



Characterization of coated biodegradable trays by spectroscopic techniques

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ABSTRACT

Biodegradable trays of thermoplastic starch (TPS)/poly (lactic acid) (PLA) blends were produced by flat extrusion followed by thermopressing. The trays were coated by immersion in beeswax (BW) emulsion (1, 2, and 3 g BW/100 g ethyl alcohol + Tween 80 solution). The structural properties of the coated trays were characterized by Confocal Raman and Infrared spectroscopies to verify the coating-tray and TPS-PLA interactions. The characterization of the TPS/PLA biodegradable trays revealed that despite the low compatibility between starch (hydrophilic) and PLA (hydrophobic) there was interaction by hydrogen bonding between the starch and PLA carbonyl group, characterizing them as an immiscible blend. The BW showed weak interaction with PLA, but this interaction was sufficient to provide a good adhesion of the BW on the surface of the trays, reducing their hygroscopicity and enabling a commercial scale production of this biodegradable trays type.

1. Introduction

Starch-based trays are interesting due to their biodegradability and low cost, but they are highly hygroscopic and hydrophilic because of the thermoplastic starch (TPS) (Avérous et al., 2001; Huneault and Li, 2012). An alternative is to blend TPS with poly (lactic acid) (PLA) to produce less hygroscopic/hydrophilic materials and increased mechanical properties (Martin and Avérous, 2001; Ohkita and Lee, 2006; Shirai et al., 2013; Shirai et al., 2015; Soares et al., 2014; Teixeira et al., 2012; Wang et al., 2008; Xiong et al., 2013). Coating trays with food-grade waxes is also an option, such as beeswax (BW), which comprises a mixtures of esters (67 wt%), hydrocarbons (14 wt%), fatty acids (12 wt %), alcohols (1 wt%) and others (6 wt%) (Bonvehi and Bermejo, 2012; Polat et al., 2013; Tulloch, 1980) and has been studied by several researches (Cuq et al., 1995; Fabra et al., 2008; Martínez-Abad et al., 2014; Polat et al., 2013; Velickova et al., 2013).

The coating when applied on the trays surface can migrate, and to verify if the tray components are interacting among them and/or with the coating, the infrared spectroscopy techniques (IR) can be used, because they are able to identify and elucidate the structure of organic substances (Lopes and Fascio, 2004).

Another technique used to characterize materials is the Raman spectroscopy, a non-destructive, fast analysis technique that requires only small sample volumes and nearly no interference of water occurs (Edwards et al., 1996; Gelder et al., 2007; Kizil et al., 2002; Nawrocka

and Lamorska, 2013; Vano-Herrera et al., 2015). Moreover, bands in Raman spectra are well resolved compared to similar spectroscopic techniques, such as infrared spectroscopy (Gelder et al., 2007).

In Raman technique with the aid of Confocal microscopy the Raman images of the trays are obtained, showing the distribution of starch, PLA and beeswax, and it is possible to identify the coating layer at the interface of the tray.

There are several techniques for the characterization of polymers, in this study the biodegradable trays were characterized in terms of their structural properties. The goal of this study was to characterize the components of biodegradable trays coated with beeswax and the interactions between them through Infrared and Confocal Raman spectroscopies.

2. Experimental

2.1. Materials

The trays were produced with native cassava starch (17% wt amylose, 11% wt moisture) (Tereos Syral do Brasil, Brazil), poly (lactic acid) (PLA) (Ingeo 4043D, Nature Works LLC, Cargill, USA) and glycerol (Dinâmica, Brazil).

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

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2.2. Trays production

Blends of 52.5g.100g⁻¹ starch, 17.5g.100g⁻¹ glycerol, and 30g.100g⁻¹ PLA were manually mixed and then extruded to produce pellets. The extrusion was carried out in a pilot single-screw extruder (BGM, EL-25 model, Brazil), with 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. The barrel temperature profile was set at 90/180/180/140 °C with screw speed of 30 rpm.

The pellets were extruded to produce sheets 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 of 1.74 mm, and coupled with a three-rolls calender (AX Plásticos, Brazil). The temperature profile was set at 90/170/170/170/170 °C and the screw speed at 100 rpm.

The sheets were thermopressed in a hydraulic press (JOMAO, Brazil) to produce trays. The hydraulic press had electric heating system, PID controller and it was equipped with a tray-shape mold (82 × 70 × 23 mm) plated with PTFE. The sheets were pressed in the mold (100 °C/2 min/100 bar), and demolded.

2.3. Coating

The trays were coated with 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 solution for 3 s and then dried at room temperature for 7 days.

The samples were coded as BCX, where X corresponds to the concentration of beeswax in the coating solution.

2.4. Characterization of the trays

2.4.1. Confocal Raman spectroscopy

Raman spectra of samples was recorded on a WITec Confocal Raman Microscope System alpha300+. The excitation wavelengths were at 532 and 785 nm. The Raman images were obtained with the aid of the confocal microscope using an objective Zeiss EC 100x of field, numerical aperture (NA) of 0.90, working distance (WD) of 0.31 mm; in different thicknesses of the sample and associated with the Raman spectra.

