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Mixture design applied for the study of the tartaric acid effect on starch/polyester films

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ABSTRACT

Tartaric acid (TA), a dicarboxylic acid, can act as a compatibiliser in starch/polyester blends. A mixture design was proposed to evaluate the effect of TA on the properties of starch/poly (butylene adipate co-terephthalate) (PBAT) blown films plasticised with glycerol. The interaction between the starch/PBAT and the TA has a positive effect on the tensile strength and puncture force. Additionally, greater proportions of TA increased Young's modulus. The starch + PBAT/TA and Gly/TA interactions contributed to a reduction in the water vapour permeability of the films. The inclusion of TA did not change the crystallinity of the samples. Formulations with intermediate proportions of TA (0.8 g/100 g) were shown to produce the best compatibilising effect. This was observed by DMA analysis as a consequence of the perfect equilibrium between the contributions of TA as a compatibiliser and in the acidolysis of starch, resulting in films with a tensile strength of 5.93 MPa, a possible alternative to non-biodegradable packaging.

1. Introduction

Starch has been the focus of several studies whose objective has been to take this biodegradable, inexpensive, and abundant material, obtained from renewable resources and create packaging (Lu, Xiao, & Xu, 2009). During the extrusion process, the granular structure of starch is disrupted by the combination of temperature and shear forces and, in the presence of a plasticiser, forms a melted material called thermoplastic starch (TPS) (Avérous, Fringant, & Moro, 2001).

The use of pure TPS in packaging materials is limited by its low mechanical resistance, the deterioration of its mechanical properties when exposed to environmental conditions (mostly in high humidity conditions) and the difficult processing due to its inherently high viscosity (Contreras, Perilla, & Enciso, 2008; Yoon, Chough, & Park, 2006). A proposed alternative that could potentially overcome these deficiencies is to blend TPS with good performance biodegradable polyesters, such as PBAT (poly (butylene adipate co-terephthalate)).

The melting and mixing of TPS with PBAT results in an immiscible blend with high interfacial tension between the phases (Taguet, Huneault, & Favis, 2009). A compatibiliser could be added to interact with the starch hydroxyl to improve the adhesion between the polymeric phases, producing blends with improved properties (Orozco, Brostow, Chonkaew, & López, 2009; Ren, Fu, Ren, & Yuan, 2009).

In previous studies (Olivato, Grossmann, Bilck, & Yamashita, 2012; Olivato, Grossmann, Yamashita, Eiras, & Pessan, 2012) we observed that multifunctional organic acids, such as citric, malic and tartaric acids, could improve the compatibility between the polymeric phases, producing structurally more homogeneous blends with better mechanical properties. These acids have the added advantage of health safety when the objective is food packaging, once they are non-toxic and non-volatile (Da Róz, Zambon, Curvelo, & Carvalho, 2011). Tartaric acid was also evaluated by Yun, Na, and Yoon (2006), resulting in starch/PVA films with improved properties.

Using a mixture design and low concentrations of PBAT (<40 wt%), this paper aims to evaluate the influence of TA, glycerol as a plasticiser, and a third component represented by a starch + PBAT mixture, on the mechanical, thermal and barrier properties of blown-films obtained by reactive extrusion.

2. Materials and methods

2.1. Materials

Native cassava starch was obtained from Indemil (Paranavaí, PR/Brazil) (amylose 20.8 ± 0.6 wt%), PBAT (poly (butylene adipate co-terephthalate)), was supplied by BASF (Ludwigshafen, Germany); glycerol, supplied by Dinâmica (Diadema, SP/Brazil) and tartaric acid, supplied by Sigma–Aldrich (Steinheim, Germany).

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2.2. Methods

2.2.1. Mixture design

A mixture design, with constraints on the lower and upper levels of each component (determined from previous tests), was used for the development of the films. Table 1 shows the concentration (in real values and as pseudo-components) of each component in the different samples. The components of the blends were the tartaric acid (TA), glycerol (Gly) and the third component was represented by a mixture of cassava starch and PBAT (starch + PBAT) in a proportion of 55:45, respectively. Two replicates of the T5 sample (T5.1 and T5.2) were used.

The mechanical properties and water vapour permeability of the films were analysed with STATISTICA 7.0 software (Statsoft, Tulsa/USA) using data modelling and analysis of the surface contours of the mixture design. Quadratic models (Eq. (1)) better fit the results.

