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Effect of organic acids as additives on the performance of thermoplastic starch/polyester blown films

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ABSTRACT

The influence of citric acid (CA), malic acid (MA) and tartaric acid (TA) in starch/poly (butylene adipate co-terephthalate) blown films was evaluated by examining the barrier, structural and mechanical properties of the films. These properties were analysed in different relative humidities. Greater concentrations of TA and CA (1.5 wt%) produced films with improved tensile strength (6.8 ± 0.3 and 6.7 ± 0.3 MPa, respectively), reduced water vapour permeability and a more homogeneous structure. The compatibilising effect of MA was less efficient, as shown in the scanning electron microscopy (SEM) images. Changes in the relative humidity (RH) affected the elongation of the films, which reached values of 5.7 ± 0.5 at 33% RH and increased to 312.4 ± 89.5% at 53% RH. The FT-IR spectra showed no additional reactions caused by the incorporation of the additives, and the observed results are attributed to the esterification reactions and/or hydrolysis of the starch, producing films with interesting properties. This process represents an alternative to the use of non-biodegradable materials.

1. Introduction

Efforts have been made to produce totally biodegradable packaging that exhibits a good performance to ensure market needs. Starch is an inexpensive polysaccharide that is obtained from renewable resources. Its use in packaging development has been extensively studied, and it can be transformed to a melted thermoplastic (TPS) by an extrusion process with the inclusion of plasticisers, such as glycerol, which is the most used (Liu, Xie, Yu, Chen, & Li, 2009; Nabar, Raquéz, Dubois, & Narayan, 2005). Chemical modification by reactive extrusion using organic acids could be useful to obtain TPS with modified properties (Carvalho, Zambon, Curvelo, & Gandini, 2005). However, the mixture of the thermoplastic starch with another polymer is necessary to improve the properties of the final product (Lu, Xiao, & Xu, 2009).

The main drawback of starch-based biodegradable films is their sensitivity to environmental conditions. Because of its high character hydrophilic, starch tends to absorb greater quantities of water under conditions of high relative humidity (Galdeano, Mali, Grossmann, Yamashita, & García, 2009; Mali, Sakanaka, Yamashita, & Grossmann, 2005). Blends containing TPS and biodegradable synthetic polyesters, such as poly (butylene adipate co-terephthalate) (PBAT), are interesting for these applications because the polyester has good mechanical and barrier properties that could overcome the limitations of TPS (Nabar et al., 2005; Raquéz, Nabar, Srinivasan, Shin, Narayan, & Dubois, 2008; Ren, Fu, Ren, & Yuan, 2009).

Organic acids are naturally present in fruits and vegetables, and they are synthesised by microorganisms during the fermentation process (Eswaranandam, Hettiarachchy, & Meullenet, 2006). Citric acid has been used as an additive in corn starch films to promote crosslinking (Reddy & Yang, 2010), it has been used in TPS/PLA (polylactic acid) blends to improve the interaction between the polymeric phases and produce films with better properties (Wang, Zhang, Han, & Fang, 2010) Yun, Na, & Yoon (2006) and it has been used in TPS/PVA (polyvinyl alcohol) blends to improve the compatibility of the polymeric phases and the mechanical stability of the materials (Shi et al., 2008).

In this context, it is expected that citric, malic and tartaric acids, which are polycarboxylic acids, will act to promote esterification (grafting) and transesterification reactions (cross-linking) between polymers, improving the compatibility between the starch chains (hydrophilic) and the PBAT (hydrophobic), which will add to the plasticising effect and acid hydrolysis of the starch. Consequently, the influence of citric acid (CA), malic acid (MA) and tartaric acid (TA) on the mechanical, structural and barrier properties of cassava starch/PBAT blown films produced by reactive extrusion were evaluated in this study. The influence of the relative humidity on the mechanical properties of the films was also investigated.

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Table 1
Concentration of the organic acids and glycerol in the formulations.

