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Physicochemical characterization of chitosan-based coating-forming emulsions: Effect of homogenization method and carvacrol content

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Glycerol (PubChem CID: 753)
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Absolute ethanol (PubChem CID: 702)

ABSTRACT

The effect of carvacrol content and two homogenization methods on the physicochemical properties of chitosan-based coating-forming emulsions were evaluated. Coating-forming emulsions were developed based on chitosan (1.5% w/v) and carvacrol (0.25%, 0.5% and 1.0% v/v) and using two homogenization methods (rotor-stator and rotor-stator followed by high-pressure homogenization). Emulsions were characterized in terms of droplet size, polydispersity index, ζ-potential, rheological behavior, and surface tension. Wettability was evaluated on the cherry tomato epicarp by measuring the critical surface tension and contact angle. Emulsions with smaller droplet size, lower polydispersity index, and higher ζ-potential were obtained by high-pressure homogenization (HPH). Emulsions viscosity decreased when high pressure was applied. Emulsion wettability improved with carvacrol content and HPH. Incorporating carvacrol and using HPH produced emulsions with better functional properties, which could be used as a coating for fruit and vegetable products.

1. Introduction

In recent years, exploring the potential of edible coatings to maintain the quality and extend shelf life of fresh and minimally processed fruit and vegetables has been addressed (Dhall, 2013; Lin & Zhao, 2007). Their use in fresh produce is based on their potential to decrease moisture loss, limit oxygen entrance, reduce respiration, retard ethylene production, and decreases the oxidative reaction rate (Baldwin, Nisperos, Chen, & Hagenmaier, 1996; Park, 1999). Additives, such as antimicrobial and antioxidant agents, nutraceuticals, colorants, flavors, nutrients, and essential oils, have now been included to increase the effectiveness of edible coatings to reduce microbial loads and delay oxidation and discoloration; they have been reported and patented (Antunes, Gago, Cavaco, & Miguel, 2012; Pranoto, Salokhe, & Rakshit, 2005; Rooney, 2005)

Various materials are used to manufacture edible coatings, but most can be included in one of three categories: hydrocolloids (polysaccharides, proteins), lipids (fatty acids, waxes), and composites (Donhowe & Fennema, 1993). Chitosan is among the most attractive and promising coating biomaterial for fresh produce because it has been proven to be non-toxic and biodegradable; it also has an excellent film-forming ability, broad antimicrobial activity, and compatibility with other substances, such as vitamins, minerals, and antimicrobial agents (Durango, Soares, & Andrade, 2006; Li, Dunn, Grandmaison, & Goosen, 1992; Park & Zhao,

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2004; Ribeiro, Vicente, Texeira, & Miranda, 2007; Rinaudo, 2006; Shahidi, Arachchi, & Jeon, 1999). The cationic properties of chitosan can be used to modify material properties by incorporating and/or slowly releasing active components (Hoagland & Parris, 1996). Chitosan-based films have exhibited selective permeability to O_2 and CO_2 as well as good mechanical properties. However, one major limitation of chitosan coatings is their hydrophilic character and weak water resistance (Butler, Vergano, Testin, Bunn, & Wiles, 1996). This is an important drawback because effective moisture transfer control is a desirable property in most foods.

In general, the water vapor barrier property of polysaccharide- and protein-based coatings has been poor due to their hydrophilic nature. Recent research has therefore focused on the development of composite coatings (Bourtoom, 2008). Polysaccharides or proteins are combined with hydrophobic compounds (fats and oils) in this system; this result in better functionality compared to the pure hydrocolloid coating, especially with respect to their moisture barrier properties. Composite coatings can be categorized as bilayer or emulsion. In a bilayer coating, lipids generally form an additional layer over the polysaccharide or protein layer. In the emulsified systems, lipids are dispersed and entrapped in the hydrocolloid matrix (Galus & Kadzinska, 2015).

One current approach is using essential oils and their components, such as hydrophobic constituents, in the coating compounds. These also have great antimicrobial activity against a wide variety of bacteria, molds, and yeasts (Fischer & Phillips, 2006); they are considered as natural preservatives and are generally recognized as safe (GRAS) for human consumption. Carvacrol is a phenolic compound primarily found in oregano, thyme, and marjoram essential oils, and it is recognized as a safe additive (Alvarez, Niemira, Fan, & Sommers, 2007).

