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Physical, antioxidant and antimicrobial properties of chitosan–cinnamon leaf oil films as affected by oleic acid

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ABSTRACT

The physical, antioxidant and antimicrobial properties of chitosan (CH)–cinnamon leaf essential oil (C) films, containing or not oleic acid (OA), were evaluated. The addition of OA led an increase in surface charge and particle size of the film-forming dispersions. This is in agreement with a greater CH adsorption on the droplets containing OA and the entrapment of C compounds in the non-polar core of the OA molecule associations. OA contributed to a better retention of C in the film during its drying, diminished the changes in colour parameters provoked by C addition and reduced the film transparency. Water vapour permeability of CH films was reduced by OA incorporation while it increased when they contained only C. Every film containing C showed antioxidant and antifungal properties, depending on the C content (the higher the C content, the greater the effect). OA reduced the antifungal effectiveness of C containing films in line with its encapsulating effect on C compounds. All the coatings were effective in extending the shelf-life of cold-stored strawberries, mainly when CH was combined with C at the ratio 1:0.5.

1. Introduction

Chitosan is a biopolymer that has film-forming ability and shows antimicrobial activity (No, Park, Lee, & Meyers, 2001; Tharanathan & Kittur, 2003). One of the most important drawbacks to the application of chitosan films to fresh food products is their poor water vapour barrier properties (Vargas, Sánchez-González, Chiralt, Cháfer, & González-Martínez, 2012), which can be improved by the incorporation of lipid compounds, such as oleic acid (Vargas, Pastor, Chiralt, McClements, & Gonzalez-Martinez, 2008).

Essential oils (EOs) are natural antioxidant and antimicrobial substances, extracted from vegetables. Most of them consist of a mixture of terpens, terpenoids and other aromatic and aliphatic compounds (Bakkali, Averbeck, Averbeck, & Idaomar, 2008), but their composition can vary markedly depending on the origin. Cinnamon leaf essential oil has shown not only antifungal and antibacterial properties against a broad spectrum of food spoilage microorganisms but also antioxidant activity (Singh, Maurya, de Lampasona, & Catalan, 2007). The main compound of cinnamon leaf essential oil is eugenol (70–95%), followed by cinnamaldehyde which can be present in a proportion of 1–5% (Vangalapati, Satya Prakash & Avanigadda, 2012).

The use of EOs in food preservation is often limited because of their application costs and other drawbacks, such as their intense aroma and potential toxicity. An interesting approach to reduce the doses of essential oils, while maintaining their effectiveness, could be to incorporate these compounds into the formulation of edible coatings (Sánchez-González, Vargas, González-Martínez, Chiralt, & Cháfer, 2011). In this sense, Sánchez-González, Cháfer, Chiralt, and González-Martínez (2011) developed antibacterial composite films based on chitosan and different EOs (lemon, tea tree or bergamot), which were proved to inhibit the growth of bacteria (*Escherichia coli*, *Listeria monocytogenes* and *Staphylococcus aureus*) in an *in vitro* study. Wang et al. (2011) prepared chitosan films incorporated with cinnamon, clove and anise essential oils. Cinnamon oil–chitosan films exhibited a synergistic effect, which was related to the constant release of cinnamon essential oil.

The antifungal effect of bioactive coatings prepared with chitosan and essential oils, such as peppermint and lemon, on the fungal decay of cold-stored strawberries has recently been evaluated (Perdones, Sánchez-González, Chiralt, & Vargas, 2012; Vu, Hollingsworth, Leroux, Salmieriv & Lacroix, 2011). Nevertheless, there are no published studies on the antifungal effect of chitosan–cinnamon essential oil composite coatings applied to strawberry. In addition, the studies into film development based on chitosan and cinnamon leaf oil are scarce.

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The aim of this work was to characterize the film forming dispersions and physical, antioxidant and antimicrobial properties of chitosan–cinnamon leaf essential oil films, containing or not oleic acid. The potential application of such coatings to control the fungal decay of strawberries was also evaluated.

2. Materials and methods

2.1. Reagents

High molecular weight chitosan (Batch MKBD1916V, 0.8 Pa s viscosity, at 1% w/w in 1% w/w glacial acetic acid, acetylation degree: 22%), ABTS (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt), Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and potassium persulfate was provided by Sigma–Aldrich Quimica (Madrid, Spain). Cinnamon leaf essential oil was supplied by Herbes del Moli (Alicante, Spain). Acetic acid, oleic acid and magnesium nitrate were purchased from Panreac Química, S.A. (Castellar del Vallés, Barcelona, Spain).

2.2. Preparation and characterization of the film-forming dispersions

Chitosan (CH) was dispersed at 1 wt% in an aqueous solution of acetic acid (1% v/w) and Tween 80 (0.1% w/w). After at least 8 h of magnetic stirring, chitosan solution was vacuum-filtered. Cinnamon leaf oil (C) or oleic acid (OA) or both compounds were added at different concentrations as described in Table 1. Film-forming dispersions (FFDs) were prepared by means of a rotor-stator homogenizer (Ultraturrax DI 25 basic-Yellowline, Janke & Kunkel, Staufen, Germany). After homogenization, the formulations were degassed at room temperature and at 7 mbar with a vacuum pump (Wertheim, Germany).

