Food Packaging and Shelf Life 18 (2018) 37–41

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

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

Coffee-cocoa additives for bio-based antioxidant packaging

Pricila Veiga-Santos[a,*], Luciana T. Silva[b], Carolina O. de Souza[b], Jaff R. da Silva[b], Elaine C.C. Albuquerque[b], Janice I. Druzian[b]

[a] São Paulo State University-UNESP, FCA, 18603-970, Botucatu, Brazil
[b] UFBA-Faculty of Pharmacy, Salvador, BA, 40171-970, Brazil

ARTICLE INFO

Keywords:
Oxidation
Intelligent
Packaging
Eco-friendly
Biodegradable polymers

ABSTRACT

Coffee and cocoa antioxidant capacity is well known, and besides its health benefits, great acceptance and availability; there is few information about their utilization, especially simultaneously, as antioxidant packaging additives. The antioxidant capacity of a coffee-cocoa-cassava starch polymer was evaluated *in-vitro* (through DPPH scavenging %, flavonoid and total phenolic content) and *in-vivo* (by packaging palm oil and monitoring its oxidation during a 45-days storage at 63%RH/30 °C). *In-vivo* investigations indicated a protective effect up to 6.09 times against peroxide index increase, up to 60.4 times against hexanal production, and up to 6.88 times against conjugated dienoic acid production, compared to a commercial polymer. Simultaneous utilization of the additives presented a synergistic antioxidant effect. Additives negatively affected films mechanical properties and homogeneity, but presented a decreased water vapor permeability and dark pigmentation that could help avoiding the catalytic oxidationn effect of water and light.

1. Introduction

Oxidation, especially on high fat content foods, is one of the most important degradation reaction, compromising its quality and shelf life (Louli, Ragoussis, & Magoulas, 2004; Nerín, Tovar, & Salafranca, 2008) and developing harmful compounds (Estévez, Li, Soladoye, & Van-Hecke, 2017). Antioxidant packaging polymers appears as a safe and efficient alternative (Lin, Abdel-Samie, & Cui, 2018; Tian, Decker, & Goddard, 2013). Because synthetic antioxidants may have a toxicological long-terms effects potential (Louli et al., 2004; Nerín et al., 2008), there is an attempt of substituting them for natural and renewable antioxidants (Adilah, Jamilah, Noranizan, & Hanani, 2018; Masek, Latos, Piotrowska, & Zaborski, 2018) additives.

Coffee (*Coffea arabica* L.*)* and cocoa (*Theobroma cocoa* L.*)* are rich sources of polyphenols and flavonoids, with antioxidant capacity (Kwak, Ji, & Jeong, 2017; Martín & Ramos, 2016; Żyżelewicz et al., 2016), potential health benefit; preventing cardiovascular, cancer, diabetes, obesity, and neurodegenerative diseases (Martín & Ramos, 2017; Martinez-Saez & del Castillo, 2018) and great acceptance among consumers (Moreira et al., 2018). Recently, Çelik and Gökmen (2018) have observed that simultaneous use of cocoa and coffee can result in bound antioxidants instead of free antioxidants, which could result in an improved synergistic antioxidant effect. Besides all this potential, great availability and the recognition of being safe for food contact, only few works have applied coffee and cocoa (Cacciotti, Mori, Cherubini, & Nanni, 2018; Calatayud et al., 2013) into packaging materials, and the simultaneous effect of coffee and cocoa in active packaging is unknown. For this matter, this work have investigated the simultaneous use of coffee extract and cocoa powder as antioxidant additives for cassava starch bio-based packaging, following a central composite experimental design.

Polymers antioxidant capacity were evaluated *in-vitro,* through coffee and cocoa 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging %, flavonoid concentration and total phenolic content. Palm oil was packed with the coffee-cocoa films and the increase in oxidation compounds (peroxide index, hexanal and conjugated dienoic acid) during a 45-days of accelerated storage (63%RH/30 °C), have indicated polymers *in-vivo* antioxidant capacity. Palm oil packed with cassava starch films (without the antioxidant compounds) (C1), with low-density polyethylene-LDPE films (C2), and without any packaging (C3), served as controls.

2. Material and methods

2.1. Materials

Cassava starch (amylose – 23.5% and amylopectin – 64,2%), defatted ground cocoa beans (donated by Cargill Agrícola SA, Brazil),

* Corresponding author.
E-mail address: priveiga@fca.unesp.br (P. Veiga-Santos).

https://doi.org/10.1016/j.fpsl.2018.08.005
Received 4 January 2018; Received in revised form 3 August 2018; Accepted 9 August 2018

medium roasting arabica ground coffee (Mellita®, purchased at Brazilian local market), industrialized palm oil (donated by Odelsa SA, Brazil), commercial sucrose and inverted sugar (60% inversion) (donated by Açúcar Guarani SA, Brazil) and low-density polyethylene (LDPE) films (PolyPlastic®, 0.120 mm thickness-purchased at Brazilian local market).

2.2. Coffee extract

Coffee powder (0–2.0 %) were extracted with hot deionized water (90 °C) for optimal extraction and preservation of its antioxidant compounds (Famá et al., 2006) and then filtered through Whatman No.1 filter paper.

2.3. Active packaging film preparation

Cassava starch (4%), plasticizers (0.7% sucrose and 1.4% inverted sugar) and cocoa powder (0-0.46%) were directly dissolved in the coffee extract (0–2.0%) in combinations according to a 2^2 factorial central composite design.