Formulations	Concentrations (wt%)[a]			
	TA	MA	CA	GLY
Control	0.0	0.0	0.0	10.00
TA0.375	0.375	0.0	0.0	9.625
TA0.75	0.75	0.0	0.0	9.25
TA1.5	1.50	0.0	0.0	8.50
MA0.375	0.0	0.375	0.0	9.625
MA0.75	0.0	0.75	0.0	9.25
MA1.5	0.0	1.50	0.0	8.50
CA0.375	0.0	0.0	0.375	9.625
CA0.75	0.0	0.0	0.75	9.25
CA1.5	0.0	0.0	1.50	8.50

TA = tartaric acid; MA = malic acid; CA = citric acid; GLY = glycerol.

[a] In relation to the total weight of the ternary mixture, the remainder 90 wt% corresponding to cassava starch/PBAT at a ratio of 55:45 wt.

2. Materials and methods

2.1. Materials

The films were produced with native cassava starch obtained from Indemil (Brazil), glycerol, which was used as a plasticiser, (Dinâmica, Brazil) and PBAT (poly(butylene adipate co-terephthalate)), supplied by BASF (Ludwigshafen, Germany) under the commercial name Ecoflex®. The tartaric acid, malic acid and citric acid were supplied by Sigma–Aldrich (Steinheim, Germany).

2.2. Methods

2.2.1. Film production

Pellets were processed using a laboratory single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter (*D*) of 25 mm and a screw length of 28*D*. The components, PBAT, glycerol, acids and starch (in this order) were manually mixed at the time of extrusion and pelleted with a barrel temperature profile of 100/120/120/120 °C from the feeding zone (zone 1) to the die zone (zone 4) at a screw speed of 40 rpm, using a die with six holes of 2 mm diameter. Then, the pellets were extruded again to produce films with a barrel temperature profile of 100/120/120/130 °C for the four zones and 130 °C for the 50 mm film-blowing die with internal air for the formation of the film "bubble" and a screw speed of 40 rpm was maintained.

All of the developed formulations contain the same concentration of starch/PBAT (a proportion of 55:45, respectively), corresponding to 90 wt% of the total, with the remaining 10 wt% contributed by glycerol and acids, as shown in Table 1, including a control formulation without acid.

The feed rate was maintained to ensure that the screw operated at full load, and the film thickness was controlled by the roll speed control and the air-flow rate. These parameters were adjusted for each formulation to maintain a thickness of 100–150 μm.

2.2.2. Water vapour permeability (WVP)

The tests were conducted using the American Society for Testing and Materials ASTM E-96-95 (1996) standard with some modifications. Before the analysis, the samples were stored at 25 °C and 53% RH for 48 h. Each film sample was fixed in the circular opening of a permeation cell with a 60 mm internal diameter, and silicone grease was applied to ensure that humidity migration occurred only through the film. The interior of the cell was filled with a magnesium chloride solution ($MgCl_2$/32.8% RH), and the device was stored at 25 °C in a desiccator to maintain a 42% RH gradient across the film. A saturated sodium chloride solution was used in the desiccator to provide 75% RH.

The samples were weighed every 3 h during the 72 h of testing time. Changes in the weight of the cell or mass gain (m) were plotted as a function of time (t). The slope of the line was calculated by linear regression ($R^2 > 0.99$), and the water vapour permeation ratio (WVPR) was obtained with Eq. (1):

$$\mathrm{WVPR} = \frac{m}{t} \cdot \frac{1}{A} \tag{1}$$

where m/t is the angular coefficient of the curve and A is the sample permeation area. The WVP (g/m s Pa) was calculated as follows:

$$\mathrm{WVP} = \frac{\mathrm{WVPR.st}}{\mathrm{sp}(\mathrm{RH}_1 - \mathrm{RH}_2)} \tag{2}$$

where *st* is the mean sample thickness (m), *sp* is the water vapour saturation pressure at the assay temperature (Pa), RH_1 is the relative humidity of the desiccator and RH_2 is the relative humidity in the interior of the permeation cell. These tests were conducted in duplicate.

2.2.3. Weight loss in water

Samples were previously dried for three days in a desiccator containing anhydrous $CaCl_2$ (0% RH). After weighing, the films were immersed in distilled water, maintaining a proportion of 30:1 (water/sample), for 48 h at 25 °C. The samples were then removed and dried at 105 °C for 4 h, and the weight of the conditioned specimen after treatment was used to determine the % weight loss in water.

