 80% starch (F80), it appears that the k value of the film produced by method M2 was lower than that produced by M1, 0.84 and 0.94, respectively (Table 2). The other films did not show a significant difference between M1 and M2.

The values of m_0 (Table 2) did not correlate with the starch content of films. The films presented an F80-M2 value of m_0 similar to the films with 50% starch (F50), indicating that the M2 method provided greater association between starch and PBAT.

3.2. Water vapor permeability (WVP)

The films produced by blends of starch + PBAT showed WVP that were smaller than those of the films of 100% thermoplastic starch (FTPS) and similar to those of the films of PBAT (FPBAT) in different RH gradients, with the exception of the F65-M2 and F80-M2 films that showed WVP greater than those of the FPBAT films in the range of RH of 32.8–64% (Table 3).

According to Table 3, the films prepared by method M1 showed a reduced value of D^w with increased starch content in the blend. The films produced by M2 had values of D^w that were similar and larger than films produced by M1. The M1 method probably allowed the formation of films that were structurally more compact because the starch undergoes a greater shear. In the case of method M2, the extrusion of the granule starch with the PBAT increases the specific mechanical energy dissipation. Hence, the starch undergoes a lower shear, decreasing the flexibility of TPS due to the lower degree of gelatinization. According to Mali, Grossmann, García, Martion, and Zaritzky (2006), for starch films, the higher the stiffness is, the higher the WVP is due to cracks and pores in their structure, which could explain the higher values of the diffusion coefficient for films prepared by method M2.

With increasing concentration of starch in the blends, the values of the solubility coefficient (β) increased, with the exception that of films F80-M2, which showed lower β values because the WVP films did not vary with the extrusion method.

Table 3
Water vapor permeability (WVP), solubility coefficient (β) and diffusivity coefficient (D^w) of starch films + PBAT.

Film	ΔRH (%)	WVP[a] ($\times 10^7$) (g dia^{-1} Pa^{-1} m^{-1})	β ($\times 10^6$) (g/g Pa)	D^w ($\times 10^7$) (m^2/dia)
FPBAT	2.00–32.8	$0.82 \pm 0.01^{b,A}$	–	–
	32.8–64.5	$0.80 \pm 0.01^{d,A}$	–	–
	64.5–90.0	$1.06 \pm 0.07^{b,B}$	–	–
F50A30G-M1	2.00–32.8	$0.57 \pm 0.02^{b,B}$	0.84	0.57
	32.8–64.5	$2.51 \pm 0.23^{cd,B}$	1.33	1.60
	64.5–90.0	$2.42 \pm 0.24^{b,A}$	3.30	0.62
F65A30G-M1	2.00–32.8	$0.60 \pm 0.17^{b,B}$	0.80	0.60
	32.8–64.5	$2.41 \pm 0.40^{cd,B}$	1.96	0.92
	64.5–90.0	$3.11 \pm 0.17^{b,A}$	7.22	0.32
F80A-30G-M1	2.00–32.8	$1.09 \pm 0.09^{b,B}$	0.82	0.93
	32.8–64.5	$0.95 \pm 0.30^{d,B}$	1.86	0.36
	64.5–90.0	$3.94 \pm 0.03^{b,A}$	7.74	0.36
F50A30G-M2	2.00–32.8	$0.93 \pm 0.14^{a,C}$	0.93	1.33
	32.8–64.5	$1.83 \pm 0.86^{d,B}$	1.33	1.23
	64.5–90.0	$5.78 \pm 0.31^{b,A}$	2.38	1.29
F65A30G-M2	2.00–32.8	$0.70 \pm 0.01^{b,B}$	0.74	1.01
	32.8–64.5	$4.60 \pm 0.01^{bc,B}$	1.76	2.79
	64.5–90.0	$4.92 \pm 1.00^{b,A}$	6.90	0.75
F80A30G-M2	2.00–32.8	$2.98 \pm 1.96^{b,A}$	1.21	1.79
	32.8–64.5	$6.75 \pm 0.80^{ab,A}$	1.60	3.07
	64.5–90.0	$7.35 \pm 2.51^{b,A}$	4.40	1.23
FATP30G	2.00–32.8	$2.84 \pm 0.31^{b,A}$	1.49	0.85
	32.8–64.5	$7.52 \pm 1.16^{a,A}$	2.10	1.61
	64.5–90.0	$20.5 \pm 3.75^{a,B}$	8.30	1.10

[a,b,c,d] Averages with same lowercase letters of films with different formulations in the same range of moisture content did not differ at $p < 0.05$, according to the Tukey test.
[A,B] Averages with capital letters equal to films with the same formulation in different ranges of humidity did not differ at $p < 0.05$, according to the Tukey test.

