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Stability and rheology of water-in-oil-in-water multiple emulsions made with protein-polysaccharide soluble complexes

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ABSTRACT

The morphology, stability, and rheological properties of water-in-oil-in-water ($W_1/O/W_2$) multiple emulsions (ME) stabilized by whey protein concentrate (W)-carboxymethylcellulose (C) soluble complexes ($SC_{W/C}$) were evaluated. The interaction pH values (pH_i) to generate $SC_{W/C}$ were established through zeta potential and turbidity determinations. Six ME variations were prepared using a constant weight ratio (WR) between W and C of 3:1 (where maximum interaction occurred) and by varying the way in which the biopolymers were adsorbed at the interface (layer-by-layer, LL, or pre-formed complex, PF) and pH_i (3.7, 4.0 and 4.3). The ME initial volume-surface diameter ($D_{3.2}$) of the oil droplets ranged from 2.4 to 3.2 μm, which on turn contained numerous flocculated water droplets. Higher viscoelastic moduli values (G' and G''), more pronounced shear thinning behaviour and smaller changes in droplet size with storage time were displayed by ME made with a pH_i value of 4.3, $WR_{3:1}$, and LL biopolymers adsorption technique.

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1. Introduction

In water-in-oil-in-water ($W_1/O/W_2$) multiple emulsions (ME) the internal (W_1) and external (W_2) phases are chemically alike, and an intermediate immiscible (O) phase physically separates the two like phases (Dickinson and McClements, 1996). Bioactive compounds can be incorporated within the W_1 or O phases, making ME carriers for non-polar and polar ingredients, and ideal for the development of novel food products with enhanced functional properties (Murillo-Martínez et al., 2011; Nisisako et al., 2012). ME have been used in the manufacture of reduced-fat yoghurt (Lobato-Calleros et al., 2009) and edible films (Murillo-Martínez et al., 2011). The most used method for forming kinetically meta-stable ME is the two-step emulsification method process, where in the first step a water-in-oil emulsion (W_1/O) is formed, which is then re-emulsified in an aqueous phase (W_2) containing a combination of emulsifiers and/or stabilizing agents (Lobato-Calleros et al., 2009). Actual development of food emulsions usually includes the use of two or more biopolymers for enhancing their individual functional properties (Ramírez-Santiago et al., 2012). For instance, the combined use of proteins and polysaccharides would be expected to bring together the emulsifying role of the protein with the stabilizing role of the polysaccharide (Dickinson and Euston, 1991). The improved functional properties resulting from the protein–polysaccharide complexes in comparison to the proteins and polysaccharides alone could be attributed to the structure of their complexes. There are many ways in which biopolymers can interact at the molecular level, and so it is important to determine which parameters influence the formation of the complexes and their effect on the main functional properties that they impart to the systems to which they are incorporated (Espinosa-Andrews et al., 2008; Schmitt and Turgeon, 2011). Oppositely charged protein and polysaccharides are generally known to form stable inter-biopolymer complexes that have the capacity to form and stabilize effectively emulsions (Ruíz-Ramos et al., 2006). The mechanical, thermal, emulsifying properties of these complexes are better than those of the individual biopolymers (Ye, 2008) with the additional advantage that the electrostatic interactions and in consequence the complexes properties can be modulated. The actual chemical composition of the emulsion droplet surface will depend on how the protein and polysaccharide molecules adsorb at the interface, this being the key factor which determines most of the surface interactions (Bergenståhl, 1995). Thus, the interface may arise by two routes: (i) aggregates of pre-formed (PF) protein–polysaccharide soluble complex which may adsorb together at the interface from a mixed bulk solution; or alternatively (ii) a pure protein layer may be formed first, with interfacial complexation following on after subsequent addition of polysaccharide (LL). Hence, surface composition and structure may be determined by a

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delicate dynamic balance of competitive and cooperative (associative) processes, leading to possibilities for evolving structural heterogeneity in both the plane of the interface (surface phase separation) and normal to the interface (multilayer formation) (Dickinson, 2008; Jourdain et al., 2009).

The aim of this work was to determine the influence on the morphology, droplet size, rheological properties and stability of water-in-oil-in water multiple emulsions formed by the layer-by-layer and pre-formed whey protein concentrate–carboxymethylcellulose biopolymers adsorption at the interface at different pH values.