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (1)$$

where y is the dependent variable, β is the regression coefficient for each component, x_1 is the starch + PBAT, x_2 is the glycerol and x_3 is the tartaric acid.

2.2.2. Film production

All components of the formulations (Table 1) were manually mixed at the time of extrusion and processed to produce pellets using a laboratory single-screw extruder (model EL-25, BGM, São Paulo, Brazil) with a screw diameter (D) of 25 mm and a screw length of 28D. A barrel temperature profile of 100/120/120/120 °C from the feed zone (zone 1) to the die zone (zone 4) was used. The screw speed was set to 40 rpm using a die with six 2 mm diameter holes. The pellets were then extruded, using the same equipment, to obtain the films. The barrel temperature profile was set to 100/120/120/130 °C and 130 °C for the 50 mm film-blowing die and screw speed was set to 40 rpm. The feed rate was maintained to ensure that the screw operated at full load. The film thickness (maintained between 80 and 100 μm) was controlled via roll speed control and the air flow.

2.2.3. Water vapour permeability (WVP)

The tests were conducted using ASTM method E-96-95 (1996) with some modifications. Before 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 using silicone grease 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 containing a saturated sodium chloride solution that provided 75% RH and maintained a 42% RH gradient across the film. The samples were weighed every 3 h during the 72 h 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 ($R^2 > 0.99$). The water vapour permeation ratio (WVPR) was obtained with Eq. (2):

$$\text{WVPR} = \left(\frac{m}{t}\right) \cdot \left(\frac{1}{A}\right) \quad (2)$$

where m/t is the angular coefficient of the curve and A is the sample permeation area. The WVP ($\text{g Pa s}^{-1}\,\text{m}^{-1}$) was calculated using Eq. (3):

$$\text{WVP} = \frac{\text{WVPR} \cdot \text{st}}{\text{sp}(\text{RH}_1 - \text{RH}_2)} \quad (3)$$

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 of the interior of the permeation cell. The tests were conducted in duplicate.

2.2.4. Mechanical properties

A texture analyser model TA.XT2i (Stable Micro Systems, Surrey/England) fitted with a 50 kg load cell was used to conduct the tensile and puncture tests of the films. Tensile tests were based on the ASTM method D882-91 (1996). Ten samples from each formulation were cut along the longitudinal direction (50 mm in length and 20 mm in width) and fit in the tensile grips. The crosshead speed was set at 0.8 mm/s and the initial distance between the grips was 30 mm. The tensile strength (MPa), elongation at break (%) and Young's modulus (MPa) were determined.

Puncture tests were performed using 10 samples from each formulation. These were fixed in an appropriate apparatus that allowed exposure to 35 mm of the sample. The perforation was conducted using a cylindrical probe 3.0 mm in diameter at a speed of 0.4 mm/s which pierced perpendicular to the sample. The puncture force (N) was determined (Gontard, Guilbert, & Cuq, 1993). Before all tests, the samples were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h.

2.2.5. Dynamical–mechanical analysis (DMA)

A Dynamical Mechanical Analyser (DMA-Q800, TA Instruments, USA) was used to determine the storage modulus (MPa) and loss factor (tan δ) of the blown films. The samples were subjected to a sinusoidal strain in traction mode and scanned from −50 °C to 100 °C with a heating rate of 3 °C/min and fixed frequency of 1 Hz. Glass transition temperatures (Tg) were expressed as the temperature of the tan δ peaks. For clarity, the analysis was done for samples C, T1 and T5, which contained different levels of tartaric acid.

2.2.6. X-ray diffraction (XRD)

X-ray patterns of the samples were taken using an XPert PRO (Panalytical, Philips) machine with Cu(kα) radiation (λ = 1.5406 Å) operating at room temperature, 30 mA and 40 kV. The scanned region ranges from $2\theta = 3.0–70.0°$, with a step size of 0.01° and dwell time of 4.0. The relative crystallinity index (CI) was estimated from the relative areas of crystalline and amorphous regions, according to the relationship described by Müller, Laurindo, and Yamashita (2009). For clarity, the analysis were shown for samples C, T1 and T5, which contained different levels of TA.

