Fabrication and physicochemical characterization of HPMC films with commercial plant extract: Influence of light and film composition

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A B S T R A C T

Betacyanins used as natural red color (NRC) are known as antioxidants. The present paper was focused on their effect on physicochemical properties of hydroxypropyl methylcellulose (HPMC) films. All the films were evaluated for their photo-aging stability on optical, mechanical, barrier, thermal and structural properties. Both, tensile strength and Young's modules of NRC composite films decreased, while elongation significantly increased compared to control films. Dynamic vapor sorption data fitted by Guggenheim–Anderson–de Boer (GAB) model showed lower values of sorption energy for NRC composite films. NRC films showed an initial decrease in oxygen permeability that was more decreased after 20 days of photo-aging. Inversely, a significant increase in water vapor permeability of films by increasing NRC was observed. The films composed of 4% NRC (v/v) showed the highest WVP and lowest oxygen permeability. HPMC films transparency decreased with NRC contents.

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1. Introduction

Face to increased health and environmental concerns replacement of synthetic chemical additives with natural edible compounds in packaging is a modern concept in the food industry. In response to this consumer requirement, bioactive films based on natural biodegradable polymers, such as structural polysaccharides, gums, proteins, lipids and their complexes (Ray & Bousmina, 2005), combined with natural antioxidants are one of the most promising technologies. Development of such bioactive films can protect food against chemical and physical damages and reduce food preservatives.

Selection of bio-polymers depends on their barrier properties like oxygen, water vapor and light because they cause adverse affect on product quality and limit shelf life (Turhan & Sahbaz, 2004). Polysaccharides are important biopolymers used to prepare edible films and coatings (Gontard, Guilbert, & Cuq, 1993; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2006; Peressini, Bravin, Lapasin, Rizzotti, & Sensidoni, 2003). Cellulose-based materials are widely used because of their biocompatibility, edibility and barrier properties. Moreover, they are non-polluting and economical materials (Vasconez, Flores, Campos, Alvarado, & Gerschenson, 2009). Use of hydroxypropyl methylcellulose is

attractive because, it is a readily available non-ionic edible plant derivative forming transparent, odorless, tasteless, oil resistant, and water soluble edible films. It has also the ability to absorb and retain the color pigments (Akhtar et al., 2010). HPMC is approved for food uses by the FDA (21 CFR 172.874) and the EU (EC, 1995); its safety in food use has been confirmed by the (ECFA) "Joint expert committee on food additives" (Burdock, 2007). Food grade HPMC is listed as suitable for use in applications falling under the provisions of the regulation as additive or polymer production aid with no specific migration limit (Annex I UE N. 10/2011). The tensile strength of HPMC films is high with medium flexibility, which makes them suitable for edible coating purposes (Brindle & Krochta, 2008).

Recently, the use of plant natural products such as fruit or vegetable extracts has gained a considerable market, not only because of their coloring potential but also the positive physiological attributes of their pigments (Frank et al., 2005). These phenolic compounds are among the most effective and abundant bioactive compounds from different fruits and vegetables, agro-industrial wastes, and by-products (Ali et al., 2008; Bonilla, Mayen, Merida, & Medina, 1999; Liu, Qiu, Ding, & Yao, 2008). Several studies on the anti-inflammatory, antioxidant and anti-radical activity of betalains (mainly betanin) from red beetroot extract (*Beta vulgaris* L.) have been published (Gentile, Tesoriere, Allegra, Livrea, & Alessio, 2004; Kanner, Harel, & Granit, 2001; Pedreño & Escribano, 2000). Anthocyanins play a role in industry as synthetic colorant replacer and have health benefits, including

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reduced risk of cancer and heart diseases (Bell & Gochenaur, 2006; Dai, Patel, & Mumper, 2007).

As opposed to mixing these phenolic compounds directly in foods, their incorporation into edible packaging is particularly encouraged since they can improve antioxidant, antimicrobial, mechanical, barrier, thermal and coloring properties of edible packaging (Akhtar et al., 2010; Bifani et al., 2007). The molecular weight and structure of these phenolic compounds show great variations and contain different numbers of hydroxyl groups capable to interact with cellulosic OH groups (Bifani et al., 2007).

The aim of this work was to investigate the effect of natural red color (NRC) addition on HPMC films properties, such as optical, mechanical, barrier, thermal and structural properties. Films and NRC stability during storage under fluorescent light were also investigated.

2. Materials and methods

2.1. Raw materials

The HPMC (Fluka-Biochemika, Japan) contained 9% of hydroxylpropoxyl and 28% of methyl radicals and had a viscosity of 15 mPa s and a water solubility of 2% at 25 °C. Ethanol 96.2% (Pharmaceutics Carlo Erba) was used to improve HPMC solubilization. Phosphorus pentoxide (P_2O_5) was purchased from Sigma–Aldrich (France). Petri-dishes (optilux) were provided by Nunclon™ Fisher (DK-4000 Roskilde, Denmark). A liquid (NRC) "Natural Red Color blend" of beetroot juice (E162) and purple carrot extract (E163) containing 20% glycerin was obtained from Color-Maker, California, USA, and used as coloring agent to investigate changes in physico-chemical properties of HPMC films.