2.2.4. Mechanical properties

A texture analyser, model TA.TX2 *plus* (Stable Micro Systems, Surrey-England) fitted with a 50 kg load cell, was used to determine the tensile properties of the films. The tensile tests were based on the ASTM standard D882-91 (1996). Ten samples of each formulation were cut in the longitudinal direction to a length of 50 mm and a width of 20 mm and fit to the tensile grips. The crosshead speed was set at 0.8 mm/s, and the initial distance between the grips was 30 mm. Before testing, the samples were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h. The tensile strength (MPa) and elongation at break (%) were determined.

2.2.5. Scanning electron microscopy (SEM) analysis

A scanning electron microscope FEI model Quanta 200 (FEI Company/Tokyo, Japan) was used to observe the fractured surface of the blown film samples. The samples were submerged in liquid nitrogen and then broken (cryogenic fracture). Before coating with a gold layer, the samples were stored at 25 °C in a desiccator with $CaCl_2$ (≈0% RH) for 3 days. The coating was produced with a Sputter Coater (BAL-TEC SCD 050). Images were taken of the fractured surface at a magnification of 800×.

2.2.6. Fourier transform infrared spectroscopy (FT-IR)

FT-IR analyses were conducted on the blown films from 4000 to 500 cm^{-1} with a spectral resolution of 4 cm^{-1}. A Perkin-Elmer Spectrum 2000 FT-IR with a Universal Attenuated Total Reflectance (UATR) Pike Miracle module was used. The samples were conditioned in a desiccator containing anhydrous calcium chloride ($CaCl_2$) for 10 days before the analysis.

2.2.7. Statistical analysis

The data were analysed using STATISTICA 7.0 software (Statsoft, Oklahoma), with analysis of variance (ANOVA) and Tukey's test at a 5% significance level.

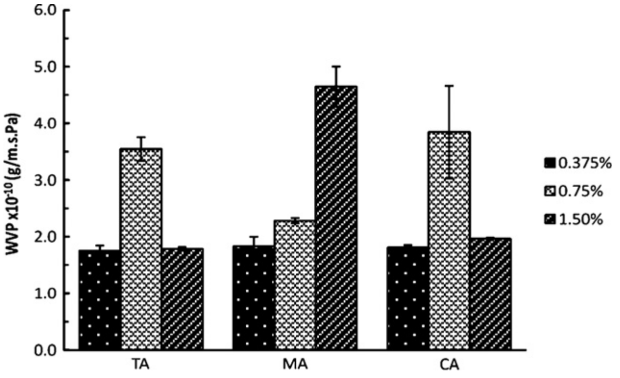

Fig. 1. WVP of the films with TA, MA and CA in different concentrations.

3. Results and discussion

3.1. Water vapour permeability (WVP)

The WVP results showed two different response profiles (Fig. 1). An increase in the concentration of the citric and tartaric acids from 0.375 wt% to 0.75 wt% led to higher WVP values of the films. However, at a concentration of 1.5 wt%, the opposite effect was observed, and the WVP was reduced. The results suggest that in lower concentrations, both CA and TA are present in small quantities, insufficient to contribute to the cross-linking reactions. The reduction of the mobility of the polymeric chains, as a result of cross-linking reactions and making the diffusion of water across the film matrix more difficult, can be observed by the lower WVP results when greater concentrations (1.5 wt%) of these acids are used. In intermediary proportions (0.75 wt%), the hydrolytic actions of both CA and MA are more pronounced, resulting in films with greater molecular mobility and as consequence, more permeable to water.

A higher concentration of MA produced films with greater water vapour permeability, possibly because of the difficulty in promoting transesterification reactions than the other acids evaluated and because it may have contributed to the plasticising effect. The effects of plasticisers on the water vapour permeability of starch-based films have also been evaluated by other authors (Alves, Mali, Beléia, & Grossmann, 2007; Müller, Yamashita, & Laurindo, 2008; Parra, Tadini, Ponce, & Lugão, 2004).