3. Results and discussion

3.1. Modelling of mixture design

Compatibilised blends containing starch/polyester produce films with improved mechanical and barrier properties that represent a potential substitute for plastic packaging available today (Nabar, Raquéz, Dubois, & Narayan, 2005; Yu, Dean, Yuan, Chen, & Zhang, 2007). In Table 2, the regression coefficients of the models adjusted for the mechanical and barrier properties are listed. The presented determination coefficients (R^2) that are higher than 0.70 indicate good fit with experimental data, except in the case of elongation ($R^2 = 0.474$), whose model cannot be considered for prediction purposes.

The influence of the components on the mechanical resistance of the films were evaluated based on modelling coefficients for the tensile strength and puncture force, which both showed similar effects. The inclusion of tartaric acid exerted a negative effect on the tensile strength (β_3 −16.97) and the puncture force (β_3 −52.34), i.e., when the concentration of TA increases, the film's tensile strength and puncture force were reduced. On the other hand, the interaction between the mixture of starch/PBAT and TA (β_{13}) had a more significant positive effect on the response, producing more

Table 1
Concentrations of the components in the film formulations according to the mixture design.

Samples	Components			Pseudo-components[a]		
	Starch + PBAT[c] (wt%)	Glycerol (wt%)	Tartaric acid (wt%)	x_1	x_2	x_3
C	88.0	12.0	0.0	0.3	0.7	0.0
T1	87.0	11.9	1.1	0.0	0.6	0.4
T2	89.5	9.9	0.5	0.8	0.0	0.2
T3	87.5	11.9	0.5	0.2	0.6	0.2
T4	89.0	9.9	1.1	0.6	0.0	0.4
T5[b]	88.3	10.9	0.8	0.4	0.3	0.3

[a] $x_i = c_i - a_i/1 - \sum a_i$ was used to calculate the pseudo-components values were x_1 = starch + PBAT, x_2 = glycerol and x_3 = tartaric acid (TA), c_i is the real concentration and a_i is the lower limit of each component in the mixture design.

[b] Two replicates of the T5 sample were performed.

[c] Mixture of cassava starch and PBAT (starch + PBAT) in a proportion of 55:45, respectively.

Table 2
Regression coefficients for the mechanical and barrier properties.

Coefficients	Properties				
	Tensile strength	Elongation	Young's modulus	Puncture force	WVP
β_1	3.39	197.71	29.61	2.02	9.11
β_2	8.41	960.79	50.16	13.28	4.25
β_3	−16.97	−3016.43	142.76	−52.34	32.23
β_{12}	−4.35	−794.25	−19.99	−18.59	13.02
β_{13}	41.37	6229.25	8.24	93.35	−45.57
β_{23}	16.06	3235.63	−246.78	64.77	−27.70
R^2	0.775	0.474	0.834	0.918	0.890

β_1 = starch+PBAT, β_2 = Gly (glycerol), β_3 = TA (tartaric acid), β_{12} = interaction starch + PBAT/Gly, β_{12} = interaction starch+PBAT/TA, β_{23} = interaction Gly/TA.

resistant films (Table 2). This can also be observed in Fig. 1; for tensile strength, improved results were obtained when intermediate concentrations of glycerol and TA are used (calculated value of 5.93 MPa).

Young's modulus or elastic modulus is related to film rigidity. Higher values of Young's modulus indicate a more rigid material. The resultant Young's moduli for the starch/PBAT films ranged from 29.95 to 74.87 MPa (Fig. 2). A positive effect was seen by the addition of TA (β_3 142.76). The films were more rigid when increased amounts of TA were used. At the same time, the antagonistic interaction of Gly/TA (β_{23} −246.78) results in more flexible films as a consequence of the plasticising role of the glycerol together with the TA action as a plasticiser. These components interpose themselves between the starch molecules and reduce the attractive intermolecular forces. This behaviour was also observed for citric acid in thermoplastic starch films (Garcia et al., 2011; Olivato et al., 2011; Shi et al., 2007).

