



## High methoxyl pectin–methyl cellulose films with antioxidant activity at a functional food interface

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### ABSTRACT

The effect of using increasing proportions of methylcellulose (MC) for the development of glycerol plasticized films based on high methoxyl pectin (HMP) (30:70, 50:50 and 70:30 w/w HMP:MC) and carrying L-(+)-ascorbic acid (AA) was studied with the purpose of achieving higher stability of AA and localized antioxidant activity at food interfaces. MC and 30:70 HMP:MC systems could not be casted. The shelf-life of the other AA-active films was assessed by storage at 25 °C, constant relative humidity (RH: 33.3%, 57.7% and 75.2%) and vacuum conditions. The rate constant for AA hydrolysis increased with the RH and, hence, with water mobility. Browning and AA degradation rates were directly related. When stored at 75.2% RH, both decreased as MC proportion increased. Compared to HMP film, the highest proportion of MC (50:50 HMP:MC) showed the highest AA stabilization under vacuum and greater performance under air atmosphere. They also developed localized antioxidant activity preserving the tocopherol content of walnut oil.

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### 1. Introduction

In the past, foods were primarily recognized for their essential nutrients for normal physiological activity and function. However, during the past two decades, consumers have switched from an emphasis on satisfying hunger to an emphasis on the promising use of foods to promote well-being and help reduce the risk of disease. Nowadays, there is a consensus that eating the “right” foods extends life expectancy and improves quality of life (Agriculture, 2009). The food industry shows increasing interest in product innovation in order to satisfy consumer’s demand for high-quality and option variety of healthy products. A preference for foods with natural instead of synthetic additives is also significantly related to health concerns (Devcich et al., 2007). At the same time, preservatives used in healthier food formulations (i.e.: antimicrobial agents, antioxidants) should be used at the lowest level that assures effectiveness. A localized activity of preservatives could be a way to achieve the desired reduction of concentration and edible biopolymer films can be an effective manner of carrying additives while providing localized activity and delivery at food interfaces (De’Nobili, Pérez, Navarro, Stortz, & Rojas, 2011). Known as vitamin C, L-(+)-ascorbic acid (AA) is a natural and water soluble antioxidant also useful in food preservation. AA stability is affected by processing and storage conditions, depending on a large number of factors

such as temperature, equilibrium RH, oxygen partial pressure, light, package permeability and package configuration (Kitts, 1997). AA reacts with oxygen to produce L-dehydroascorbic acid (DHA) that also has vitamin C activity in vivo. The latter is irreversibly lost when DHA is hydrolyzed in the subsequent reaction. Furthermore, anaerobic degradation of AA through hydrolysis also occurs simultaneously to AA oxidation when oxygen is present, producing 2-keto-L-gulonic acid (Kurata and Sakurai, 1967a). On the other hand, non-enzymatic browning (NEB) also proceeds with AA concentration decay since the products of the reactions that follow the first step of AA destruction are also part of the NEB reaction chain (Rojas and Gerschenson, 2001; León and Rojas, 2007). Compartmentalization of AA into an edible film network could help achieve stabilization because it can preclude the AA interaction with oxygen, other food preservatives or nutrient components and films can provide a localized antioxidant activity at interfaces.

A high methoxyl pectin (HMP) film formulated to carry AA was previously developed, during which AA degradation and browning kinetics were studied at 25 °C under vacuum conditions ( $p = 132$  Pa) (Pérez, Flores, Marangoni, Gerschenson, & Rojas, 2009) as well as under normal air conditions ( $p = 1.013 \times 10^5$  Pa) (Pérez, 2012) in order to determine the films’ shelf-life as potentially active interfaces. Methyl cellulose (MC) is a hydrophobically modified cellulose with interesting thermogelation properties (Li, 2002), and most useful in pharmaceutical and food formulation. During film development, MC was applied using polyethylene glycol 400 as plasticizer (Debeaufort and Voilley, 1997; Turhan

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et al., 2001). The hydrophobic/hydrophilic nature of MC films has been recently studied by Innis-Samson and Sakurai (2011), showing it could be able to modify the HMP film network for better immobilization of the water sorbed, necessary to preserve AA from hydrolysis (León and Rojas, 2007). Walnut oil is a valuable functional ingredient, though highly susceptible to oxidation. The aim of the present work was to study the effect of using increasing proportions of MC (compared to those of HMP) in the edible films that were developed, especially focusing on AA stability, browning development and antioxidant activity of the edible films developed. Some aspects related of the polymeric film microstructure were also analyzed.

## 2. Experimental methods

The kinetics of AA degradation and NEB development in the films were studied under vacuum at constant temperature (25 °C) and at three RH values (33.3%, 57.7% and 75.2%) to specifically determine the hydrolytic stability of AA. The film formulation that could be casted and showed the highest AA stability (50:50 w/w HMP:MC) was then used to evaluate the effect of oxygen on the AA degradation at a RH of 57.7% and 25 °C. It was also used as an antioxidant interface for precluding walnut oil oxidation at the same environmental conditions.