3.2. Weight loss in water

Whereas that the control sample (without acids) exhibited a weight loss of 10.48 ± 0.41% in water, the inclusion of organic acids in the formulations increased the weight loss of the films (Fig. 2), causing the weight loss to reach greater values when the concentration of the acids was greater (1.5 wt%).

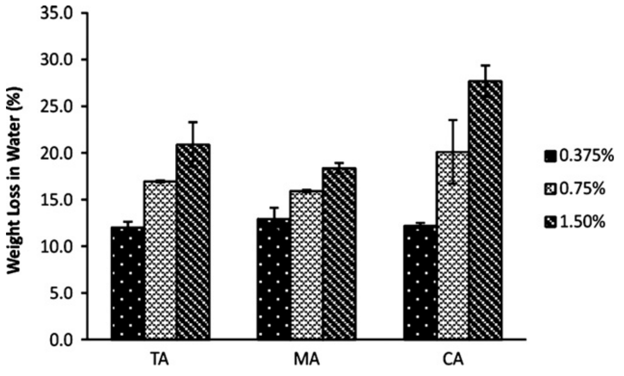

Fig. 2. Weight loss in water (%) of the films with TA, MA and CA in different concentrations.

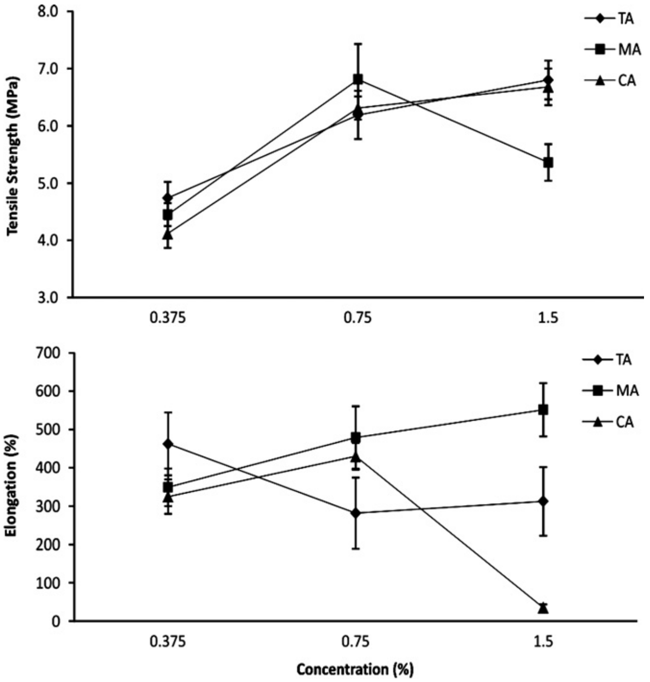

Fig. 3. Tensile strength (MPa) and elongation at break (%) of the films with TA, MA and CA at different concentrations.

The organic acids may have promoted the acid hydrolysis of the starch during the film production process, making them more soluble. Moreover, the presence of free acids, which did not react with the polymeric molecules and are broadly soluble in water, could contribute to occurrence of these reactions during the test, which may have been responsible for the observed results. Yoon, Chough, & Park (2006) observed that the inclusion of glycerol, succinic acid, malic acid and tartaric acid affects the properties of starch/PVA blends, increasing their water solubility, when greater concentrations of the additives are used.

Crosslinking reactions between the polymeric chains may be indicated by the weight loss in water of the films, as described by Reddy and Yang (2010), who reported that starch films with added citric acid underwent crosslinking reactions, producing a denser structure that experienced reduced weight loss and water vapour permeability.

3.3. Mechanical properties

The mechanical properties were affected by the inclusion of organic acids in the films. Fig. 3 shows the tensile strength and elongation of the films that were previously conditioned in 53 ± 2% RH. A difference can be noted between the results observed for the CA and TA and those observed for the MA. More resistant films (higher tensile strength) were obtained when higher concentration of CA and TA (1.5 wt%) or intermediate concentrations of MA (0.75 wt%) were used. In the elongation results, the CA caused a remarkable reduction of this property when added in a concentration of 1.5 wt%.