Ayoub and Rizvi (2009) observed that the utilisation of greater concentrations of glycerol reduces the crosslink reaction efficacy. This is because the intermacromolecular distances increase and the possibility of creating macro radical combinations is reduced, which also could be responsible for the negative effect observed with the Gly/TA interaction on Young's modulus. Additionally, Wang, Zhang, Han, and Shihe (2009), studying starch/montmorillonite nanocomposites, observed that citric acid (3 wt%) contributed to starch granule disruption and facilitated the

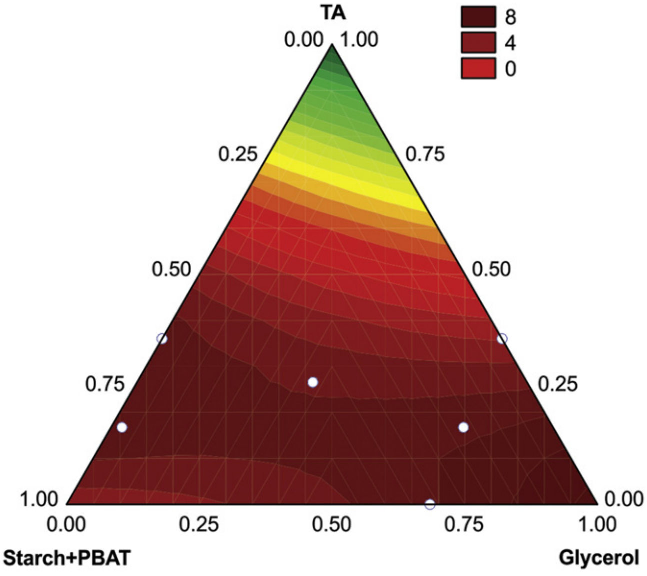

Fig. 1. Surface contour map showing the effect of the starch + PBAT, glycerol (Gly) and tartaric acid (TA) on the tensile strength (MPa), in terms of pseudo-components. The experimental area is delimitated by the shown sample points.

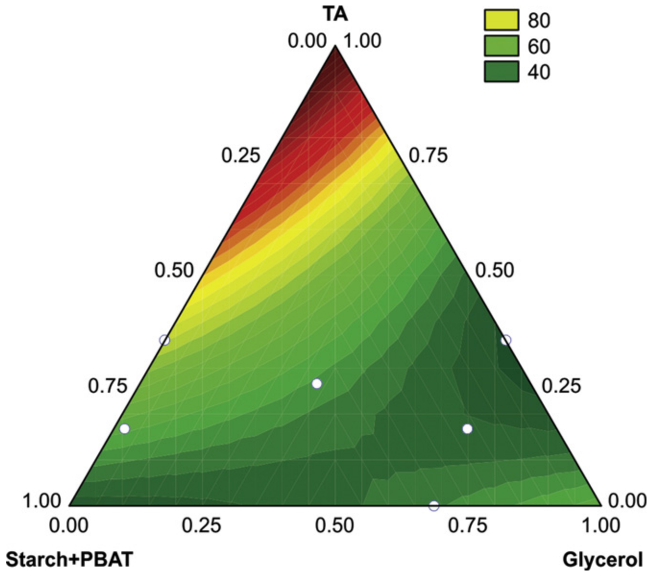

Fig. 2. Surface contour map showing the effect of the starch + PBAT, glycerol (Gly) and tartaric acid (TA) on the Young's modulus (MPa), in terms of pseudo-components. The experimental area is delimitated by the shown sample points.

penetration of the plasticiser within the film, resulting more flexible films.

The results from mechanical testing allow us to observe different and concomitant roles of TA when added to starch/PBAT blends. Organic dicarboxylic acids, such as TA, are able to promote crosslinking reactions (transesterification), connecting the starch chains together and restraining their molecular mobility, with the overall effect being to reinforce the film matrix (Olivato, Grossmann, Bilck, et al., 2012). This function can be evidenced by the positive effect of the starch + PBAT/TA interaction on the tensile strength and puncture force (Table 2), where more resistant and more rigid films (positive effect of TA on Young's modulus) were seen. The reinforcing effect could additionally be caused by the TA reaction with the hydroxyl group on the starch (grafting). This would reduce the hydrophilic character and improve their compatibility with PBAT, promoting enhanced stress transference within the polymeric matrix.

