Chitosan biobased and intelligent films: Monitoring pH variations

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ABSTRACT

Many factors can influence the shelf-life product, such as pH, water activity, nutrient levels available oxygen, etc. Variations in food pH could occur due to microorganism growth and chemical reactions that may impact flavour, consistency and shelf-life. The objective of this paper was to obtain and characterize the fast pH-colourimetric indicator device, applying a simple manufacturing technique, using food grade and biodegradable materials. The intelligent film was based on natural compounds as chitosan and anthocyanin (pH-colourimetric indicator). Chitosan intelligent films (C-ATH, 2.0 g/100 g) were obtained incorporating anthocyanin (1.0 g/100 g) in matrix films. Initially, a dark violet colour was observed in chitosan films dried. When immersed in different pH buffers, the colour range of the films varied from pink (in acid pH) to bluish-green (in neutral pH) and to violet (in basic pH). The water solubility and water vapour transmission rate of C-ATH were decreased to 60% and 48%, respectively, as compared to control film (CF, without indicator). The mechanical properties such as tensile strength and rigidity were maintained, and the elongation at break was reduced to 47% compared to CF. The advantages of this system were the simple manufacturing process, biodegradability and usage of natural and safe compounds.

1. Introduction

Innovative packaging with enhanced functions is constantly being studied in response to consumer demands for minimally processed foods with fewer preservatives, increase in regulatory requirements and market globalization (Yam, Takhistov, & Miltz, 2005). Intelligent packaging is a concept that detects, senses, records, traces and monitors the condition of packaged products to provide information, extend shelf-life, enhance safety, improve quality (Ahvenainen, 2003; Yam et al., 2005).

The intelligent package devices are classified as data carriers (such as barcode labels and radio frequency identification (RFID)) tags and package indicators (such as time–temperature, gas, biosensors). Indicator systems usually provide qualitative information through visual colourimetric changes. These intelligent devices may be incorporated in packaging materials or attached to the inside or outside of a package (Brody, Bugusu, Han, Sand, & McHugh, 2008).

Colour based pH indicators offer a potential use as indicators of microbial metabolites (Kerry, O'Grady, & Hogan, 2006), as a microbiological growth could induce a pH change (Smolander, 2003). Mills (2005) suggested that an ideal indicator for intelligent packaging should be inexpensive or should not require an expensive piece of analytical instrumentation. Veiga-Santos, Ditchfield, and Tadini (2011) developed a pH indicator biodegradable film based on cassava starch plasticized with sucrose and inverted sugar containing grape and spinach extracts as a pH indicator. Maciel, Yoshida, and Franco (2012) developed a prototype of a colourimetric temperature indicator for monitoring food quality using chitosan suspensions containing anthocyanin applied on card paper sheets. Kato, Yoshida, Reis, Melo, and Franco (2011) studied a colourimetric indicator of hydrogen sulfide based on chitosan matrix. Almeida, Estela, Segundo, and Cerdà (2011) proposed a membraneless gas-diffusion unit containing a pH indicator to determinate ammonium in wastewater and river water. Capel-Cuevas, Cuéllar, Orbe-Payá, Pegalajar, and Capitán-Vallvey (2011) studied different matrices containing different synthetic pH indicators to form optical pH sensor array based on neural networks.

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There is a growing interest in the development of packaging that use natural polymer, such as chitosan, due to biodegradability and ability to retard the transport of moisture, gas, flavour and lipids (Dutta, Tripathi, Mehrotra, & Dutta, 2009; Yoshida, Bastos, & Franco, 2010; Yoshida, Oliveira-Junior, & Franco, 2009).

Anthocyanins (ATH) represent a large group of natural, water-soluble, nontoxic pigments (Janik, Cozzolino, Dambergs, Cynkar, & Gishen, 2007). They are polyphenolic plant pigments, responsible for the red, blue and purple colours of many fruits, vegetables and grains (Wrolstad, 2004). ATH are most frequently o-glycosylated (usually glucosylated) at the C3-position, followed by the C5-position. Glycosylation at C-7, C-3 or C-5 is often found. The colour of ATH changes depending on the pH, co-existing colourless compounds (co-pigments, typically flavones and flavonoids), storage temperature, chemical structure, concentration, light, oxygen, solvents and the presence of enzymes, proteins and metallic ions (Castañeda-Ovando, Pacheco-Hernandez, Paez-Hernandez, Rodriguez, & Galan-Vidal, 2009; Tanaka, Sasaki, & Ohmiya, 2008).

The aim of this study was to develop a biobased and intelligent packaging material system made of natural ingredients: chitosan film containing ATH as a natural pH-colourimetric indicator. The chitosan intelligent films were characterized for water solubility, water vapour transmission rate, mechanical and thermogravimetric properties, adsorption isotherm and colour response efficiency.