### 2.1. Chemicals

The MC used was M0512 (molecular weight  $\approx$  85,000 Da; methoxy substitution  $\approx$  27.7–31.5%; degree of substitution or average number of substituent groups attached to the ring hydroxyls  $\approx$  1.5–1.9; viscosity  $\approx$  4.2 Pa s for a 2% solution in water at 20 °C) from Sigma–Aldrich (St. Louis, MO, USA). Food grade pectin with a high degree of methylation (GENU pectin type B rapid set-Z) was from CP Kelco (Denmark). Its chemical composition was determined and reported by Pérez et al. (2009). All other chemicals were of analytical grade from Merck (Argentina) and Sigma–Aldrich.

In order to evaluate the antioxidant capacity of films containing AA, walnut oil (IL Noce™, Escobar, Buenos Aires province, Argentina) was used. It was the product of the first cold pressing of *Juglans regia* L. edible seeds, whose ripened fruits were harvested in 2010 in the Argentine province of Catamarca.

### 2.2. Film making procedure

Films constituted only by MC or by 70:30, 50:50 or 30:70 (w/w) HMP:MC ratios were developed for the purpose of this study. Also, HMP film samples were made according to Pérez et al. (2009). For this trial, a 2% (w/w) total polymer concentration was used for film making solution, thus permitting to obtain plasticized films with the adequate handling resistance. This solution was continuously stirred under controlled high speed (1400 rpm-constant) using a vertical stirrer (model LH, Velp Scientifica, Italy) in order to reach homogeneous hydration. While stirring, the obtained viscous, homogeneous and transparent system was then heated up to 75 °C at a constant heating rate (5.0 °C/min) by means of a hot plate (Velp Scientifica, Italy) and with simultaneous recording of the temperature by using a thermocouple connected to a Consort millivoltmeter (P 901, Belgium). Subsequently the following substances were added: Glycerol [36.84 g per 100 g of (polymer + glycerol)] for plasticization (Yang and Paulson, 2000), potassium sorbate (0.03% w/w) as a antimicrobial agent and finally AA (0.100% w/w). The obtained hot solution was placed under vacuum for 20 s to remove air bubbles and then immediately poured onto horizontally leveled polystyrene plates. The fractionated system was dried in a forced convection oven at 60 °C. The films were

peeled from the polystyrene plates and stored in light-protected desiccators over saturated solutions of known water activity ( $a_w$ ), in order to maintain a constant relative humidity ( $a_w^\circ = \text{RH}\%/100$ ) for film equilibration. The salts used were  $\text{MgCl}_2$  ( $a_w^\circ = 0.333$ ), NaBr ( $a_w^\circ = 0.577$ ) and NaCl ( $a_w^\circ = 0.752$ ) at 25 °C (Greenspan, 1977). Equilibration was followed by the measurement of  $a_w$  of the film samples daily until attaining the final equilibrium. Afterwards, the sample thickness was measured at six different locations in each of ten specimens by using a digital micrometer (Mitutoyo, Kawasaki, Japan).

Three batches of films (replicates) were prepared as above described. The film samples obtained from each batch were identified and distributed among light-protected desiccators with different RHs (33.3%, 57.7% or 75.2%) and stored at 25 °C in order to establish the influence of the film making in the following determinations. Storage was first performed under vacuum ( $p = 132$  Pa) with controlled RH in order to ensure that AA degradation was initiated through the irreversible hydrolysis of its lactone ring as the first and limiting reaction step (León and Rojas, 2007). Hence, the specific influence of water in the AA stability could be analyzed. On the other hand, samples of the three batches of the 50:50 HMP:MC film were further stored under air ( $p = 1.013 \times 10^5$  Pa) protected from the light, at 25 °C and 57.7% RH, in order to infer the specific influence of oxygen on the total AA kinetics.

The following analyses were performed on each film sample collected from the three batches at each corresponding time and RH of interest.

### 2.3. Water activity

To evaluate film equilibration, the  $a_w$  was determined on the film samples with a Decagon AquaLab (Series 3 Water activity meter, USA) at 25 °C using a calibration curve made with the standard saturated salt solutions above mentioned.

### 2.4. Measurement of pH

This was performed on the film-forming solutions as well as on the casted films after their equilibration at the corresponding RH, as informed by De'Nobili et al. (2011).

### 2.5. Determination of L-(+)-ascorbic acid (AA)

A film sample was taken from each of the three batches obtained in order to determine the AA kinetics from the triplicates of film making. The AA concentration was determined by using the 2,6-dichlorophenolindophenol (2,6-DPIP) spectrophotometric method detailed by De'Nobili et al. (2011). The AA concentration was determined from two different aliquots (duplicate) for each film sample.

### 2.6. Color

Measurement of the film color was performed employing a Minolta colorimeter (Minolta CM-508d) using an aperture of 1.5 cm-diameter, as previously reported by De'Nobili et al. (2011). Film samples for color measurement were taken from each of the three batches of films obtained in order to determine browning (yellowness index, YI%) kinetics. Also,  $L$ ,  $a$ , and  $b$  (HunterLab) color parameters were measured, which ranged from  $L = 0$  (black) to  $L = 100$  (white) for lightness;  $-a$  (greenness) to  $+a$  (redness), and  $-b$  (blueness) to  $+b$  (yellowness). Standard values considered were those of the white background.

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