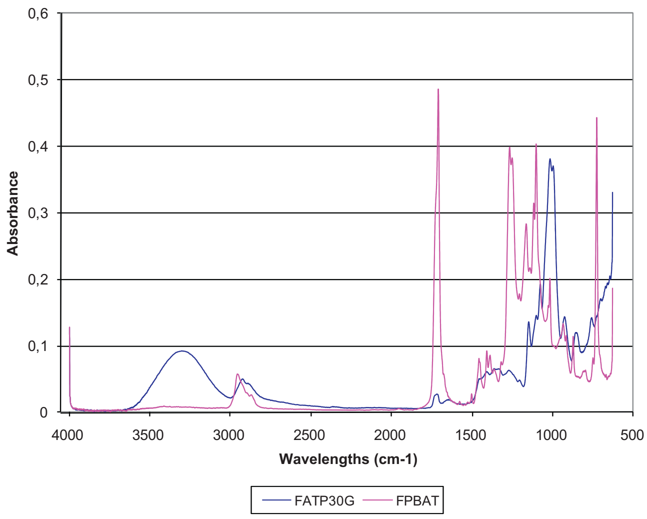

Fig. 1. Infrared spectra of 100% starch (FTPS) and 100% PBAT (FPBAT) films.

The F80 films had β values for different ΔRH conditions (2.00–32.8, from 32.8 to 64.5, from 64.5 to 90.0) equal to 0.82, 1.86 and 7.74, respectively, when prepared by the method M1, and values of 1.21, 1.60 and 4.40, respectively, when prepared by method M2, indicating a 43% reduction in the coefficient of solubility when the film was prepared by method M2 and conditioned at high relative humidity (64.5–90% RH).

The WVP and β values increased with increasing RH (Table 3), indicating that increasing the relative humidity increases the solubility of water in the film matrix, leading to saturation of binding sites and a decrease of the energy of sorption. Under these conditions, increasing the values of WVP facilitates the permeation of water vapor.

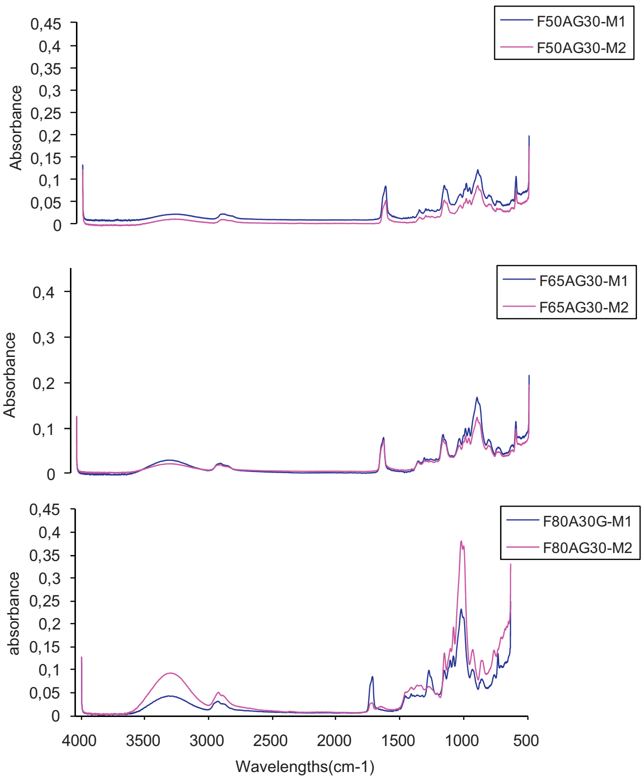

Fig. 2. Infrared spectra of starch + PBAT films produced by M1 and M2.