2.4.2. Fourier transform infrared spectroscopy (FT-IR)

The samples were dried in a desiccator containing anhydrous calcium chloride (CaCl₂) prior to the analyses. The Fourier transform infrared (FT-IR) spectra were obtained with a FT-IR spectrophotometer (IRPrestige-21, Shimadzu, Japan) through KBr pellets. The analyses were performed on the Fourier transform mid-infrared zone with wavenumbers ranging from 4000 to 400 cm⁻¹ and a spectral resolution of 2 cm⁻¹. Thirty-two scans were performed on each sample.

3. Results and discussion

3.1. Confocal Raman spectroscopy

Fig. 1 shows the Raman spectra of solid samples of the beeswax, PLA and starch. The spectra of the solid materials were used to check the nature of the material, based on the characteristic frequencies, and for the beeswax (Fig. 1a) the frequencies at 1463, 1441, 1419 and 1296 cm⁻¹ correspond to the CH₂ deformations and the band at 1173 cm⁻¹ is due to the C–C stretching (Edwards et al., 1996; Zimnicka and Hacura, 2006). The band of several esters of acetic acid, sulfonic acid, which are the main components of beeswax, was verified

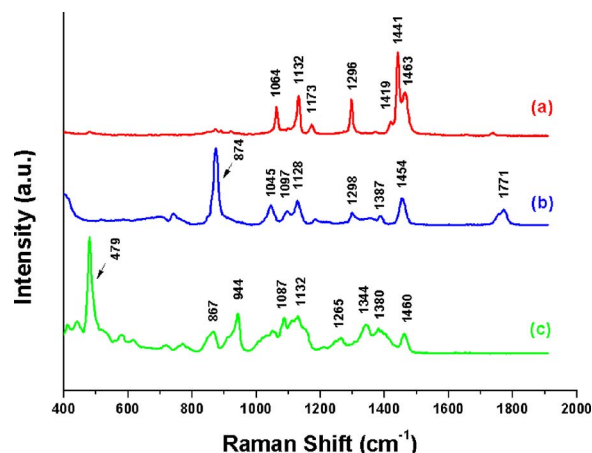


Fig. 1. Raman spectra of beeswax (a), PLA (b) and starch (c).

at 1132 cm⁻¹, which corresponds to the C–O–C and C–C stretching mode. The band at 1064 cm⁻¹ is relative to the Si–O stretching due presence of the silicon compounds (Zimnicka and Hacura, 2006).

In the Raman spectrum of PLA (Fig. 1b), the band associated with stretching of the carbonyl group (C=O) was observed at 1771 cm⁻¹. The bands at 1454 and 1387 cm⁻¹ correspond to the CH₃ asymmetric and symmetric deformations mode, respectively (Jarmelo et al., 2012; Vano-Herrera et al., 2015). The C–H deformation showed band at 1298 cm⁻¹, CH₃ rocking modes at 1128 cm⁻¹, C–O–C bond stretching at 1097 cm⁻¹ and the stretching vibration of the C–C at 1045 cm⁻¹. The C–COO stretching was responsible for the very strong band at 874 cm⁻¹ and has been assigned to semicrystalline and amorphous polymers (Auras et al., 2010; Jarmelo et al., 2012; Vano-Herrera et al., 2015).

In Fig. 1c the Raman frequencies between 800 and 1500 cm⁻¹ are characteristic of polysaccharides (amylose, amylopectin, and starch) and mainly originate from the vibrational state of its monomer glucose unit (Kizil et al., 2002). The Raman band at 479 cm⁻¹ is attributed to the vibrations of the pyranose ring in the glucose unit of starch. The band at 867 cm⁻¹ is assigned to the C(1)-H and CH₂ deformation, and the 944 cm⁻¹ band is related to the skeletal modes vibrations of α-1,4 (C–O–C) glycosidic bonds. Raman band at 1087 cm⁻¹ could be attributed to the C–O–H deformation, the band at 1132 cm⁻¹ was attributed to the contribution of two main vibrational modes: C–O stretching and C–O–H deformation and at 1265 cm⁻¹ to the side chain related CH₂OH, that is characteristic of the V-form amylose. The band at 1344 cm⁻¹ is due to C–H deformation and the bands at 1380 and 1460 cm⁻¹ were attributed to CH₂ deformation (Kizil et al., 2002; Wang et al., 2015).

Fig. 2 shows the Raman spectra of the surface BC0 tray, with a highlight at the region around 1770 cm⁻¹ (insert b) and a highlight at the same region of the PLA Raman spectra (insert a).

No significant variations were observed in the starch bands, at 483, 942, 1085, 1133, 1340 and 1389 cm⁻¹, and at 875, 1045, 1296, 1458 and 1775 cm⁻¹, relative to PLA. However, as can be seen in the highlight of the region around 1770 cm⁻¹ (Fig. 2 – insert a), the band referring to the C=O stretch of the PLA presents three distinct bands in 1756, 1771 and 1779 cm⁻¹, that suffer displacement and variation of the same relative intensity in the spectrum BC0 sample, where two well-defined bands were observed in 1766 and 1778 cm⁻¹ (Fig. 2 – insert b).

Observing the structure of these compounds, it can be considered weak hydrogen bonds interaction between the starch groups and carbonyl of the PLA.

Fig. 3 shows the Raman spectra of the BC1 tray at different points, depending on the thickness of the sample. The image was obtained simultaneously with the Raman spectra and the characteristic spectral

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