2.2. HPMC solution making and films casting

Film forming solutions (FFS) were prepared according to Akhtar et al. (2010) by dissolving 6 g of HPMC in 35% solution of ethanol for 40 min at 65 °C using a heating magnetic stirrer (Fisher Bio-block Scientific). NRC was dissolved separately in 35% solution of ethanol at room temperature to avoid oxidation. Both, HPMC and NRC solutions were then centrifuged together at 4000 rpm for 30 min at 20 °C to obtain homogeneous solution. The pH of NRC solutions was controlled with HCl (0.1 M) and fixed at 3.2 ± 0.1. After mixing, solutions were degassed at room temperature under vacuum "Handy Aspirator WP-15 (YAMATO®)" for 30 min. Films were made by pouring 6 g of each FFS in the lids of Petri-dishes and then left to dry at 20 °C and 50% relative humidity for 48 h, in a dark room.

2.3. Film conditioning for photo-aging

Films were placed under the fluorescent light (Osram L36w/640) for 20 days in an experimental chamber with controlled conditions of temperature (20 ± 1 °C) and relative humidity (50 ± 2%). The distance from fluorescent tube to films was 14 cm.

2.4. Thickness measurement

Thickness was measured according to the standard NF Q 03-016 with a manual micrometer (Messmer, London, England) equipped with a measuring head of 1 cm in diameter and a sensitivity of 2 μm. The thickness was measured in 8 randomly selected points on each film and then an average value was calculated.

2.5. Mechanical properties

A universal testing machine Lloyd instrument (AMETEK, United Kingdom) was used to determine mechanical properties, i.e. tensile strength (TS, MPa), ultimate elongation (UE, percent at break point) and Young's modulus (YM, MPa) according to ASTM D882. Tests were performed on 6 specimens previously stored for 48 h at 50 ± 2% relative humidity (RH) in a container using magnesium nitrate saturated solution at 20 ± 1 °C. Equilibrated film samples of 6 × 2 cm were stretched at a rate of 10 mm/min until breaking. The RH and temperature of the testing environment was held at 50 ± 2% and 20 ± 2 °C, respectively. The stress–strain curves were recorded and exploited with Nexygen software.

2.6. Light transparency

UV–visible light barrier properties of films (1 cm × 3 cm) were measured using a UV–visible recording spectrophotometer (Ultro-Spec 4000 UV/visible, Pharmacia Biotech, UK) at selected wavelengths from 200 to 900 nm following the ASTM method D 1746-92 with slight modifications (Fang, Tung, Britt, Yada, & Dalgleish, 2002; Hamaguchi, Weng, & Tanaka, 2007). The transparency was calculated from Han and Floros (1997) equation:

$$\text{Transparency } (T) = -\log(T_{600}/X) \tag{1}$$

where T_{600} is the transmittance (%) at 600 nm and X is film thickness in mm. Three replicates of each treatment were tested.

2.7. Water vapor permeability

Films water vapor permeability (WVP) was determined by using a gravimetric method described in the AFNOR NFH00-030 standard (1974), at 38 °C and 90% RH gradient. The film was sealed in a permeation cell containing a desiccant (silica gel). The plastic permeation cells used had an exposed film area of 26.42 cm^2. The permeation cells were placed in a close chamber having controlled conditions of temperature, (38 °C) and RH, (90%). The water vapor transport was determined from the weight gain of the permeation cell that was determined each hour of experiment up to 10 h. At least three replicates were made for each film. WVP was calculated as follows (Khwaldia, Banon, Perez, & Desobry, 2004):

$$\text{WVTR} = \Delta M/\Delta T \times 1/A \left(\text{gh}^{-1}\text{m}^{-2}\right) \tag{2}$$

$$P = \text{WVTR}/\Delta P \times 3600 \left(\text{gs}^{-1}\text{m}^{-2}\text{Pa}^{-1}\right) \tag{3}$$

$$\text{WVP} = P \times X \left(\text{gm}^{-1}\text{s}^{-1}\text{Pa}^{-1}\right) \tag{4}$$

where (ΔM) is the weight gain of the permeation cell over time (Δt), (A) is the exposed film area, (Δp) is the differential vapor pressure across the film and (X) is the film thickness.

2.8. Oxygen permeability

Control and NRC films were conditioned under controlled relative humidity (50%) and temperature (20 °C) for one week. Gas chromatography system (Shimadzu GC-4A; Shimadzu Corp., Kyoto, Japan) was used to measure films oxygen permeability by directly injecting samples with a gas sampling syringe (Dynatec Pressure Lok, Baton Rouge, LA, USA) into a gas chromatograph equipped with a thermal conductivity detector and molecular sieve columns (Desobry & Hardy, 1997). Helium gas at flow rate of 25 mL/min was used as carrier gas and column temperature was 50 °C. Method was based on measurement of oxygen diffusing through film over time. The film was first sealed into a test cell of 26.42 cm^2 exposed area and 0.8 bar oxygen pressure gradient across the film, which was