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Active and sustainable materials from rice starch, fish protein and oregano essential oil for food packaging

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ABSTRACT

The development of blends using sustainable raw materials promises to reach superior properties compared to biodegradable materials in general, besides the low cost and environmental appealing. This study investigates the addition of oregano essential oil (OEO) in blends from rice starch/fish protein to be used as active packaging. For this purpose, rice starch was extracted from broken grains and fish protein was recovered from Withemouth Croacker (*Micropogonias furnieri*). The influence of different ratios of starch/protein was confirmed by mechanical properties, solubility, water vapor permeability, opacity and color parameters. The results showed that the ratio 50/50 of starch/protein was the most suitable for packaging materials development. It had the lower solubility (8.0%), water vapor permeability (0.18 g mm kPa^{-1} h^{-1} m^{-2}), and intermediate mechanical properties (Tensile strength 5.69 MPa, Elongation 85.5%). Morphology and thermal tests were related to the properties of the films and confirmed that the matrix was homogeneous and cohesive. The antioxidant tests confirmed the activity of the blends in inhibition of peroxidase suggesting its promising application as anti-browning packaging in fruits and vegetables. Based on the results, this research demonstrated that the use of rice starch and fish protein to form sustainable blends represents an interesting alternative for the production of active packaging and for the development of eco-friendly technologies.

1. Introduction

Conventional packaging based on petroleum is used in a wide variety of application due to its durability, mechanical and barrier properties, ease processing and low cost. However, in recent years there is an increasing concern due to environmental problems because such packaging takes hundreds of years to decompose (Debiagi et al., 2014; Sun et al., 2013). Sustainable packaging from renewable resources has been widely studied for replacement of synthetic polymers. Bioplastics is a nascent market capturing plastics market at a growth rate of 30% annually (Reddy et al., 2013). A broad spectrum of materials may be used for biodegradable polymers production, such as proteins, polysaccharides and lipids (Debiagi et al., 2014; Peelman et al., 2013).

Starch is used to develop films due to its high availability, low cost and its ability to form odorless and colorless polymer matrices with low oxygen permeability (Cano et al., 2014; Jiménez et al., 2012). Starch is the major chemical component of cereal grains, comprising approximately 90% of the dry weight of rice grain (Zhou et al., 2002). The rice industry produces a large quantity of by-products, including broken grains, which are normally used as animal feed or treated as waste products incinerated for energy purposes (Li et al., 2010; Yun et al., 2005). The use of rice by-products is feasible since the rice processing yields approximately 14% of broken grains (Dias et al., 2010). Therefore, starch extraction is an alternative to add value to broken rice grains, transforming this material into a product with increased industrial interest. One of the most interesting potential uses of starch is the production of biodegradable food packaging, contributing positively to reduce the problem of environmental pollution.

Proteins are among the most promising raw materials for biodegradable polymers development due to its ability to form three-dimensional macromolecular networks, stabilized and strengthened by hydrogen bonds, hydrophobic interactions, and disulfide bonds (Thomas et al., 2013). Fish is an important source of proteins that contains considerably higher quantity of myofibrillar proteins in comparison to land animals and play significant role in three-dimensional networks formation (Lanier et al., 2005; Shiku et al., 2004). With the decline in wild fish species abundance, better utilization is called for marine by-products and underutilized fish that is currently used for animal feed (Brenner et al., 2009).

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In line with the new technologies for food packaging, the study of the incorporation of active agents in bio-based films to improve their functional and food-protective properties plays an important role (Nur Hanani et al., 2014). Natural compounds, such as plant extracts and essential oils from herbs incorporated in packaging films is a promising way to prevent or reduce deterioration of foods caused by oxidation (López-de-Dicastillo et al., 2012). Once enzymatic browning, the reaction of enzymes (polyphenol oxidase and peroxidase) and phenolic substrates that produces darker pigments on the surface (Song et al., 2007), impacts the appearance and the consumer acceptance of fruits, it is relevant to find alternatives to minimize these oxidative reactions. Oregano essential oil is well recognized for its antioxidant and antimicrobial action (Burt, 2004) and consists in an interesting compound to incorporate in bio-based materials.

Some drawbacks of biodegradable plastics still limit their commercial application, such as poor mechanical and water barrier properties, which make them difficult to use in food packaging (Jeya Shakila et al., 2012). Different strategies have been used to overcome these limitations, including blending, cross-linking and composites with nanoparticles (Martucci and Ruseckaite, 2010). Blending materials has been related using many types of raw materials, such as whey protein and lotus rhizome starch (Sukhija et al., 2016), pea starch and peanut protein (Sun and Xiong, 2014), pectin and bitter vetch protein (Porta et al., 2016), among others. However, blending rice starch and fish proteins has not been related. The use of these raw materials is promising due to their sustainability and the low cost involved. Thus, this work was aimed to evaluate the influence of different ratios of rice starch/fish protein in blends incorporated with oregano essential oil and also verify its antioxidant activity against enzymatic browning.

