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Characterization of active biodegradable films based on cassava starch and natural compounds

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ABSTRACT

Biodegradable films with antimicrobial and antioxidant properties were developed from cassava starch with the addition of minimally processed pumpkin residue extract (PRE) (0 to 6%) and oregano essential oil (OEO) (0 to 2%). The films were characterized regarding their physicochemical, mechanical, barrier, and antioxidant (DPPH and TBARS) properties. The films that had the best barrier, mechanical and antioxidant properties were selected and further characterized by their optical, thermal, and antimicrobial properties. Oregano essential oil and glycerol contributed to increasing the elongation and reducing the tensile strength of the films. The films showed satisfactory antioxidant and antimicrobial activity when tested *in vitro*. From these results, two formulations were selected to test the protection against oxidation in ground beef (F8, with 4.8% PRE and 1.6% OEO and F12 with 3% PRE and 2% OEO). It was observed that adding pumpkin residue extract was important to provide opacity to the films, but it was not effective in improving the antioxidant or antimicrobial activity when compared to adding essential oregano oil. When applied to ground beef, the films protected the meat against lipid oxidation until the third day of storage.

1. Introduction

This work aims to contribute to the biodegradable packaging development, through the use of renewable sources to obtain the polymeric matrix (cassava starch) and using minimally processed (pumpkin peel) industry waste. Essential oils also can be added to produce antimicrobial packaging. Biodegradable packaging can be reducing the amount of non-biodegradable plastics and industrial waste, which are disposed of without proper reuse and has antioxidant properties.

Some researchers also target the use of by-products and food waste from which to extract bioactive compounds to be added to the film or be used as base material to produce films. Several studies show that these residues are sources of bioactive compounds with significant antioxidant activity (Galanakis, 2012; Martin-Sanchez et al., 2014; Oreopoulou & Tzia, 2007). The minimally processed-food industry generates large amounts of waste such as peels and seeds, among others. When processed, pumpkin seeds and skins are discarded, and these residues are sources of bioactive compounds such as carotenoids and phenolic compounds with relevant antioxidant activity.

Technologies to improve the food shelf life are the main motivator for further research on new packaging (Martucci, Gende, Neira, & Ruseckaite, 2015; Peighambardoust, Beigmohammadi, & Peighambardoust, 2016). In this way, active packaging offers conditions to improve safety and/or sensory properties and extend the food shelf life (Vermeiren, Devlieghere, van Beest, de Kruijf, & Debevere, 1999; Yang et al., 2016). Hence, substances with antioxidant and antimicrobial properties can be added to the polymer matrix to form active films (Muriel-Galet, Cran, Bigger, Hernández-Muñoz, & Gavara, 2015). Thus, the use of bioactive packaging is an alternative to replace the use of synthetic preservatives that may be harmful to health.

The packaging is generally made of plastic, which causes a great environmental impact. However new technologies are being developed to replace non-biodegradable plastics. Cassava starch is a raw material very common because it is a widely available and cheap biopolymer (Gutiérrez, Morales, Pérez, Tapia, & Famá, 2015; Moorthy, 2002) and, when compared to other starches, its extraction generates fewer impurities, which improves the efficiency of extraction (Auras, Arroyo, & Selke, 2009). However, for use in the production of films, starch alone does not result in suitable mechanical and barriers properties for packaging (de Moraes, Scheibe, Sereno, & Laurindo, 2013). Therefore,

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plasticizers as glycerol must be added (Auras et al., 2009). However glycerol produces hygroscopic films with high permeability to water vapor, and these properties can be improved by adding hydrophobic components such as lipids to the films (Santos et al., 2014).

Essential oils are used as natural ingredients and promote modifications in the characteristics of the films, such as improvement in the mechanical and barrier properties. In addition, they often have other beneficial properties in the development of films such as antioxidant and/or antimicrobial activity. Oregano essential oil is known for its antimicrobial, antioxidant, and anti-inflammatory properties and it is a natural alternative for food preservation (Almeida et al., 2013). Therefore, this study aimed to investigate the effect of oregano essential oil and pumpkin residue extract on antimicrobial, antioxidant, mechanical, physicochemical, barrier, structural, optical, and thermal properties of biodegradable starch films.

2. Materials and methods

2.1. Materials

Pumpkin residues (skin) obtained from minimally processed crossbred C. maxima and C. moschata var. Tetsuka Buto were donated by Degasperi Atacadista (Rio Grande do Sul, Brazil); soy lecithin (Giro Verde) and cassava starch (Yoki) were purchased at a local market (Porto Alegre, Brazil); oregano essential oil was purchased from Mundo dos Óleos (Brasília, Brazil); Glycerol was from Dinâmica (São Paulo, Brazil); **Chemicals**: 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) was purchased from Sigma-Aldrich (São Paulo, Brazil); thiobarbituric acid (TBA) from JT Baker (Brazil); trichloroacetic acid (TCA) from Neon (Brazil); butyl hydroxyl toluene (BHT) from Dinâmica (Brazil); 1,1,3,3-tetraethoxypropane (TEP) from Sigma-Aldrich (Brazil).