Multifunctional organic acids, such as CA, MA and TA, are able to interact with the hydroxyls of the starch, introducing new groups (carboxyls and esters) to their structure. These new groups represent new potential reactive points for crosslinking reactions, improving the compatibilisation between the polymeric molecules resulting in more resistant films. The action of the organic acids on the acid hydrolysis of starch molecules is known, and it has already

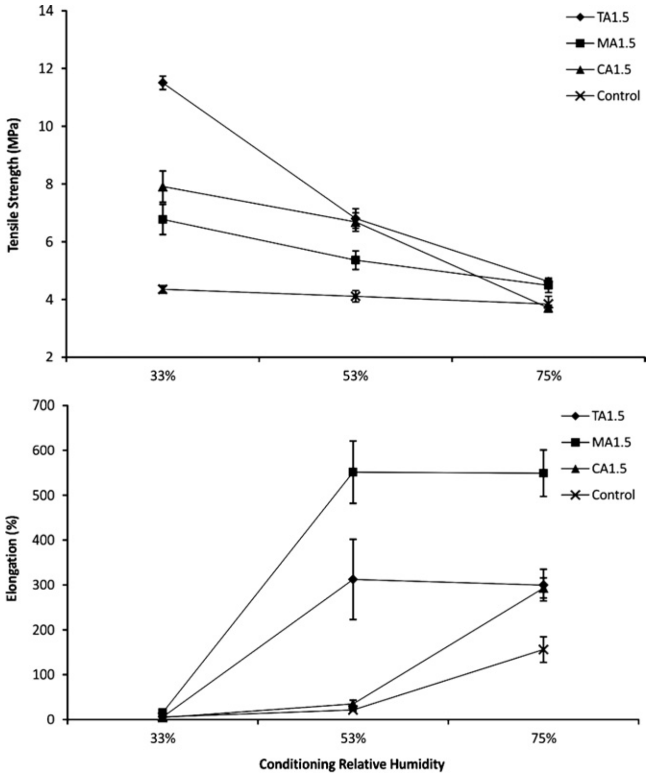

Fig. 4. Tensile strength (MPa) and elongation (%) of the analysed films at relative humidity of 33, 53 and 75% at formulations of TA1.5, MA1.5, CA1.5 and the control.

been evaluated in other papers (Carvalho et al., 2005; Da Róz, Zambon, Curvelo, & Carvalho, 2011), which proves that increasing the concentration of acids leads to a reduction of the molecular weight of the starch chains. Consequently, the results shown in this work suggest a combination of these actions, in addition to the plasticising role of the organic acids reported in the study by Shi et al. (2007). This effect causes greater compatibilisation of the polymeric blends.

The citric and tartaric acids contribute to the production of a material with increase tensile strength and reduced elongation when their concentration in the starch/PBAT blend is increased. This result is most likely caused by crosslinking reactions, which interconnect the polymeric molecules and restrict their mobility, in agreement with the results of WVP. The effect of the citric acid and maleic anhydride in the starch/PBAT blends has already been discussed in a previous study (Olivato, Grossmann, Yamashita, Eiras, & Pessan, 2012), and Shi et al. (2008) and Reddy and Yang (2010) also reported similar results with the inclusion of CA in starch-based materials.

Although both showed similar behaviour, the addition of CA caused a pronounced decrease in the elongation of the films (with 1.5 wt%), while TA did not significantly alter the results obtained at concentrations of 0.75 wt% or 1.5 wt%. This result shows that, beyond the crosslinking reactions, CA interacts with the polymeric molecules and produces strong hydrogen bonds (Shi et al., 2007). The proliferation of hydrogen bonds makes the movement of chains past each other more difficult, reducing the elongation as a consequence.

With the objective of evaluating the influence of the relative humidity on the mechanical properties, films were conditioned at three relative humidities (33, 53 and 75 ± 2%RH), and these results are shown in Fig. 4. In general, as the RH was increased, the tensile strength was reduced for all film formulations. In other words, their mechanical properties deteriorated, and the films became fragile. Greater water content resulted in a pronounced plasticising effect, weakening the polymeric matrix. In the case of the films with added CA, TA and MA, the gain of water favours acidolysis reactions, which may have been the cause of the lower tensile strength and higher elongation at break, which changed only slightly for the control films (containing only glycerol) as the RH increased.

