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Effect of the weight ratio of alginate-modified tapioca starch on the physicochemical properties and release kinetics of chlorogenic acid containing beads

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ABSTRACT

Sodium alginate (SA)-modified tapioca starch (TS) solutions ($R_{SA/TS}$) in different weight ratios (1/0, 0.75/0.25, 0.5/0.5 and 0.25/0.75), added with chlorogenic acid (CGA), were dripped into $CaCl_2$ solution for obtaining calcium alginate (CA) hydrogel beads filled with TS containing chlorogenic acid ($HB_{CA/TS}$). The beads size, morphology, encapsulation efficiency, textural and viscoelastic properties, CGA release in simulated gastrointestinal conditions, and the molecular interactions between beads components using DSC and FTIR were evaluated. The sphericity of the $HB_{CA/TS}$ filled with TS was lower than that made with only calcium alginate, but the diameter was larger. CGA release from the beads was due to a complex interplay between matrix porosity and tortuosity. Highest release % of CGA occurred for $HB_{0.75/0.25}$ which showed the lowest Tan δ-strain %, hardness and cohesiveness values. The diffusion-relaxation model involving two mechanisms described better the CGA release experimental data.

1. Introduction

The roles of antioxidants on human health have been widely recognized by numerous researches, and there has been an increasing interest by the food industry and a growing trend in consumer preferences for natural antioxidants over synthetic compounds for food applications (Fu et al., 2011; Xi & Shouqin, 2007). However, natural antioxidants are easily oxidized and sensitive to heat and light, which limit their application in the food industry (Chao, Wang, Zhao, Zhang, & Zhang, 2012). Thus, the development of carriers systems for these compounds that may help to protect them against deleterious environmental factors and to incorporate them into more complex food systems in an efficient manner is a current topic of study.

Microencapsulation is a reliable technique that has been in use for many decades for protecting bioactive compounds from degrading under the influence of environmental factors. This technique relies on surrounding the bioactive compounds with a semi-permeable biopolymeric matrix, avoiding or retarding their coming into contact with the deleterious environmental factors. An ongoing research topic is how to improve the physicochemical, functional, and release properties characteristics of these biopolymeric matrices, and to make them more cost efficient.

The most widely used encapsulating material is alginate, a natural anionic polyelectrolyte extracted from various species of algae, and composed by (1-4)-linked β-D-mannuronate (M) and α-L-guluronate units (G), which are present in the linear macromolecule in homopolymeric blocks of each monomer, together with blocks of alternating sequence (Donati et al., 2005). Alginate has several features that make it a suitable choice material for encapsulation such as low cost, simple use, biodegradability, biocompatibility, capability to undergo chain–chain association and forming three dimensional gels in the presence of divalent cations (e.g., Ca^{2+}) (Fang et al., 2008). However, alginate gels are susceptible to disintegrate in the presence of excess monovalent ions, Ca^{2+}-chelating agents, and harsh chemical environments (Smidsrod & Skjak-Braek, 1990). They also present high permeability, due to their porous and hydrophilic structure which causes

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rapid release of entrapped materials (Chan et al., 2011; Hosseini et al., 2014; López-Córdoba, Deladino, & Martino, 2013; Martin, Lara-Villoslada, Ruiz, & Morales, 2013), which may be considered a drawback in some applications. Some authors have reported that alginates can form matrices with improved structural and functional properties by the addition of other polymers as fillers (Chan et al., 2011; López-Córdoba, Deladino, & Martino, 2014; Wu, He, Chen, Han, & Li, 2014). Hosseini et al. (2014) informed that the presence of resistant starch in alginate microcapsules resulted in higher nisin encapsulation efficiency and loading capacity, while López-Cordoba et al. (2013) found that the incorporation of starch granules improves the release characteristics of alginate-based capsules.

There are very few researches about the combination of alginate with chemically modified starch. It is interesting to note that chemically modified starches exhibit reduced digestibility, so they qualify as resistant starches, and may have an important role in human health (Chung, Shin, & Lim, 2008). No reports are available characterizing the effect of the alginate-chemically modified starch weight ratio on the structural, mechanical, loading, and release properties of microcapsules containing bioactives. This knowledge is relevant considering that the most important mechanisms that regulate the release rate of bioactive compounds (diffusion, swelling, biodegradation/erosion and osmotic pressure) will depend on the composition of the biolymeric matrix and the surrounding fluid (Barba, d'Amore, Chirico, Lamberti, & Titomanlio, 2009; Pothakamury & Barbosa-Cánovas, 1995).

Chloragenic acid (CGA, 5-caffeoylquinic acid) is a widely used bioactive in functional foods due to its antioxidant activity and scavenging of reactive oxygen species capacity (Pal, Banerjee, & Ghosh, 2012; Pal & Mitra, 2010; Sato et al., 2011), and for preventing diverse health conditions (Shin et al., 2015). CGA is easily oxidized and sensitive to heat and light (Chao et al., 2012), and for this reason was chosen as the bioactive to be encapsulated in this work.

The objectives of this work were to: (a) encapsulate chlorogenic acid (CGA) in modified tapioca starch-filled calcium alginate hydrogel beads ($HB_{CA/TS}$); (b) evaluate the size, textural, microstructural, and viscoelastic properties of the beads; (c) determine the CGA entrapment efficiency, antioxidant activity, and release kinetics under simulated gastrointestinal conditions; and (c) evaluate the starch-alginate-CGA interactions on the beads.

