Industrial Crops & Products 112 (2018) 481–487

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Biodegradable trays of thermoplastic starch/poly (lactic acid) coated with beeswax

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ARTICLE INFO

Keywords:
Biodegradable material
Extrusion
Coating

ABSTRACT

Biodegradable trays of thermoplastic starch (TPS)/poly (lactic acid) (PLA) blends were produced by flat extrusion, calendering, and thermopressing. The trays were coated by immersion in beeswax (BW) emulsion (1, 2, and 3 g BW/100 g ethyl alcohol + Tween 80 solution) to improve their barrier properties. The trays coated with 1% BW had the higher tensile strength (11.5 ± 1.0 MPa), and the lower solubilization capacity in water (22.8 ± 0.8%) and trays coated with higher BW content emulsion decreased their tensile strength, stiffness, and water vapor permeability (from 7.9 to 0.2 × 10^{-11} g/m.s.Pa). It was possible to produce TPS/PLA biodegradable trays by flat extrusion, calendering and thermopressing, with adequate mechanical properties and processability to be produced in large scale. The coating with beeswax is an interesting technique for reducing the water vapor permeability of hygroscopic biodegradable materials.

1. Introduction

Ecological concern and the difficulty to recycle packaging materials has promoted the development of biodegradable materials (Brandelero et al., 2010; Olivato et al., 2013a; Reis et al., 2014; Shirai et al., 2013a; Zanela et al., 2015). The high cost of the commercial biodegradable polymers such as poly (lactic acid) (PLA) compared to the conventional ones like low-density polyethylene (LDPE), and polypropylene (PP) is an obstacle to their popularization. Thermoplastic starch (TPS) materials are biodegradable and have relatively low cost, but they have some limitations as deficient mechanical properties and high hygroscopicity. An alternative to producing biodegradable materials with low cost and adequate mechanical and barrier properties is to blend TPS with biodegradable polyesters (as PLA) (Li and Huneault, 2007; Martin and Avérous, 2001; Ren et al., 2009; Shirai et al., 2015). PLA is an aliphatic, biodegradable, and hydrophobic polyester with a high molar mass (> 100 kDa) produced by the polymerization of lactic acid molecules (Auras et al., 2004; Martin and Avérous, 2001).

The beeswax coating can reduce the hygroscopicity of starch-based materials due to its hydrophobic characteristics and it is compatible for use in pharmaceutical, cosmetic and food contact applications (Cuq et al., 1995; Fabra et al., 2008; Martínez-Abad et al., 2014; Polat et al., 2013; Velickova et al., 2013). Beeswax is a natural wax composed of a mixture of esters (67 wt%) hydrocarbons (14 wt%), fatty acids (12 wt %), alcohol (1 wt%) and others (6 wt%) (Bonvehi and Bermejo, 2012; Polat et al., 2013; Tulloch, 1980).

Lipid coatings are good moisture barrier but exhibit some disadvantages such as brittleness, and lack of homogeneity (Khawaldia et al., 2010). According to Zhang et al. (2014), the use of lipids coating is an effective barrier to water vapor, but it can reduce the mechanical strength of the materials. Cuq et al. (1995) reported that the addition of beeswax in wheat protein films reduced their water vapor permeability from 69.7 to 0.0230 × 10^{-12} mol mm^{-2} s^{-1} Pa^{-1}.

The goal of this study was to produce TPS/PLA biodegradable trays coated with beeswax emulsion with adequate mechanical and barrier properties, and processability.

2. Experimental

2.1. Materials

The trays were produced with native cassava starch (17 g.100 g^{-1} amylose, 11 g.100 g^{-1} moisture) (Tereos Syral do Brasil, Brazil), glycerol (Dinamica, Brazil), and poly (lactic acid) (PLA) (Ingeo 4043D, NatureWorks LLC, Cargill, USA). According to the manufacturer, PLA Ingeo 4043D is a semi-crystalline polymer with glass transition

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https://doi.org/10.1016/j.indcrop.2017.12.045
Received 15 December 2016; Received in revised form 8 November 2017; Accepted 17 December 2017

temperature of 55–60 °C, peak melt temperature of 145–170 °C, molecular weight of ~150 kDa, and adequate characteristics to produce films and sheets by extrusion.

The coating was produced with beeswax (BW), courtesy of APOMEL (Associação dos produtores de mel de Ortigueira – PR, Brazil), ethyl alcohol P.A. (Exodo Cientifica, Brazil) and Tween 80 (CAAL, Brazil).

2.2. Trays production

The ingredients (52.5 g.100 g^{-1} starch, 17.5 g.100 g^{-1} glycerol, and 30 g.100 g^{-1} PLA) were manually mixed, and extruded in a pilot single-screw extruder (BGM, EL-25 model, Brazil) to produce pellets. The extruder had a screw diameter (D) of 25 mm, screw length (L) of 750 mm (L/D ratio of 30), five heating zones and a matrix six 2-mm holes, and the barrel temperature profile was set at 90/180/180/140 °C with a screw speed of 30 rpm.

The pellets produced in the previous step were extruded in a pilot co-rotating twin-screw extruder (BGM, D-20 model, Brazil) with a screw diameter of 20 mm and L/D ratio 34, five heating zones, flat-die slot gap of 1.74 mm coupled with a calender (AX Plásticos, Brazil) to produce biodegradable sheets. The calender roll speed was set for each formulation to ensure continuous and cohesive sheets, with homogeneous thickness. The temperature profile was set at 90/170/170/170/170 °C, and the screw speed maintained at 100 rpm.