2. Materials and methods

2.1. Materials

Chitosan was supplied by Primex (Iceland; degree of acetylation (DA) of 18% and molecular weight (Mw) of 238 000 g mol^{-1}), anthocyanin AC-2-12R-WS-P extracted from grapes (Christian Hansen, Brazil), acetic acid (Synth, Brazil) and sodium chloride and other salts (Synth, Brazil).

2.2. Film formation

Film suspensions were prepared by dispersing chitosan (2.0 g/100 g) in aqueous acetic acid according to Maciel et al. (2012). The stoichiometric amount of acetic acid was calculated from weight of sample, and taking into account the value of DA to achieve the protonation of the NH_2 sites (Notin et al., 2006). The suspensions were homogenized by magnetic stirring at room temperature for 60 min until complete dissolution. Then, 1.0 g/100 g of ATH was homogenized in filmogenic suspension, and 4.0 g of aliquots were poured into Petri dishes (diameter = 4 cm) and dried overnight at room temperature. The mass of the solution applied onto Petri dishes was kept constant and the total solids content per gram of dried films were 95 g/m^2 for control films (CF) and 127 g/m^2 for chitosan intelligent films (C-ATH).

2.2.1. Colour response efficiency

Colour variation was measured using a colorimeter (Chroma Meter CR 400, Konica Minolta, Japan). The colour parameters (L^*, a^*, b^*) were determined using white and black patterns. The total difference of colour (ΔE^*) was calculated according to Equation (1) (Gennadios, Weller, Hanna, & Froning, 1996):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (1)$$

where, $\Delta L^* = L^*_{standard} - L^*_{sample}$; $\Delta a^* = a^*_{standard} - a^*_{sample}$; $\Delta b^* = b^*_{standard} - b^*_{sample}$.

2.2.2. Water vapour transmission rate (WVTR)

Water vapour transmission rate (WVTR) was determined by standard gravimetric method ASTM E96/E96M (ASTM, 2012b). The films were fixed on top of test cells containing a desiccant (silica gel). These cells were weighed and placed in a chamber with controlled temperature (25 °C) and relative humidity (75% rh). After five days of incubation, WVTR was determined. There were at least five replicates per experiment.

2.2.3. Soluble matter (SM)

The percentage of water-soluble matter (SM) was determined according to the method adapted from Hosseini, Razavi, and Mousavi (2009). Samples (2.0 cm in diameter) were immersed in 50 mL of distilled water. The system was kept under slow mechanical stirring (25 °C, 24 h). The samples were removed from the solution and dried in a forced air oven (105 °C, 24 h). The determinations were carried out in at least five replicates. SM (%) was calculated as Equation (2):

$$SM(\%) = \left(\frac{\text{Initial dry weight} - \text{Final dry weight}}{\text{Initial dry weight}} \right) \times 100 \qquad (2)$$

2.2.4. Moisture content (MC)

Moisture content of films was determined measuring weight loss of films, upon drying in an oven at 110 °C for approximately 12 h, until a constant weight was reached (dry sample weight).

2.2.5. Mechanical properties

Tensile strength (TS), Young's Modulus (E) and percentage elongation at break (ε_r) were determined based on ASTM D882 (ASTM, 2012a). Films were cut into 25.4 × 100.0 mm strips and then preconditioned at 75% rh and 25 °C for 48 h. TS and E were measured with a TA.XT2 texture analyser (Stable Micro Systems, Godalming, UK). The initial grip separation was set at 50 mm, and crosshead speed, at 1 mm/s. There were at least ten replicates per experiment.

2.2.6. Sorption isotherms

Adsorption isotherms were determined according to COST 90 Project (Jowitt et al., 1983) adapted. The films were cut (squares of 1 cm) and dried over silica in a desiccator during at least 7 days. Approximately 1 g of each film was weighted and placed in hermetic chambers containing saturated salt solutions with different water activity (a_w): 0.11 (LiCl), 0.32 ($MgCl_2$), 0.52 ($MgNO_3$), 0.75 (NaCl), 0.83 (KCl), 0.89 ($BaCl_2$), 0.94 ($CuSO_4$) at temperature of 30 ± 1 °C. The initial moisture content of films was measured in triplicate on dry basis. The adsorption experiments were carried out using an incubator (BOD, Tecnal, Brazil), removing the samples at frequent intervals and weighing until they reached a constant weight (within ±5%). Equilibrium moisture content of the films was measured in triplicate. Guggenheim, Anderson and de Boer (GAB) isotherms equation (Equation (3)) was used for fitting the sorption data, describing the dry basis moisture content (X) as a function of a_w:

$$GAB\ Model: X = \frac{X_m * C * k * a_w}{(1 - k*a_w)*(1 - k*a_w + C*k*a_w)} \qquad (3)$$

where, X_m is the monolayer moisture content, C is a constant related to thermal effects and k is the GAB constant related to the properties of multilayer water molecules with respect to bulk liquid. Equations parameters were estimated by non-linear