Residual TA, which did not participate in esterification and/or transesterification reactions, can cause starch acidolysis, which factors into viscosity control of the molten thermoplastic starch. As shown by Da Róz et al. (2011), the addition of organic acids during thermoplastic starch melting results in a reduction of molecular weight. The acid hydrolysis of starch resulted in more brittle films when higher proportions of TA were used (negative effect on tensile strength and puncture force) (Fig. 1 and Table 2).

3.2. Water vapour permeability (WVP)

To use starch films for food packaging, in place of synthetic plastics, it is important to minimise water vapour permeability in order to avoid the moisture transference between the packaged material and the atmosphere (Gontard, Guilbert, & Cuq, 1992). The WVP of the films ranged from 6.44×10^{-10} to 8.80×10^{-10} g s^{-1} m^{-1} Pa^{-1} and are lower than those found for cassava starch/glycerol films, which reach WVP values of $3.20 \pm 0.20 \times 10^{-9}$ (Alves, Mali, Beléia, & Grossmann, 2007). The improvement was promoted by the inclusion of PBAT, which added a hydrophobic character to the films. The results, however, are closer to those of our previous works (Olivato et al., 2011) and also to those of Wang et al. (2009), who observed a WVP of 2.0×10^{-10} g s^{-1} m^{-1} Pa^{-1} for starch/montmorillonite nanocomposites containing citric acid, and to the results obtained by Pelissari, Grossmann, Yamashita, and Pineda (2009), which ranged from $0.62 \pm 0.15 \times 10^{-10}$ to $1.39 \pm 0.15 \times 10^{-10}$ g s^{-1} m^{-1} Pa^{-1} for cassava starch/chitosan films.

The WVP increased (positive effect on the response) when the proportions of any component in the blends was increased (Table 2). According Wang and Padua (2005), the permeability of a material is strongly influenced by the hydrophobic or hydrophilic nature of its components. For hydrophilic molecules, the inclusion of higher proportions of glycerol or TA resulted in a greater affinity of the polymeric matrix for water, contributing to an increase in the WVP (Fig. 3). Similar results were observed by Galdeano, Mali, Grossmann, Yamashita, and García (2009) in oat starch films and Parra, Tadini, Ponce, and Lugão (2004) for cassava starch samples.

Considering the component interactions, a reduction in WVP was promoted by the β_{13} (starch + PBAT/TA) and β_{23} (Gly/TA) interactions (Table 2). The role of TA as a compatibiliser, through transesterification reactions and/or single esterification reactions with starch hydroxyls (which formed a more hydrophobic starch), could contribute to the WVP decrease (Fig. 3). Ren et al. (2009) observed that the reaction of the compatibiliser with the starch —OH group (ester bonds) causes the "coating" of the hydrophilic centres of the starch by a hydrophobic layer. This could be making the starch more compatible with PBAT, thus decreasing WVP.

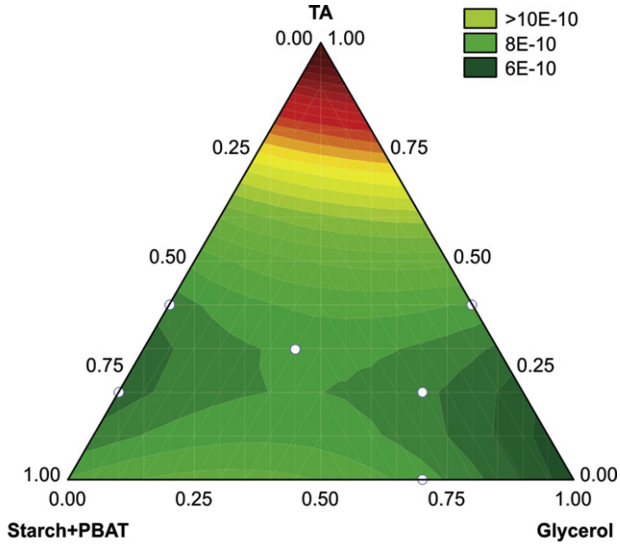

Fig. 3. Surface contour map showing the effect of the starch + PBAT, glycerol (Gly) and tartaric acid (TA) in the WVP (g/s m Pa), in terms of pseudo-components. The experimental area is delimitated by the shown sample points.