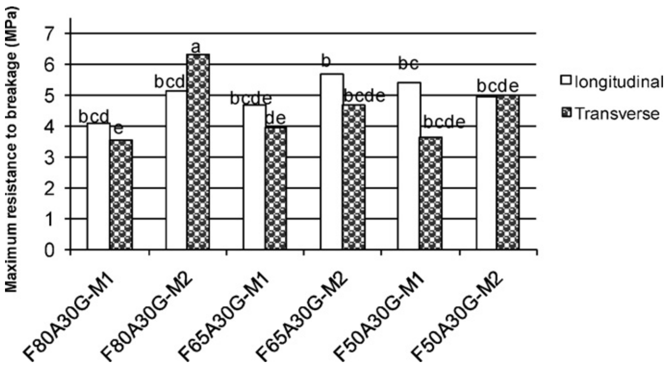

Fig. 3. Maximum tensile strength of starch + PBAT films produced by M1 and M2.

Müller, Yamashita, and Laurindo (2008) determined the WVP of cassava film with 30% glycerol. The values were 5.6, 8.2 and 25×10^{-6} g day^{-1} Pa^{-1} m^{-1} in intervals of 2–33% RH, 33–64% RH and 64–90% RH, and values of β equal to 1.99, 3.09 and 10.5×10^{-6} g/g Pa in the respective ranges of humidity. Comparing these results with the data in Table 3, it appears that the addition of PBAT decreased the WVP as the solubility coefficients (β), especially under high relative humidities, due to the reduced hydrophilicity of the films.

3.3. Infrared spectrum

The spectrum obtained for the starch films (FTPS) is characterized by the presence of a broad band in the 3300 cm^{-1} region due to the vibrational stretching of hydroxyl groups linked inter- and intra-chain. In the 2968 cm^{-1} region, there is a band due to stretching related to C–H groups attached to the ring and a peak in the region of 1151–931 cm^{-1} due to CO stretching vibrational groups, with peaks at 1080 and 1020 cm^{-1} characteristic of the stretching of CO groups attached to the glucose ring and a peak at 1695 cm^{-1} related to H_2O bound to starch, as showed in Fig. 1. The spectrum obtained for the FTPS film was similar to that found by Fang, Fowler, Tomkinson, and Hill (2002) and Zullo and Iannace (2009) for, respectively, potato starch and cornstarch.

The spectrum determined for the film PBAT (FPBAT) was similar to the spectrum determined for PBAT by Kijchavengkul, Auras, and Rubino (2008), with a peak at 2970 cm^{-1} for the stretching of CH group connected to aromatic and aliphatic regions of the polymer, in the 1708 cm^{-1} region due to stretching of carbonyl (C=O) and in the 1269 cm^{-1} region due to stretching of the C–O groups. For both ester linkages, in the region of 727 cm^{-1}, there is a broad band due to the stretching of CH_2 groups and between 1020 and 880 cm^{-1} for stretching due to the presence of substituted benzene rings (Fig. 1).

Comparing the spectra for the blends according to the extrusion method, as shown in Fig. 2A–C, there is similarity between

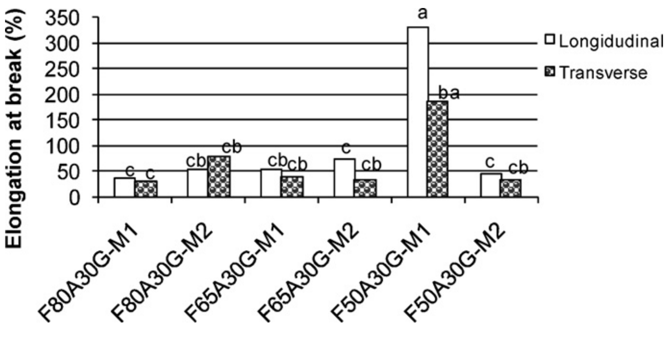

Fig. 4. Elongation at break of the starch + PBAT films produced by M1 and M2.

