



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.

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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.

$$y = \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 \quad (1)$$

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 28 D . 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 (MgCl₂/32.8% 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 ($\tan \delta$) 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 (T_g) were expressed as the temperature of the $\tan \delta$ 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($K\alpha$) radiation ($\lambda = 1.5406$ 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 was 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 ($\beta_3 - 16.97$) and the puncture force ($\beta_3 - 52.34$), 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

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