Greater film tensile strengths were observed at lower relative humidities (33 ± 2%). Nevertheless, in these conditions, the materials are rigid and brittle, making their utilisation as packaging difficult. Galdeano et al., 2009 and Mali et al. (2005) found the same comportment in oat starch- and cassava starch-based films, respectively.

The role of water as a plasticiser produces materials with higher elongation, as observed at Fig. 4. In this case, the results were similar, regardless of the organic acid used, and it was observed that the water content in the films had no clear influence on the mechanical properties past an RH of 53 ± 2%, possibly because the maximum capacity of water absorption of the films was achieved.

3.4. Scanning electron microscopy (SEM) analysis

The sample morphology was evaluated by scanning electron microscopy, and the resulting images are presented in Fig. 5. In these images, it is possible to observe partially disrupted granules of starch in the control sample and the sample containing malic acid (MA1.5), although it is present in small quantities for this sample, which shows that the starch was not completely fragmented. Consequently, a continuous thermoplastic phase is not observed, interfering with the homogeneity of the blend. In the samples with citric acid (CA1.5) and tartaric acid (TA1.5), starch granules are not observed in the images (i.e., a homogeneous structure composed of only one phase was formed). Therefore, we can conclude that both CA as TA acted as better compatibilisers than MA, producing a more uniform and smooth material, which was also indicated by in the improvement of their mechanical properties. The effect of citric acid on the morphology of blends containing thermoplastic starch was already evaluated in previous works (Olivato et al., 2011; Wang et al., 2010).

When considering the dicarboxylic organic acids (TA and MA) and the polycarboxylic acid (CA), we should consider the possibility of intramolecular hydrogen bonds (Rodrigues, 2000). This phenomenon could explain the difference in the behaviour of these acids. Citric and tartaric acid have substitution in the carbonic chain, which makes more difficult for the molecule acquire the necessary conformation to form intramolecular hydrogen bonds (steric blocking), which is opposed to MA, that is able to perform intramolecular hydrogen bonds. This could explain the lower efficiency of MA in disrupting the starch granules and promoting esterification reactions. Also, the differences in the molar concentrations for the tested acids must be taken into consideration to explain the results.

This effect would compromise the mechanical properties of the blends because these intermolecular bonds retard the interaction of the acid with the other components of the film. However, some adjustments in the process parameters could be useful to provide the necessary energy for the complete fragmentation and melting of the starch. Wang et al. (2010) observed that the addition of greater quantities of CA to the starch/PLA blends improved both the plasticisation of the starch and the phase dispersion, leading to the production of more homogeneous blends, which could be attributed to acceleration of the fragmentation and dissolution of the starch granules by the acid.

3.5. Fourier transform infrared spectroscopy (FT-IR)

Fig. 6 shows the FT-IR spectra (wave numbers between 1800 and 1000 cm^{-1}) of the control starch/PBAT films and those with