Possible reactions between tartaric acid and glycerol should also be considered. The availability of both molecules acting as plasticisers was reduced and, as a consequence, the diffusion of water through the film matrix became more difficult. Raquéz, Nabar, Narayan, and Dubois (2008), studying melt-blends of TPS/PBAT, also reported the occurrence of glycosylation reactions during the process of reactive extrusion. This was also the case when decreasing the glycerol available to act as a plasticiser.

3.3. X-ray diffraction (XRD)

Similar X-ray patterns were obtained for samples C, T1 and T5 (Fig. 4). For all the samples, the peaks identified at $2\theta = 13.1^\circ$ and 19.8° are due to the crystallisation of the starch induced by processing (type V_H). No residual native crystallinity was observed in the films, leading to the conclusion that complete starch melting occurred. Van Soest, Hulleman, de Wit, and Vliegenthart (1996) found similar results for TPS processed at temperatures lower than 180 °C. Moreover, the peaks at $2\theta = 17.6^\circ$ and 23.2° are related to the PBAT crystallinity, which is in agreement with those observed by Raquéz et al. (2008) for thermoplastic starch/PBAT blends.

Shi et al. (2007) observed that starch has its crystallinity reduced when citric acid is added. However, in this work, the inclusion of tartaric acid did not change the crystallinity index (CI) of the films, as can be observed in Fig. 4. The sample T1 has a slightly greater CI (19.2%) and the C sample, without acid, had a CI of 18.1%, which is similar to those of the T5 sample (18.25%).

3.4. Dynamical mechanical analysis (DMA)

The viscoelastic response of the material can be studied using a temperature sweep at a fixed frequency by dynamical mechanical analysis (DMA). The storage modulus is related to the potential energy stored by the material under deformation and is closely related to the load bearing capacity of the material (Mohanty, Verma, & Nayak, 2006; Vaidya, Bhattacharya, & Zhang, 1995). The higher storage modulus was obtained for sample T5 (Fig. 5), indicating an increase in the viscoelastic stiffness, which could be a consequence of the more pronounced compatibiliser effect of the TA, at intermediate proportions. Sample T1 was similar to sample C, i.e., without acid.

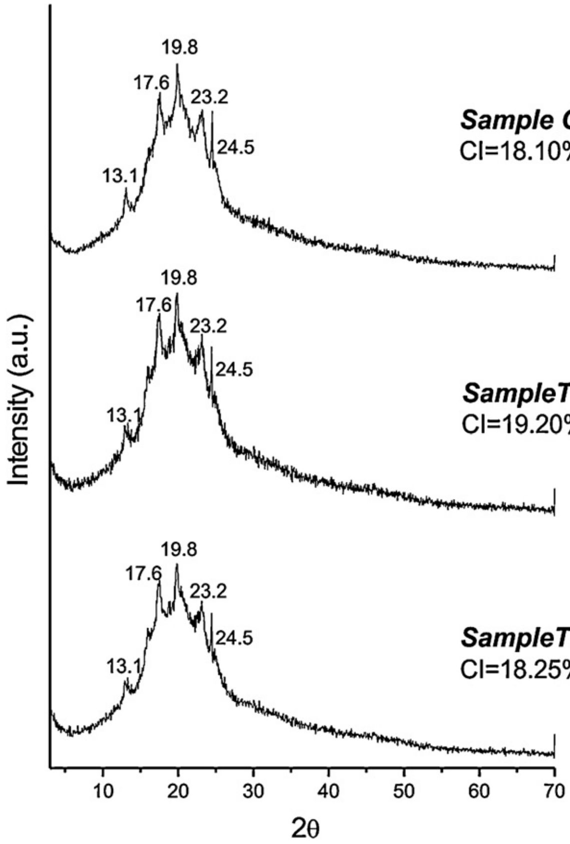

Fig. 4. X-ray diffractograms for samples C (without TA), T1 (1.1 wt% TA) and T5 (0.8 wt% TA). Relative crystallinity index (CI) was calculated and is indicated on the plots.

Liang and Williams (1992) observed that poor adhesion between the co-continuous phases in blends results in a lower storage modulus. With the addition of a compatibiliser the adhesion is improved and results in a greater storage modulus. Comparing the results of our work, it is possible to conclude that sample T5 contained the better proportion of TA for the compatibiliser effect.