2.2.1. Particle size distribution, zeta potential and rheological behaviour

The particle size analysis of the FFDs was carried out by means of a laser diffractometer (Mastersizer 2000, Malvern Instruments, Worcestershire, UK). The samples were diluted in the acetic acid solution (pH = 4.8) at 2000 rpm until an obscuration rate of 10% was obtained. Mie theory was applied considering a refractive index of 1.47 and 1.50 for C and OA, respectively, and 0 absorption in both cases. Three replications per formulation were made. ζ-potential was measured in triplicate by Laser-Doppler electrophoresis performed with a Zetasizer nano-Z (Malvern Instruments, Worcestershire, UK). The electrophoretic mobility of the droplets was transformed into ζ-potential values using the Smoluchowsky model. The samples were diluted to a droplet concentration of 0.02% with an acetic acid solution (pH 4.8).

The rheological behaviour of FFDs was analysed in triplicate at 25 °C using a rotational rheometer (HAAKE Rheostress 1, Thermo Electric Corporation, Karlsruhe, Germany) with a sensor system of coaxial cylinders, type Z34DIN Ti. Samples were left to rest for 5 min before the measurements were taken. The shear stress (σ) was obtained as a function of shear rate ($\dot{\gamma}$) between 0 and 300 s^{-1}, taking 3 min for each (up and down) cycle. Experimental data were fitted to the Ostwald de Waale model (Eq. (1)) in order to determine the consistency (K) and the flow behaviour indexes (n).

$$\sigma = K \cdot \dot{\gamma}^n \quad (1)$$

Table 1
Composition of the film-forming dispersions (FFDs). CH: chitosan. OA: oleic acid. C: Cinnamon leaf essential oil. Subscripts indicate the ratio of film components.

FFDs	Chitosan (% w.b.)	Oleic acid (% w.b.)	Cinnamon leaf EO (% w.b.)	Total lipid (% w.b.)
CH_1	1	–	–	–
$CH_1:OA_{0.25}:C_{0.25}$	1	0.25	0.25	0.5
$CH_1:C_{0.5}$	1	–	0.5	0.5
$CH_1:OA_{0.5}:C_{0.5}$	1	0.5	0.5	1
$CH_1:C_1$	1	–	1	1
$CH_1:OA_1$	1	1	–	1

2.3. Preparation and characterization of the films

FFDs were casted in Teflon® plates (diameter = 15 cm), so as to keep CH amount constant in the dry films (28 g/m^2). The films were dried at room temperature and 60% relative humidity (RH) and were conditioned in desiccators with an oversaturated salt solution of magnesium nitrate at 20 °C or 5 °C. Film thickness was determined with a Palmer digital micrometer (Comecta, Barcelona, Spain) to the nearest 0.001 mm.

2.3.1. Microstructure

Microstructure was observed by SEM in cross-sectioned cryo-fractured film specimens, using a JEOL JSM-5410 (Japan) electron microscope. The films (2 samples per formulation) were equilibrated in P_2O_5 to eliminate water, cryofractured by immersion in liquid nitrogen, and then mounted on copper stubs perpendicularly to their surface. After gold coating, the images were captured using an accelerating voltage of 10 kV.

2.3.2. Optical and mechanical properties

Gloss of the films was measured with a gloss meter (Multi Gloss 268, Minolta, Germany) on their shiny side, using a black matte background and at an incidence angle of 60° (ASTM D523, 1999). Nine replicates were made per each formulation. Results were expressed as gloss units, relative to a highly polished surface of black glass standard with a value near to 100.

Colour of the films was determined through the surface reflectance spectra with a spectrocolorimeter CM-3600d (Minolta Co, Tokyo, Japan) with a 10 mm illuminated sample area. Measurements were taken from nine replicates per formulation by using both a white and a black background and Kubelka–Munk theory for multiple scattering was applied to the sample reflection spectra. Internal transmittance (Ti) was calculated from the reflectance of the sample layer backed by a known reflectance and the reflectance of the film on an ideal black background (Hutchings, 1999). Moreover, CIE-L^* a^* b^* coordinates (CIE, 1986) were obtained by the infinite reflection spectra of the samples, using D65 illuminant/10° observer in order to calculate the whiteness index (WI) of the samples (Eq. (2)).

$$WI = 100 - \left(\left(100 - L^*\right)^2 + a^{*2} + b^{*2}\right)^{0.5} \quad (2)$$

Mechanical properties were analysed by means of tensile tests (ASTM D882, 2001), to obtain the true stress (α) vs. Hencky strain (ε_H) curves. The mechanical parameters: elastic modulus (EM), tensile strength at break (TS) and elongation percentage at break (% E) were obtained. A Universal Testing Machine (TA.XT plus model, Stable Micro Systems, Haslemere, England) with a 500 N load cell was used to perform the tests. Film specimens were mounted in the film-extension grips and stretched at 50 mm min^{-1} until breakage. Nine to twelve replicates of each formulation were tested.

2.3.3. Water vapour and oxygen permeability

Water vapour permeability (WVP) was determined gravimetrically at 5 °C and 20 °C and 58–100% and 54–100%, RH gradient, using a modification of the ASTM E96-95 gravimetric method (1995) for hydrophilic films (Gennadios, Weller, & Gooding, 1994).