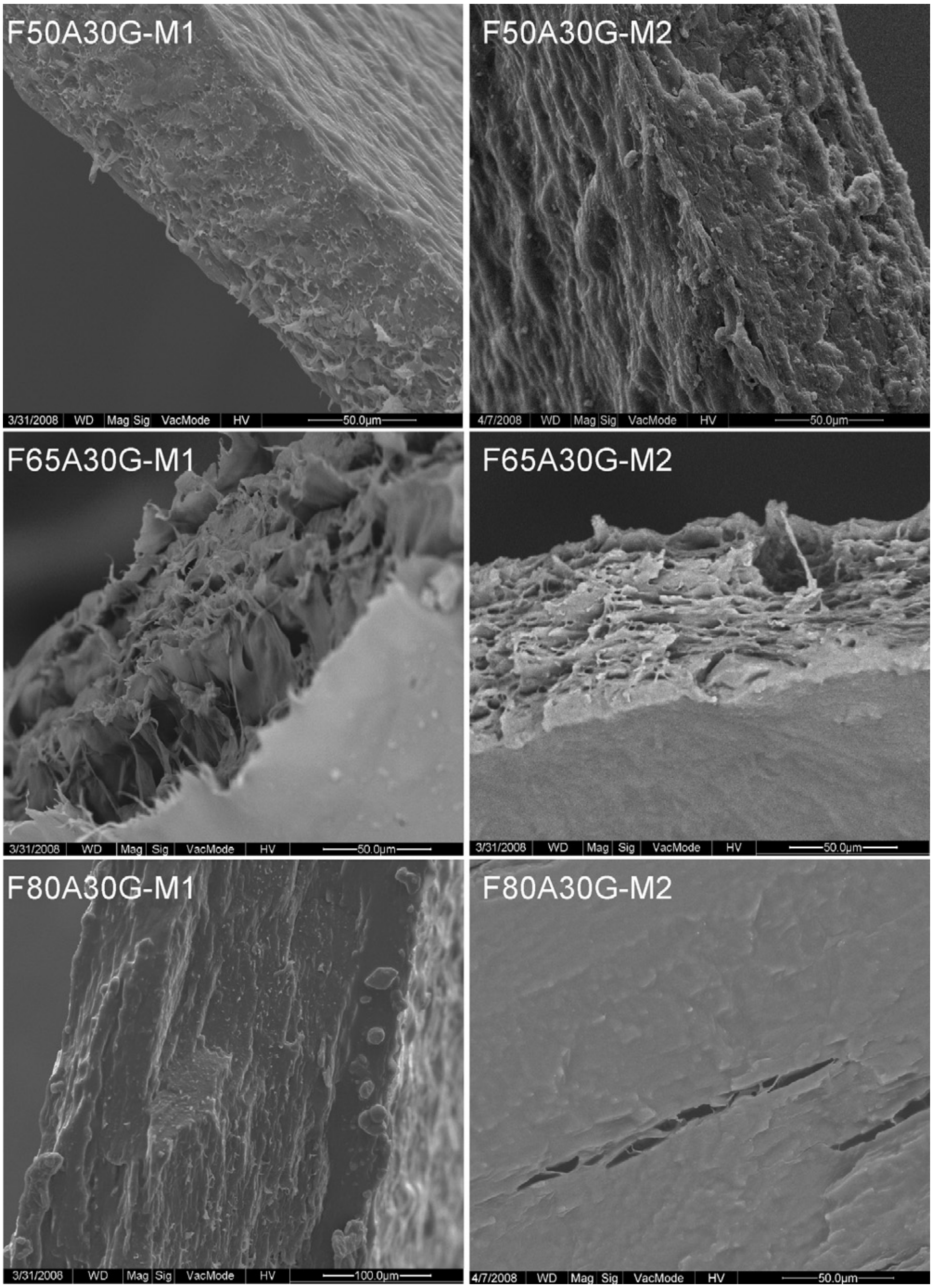

Fig. 5. Micrographs of starch + PBAT films produced by M1 and M2 methods (600× increase).

the spectra of the films with 50% or 65% starch, the main difference being the greater intensity of the peaks when method M1 was used. However, for films with 80% starch, it is possible to verify the spectral variation with extrusion method (Fig. 2C). The films of F80-M2 treatment showed higher absorbance at 3300 cm^{-1} and 1080 cm^{-1} in the F80-M1 films, indicating an increase of hydroxyl groups linked to the polymer and of CO groups attached to the glucose ring, respectively. It was also observed that the absorbance was lower at 1710 cm^{-1} and the peak was suppressed at 1269 cm^{-1} when films with 80% starch were processed by M2 (M2-F80), the latter regions characterized by stretching due to carbonyl groups of ester bonds present in PBAT, indicating that there was a decrease of these bonds in M2-F80 films.

The differences observed in the spectra of films with 80% starch in relation to the extrusion method (Fig. 2C) indicate that PBAT molecules were probably associated with the starch, breaking the PBAT esters links. C–O groups from the rupture of these bonds were associated with starch, suggesting an acetylation reaction between starch and PBAT. The F80-M2 films were less hydrophilic than the F80-M1 films (Table 3), confirming that the M2 method allowed the reduction of binding sites for water.

