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Properties of film-forming dispersions and films based on chitosan containing basil or thyme essential oil

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ABSTRACT

Film-forming emulsions and films of chitosan containing basil or thyme essential oil, with and without oleic acid were characterised as to the emulsion stability (particle size, ζ-potential and rheological behaviour) and barrier, mechanical and optical properties of the films. The losses of the essential oil during the film formation were also quantified as well as the antifungal effect of the films against *Aspergillus niger*, *Botrytis cinerea* and *Rhizopus stolonifer*.

The retention of essential oil in the films was greatly dependent on the stability of the film-forming emulsion. The addition of oleic acid (OA) to the chitosan-essential oil formulations enhanced the emulsion stability and oil retention in the film, at the same time that it improved the water vapour barrier properties of the film. Lipids reduced the film stretchability but when OA was present in the formulation, this reduction was mitigated, as well as the changes in colour provoked by the essential oils, whereas OA reduced the film transparency. Chitosan films with thyme or basil essential oil did not inhibit the growth of the tested fungi.

1. Introduction

Chitosan-based films can encapsulate essential oils (EO) so that these natural compounds can be used in food preservation. In order to achieve effective antimicrobial activity, high concentrations of essential oils are generally needed. The incorporation of essential oils into edible films can be a useful strategy to improve coating functionality in terms of the enhancement of antimicrobial properties of chitosan, at the same time that the matrix hygroscopic character can be reduced. Likewise, reduction of the cost of applying EO and minimisation of their intense aroma perception could be achieved (Sánchez-González, Vargas, González-Martínez, Chiralt, & Cháfer, 2011a).

The release rate of the encapsulated essential oil from the polymer matrix could be controlled, thus enlarging its antimicrobial action on the product by both direct contact or through the head space of the packaging due to the volatile nature of these components. One way to encapsulate essential oils into the polymer matrix consists of their emulsification in the aqueous film-forming dispersions of polymer and subsequent casting and drying processes under controlled conditions. Nevertheless, previous studies have shown notable losses of the essential oils during the film formation step by casting technique (Sánchez-González, Chafer, González-Martínez, Chiralt, & Desobry, 2011b).

Solvent evaporation in the casting plate occurs overlapped with destabilisation phenomena of the film-forming emulsion: droplet flocculation, coalescence and creaming to the liquid surface. On this surface, water and essential oil components form immiscible blends, which evaporate at lower temperature than pure compounds (steam distillation process). To minimise this negative effect, the enhancing of the stabilisation factors of the initial emulsions (i.e. reduction of particle size, increase in the viscosity of the continuous phase or incorporation of emulsifiers) is key.

Thyme essential oil contains more than 60 compounds, most of them show antioxidant and antimicrobial properties against a broad spectrum of gram-negative or gram-positive bacteria (Gaysinsky, Davidson, Bruce, & Weiss, 2005; Singh, Falahee, & Adams, 2001; Baranauskiene, Venskutoni, Viskelis, & Dambrauskiene, 2003; Burt & Reinders, 2003). The most important active compounds of thyme EO are the phenols thymol, rosmarinic acid and carvacrol (Di Pasqua, Hoskins, Betts, & Mauriello, 2006; Shan, Cai, Sun, & Corke, 2005). Similarly, basil essential oil consists of more than 30 compounds; the main constituent being estragole (Baratta et al., 1998; Bozin, Mimica-Dukic, Simin, &

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Anackov, 2006; Tampieri et al., 2005). Basil EO has been proven to exhibit antimicrobial effect against different bacteria such as *Escherichia coli*, *Enterobacter aerogenes*, *Enterobacter agglomerans*, *Listeria innocua*, *Listeria monocytogenes* and *Salmonella typhimurium* (Wan, Wilcock, & Coventry, 1998) and against different fungi, such as *Aspergillus niger*, *Mucor mucedo*, *Fusarium solani*, *Botryodiplodia theobromae*, *Rhizopus solani*, *Botrytis cinerea* (Hussain, Anwar, Sherazi, & Przybylski, 2008; Wilson, Solar, El Ghaouth, & Wisniewski, 1997). Incorporation of these EO into chitosan films could be an interesting option to obtain controlled-release active film, which could be used in preservation of foods, where the aroma of EO are compatible, such as meat or vegetable products.

The aim of this work was to characterise relevant physicochemical properties of film-forming dispersions and films based on chitosan containing thyme or basil essential oil, and to assess the effect of oleic acid addition, as emulsifier, on the final retention of essential oil in the films and on the film properties. Antifungal effect of the films containing EO was also tested.