Loss factor (tan δ) is the ratio between the loss and storage modulus. Their peaks are usually used as an indicator of glass transition temperature (Tg) for materials (Vaidya et al., 1995). tan δ curves for the samples (Fig. 6) reveal two thermal relaxations, characteristic of an immiscible blend. The first transition, at approximately −25 °C, is attributed to the glass transition temperature of the PBAT rich phase and the second one, above room temperature, corresponds to the glass transition temperature (Tg) of the TPS rich phase.

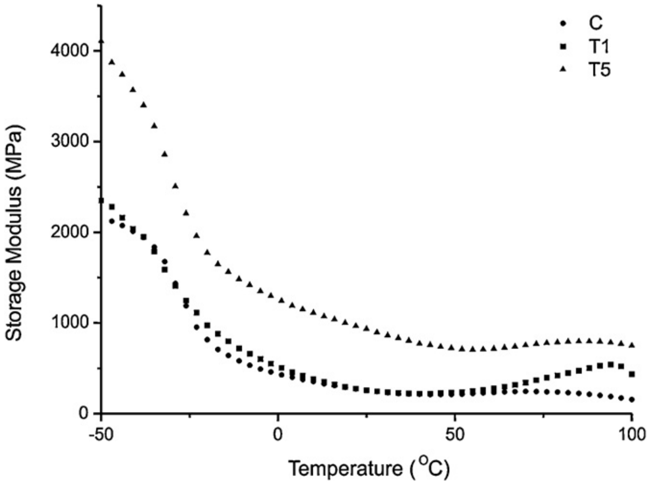

Fig. 5. Storage modulus (MPa) for samples C (without TA), T1 (1.1 wt% TA) and T5 (0.8 wt% TA).

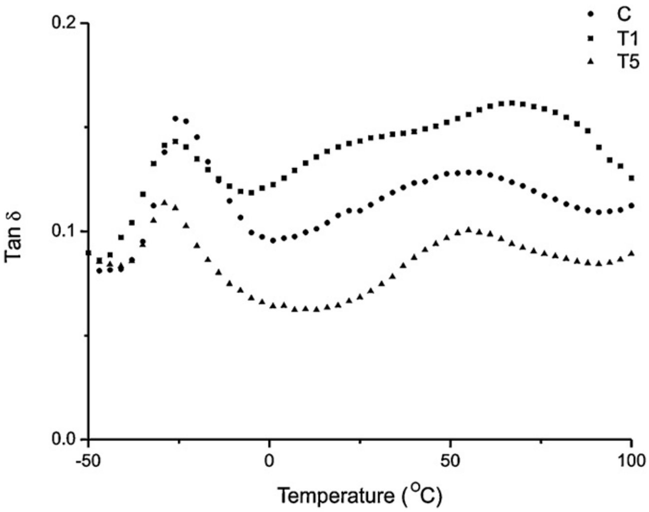

Fig. 6. Loss factor (tan δ) for samples C (without TA), T1 (1.1 wt% TA) and T5 (0.8 wt% TA).

The Tg of the samples with TA, in general, showed a slight decrease when compared to the control (C), except for T1, whose loss factor curves showed a broadening of the glass transition of TPS. This could be attributed to the higher proportion of TA in the sample favouring acidolysis reactions and resulting in starch chains with several molecular weights, i.e., polymeric chains with various sizes and consequently different molecular mobility. The reduction of Tg with the inclusion of TA could be related to its behaviour as a compatibiliser, improving the interaction between the polymeric phases (Wang, Zhang, Han, & Fang, 2010), and potentially due to its role as a plasticiser and promoter of acidolysis (Mani & Bhattacharya, 2001; Shi et al., 2008).

4. Conclusions

The proposed mixture design was efficient for evaluating the influence of tartaric acid in starch/PBAT blown films. TA proved to be a good compatibiliser at intermediate levels (0.8 g/100 g), improving the interfacial interaction between the polymeric phases and the transference of stress in the films. This resulted in greater resistance and more rigid materials. TA also acted as a plasticiser and in the acidolysis of the starch; however, it did not change the crystallinity of the films.

In conclusion, TA contributes to the improvement of the mechanical and barrier properties of films in which adequate concentrations is necessary to reach the optimal properties, as shown in the DMA analysis. Thus, the obtained biodegradable films containing reduced proportions of PBAT show good performance and represent an interesting alternative to non-biodegradable packaging.

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