2. Materials and methods

2.1. Materials

Sodium alginate (SA; FD 175, 60.5% guluronic acid content) was purchased from CP Kelco (Lille Skensved, Denmark). A hydroxypropyl distarch phosphate from tapioca starch (TS; INS number 1442; $D_{4,3}$ = 13.26 μm) was obtained from Ingredion Mexico (Guadalajara, State of Jalisco, Mexico). Chlorogenic acid (CGA, molecular weight = 354.31 Da), porcine bile extract (B8631), and DPPH (2, 2-di (4tert-octylphenyl)-1-picrylhydrazyl) free radical were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Other reagents used were of analytical grade. All water used was double distilled and deionized (DDW).

2.2. Preparation of hydrogel beads using different weight ratio of sodium alginate/Ca^{+2}

When SA is contacted with Ca^{+2} in solution, cross-linking between the carboxylate anions of the alginate guluronate units and the calcium ions occurs, resulting in the formation of a gel (Reis, Neufeld, Ribeiro, & Veiga, 2006). Thus, the weight ratio between SA/Ca^{+2} ($R_{SA/CaCl2}$) is crucial in influencing the gel properties. The total milliequivalents (meq) of carboxylate groups of SA was determined by potentiometric titration: 40 mL of an aqueous solution containing 2 g of SA per 100 mL^{-1} DDW (pH 6.7) was titrated with hydrochloric acid (0.1 N) to the pKa value (pH 3.5) (Mi, Sung, & Shyu, 2002). A 60 s time lag elapsed between two aliquots (0.1 mL) to allow the reaction to reach equilibrium. The solution pH was continuously monitored with a pH meter (Hanna Instruments, model HI 98240, Smithfield, RI, USA) at 25 °C. The meq of HCl necessary to reach pKa were doubled in order to calculate the total meq carboxylate groups present in SA (1.86 meq per g^{-1}). This means that 1 g of SA required 0.128 g of $CaCl_2$ (0.046 g Ca^{+2}). From these results six hydrogel calcium alginate beads variations (HB_{CA}) were prepared using different $R_{SA/CaCl2}$ as follows: 1/0.128, 1/0.256, 1/1.28, 1/2.56, 1/6.4, and 1/12.8. In this way, the amount of $CaCl_2$ added to each SA solution was 0.256, 0.512, 2.56, 5.12, 12.8 and 25.6 g per 100 ml. The beads were coded as $HB_{0.128}$, $HB_{0.256}$, $HB_{1.28}$, $HB_{2.56}$, $HB_{6.4}$, and $HB_{12.8}$, after the amount of $CaCl_2$ in $R_{SA/CaCl2}$. HB_{CA} were prepared by the extrusion technique (Sandoval-Castilla, Lobato-Calleros, García-Galindo, Alvarez-Ramírez, & Vernon-Carter, 2010) with slight modifications. Solutions of SA (2 g per 100 mL) were prepared, stored for 24 h at 4 °C for allowing full hydration, and degassed by ultrasound. The beads were formed by dripping 20 mL of SA solution into 160 mL of different $CaCl_2$ solutions containing the weight concentrations required for achieving each $R_{SA/CaCl2}$ mentioned above with the help of a 0.8 mm (30½ G) needle (Muthukumarasamy, Allan, & Holley, 2006). The HB_{CA} were maintained in the gelling bath to harden for 30 min at room temperature (20 ± 2 °C), harvested by filtration through a plastic mesh of 0.19 mm, and washed with DDW thrice. The $R_{SA/CaCl2}$ which produced the HB_{CA} with best sphericity and textural properties was used for preparing the calcium alginate-modified starch hydrogel beads containing CGA ($HB_{CA/TS}$).

2.3. Preparation of the calcium alginate-modified starch hydrogel beads

Four $HB_{CA/TS}$ variations were prepared from 100 mL of solutions containing 2 g of SA and different amounts of TS: 0.0, 0.67, 2.0 and 6.0 g to achieve weight ratios ($R_{SA/TS}$) of 1/0, 0.75/0.25, 0.5/0.5 and 0.25/0.75, respectively. The $HB_{CA/TS}$ beads were coded as $HB_{1/0}$, $HB_{0.75/0.25}$, $HB_{0.5/0.5}$, and $HB_{0.25/0.75}$. The solutions were stored for 24 h at 4 °C for allowing full hydration, degassed by ultrasound, and added with 40 mg of CGA. The $HB_{CA/TS}$ were formed by dripping the SA/TS solutions into a $CaCl_2$ solution at the $R_{SA/CaCl2}$ that resulted in the best beads (Subsection 2.2). The $HB_{CA/TS}$ were maintained in the gelling bath for hardening for 30 min. Subsequently, the $HB_{CA/TS}$ were filtered, washed with buffer solution (acetic-acetate, pH 5.5). Samples of fresh made beads were used for determining the diameter, sphericity and textural characteristics. Surplus beads were dried in a vacuum (304 mm Hg) convection oven (Shellab model 1410 vacuum oven, Sheldon Manufacturing Inc., Cornelius, OR, USA) at 45 °C until reaching constant weight and a water activity of about 0.35. The dried beads were placed into a desiccator containing a saturated solution of $MgCl_2$ at room temperature until required for their characterization. The water activity in the desiccator at this temperature was about 0.32. The dried beads were used for the rest of the experiments.

2.4. Morphology, diameter and sphericity of beads

HB_{CA} and $HB_{CA/TS}$ were observed in an Olympus BX45 phase contrast microscope (Olympus Optical Co., Ltd., Japan). Micrographs, at a magnification of 4×, were taken to thirty beads randomly selected with a digital camera MoticCam 2500 (Motic