3.4. Mechanical properties

The values of maximum resistance to breakage in the longitudinal direction showed no significant difference between the different films, as shown in Fig. 3, but the films produced by the M1 method showed greater resistance in the longitudinal direction. According to Thunwall, Kuthanová, Boldizar, and Rigdahl (2008), increased strength and elongation in the longitudinal direction occur due to the molecular alignment promoted by the winding forces of tension. The opposite was found for films prepared by the M2 method, which had similar strength values in both directions with the exception of M2-F80 films with higher tensile strength in the transverse direction (Fig. 3), differing from other treatments ($p < 0.05$). The results of the infrared spectra of the M2-F80 film suggest an association between starch and PBAT with an increase of hydrogen bonds and between starch and PBAT (Fig. 2). The appearance of these links could explain the greater resistance in the transverse direction because the presence of links between the polymers can increase the cohesion of the molecular chains and thus orient them.

The values of elongation were similar among the films, with the exception of the F50-M1 films, which had higher elongation in both directions of extrusion as shown in Fig. 4. The method M1 resulted in films with better mechanical properties when the concentration of PBAT was equal to 50%. With increasing concentration of starch (>50%), blends can be prepared using method M2 (starch granules) in a single extrusion step without loss of mechanical properties, which can result in lower production cost.

The intensity of the electric current in the extruder was recorded during the production process of the films. For the F80-M2 film, the average value was 8.1 A, while, for the F80-M1 film, the value was 7.65 A, with the screw speed equal for both methods. For blends with high concentrations of granular starch (method M1), the process required more mechanical energy compared with method M2, because the starch in the form of TPS is pre-gelatinized, which requires less shear in a second pass. According to Liu, Xie, Yu, Chen, and Li (2009), the first extrusion process is always more difficult than the second and requires more specific mechanical energy.

The M2 method may also provide a larger contact area between the polymers due to the geometry of the starch granules compared to pellets. The higher the mechanical energy during the extrusion process, the greater the likelihood of interactions between starch and PBAT, which may be related to the increased resistance and decreased hygroscopicity found for these films because, by increasing the compatibility between starch and PBAT there is a reduction of starch-water interactions. The lower β values and the characteristics of the isotherm of the F80-M2 films confirm this behavior.

3.5. Micrographs of the films obtained by scanning electron microscopy

When two polymers are mixed together by extrusion, it is interesting that the dispersion and the distribution of the particles occur, forming a single polymeric phase. Poor dispersal could result in the formation of clusters from the entanglement of the polymer chains, which reduces the transmission of tension. In the micrographs represented in Fig. 5, there are no clusters or separate phases, indicating that both methods have a good dispersion of the polymers.

Films with 50% starch showed few structural changes when changing the method of preparation of the blends, whereas films with 80% starch showed microcracks when prepared by method M2, which explains the higher values of the diffusivity coefficient (Table 3). However, the lower value of β explains the lower hydrophilicity of the F80 films produced by method M2 (Fig. 5).

Films with 50% or 80% starch, obtained by both methods, showed a matrix that was compact and without clusters, in contrast the results found by Noomhorm and Tokiwa (2006), who verified cluster formation that was smaller and better distributed when the pre-gelatinized starch was used in thermoformed obtained from blends of starch + PCL. In this work, the production of TPS prior to mixing with PBAT (method M1) caused greater shear to the starch, resulting in higher compression and lower rigidity of the starch phase, reducing the presence of fractures or pores. The lower values of D^w for some films produced by method M1 (Table 3) confirmed this behavior. The F65-M2 films showed a more compact structure than the F65-M1 film (Fig. 5), but showed no significant changes in mechanical and barrier properties.

4. Conclusions

The method of producing the blends of starch, granular (M1) or thermoplastic (M2), and PBAT had an effect on the mechanical and structural properties and the micro-structural barrier to water vapor of biodegradable films produced by blown extrusion in balloons. Films with a higher amount of starch had similar characteristics to films with a lower concentration when the blends were prepared by method M2, probably due to the increased contact area of the granular starch compared to TPS pellets, which allowed greater interaction between the starch and PBAT. The M1 method resulted in films with better mechanical properties when the concentration of PBAT was equal to 50%. With an increased concentration of starch (>50%), blends can be prepared from the M2 method (granular starch) in a single extrusion phase without loss of mechanical properties, which can result in lower production cost.

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