2. Materials and methods

2.1. Reagents

High molecular weight chitosan (CH) with a viscosity of 1.2 Pa s at 1% w/w in 1% w/w glacial acetic acid (Batch MKBD1916 V, Sigma–Aldrich Química, Madrid, Spain, 78% deacetylation degree), glacial acetic acid, oleic acid (OA) and magnesium nitrate-6-hydrate (Panreac Química, S.A., Castellar del Vallès, Barcelona, Spain), basil (BO) and thyme (TO) essential oil (Herbes del Molí, Alicante, Spain) were used to prepare the film-forming dispersions (FFDs).

2.2. Preparation and characterization of the film-forming dispersions

CH (1% w/w) was dispersed in an aqueous solution of glacial acetic acid (1% v/w) at 25 °C for 12 h. Thyme essential oil, basil essential oil or oleic acid, or a mixture of essential oil and oleic acid, were added at different concentrations as described in Table 1. FFDs were prepared by means of a rotor-stator homogeniser (Ultraturrax DI25 Yellow Line, IKA®, Germany) at 20,500 rpm for 4 min. After homogenisation, the formulations were degassed with a vacuum pump (Wertheim, Germany).

2.2.1. Particle size distribution, ζ-potential and rheological behaviour

The particle size of the FFDs was measured by using a laser diffractometer (MasterSizer 2000, Malvern Instruments, UK). The FFDs were diluted in a glacial acetic acid solution (pH = 4.8) at 2000 rpm until an obscuration rate of 10% was obtained. The Mie theory was applied considering a refractive index of 1.338 and 0 absorption. Three samples of each FFD were measured in quintuplicate. ζ-potential was measured in quintuplicate 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 a glacial acetic acid solution (pH 4.8). The rheological behaviour of FFDs was analysed in triplicate at 25 °C by means of a rotational rheometer (Haake Rheostress1, Thermo Electric Corporation, Germany) with a type Z34DIN Ti sensor system of coaxial cylinders. Rheological curves were obtained after a stabilisation time of 5 min at 25 °C. The shear stress (σ) was measured as a function of shear rate ($\dot{\gamma}$) from 0 to 512 s^{-1}, taking 5 min to reach the maximum shear rate and another 5 min to attain zero shear rate. The power law model was applied to determine the consistency (K) and the flow behaviour (n) indexes of the FFDs. Apparent viscosity values were calculated at 100 s^{-1}.

2.3. Preparation and characterisation of the films

The films were obtained by casting technique. FFDs were poured onto a framed and levelled Teflon® plate (φ = 15 cm) and were dried at room temperature for 48 h. Films were prepared by pouring the amount of FFD that would provide a constant CH surface density in the dry films of 28 g/m2. Dry films were peeled off the casting surface and preconditioned in desiccators at 5 °C and 59% relative humidity (RH), with an oversaturated $Mg(NO_3)_2$ solution (Greenspan, 1977) for one week prior to performing all the tests. Film thickness was measured using a Palmer digital micrometre (Comecta, Barcelona, Spain, ± 0.001 mm) at a minimum of 5 different points of the same sample. Losses of the essential oil during the film formation were estimated from the difference between weight of the initial solid extended in the casting plate and the final weight of the dried film. Results were expressed as wt % with respect to the initial amount of essential oil.

2.3.1. Water vapour permeability

The water vapour permeability (WVP) was measured gravimetrically at 5 °C and 59–100% relative humidity (RH) gradient, using a modification of the ASTM E96-95 gravimetric method (ASTM, 1995) for hydrophilic films (Gennadios, Weller, & Gooding, 1994). Payne permeability cups (Elcometer SPRL, Hermelle/s Argenteau, Belgium) were filled with 5 mL of deionised water (100% RH). The films were secured and the cups were placed in pre-

Table 1
Composition of the film-forming dispersions (FFDs).

FFDs	CH (g/100 g)	OA (g/100 g)	To (g/100 g)	Total lipid (g/100 g)
CH_1	1	–	–	–
CH_1:$TO_{0.5}$	1	–	0.5	0.5
CH_1:$BO_{0.5}$	1	–	0.5	0.5
CH_1:$OA_{0.25}$:$TO_{0.25}$	1	0.25	0.25	0.5
CH_1:$OA_{0.25}$:$BO_{0.25}$	1	0.25	0.25	0.5
CH_1:$OA_{0.5}$	1	0.5	–	0.5
CH_1:TO_1	1	–	1	1
CH_1:BO_1	1	–	1	1
CH_1:$OA_{0.5}$:$TO_{0.5}$	1	0.5	0.5	1
CH_1:$OA_{0.5}$:$BO_{0.5}$	1	0.5	0.5	1
CH_1:$OA_{0.75}$:$TO_{0.25}$	1	0.75	0.25	1
CH_1:$OA_{0.75}$:$BO_{0.25}$	1	0.75	0.25	1
CH_1:OA_1	1	1	–	1

CH: chitosan, OA: oleic acid, EO: essential oil, BO: basil essential oil, TO: thyme essential oil. Subscripts indicate the ratio of film components.