2.2. Proximate composition

Proximate composition (proteins, total fibers, ashes, and lipids) was analyzed in accordance with AOAC Official Methods of Analysis (AOAC, 2005). The carbohydrate content was obtained by the difference (AOAC, 2006).

2.3. Pumpkin residue extract for addition to films

Pumpkin residues were ground using a processor (Philips Walita, RI7762/91, Brazil), dried for 4 h at 60 °C in an oven with air circulation (model B5AFD, DeLeo, Brazil), vacuum-packed, and stored under refrigeration protected from light. The moisture content of the dry residue was 8.23 ± 0.02%. The extract was obtained using 5 g of the dry residue and 20 mL ethanol 100%; triturated in a Turrax dispersing instrument (Model T 25 D S1, IKA, Germany) for 10 min and centrifuged at 10,000 g (CR21GIII, Hitachi Koki Co., Japan) for 10 min at 15 °C. The antioxidant activity (DPPH scavenging method) of extracts with different concentrations of ethanol (70 to 100%) was evaluated, and the one with the best activity was at the concentration of 100%.

2.4. Film preparation

An experimental design was used to evaluate the effect of extract and glycerol concentrations in films properties, based on preliminary tests. The choice of essential oregano oil was based on a previous study by Pagno, Klug, Haas Costa, Rios, and Flores, 2016. Different concentrations (w/v) (with respect to the solution volume) of the pumpkin residue extract (PRE) (0–6%), oregano essential oil (OEO) (0 to 2%), and glycerol (GY) (0.85 to 2.55%) were used according to a central composite rotational design. Cassava starch concentration was kept at 4% (w/v). Soy lecithin was used to mix the oil with the filmogenic solution at a proportion of one-third of the amount of oil added. The films were produced by the casting technique. The additives were added according to the experimental design as shown in Table 2. The filmogenic solution was placed in acrylic plates at 0.28 g/cm^2, and the cast film was dried for about 16 h at 30 °C. Finally, the films were conditioned in a desiccator with a relative humidity of 58% for 48 h before analysis.

2.5. Film characterization

2.5.1. Film thickness measurement

The thickness of the films was measured according to Versino and Alejandra Garcia (2014), using a micrometer MDC-25, Mitutoyo Corp. Tokyo, Japan.

2.5.2. Moisture content

Moisture content was determined according to AOAC Official Methods of Analysis (AOAC, 2005).

2.5.3. Water solubility

Water solubility values were obtained following the method described by Medina Jaramillo, Gonzalez Seligra, Goyanes, Bernal, and Fama, 2015. Disks of 2 cm previously dry were submerged in 50 mL of distilled water at 25 °C for 24 h, and dried at 100 °C for 24 h to obtain the final dry weight values.

2.5.4. Mechanical properties

Tensile strength (MPa), percent elongation at break (%) and Young's Modulus (MPa) were measured using a texture analyzer (TA-XT2i, Stable Micro Systems, Surrey, UK) operating in accordance with ASTM D882-09 (ASTM, 2009). Ten strips of each film were used.

2.5.5. Water vapor permeability

Water Vapor Permeability (WVP) was determined according to ASTM E 96 (ASTM, 2001) in a desiccator (75% relative humidity).

2.5.6. Opacity and color

The opacity of cassava starch film was obtained on a UV spectrophotometer (Shimadzu UV-1800) in accordance with Santos et al. (2014). The color measurements of the films were taken using a colorimeter (CR-300, Minolta Co. Ltd., Osaka, Japan) according to Medina Jaramillo et al. (2015). For control was used a film without additives.

2.5.7. Thermal properties

Thermogravimetric analyses (TGA) of the film were evaluated using a Shimadzu device (TGA-50, Brazil). The samples were heated, using nitrogen atmosphere, from room temperature to 800 °C at a rate of 20 °C min^{-1}.

2.5.8. Film morphology

Scanning electron microscopy (SEM) was performed using a scanning electron microscope (model Jeol JSM 6060) according to with Kampeerapappun, Aht-ong, Pentrakoon, and Srikulkit, 2007. Cross sections were evaluated according to Tongdeesoontorn, Mauer, Wongruong, Sriburi, and Rachtanapun, 2012.

2.5.9. Antioxidant properties

2.5.9.1. DPPH assay. The percentage of DPPH radical-scavenging activity of the films was evaluated according to Brand-Williams, Cuvelier, and Berset, 1995 with adaptations. Film samples (0.016 g) were weighed in test tubes with screw-on caps and added to 3.9 mL of DPPH (0.06 M) methanolic solution. After 45 min reacting in the dark at 23 °C, the absorbance at 515 nm was measured with a spectrophotometer (Model UV-1800, Shimadzu, Japan).

2.5.9.2. TBARS assay. TBARs (2-thiobarbituric acid-reactive substance) analysis was performed according to Tarladgis, Watts, Younathan, and Dugan, 1960 with modifications. Ground beef (30 g)