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Thermoplastic starch/polyester films: Effects of extrusion process and poly (lactic acid) addition

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ABSTRACT

Biodegradable films were produced using the blown extrusion method from blends that contained cassava thermoplastic starch (TPS), poly(butylene adipate-co-terephthalate) (PBAT) and poly(lactic acid) (PLA) with two different extrusion processes. The choice of extrusion process did not have a significant effect on the mechanical properties, water vapor permeability (WVP) or viscoelasticity of the films, but the addition of PLA decreased the elongation, blow-up ratio (BUR) and opacity and increased the elastic modulus, tensile strength and viscoelastic parameters of the films. The films with 20% PLA exhibited a lower WVP due to the hydrophobic nature of this polymer. Morphological analyses revealed the incompatibility between the polymers used.

1. Introduction

The development of biodegradable materials has received considerable interest in recent years with the primary goal of reducing the consumption of non-biodegradable petroleum-based polymers in various applications [25]. There are currently several biodegradable polymers commercially available, and they exhibit a wide range of properties and can compete with non-biodegradable polymers in different industrial fields.

Biodegradable films composed of thermoplastic starch (TPS) and poly(butylene adipate-co-terephthalate) (PBAT) with good mechanical properties and adequate water vapor barrier properties have been obtained by Bilck et al. [4], Brandelero et al. [5] and Olivato et al. [19]. PBAT is a flexible co-polyester that can fully biodegrade within a few weeks, but it is derived from petroleum.

In this context, TPS/PBAT blends with poly(lactic acid) (PLA) are a promising option because in addition to being biodegradable, both TPS and PLA are derived from renewable resources. PLA is an aliphatic and hydrophobic polyester that is produced from the polymerization of lactic acid molecules, and it has properties that are comparable to those of plastics produced from petroleum, such as polypropylene (PP) and poly(ethylene terephthalate) (PET) [9,14]. However, the high brittleness, slow crystallization, low toughness and hydrolysis properties limit the usage of PLA in the production of flexible films [25].

The production of films of blends of TPS/PLA using the blown extrusion method is difficult because PLA is rigid and brittle. In addition, the weak interfacial affinity between these polymers results in poor mechanical properties. The brittle properties of PLA can be modified by reactive extrusion using dicumyl peroxide as a radical initiator and with the addition of PBAT [12,22]. Ren et al. [21] also reported that blending the PLA/TPS blend with another flexible polymer, such as PBAT, could be a useful method for obtaining new types of materials with excellent integrated properties.

Jiang et al. [11] studied PLA/PBAT blends and observed that the blends exhibited a decreased tensile strength and modulus; however, the elongation and toughness of these blends significantly increased when PBAT was added. Coltelli et al. [7] studied the effect of adding acetyl tributyl citrate (ATBC) as a plasticizer to the PLA/PBAT blends, and they observed that the blend with 20% ATBC with respect to PLA resulted in films with strains at break that were 30% greater than the PLA/PBAT blend.

There are a few studies on the production of ternary blends of TPS, PLA and PBAT with citric acid and magnesium stearate and their use in films obtained by blown extrusion. Citric acid, naturally present in vegetables and employed in food processing, has shown interesting effect as compatibilizer on TPS/PBAT blends, improving the interaction between the polymeric phase [19]. Furthermore, there are few reports about viscoelastic characterization of the films and their correlation with extrusion process. Ren et al. [21] produced binary and

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ternary blends of TPS, PLA and PBAT using a one-step extrusion process, but they did not employed these blends in film production.

Some studies have demonstrated that the blend production method and the processing technique influence the mechanical, morphological and barrier properties of the obtained films [1,5].

The aim of this work was to evaluate the effect of the type of the extruder (single- or a twin-screw extruder) used in the preparation of the blends and the addition of PLA on the functional properties of TPS/PBAT films produced using the blown extrusion method.

2. Materials and methods

2.1. Materials

This study used PLA Ingeo 3251D (Natureworks LLC, Cargill, USA), native cassava starch (Indemil, Brazil), poly(butylene adipate-co-terephthalate) (PBAT) (BASF, Germany) under the commercial name Ecoflex®, glycerol (Dinâmica, Brazil), citric acid (Nuclear, Brazil) and magnesium stearate (Sigma, Brazil).

2.2. Preparation of pellets and films

The blends were prepared using a single- (BS) or a twin-screw extruder (BT). PLA was added at concentrations of 10%, 20% and 30% as a substitute for TPS in the blends, and in the control samples (CS and CT), PLA was not added. The samples were labeled according to the PLA content and the type of extruder used during the production of the blends (Table 1). Citric acid and magnesium stearate were used to improve the processability of the films because they act as compatibilizer and plasticizer, respectively.