The sheets were thermopressed in a hydraulic thermo press machine (JOMAQ, Brazil) to produce the trays (82 × 70 × 23 mm). The sheets were placed in the heated mold (100 °C/100 bar), and after 2 min, the trays were then mold released.

2.3. Coating

The trays were coated with beeswax (BW) emulsion prepared according to Velickova et al. (2013), with some modifications. The BW was melted in a water bath at 65 °C and then mixed with ethyl alcohol and Tween 80 (25% w/w to the wax content). The emulsion was produced with 1, 2 and 3 g wax/100 g solution. The trays were coated by immersion in BW emulsion for 3 s and then dried at room temperature for 7 days.

The formulations were coded as BC*X*, where *X* corresponds to the concentration of beeswax in the coating emulsion.

2.4. Characterization of the trays

2.4.1. Thickness and density

The trays thickness was measured with a micrometer (± 0.001 mm) (Digimess, Brazil) at fifteen different points. To determine the trays density, three samples from each formulation with 20 mm x 20 mm were kept in a desiccator with anhydrous calcium chloride (~0% RH) for 20 days and then weighed, according to the procedure described by Müller et al. (2011).

2.4.2. Mechanical properties

Tensile tests were performed according to ASTM method D-882-02 (2002) using a texture analyzer (model TA.XT2i Stable Micro Systems, England). Ten specimens from each formulation were cut along the longitudinal direction (70 mm in length and 7 mm in width). Before testing, the specimens were conditioned at 23 ± 2 °C and 53 ± 2% relative humidity (RH) for 72 h. The crosshead speed was set at 0.8 mm/s, and the initial distance between the grips was 50 mm. The properties measured were: tensile strength (MPa), elongation at break (%) and Young's modulus (MPa).

2.4.3. Solubilization capacity in water (SCW)

Specimens were conditioned for three days in a desiccator containing anhydrous $CaCl_2$ (~0% RH). Then, the specimens were weighed, immersed in distilled water (30:1 water/sample w/w) for 48 h at 25 °C, and dried at 105 °C for 4 h. The weight of the specimen after drying was used to calculate the% of mass solubilized in water (SCW). The tests were conducted in triplicate.

2.4.4. Water vapor permeability (WVP)

The water vapor permeability (WVP) of the trays was determined gravimetrically according to the ASTM E-96-00 (2000) under a relative humidity gradient of 33–64%. The tests were conducted in duplicate.

2.4.5. Sorption isotherms

The moisture sorption isotherms of the trays were determined through the static method, using saturated saline solutions (Bell and Labuza, 2000). The Guggenheim-Anderson-de Boer (GAB) model (Eq. (1)) was used to fit the experimental data, where the *M* parameter is the equilibrium moisture content (g water/100 g dry solids) at a given water activity (a_w), m_0 is the monolayer water content, and *C* and *K* are GAB constants. The GAB model parameters were determined by non-linear regression using the Origin 8.0 software (OriginLab, EUA). These tests were performed in triplicate.

$$M = \frac{m_0.C.K.a_w}{(1\text{-}K.a_w)(1\text{-}K.a_w + C.K.a_w)} \quad (1)$$

2.4.6. Thermogravimetric analysis (TGA)

The thermal stability of the materials was determined by TGA using a gravimetric thermal analyzer of high resolution (TGA 50, Shimadzu, Japan). The samples were heated from 25 °C to 600 °C at 10 °C/min under nitrogen flow (100 mL/min). DTG curves were obtained using the Software Origin 8.0 (OriginLab, EUA), to verify the maximum degradation temperatures.

2.4.7. Scanning electron microscopy (SEM)

The microstructure of the trays was analyzed with a scanning electron microscope (FEI, Quanta 200, USA). The trays were fractured after being immersed in liquid nitrogen and gold-coated using a Sputter Coater (BAL-TEC, SCD-050, USA). All the trays were examined using an accelerating voltage of 30 kV.

2.4.8. X-ray diffraction (XRD)

X-ray patterns of the samples were obtained using an XPert PRO (Panalytical, Philips, Netherlands) machine with Cu (kα) radiation (λ = 1.5406 Å) operating at room temperature, 50 mA and 40 kV. The scanned 2θ region ranged from 2.0° to 60.0° with a step size of 0.01° and dwell time of 4.0 s. The relative crystallinity index (CI) was estimated from the relative areas of crystalline and amorphous regions (Köksel et al., 1993; Müller et al., 2011).

2.4.9. Statistical analysis

The data were analyzed using STATISTICA 8.0 software (StatSoft, Oklahoma), with analysis of variance (ANOVA) and Tukey's test at a 5% significance level.

3. Results and discussion

3.1. Trays production

All the trays produced were flexible and easy to handle (Fig. 1), however with higher beeswax content in the coating (2 wt% and 3 wt %), they were more sticky when compared to BC0 (control) and BC1 (1 wt% BW) trays.

3.2. Mechanical properties, thickness, and density

Table 1 presents the results of mechanical properties, thickness, and density of the trays. The BC1 tray had the higher tensile strength (11.5 ± 1.0 MPa), probably because of the better adherence of the