2. Material and methods

2.1. Material

Broken grains produced during rice processing were provided from Arrozeira Pelotas located in Pelotas/Brazil. Whitemouth croacker (*Micropogonias furnieri*) was acquired in trade from Rio Grande/Brazil. Oregano essential oil was purchased from Quinari (Ponta Grossa, Brazil) with a refractive index of 1.3521.

2.2. Protein isolation

Whitemouth croacker protein was extracted similar to Nolsoe and Undeland (2009) through pH shifting process. Muscle of Whitemouth croacker was homogenized with distilled water in a ratio of 1:9 (muscle:water, w/v). Alkaline solubilization was performed at pH 11.0. After solubilization, the sample was centrifuged at 9000*g* for 20 min. During centrifugation, the sample was separated into three phases. The middle phase (soluble proteins) was subjected to isoelectric protein precipitation at pH 5.5 and centrifuged again at 9000*g* for 20 min. The precipitated protein was dehydrated in an air circulation oven (Quimis, Q342, Brazil). The Whitemouth croacker protein isolate was analyzed to determine the protein content in accordance to standard method 981.10 (AOAC, 2000), and a protein content of 96.7% was obtained.

2.3. Starch extraction

Rice starch from broken grains was extracted as previously described by Wang and Wang (2004). Rice flour was soaked in 0.1% NaOH at a ratio 1:2 (w/v) for 18 h, followed by blending, passage through a 63 μm screen and centrifugation at 1200*g* for 5 min. The soft-top layer was carefully removed, and the underlying starch layer was re-slurried. The starch layer was washed twice with 0.1% NaOH, followed by centrifugation. Then, the starch layer was washed with distilled water and centrifuged again. The starch was re-slurried, neutralized to pH 6.5 and centrifuged. The neutralized starch was washed twice with distilled water and dried in an air circulation oven. The amylose content was determined according to Martinez and Cuevas (1989) generating 40.8% of amylose.

2.4. Blend preparation

Blends were prepared using 3% of total solids and different proportions of starch/protein (25/75, 50/50 and 75/25). Oregano essential oil was used in concentrations of 4%, 6% and 8%. The blends were prepared by casting technique as described by Rocha et al. (2013), with some modifications. Starch and protein were homogenized in distilled water and the pH of the solution was adjusted to 11.0. Glycerol was added as a plasticizer in a concentration of 25%. The solution was heated to 80 °C and kept 20 min under mechanical agitation to form the film solution. After cooling to 35 °C, the oregano essential oil was added, and the mixture was homogenized for 10 min.

The filmogenic solutions were placed in Petri dishes (9 cm in diameter) and dried in an oven with air circulation (BIOPAR, S150BA, Brazil) at 40 °C for 12 h. After drying, the blends remained 24 h in desiccators at 25 °C with a relative humidity (RH) of 50%. A saturated calcium chloride solution was used to control the RH.

2.5. Blend characterization

2.5.1. Thickness

Blend thickness was measured with a micrometer (Insize, IP54, precision 0.001 mm) at ten different positions for each film sample. Thickness mean values were considered in the calculations of tensile strength and water vapor permeability (WVP).

2.5.2. Mechanical properties

Mechanical properties were determined using a texture analyzer (TA.XTplus, Stable Micro Systems, England) based on the ASTM D-882-02 method (ASTM, 2002). The blends were cut into 25 by 85 mm strips. The initial grip separation and cross-head speed were set at 50 mm and 1 mm/s, respectively. The tensile strength (MPa) was calculated dividing the maximum force by the initial cross-sectional area of the film. Elongation (%) was calculated dividing film elongation at break by the initial gauge length of the specimen.

2.5.3. Solubility in water

The solubility in water (%) of the blends was measured according to method described by Gontard et al. (1994), with some modifications. The samples (2 cm in diameter) were dried in an oven (DeLeo, A15E, Brazil) at 105 °C to determine the initial dry weight. The blends were immersed in 50 mL of distilled water, and the mixtures were continuously shaken (100 rpm) at 25 °C for 24 h. After immersion, the blends were dried at 105 °C to determine final dry weight. The film solubility (%) was defined as the ratio between the water-soluble solid content and initial solid dry content.

2.5.4. Water vapor permeability

The water vapor permeability was gravimetrically determined according to the ASTM Standard Method E96-00 (ASTM, 2000), with some modifications. The blends were sealed on a permeation cell containing anhydrous calcium chloride (0% RH). The cells were placed in desiccators with a saturated sodium chloride solution