Dispersions were heated (70 °C), degassed for 30 min. in ultrasonic bath to remove the bubbles, placed in polystyrene Petri dishes (150 × 15 mm) and dehydrated at 35 °C (oven, airflow and circulation). Resulting films were stored in desiccators with a supersaturated solution of sodium chloride (23 ± 2 °C; 75 ± 2% RH) for 3 days prior testing (Souza et al., 2011). The same procedure, but without any antioxidant additives, was used to produce control C1.

2.4. In-vitro antioxidation evaluation

Cocoa powder and coffee extract were investigated through their *antioxidant capacity - DPPH scavenging %* (Brand-Wiliams, Cuvelier, & Berset, 1995). Polymer samples and additives (coffee extract and cocoa powder) were also analyzed for flavonoid concentration and total phenolic content. For the polymers analysis, 100 mg samples were defatted with petroleum ether, extracted with 10 mL of distilled water and shaken for five minutes in vortex. Samples were centrifuged in a conical flask refrigerated centrifuge (5 °C, 4400 rpm, for 3 min), and the supernatant was used as the final sample. For *flavonoid* concentration (FC) 1 mL of the final sample was added to a 10 mL volumetric flask containing 4 mL of distilled water. 0.3 mL of 5% sodium nitrite solution was added to the volumetric flask, and after 5 min; 0.3 mL of 10% aluminum chloride was added. One minute later, 2 mL of 1 M sodium hydroxide was added, volume completed with distilled water and absorbance was read at 510 nm A standard curve was prepared with dilutions of epicathechin standard (Lee, Kim, Lee, & Lee, 2003). *Total phenolic content* (PC) were determined using Folin- Ciocalteu reagent as describe by Swain and Hillis (1959). 0.5 mL of the final sample was pipette onto a glass tube, and 2.5 mL with addition of Folin-Ciocalteu reagent. After 3 min, 2 mL of sodium carbonate (7.5%) were added, mixture, heated (50 °C/5 min) and immediately frozen to stop the reaction. A gallic acid standard curve was used and absorbance was read at 760 nm.

2.5. In-vivo antioxidation evaluation

Rectangle shaped (10 × 4 cm^2) cocoa-coffee film samples were folded as an envelope and sealed (Sealer SULPACK Basic SM BL 350, Brazil) at the bottom and sides, slightly humidifying the borders before sealing for a thermoplastic closure (Fig. 1). A 10 mL volumetric pipette transferred palm oil into this envelope and finally its upper side were also sealed to simulate samples antioxidation protection during a real packed product shelf life (0, 7, 15, 30 and 45 days), in accelerated storage (63%RH, 30 °C) conditions. Storage and analyses were performed in a dark room to avoid interference of light. Controls were given by packing palm oil with a cassava starch film (without antioxidants) (Control 1 - C1), with low density polyethylene films (Control 2 - C2) and without any packages - placed in a Petri dish - (Control 3 - C3).

Fig. 1. Sealed samples packing palm oil for in-vivo shelf life evaluation (F4: maximum coffee and cocoa, F5: no cocoa, F7: no coffee and F8: maximum coffee).

The packed oil oxidation during storage was evaluated through the resulting peroxide value. Samples with better protective effect on packed products against peroxid formation were also analyzed for conjugated dienoic acid and hexanal contents. The *peroxide value* was investigated according to the Association of Official Analytical Chemists, AOAC (2001) titration procedure, for all palm oil packed samples (0, 7, 15, 30 and 45 days), in triplicate. The *conjugated dienoic acid* content was determinate by the AOCS - American Oil Chemists Society (1993) spectrophotometric procedure. 10 mL palm oil was dissolved in isooctane and absorbance was measured at 233 nm. Results were expressed in percent (%), based on reading on day 1 of storage. They were calculated according to Eq. (1), were K_0 is the absorptivity by acids equal to 0.03; A the observed absorbance at 233 nm; b the cuvette length in cm, and c, the concentration of sample in g/L of the sample used for the absorption measurement.

$$Conjugated\ dienoic\ acid\% = 0.84\left(\frac{A}{bc}\right) - Ko \quad (1)$$

Hexanal content was measured with heating (140 °C/30 min) 15 mL headspace vial of the packed palm oil (200 mL), pressurized by 2 min following a 0.5 min injection time (Amstalden, Leite, & Menezes, 2001). Separation was performed by gas chromatography (CLARUS 500, Perkin Elmer gas chromatographer fitted with a mass spectrometer (MS) coupled with a Turbomatrix Perkin Elmer Headspace) using a Wax-FFAP column (50 m × 0.20 mm × 0.2 µm) with 1.0 mL/ min helium flow. The operation parameters were as follows: Injector at 180 °C; Column oven programmed from 35 °C to 160 °C with three ramps (35 °C for 1 min, heating at 3 °C/min up to 80 °C, and at 7 °C/min up to 160 °C for 22.57 min). The mass spectrometer had an electron impact ionization and ionization energy of 70 eV. Mass spectra were collected over the mass range of m/z 50-600. Hexanal was identified by comparing the standard area retention time and mass spectra using an NIST library. The volatile constituent was quantified using a hexanal external standard (Sigma Aldrich, Saint Louis, Missouri, USA), at five different headspace vial concentrations (0.40–32.00 µg/mL) and analyzed as above. Standards peak area calibration curve was determined and expressed in µg/mL.

For comparison reasons, palm oil was packed in three different conditions: with cassava starch films (same process formation, without cocoa or coffee) (C1), with low density polyethylene LDPE films (C2) and unpacked, placed in open Petri dishes (C3).

2.6. Samples characterization

Samples *total solids* content was determined measuring weight loss of films, upon drying (105 °C) until constant weight. *Thickness* was