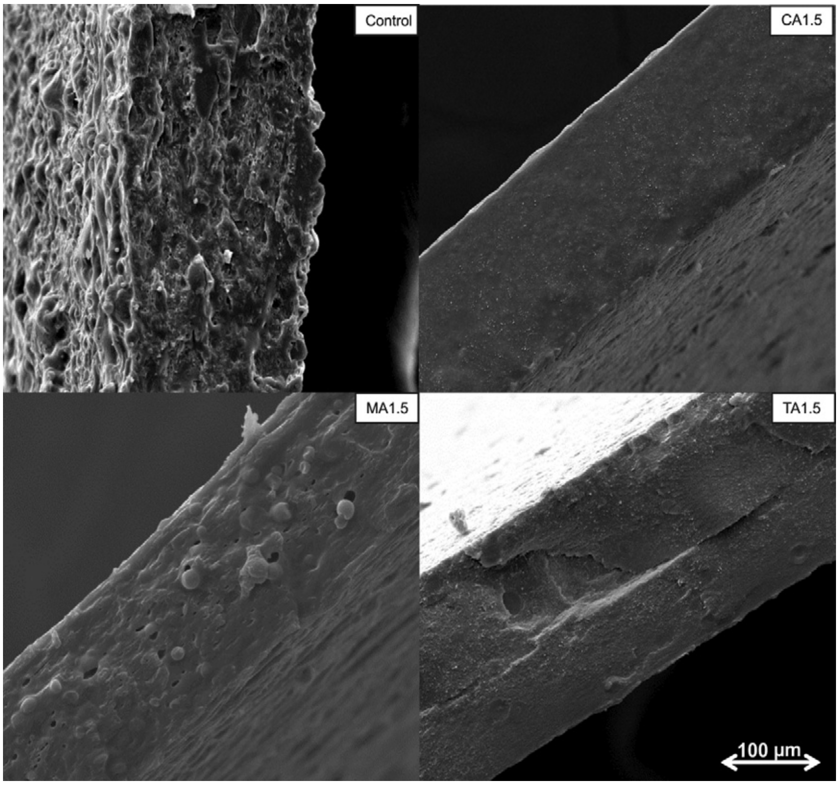

Fig. 5. SEM images of fractures of the TA1.5, MA1.5, CA1.5 and control samples (magnification, 800×).

1.5% of each organic acid. A peak at approximately 1715 cm^{-1}, produced by a carbonyl stretch attributed to esters, was observed for all of the samples. This visibility is a result of peak coalescence because of the ester bonds naturally present in the PBAT molecules, and also due those which were produced by the esterification and transesterification reactions that occurred during the reactive extrusion process. Consequently, it is not possible to obtain accurate information to discriminate the localisation of these chemical bonds.

The stretch vibrations of C—O in C—OH bonds are observed at 1150 cm^{-1}, and an increase of the peak intensity is noted when the organic acids are present. Similar behaviour is observed for the C—O bond stretching of the C—O—C group in the anhydroglucose ring at 1020 cm^{-1}, which is also amplified in the CA1.5, MA1.5 and TA1.5 samples, relative to the control. The peaks at approximately 1280 and 1123 cm^{-1} are characteristic of C—O in —O—C═O bonds, and a slight increase in their intensity could be observed in samples containing acids, of which CA exhibited the most visible peak. Similar spectra were obtained by Wang et al. (2010) and by Miranda & Carvalho (2011).

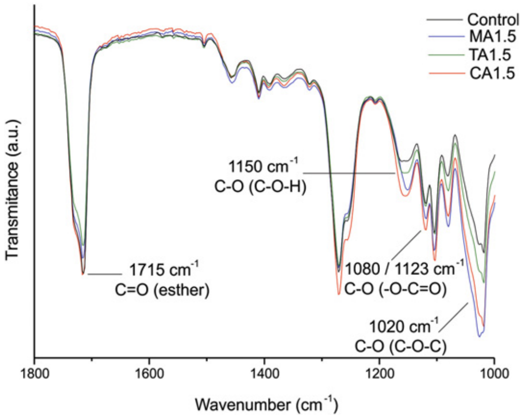

Fig. 6. Comparison of FT-IR spectra for the control, MA1.5, TA1.5 and CA1.5.

In general, all of the sample spectra are similar, showing that the results are produced by the acid hydrolysis of the glycosidic linkages and the esterification and transesterification reactions, whose definition was impaired by overlapping peaks. No additional reactions or modifications to the polymeric matrix could be observed.

4. Conclusion

The inclusion of organic acids improved the properties of starch/PBAT films because they produced crosslinks that interconnect the polymeric chains, generating more resistant and less permeable films. In addition, organic acids contribute to starch hydrolysis, facilitating the destructuring and disruption of the granules, decreasing the material viscosity, improving the processing properties and producing a more homogeneous matrix, as observed in the scanning electron micrographs.

The increase in the relative humidity led the tensile strength to decrease and increment at elongation of the films because of the role of water as a plasticiser. Thus, biodegradable films with better properties could be produced. These films represent an alternative to synthetic packaging, but their limitations should be respected.

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