In BS, the blends were processed in a pilot single-screw extruder (BGM, EL-25 model, Brazil) with screw diameter of 25 mm, screw length of 28 D, screw speed of 35 rpm and a temperature profile of 130/150/150/150 °C. In the preparation of BT, a pilot co-rotating twin-screw extruder (BGM, D-20 model, Brazil) was used with the following processing conditions: screw diameter of 20 mm, screw length of 35 D, screw speed of 100 rpm, feeder speed of 30 rpm, and a temperature profile of 100/150/150/150/150 °C. All of the extruded cylindrical profiles were pelletized and were extruded in a single-screw extruder (BGM, EL-25 model, Brazil) to produce films with the blown extrusion method under the following conditions: screw speed of 35 rpm, barrel temperature profile of 100/140/140/140 °C and a 50-mm film-blowing die. The winding speed and airflow in the matrix that formed the balloon was adjusted for each formulation to allow the formation of the balloon without tearing or cracking.

2.3. Blow-up ratio

The blow-up ratio (BUR) is the ratio between the film and the diameter of the die, and this ratio was used to express the film elongation capacity [20]. The results were expressed as the arithmetic mean values of ten random measurements.

Table 1
Composition of the films from blends processed in a single- (BS) or twin-screw (BT) extruder.

Film	PBAT (%)	*TPS (%)	PLA (%)	Citric acid (%)	Magnesium stearate (%)
CS/CT	40	59.49	0	0.01	0.5
BS-10/BT-10	40	49.49	10	0.01	0.5
BS-20/BT-20	40	39.49	20	0.01	0.5
BS-30/BT-30	40	29.49	30	0.01	0.5

*TPS = 32 g glycerol/100 g starch.
CS = control blend prepared by single-screw extruder; CT = control blend prepared by twin-screw extruder.

2.4. Mechanical properties

The tensile strength tests were performed using a texture analyzer (Stable Micro Systems, TA XTplus model, England) based on the American Society for Testing and Material standards [3]. The films were previously conditioned for 48 h at 23 ± 2 °C and 53 ± 2% relative humidity. The measured properties included the tensile strength (MPa), the elongation at break (%) and the Young's modulus (MPa). The tests were repeated ten times for each formulation.

2.5. Apparent opacity

The apparent opacity of the films were determined using a colorimeter (BYK Gardner, USA) with an illuminant D_{65} (day light) and a visual angle of 10°. The apparent opacity (Y_{ap}) was calculated according to Eq. (1), which is based on the film luminosity (L^*—CIELab system).

$$Y_{ap} = [(L*_B/L*_w)/\varphi] \times 100 \quad (1)$$

Y_{ap} apparent opacity (% μm^{-1})
L^*_B L^* measured against a black background
L^*_w L^* measured against a white background
φ film thickness (μm)

2.6. Water vapor permeability (WVP)

The water vapor permeability (WVP) of the films was determined gravimetrically, according to the American Society for Testing and Material Standards [2], under a relative humidity gradient of 33–64%. The tests were performed in duplicate.

2.7. Moisture sorption isotherm

The moisture sorption isotherms of the films were obtained using the static gravimetric method, and saturated saline solutions were used to create different relative humidities. The GAB (Guggenheim–Anderson–de Boer) model (Eq. (2)) was used to fit the experimental data. In this equation, the parameter X_w is the equilibrium moisture content (g water/g dry solid) at a water activity (a_w), m_o is the monolayer water content, C, is the Guggenheim constant, which represents the sorption heat of the first layer, and k is the sorption heat of the multilayer. The parameters of the GAB model were determined using non-linear regression with the Statistica 7.0 software (Stat-Soft, Tulsa, OK, USA).

$$X_w = m_o C k a_w/(1-k a_w)(1-k a_w + C k a_w) \quad (2)$$

2.8. Stress relaxation test and viscoelastic properties

The stress relaxation test was performed using a texture analyzer (Stable Micro Systems, TA XTplus model, England), and the test samples (25 mm × 130 mm) were conditioned for 48 h at 23 ± 2 °C and 53 ± 2% relative humidity. The initial distance between the grips was 100 mm, and the films were stretched at 0.8 mm/s until 1% deformation was achieved, which was maintained for 60 s. The force required to maintain the deformation was measured at intervals of 0.04 s. This deformation value was selected to ensure that the behavior of the material remained in the linear viscoelastic region.

Linear viscoelastic models for the static relaxation test are generally developed from two elements, a spring and a hydraulic dashpot. The