Emulsions are thermodynamically unstable colloidal systems; therefore, emulsifying agents or surfactants are often necessary to improve their stability. Droplet size is a determining factor in emulsion stability, and it also affects viscosity and other important properties (Galus & Kadzinska, 2015). Different homogenization techniques can be used to prepare emulsions. Rotor-stator, microfluidization, sonication, and high-pressure homogenization (HPH) have been used to modulate lipid droplets size in filmogenic dispersions (Ma et al., 2012). Particle size in rotor-stator systems can reach approximately 1 μm whereas the high-pressure homogenizer mechanically reduces particle size to less than 1 μm; it is used to produce a uniform emulsion composition with higher stability (Lee, Lefevre, Subirade, & Paquin, 2009)

The effectiveness of edible coatings to protect fruit and vegetables depends on controlling the wettability of coating-forming emulsions, which affects coating film thickness (Park, 1999). The coating-forming emulsions should be able to wet the product surface and spread uniformly over it; upon drying, the coating should have suitable adhesion, cohesion, and durability to function properly. Souza, Cerqueira, Teixeira, and Vicente (2010) noted that determining wettability and studying product surface properties are fundamental to correctly formulate and apply an edible coating.

To meet appropriate functional properties, emulsified coatings must be designed with suitable mechanical properties, gloss, transparency, wettability (surface adhesion), and water and gas barrier properties. However, these properties depend on factors associated with the stability of the coating-forming emulsions and their surface properties (McClements, 2007; Sánchez-González, Cháfer, Chiralt, & González-Martínez, 2010). These factors are therefore affected by the preparation technique, type and quantity of components (hydrocolloids and lipids), component compatibility, as well as microstructural heterogeneity (Fabra, Pérez-Masiá, Talens, & Chiralt, 2011).

Therefore, the aim of this study was to evaluate the effect of carvacrol content and two homogenization methods on the physicochemical properties of chitosan-based coating-forming emulsions. Parameters related to emulsion stability and wettability were evaluated, that is, particle size and distribution, ζ potential of dispersed lipid particles, rheological behavior, surface tension, critical surface tension, and contact angle.

2. Materials and methods

2.1. Materials

Carvacrol (>98% purity, CAS Number 499-75-2), chitosan with 810 KDa molecular weight and deacetylation degree > 75% (CAS Number 9012-76-4), glycerol (CAS number 56-81-5), and Tween 80 (CAS Number 9005-65-6) were obtained from Sigma-Aldrich (Santiago, Chile). Glacial acetic acid and absolute ethanol were purchased from Merck S.A. (Santiago, Chile). Ultrapure water was obtained from Direct-Q® 5 UV filtration system (Merck Millipore).

2.2. Preparation of coating-forming emulsions

2.2.1. Preparation of chitosan solution

A 1.5% (w/v) chitosan stock solution was prepared by dissolving chitosan powder in a hydroalcoholic acid solution (1% acetic acid and 2.5% ethanol). To achieve complete chitosan dispersion, the solution was stirred for 6 h at room temperature. Impurities were removed by vacuum filtration through a microfiber filter. Ethanol was used to decrease the surface tension of coating-forming emulsions, as it was described by Kurek et al. (2013). Glycerol was added as a plasticizer at 15% chitosan mass and the chitosan solution was stirred for 30 min.

2.2.2. Homogenization methods

The coating-forming emulsions were obtained by adding 0.5% (v/v) Tween 80 as an emulsifier and carvacrol at 0.25%, 0.5%, and 1.0% (v/v) to the chitosan solution; these were homogenized by two methods. In method 1, emulsions were prepared with a rotor-stator homogenizer (Ultra Turrax® T25 digital, IKA WERKE, Staufen, Germany) at 21,500 rpm for 5 min. In method 2, the coarse emulsions obtained by the rotor-stator system were subjected to a second homogenization process with a high-pressure homogenizer (model NG 12500, Stansted Fluid Power Ltd., Essex, UK) at 100 MPa. Finally, vacuum degassing was used to remove dissolved air bubbles in the emulsions. The coating-forming emulsion compositions are displayed in Table 1. For each composition, three separate batches of emulsions were prepared using both homogenization methods.

2.3. Droplet size, polydispersity index (PdI) and droplet charge (ζ-potential)

Average emulsion droplet size was determined by dynamic light scattering (DLS) with a Zetasizer Nano ZS laser diffractometer (Malvern Instruments Ltd., Worcestershire, UK). The Zetasizer operates at 633 nm and is equipped with a backscatter detector (173°) that is used to measure sub-micron particles. Emulsions were diluted 24 times with ultra-pure water to prevent the multiple-scattering effect. The carvacrol refractive index was measured with a manual refractometer (Refractometer PAL-1 Pocket, Japan), and carvacrol absorbance was measured with a spectrophotometer (Spectroquant® Pharo 300 M). Droplet size measurements were performed 24 h after preparing the emulsion at 25 °C; the average particle size was reported as z-average values. The polydispersity index was also measured. For every batch of emulsion of identical composition, three samples were used to