Physical and structural characterisation of starch/polyester blends with tartaric acid

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ABSTRACT

Starch/PBAT blends were produced by reactive extrusion with tartaric acid (TA) as an additive. The effects of TA, glycerol and starch + PBAT on the mechanical, optical and structural properties of the films were evaluated, with formulations based in a constrained mixture design. Tartaric acid acts as a compatibiliser and promotes the acid hydrolysis of starch chains. These two functions explain the observed film resistance and opacity. TA reduced the weight loss in water. Scanning electron microscopy (SEM) images showed that TA reduces the interfacial tension between the polymeric phases, resulting in more homogeneous films. Nuclear magnetic resonance (^{13}C CPMAS) and Fourier transform infrared spectroscopy (FT-IR) suggest that tartaric acid is able to react with the hydroxyl groups of the starch by esterification/transesterification reactions, confirming its role as a compatibiliser. The addition of TA results in materials with better properties that are suitable for use in food packaging.

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1. Introduction

Synthetic polymers produced from petrochemicals are a significant source of environmental pollution. Growing ecological concern has resulted in the emergence of biodegradable plastics as alternative materials to petroleum-based polymers [1].

There is strong interest in biologically based and/or biodegradable polymers. The reasons for this include the reduced cost, the abundance of the biomass and biodegradability of the materials, combined to the reduced disposal of non-degradable waste into the environment [2].

Thermoplastic starch represents an abundant, renewable and low-cost alternative to synthetic plastics but has some disadvantages, including deficient mechanical properties (crystallisation due to ageing and plasticisation by water adsorption) and hygroscopic character [2,3].

Blending thermoplastic starch (TPS) with high performance polyesters is one interesting approach to improving the properties of TPS [4]. Poly(butylene adipate co-terephthalate) (PBAT) is one such promising material, considering its good mechanical and barrier properties and its biodegradability [5,6]. However, as with most synthetic polymers, PBAT is hydrophobic and thermodynamically immiscible with hydrophilic starch, necessitating the use of a compatibiliser to improve the interfacial adhesion between the polymeric phases and produce blends with good morphology and improved mechanical properties [7,8].

The most important processing method for thermoplastic materials is most likely extrusion, with film blowing as a commonly used method for producing self-supporting plastic films [9]. Reactive extrusion combines the thermo-mechanical energy necessary to disrupt/melt the starch with chemical reactions in a single and continuous process without the use of solvents.

Starch can be chemically modified by reactive extrusion using various processes. Esterification with carboxylic acids, such as citric acid [10–14], formic acid [15] and ascorbic acid [16], has been studied as a way to produce more hydrophobic starch esters and to promote transesterification reactions. Taking health and safety into consideration, the use of organic acids seems advantageous because they are non-toxic and are used as additives in food products.

Tartaric acid was demonstrated to be a good compatibiliser for starch/PBAT blends [17,18]. One-step reactive extrusion was performed using tartaric acid (TA) as the compatibiliser with the objective of evaluating the structural and physical properties of starch/PBAT blends with formulations based on a constrained mixture design.

2. Experimental

2.1. Materials

Native cassava starch was supplied by Indemil (Paranavaí, Brazil), PBAT (poly(butylene adipate co-terephthalate)) by BASF (Ludwigshafen, Germany), glycerol by Dinâmica (Diadema, Brazil) and tartaric acid by Sigma-Aldrich (Steinheim, Germany).

2.2. Experimental design

With the aim of observing the effect of TA on the properties of starch/PBAT, a constrained mixture design was proposed with TA

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proportions ranging from 0 to 1.1 g.100 g^{-1}. The maximum proportion of glycerol was set to 12.0 g.100 g^{-1}, and the third component was a mixture of starch and PBAT with a 55:45 proportion between the phases. Table 1 shows the complete list of experimental conditions.

The films produced in this experiment were evaluated for their mechanical properties, opacity and weight loss in water. The results were analysed with STATISTICA 7.0 software (Statsoft, Tulsa/USA) by data modelling (Scheffé's canonical polynomial models) and the analysis of the surface contours of the mixture design.

2.3. Film production by reactive extrusion

The formulations were processed using a laboratory single-screw extruder (model EL-25, BGM, São Paulo, Brazil) with a screw diameter (D) of 25 mm, a screw length of 28D, and a barrel temperature profile of 100/120/120/120 °C. The screw speed was set to 40 rpm using a die with six 2 mm diameter holes. This first step produced pellets that were then extruded to obtain the films. The same equipment was used with a barrel temperature profile of 100/120/120/130 °C and 130 °C for the 50 mm film-blowing die, with a screw speed of 40 rpm. The film thickness (maintained between 80 and 100 μm) was controlled by controlling the roll speed and the air flow.

2.4. Film characterisation

2.4.1. Tensile test
A texture analyser model TA.XT2i (Stable Micro Systems, Surrey/ England) was used for the tensile testing of the materials. Tensile tests were performed based on the ASTM method D882-91 (1996) [19] using ten samples from each formulation and a crosshead speed of 0.8 mm/s. The tensile strength (MPa) was determined.

2.4.2. Opacity
Opacity was determined by a colorimeter (BYK Gardner-USA) at a 10° angle using illuminant D65 (day light), following the methods of Hunterlab [20]. The sample opacity was calculated as the ratio between the opacity of a sample placed under a black pattern and the opacity of a sample placed under a white pattern. The opacity results were expressed as a function of thickness using an arbitrary scale (0–1%.μm^{-1}). Opacity experiments were performed in triplicate.

2.4.3. Weight loss in water
This test was conducted according to Reddy and Yang [21], with some modifications. The samples were previously desiccated for three days in a desiccator containing anhydrous CaCl$_2$ (0% RH). After weighing, the films were immersed in distilled water at 30:1 (water: sample) for 48 h at 25 °C. The samples were then removed and dried using the same conditions. The weight of the conditioned specimen

after treatment was used to determine the % weight loss in water. The analysis was performed in triplicate.

2.4.4. Scanning electron microscopy (SEM)
A scanning electron microscope FEI model Quanta 200 (FEI Company/Tokyo, Japan) was used to observe the cryogenically fractured surfaces (under liquid nitrogen) of the blown film samples. The samples were then coated with gold using a sputter coater (BAL-TEC SCD 050). Images were taken of the fractured surface at a 1600× magnification.

2.4.5. 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.

2.4.6. Solid-state ^{13}C cross-polarisation/magic angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR)
Solid-state ^{13}C NMR spectra were obtained on a Mercury 300BB spectrometer operating at 300 MHz for carbon-13. The CPMAS conditions were as follows: spectral width: 75,000 Hz; acquisition time: 0.05 s; pulse width: 90.0°; recycle delay: 3 s; and number of transients: 712.

3. Results and discussion

3.1. Mixture design

The results of tensile strength, opacity and weight loss in water were analysed and the models were fitted to the data (Table 2). While the models of tensile strength and weight loss in water achieved a satisfactory fit ($R^2 = 0.8$), those relative to opacity must be used with caution due its low R^2 (0.6). Tartaric acid is able to act as a compatibiliser through esterification/transesterification reactions with the polymeric chains, restraining their mobility. Additionally, tartaric acid promotes acid hydrolysis of the starch chains. These two functions explain the results of the film resistance, which is mostly influenced by the positive effects of starch + PBAT/TA (β_{13}), which increases the film resistance, and of the negative effect of TA ($\beta_3 - 16.97$), which at high concentrations, causes excessive hydrolysis of the starch and decreases the tensile strength of the material. Similar results related to the mechanical properties were discussed in our previous works [17,18].

The opacity of the films was positively influenced by all components, with almost no difference observed between the effects of each component (Table 2). This result shows that the opacity increases as the concentrations of the evaluated components increase. Glycerol and starch exhibited the same behaviour in starch/chitosan films [22]. Olivato et al. [23] observed that greater concentrations of citric acid could increase the opacity of films based on starch/PBAT by acting as a compatibiliser and reducing the interfacial tension between the polymeric phases, increasing the density of the structure and thus increasing the opacity. The same effect of an increase in opacity with increasing concentration was also observed for TA (β_3) in this work.

The addition of greater proportions of TA reduces the weight loss in water of the films (negative effect of β_3). The inclusion of carboxyl groups in the starch chains and subsequent transesterification is able to improve the resistance to the dissolution of the materials, as was also shown by Reddy and Yang [21] for cross-linked starch, in accordance with the results of Table 2. Considering the hydrolytic action of TA, the interaction between starch + PBAT/TA (β_{13}) had a significant positive effect on the response. Based on these different effects, intermediate component proportions will increase the weight loss in water of the films (Fig. 1).

Table 1
Components and pseudo-components according to the constrained mixture design.

Samples[a]	Pseudo-components[b]			Components		
	x_1	x_2	x_3	Starch + PBAT g.100 g^{-1}	Glycerol g.100 g^{-1}	Tartaric acid g.100 g^{-1}
T0/G12	0.3	0.3	0.3	88.0	12.0	0.0
T1.1/G11.9	0.0	0.0	0.0	87.0	11.9	1.1
T0.5/G9.9	0.8	0.8	0.8	89.5	9.9	0.5
T0.5/G11.9	0.2	0.2	0.2	87.5	11.9	0.5
T1.1/G9.9	0.6	0.6	0.6	89.0	9.9	1.1
T0.8/G10.9	0.4	0.4	0.4	88.3	10.9	0.8

[a] T/G = levels of tartaric acid and glycerol in the formulations (g.100 g^{-1}).
[b] $x_i = c_i - a_i/1 - \Sigma a_i$ was used to calculate the pseudo-component values, where 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.