2. Materials and methods

2.1. Materials

Canola oil (CO; Capullo®, Unilever de Mexico, S.A. de C.V., Mexico, Mexico) was used as the oil phase of the ME. The hydrophilic emulsifier (Panodan® SDK Datem, esters of monoglycerides and diglycerides of diacetyltartaric acid) and hydrophobic emulsifier (Grinsted® PGPR 90, esters of polyglycerol and polyriciniolate fatty acids) were purchased from Danisco Mexico, S.A. de C.V., Mexico City, Mexico). The biopolymers used were whey protein concentrate (W; 83.7 g protein/100 g and 6.4 g fat/100 g, Hilmar 8000, CA, USA) and carboxymethylcellulose (C; CMC® CEROL; viscosity of 50 000 mPa s for a 2 g/100 g solution at 60 rpm and 25 °C; Grupo Dermet, S.A. de C.V., Mexico City, Mexico). Analytical grade reagents used were hydrochloric acid (HCl), sodium hydroxide (NaOH), all purchased from Quimica Laitz, S.A. de C.V., Mexico City, Mexico. All water used in the experiments was double distilled and deionized.

2.2. Complexes formation

In order to obtain a general picture for the complexation phenomena between W and C, the impact of the protein to polysaccharide weight ratios ($WR_{W/C}$) at a given pH value was evaluated using turbidity measurements (Ramírez-Santiago et al., 2012). $WR_{W/C}$ ratios ranging from 2:1 to 1:6 were obtained by blending the C (0.5 g/100 g) solution with W (1.0, 1.5, 2.0, 2.5, and 3.0 g/100 g) solutions, adjusting the pH values of the mixtures in the range of 2.0–6.0. The mixtures were gently stirred for 1 h at room temperature, and let to stand for 48 h at 4 ± 1 °C. Soluble complexes exist in solution prior to onset of macroscopic phase separation, and this phenomenon may be effectively monitored through turbidity measurements. The % transmittance (%T) of the biopolymers mixtures was measured at 400.5 nm with a Spectronics Genesys 5 UV/Vis (Spectronic Unicam, Rochester, NY, USA). The turbidity was calculated as:

$$\text{Turbidity } (\tau) = \frac{1}{L} Ln \frac{Io}{It}$$

where τ = turbidity (cm^{-1}); L = optical length (1 cm); I_t = intensity of transmitted light (%T); and I_o: intensity of incident light (100) (Skoog et al., 1995). High turbidity measurements are indicative of the formation of soluble complexes, while low turbidity measurements are indicative of insoluble complexes formation (complex coacervate).

2.3. Zeta potential measurements

To understand the driving force for electrostatic interaction between W and C, the zeta potential of the W (1.5 g/100 g) and C (0.5 g/100 g) solutions was determined with a Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, Worcestershire, UK) at pH values ranging between 2.0 and 8.0. The pH of the solutions was adjusted to the desired value by the addition of either 0.1 N NaOH or 0.1 N HCl.

2.4. Formulation and preparation of the ME

ME variations were prepared using a 2 × 3 factorial experiment, maintaining constant the $WR_{W/C}$ at which maximum turbidity was obtained. The independent variables were the way in which the biopolymers adsorbed at the outer oil–water interface (LL or PF) and pH of interaction (pH_i). These pH_i values were selected in order to comprise different conditions of charge density driving the complexation between the biopolymers, mainly: (i) pH_i of 3.7 where dissociation of W was relatively high and that of C quite suppressed; (ii) pH_i of 4.0, slightly below that of the isoelectric point of W (pI = 4.2), where the positive charges of W and negative charges of C are more balanced, but sufficiently far away from a stoichiometric relationship between the biopolymers that would lead to the formation of insoluble complexes; and (iii) a pH_i of 4.3 above the pI of W, where both W and C are negatively charged. It is known that anionic polysaccharide can interact with positively charge "patches" on the protein surface (Dickinson, 2008). The resulting multiple emulsions were coded as $ME_{x,y}$, where x = biopolymers interfacial adsorption technique employed (LL or PF) and y = pH_i of manufacture (3.7, 4.0 or 4.3). ME_{PF} were prepared by a two-step procedure (Lobato-Calleros et al., 2008), while the ME_{LL} were prepared by a three step procedure (Mora-Huertas et al., 2010).

In the case of both ME_{PF} and ME_{LL}, the first stage consisted in the formation of a W_1/O primary emulsion with a 0.4 disperse mass fraction (ϕ_1). The aqueous phase (37.9 g of distilled water per 100 g + 2.1 g of Panodan per 100 g) was poured drop-wise with continuous agitation into the oil phase (51.5 g of CO per 100 g + 8.5 g of Grinsted per 100 g) with the help of a high shear Ultra-Turrax® T50 basic homogenizer (IKA Works, Inc. Wilmington, USA) operated at 6 400 rpm during 5 min.

The second stage procedure was slightly different for ME_{PF} and ME_{LL}, but both types of emulsions had dispersed mass fraction (ϕ_2) of 0.3, total biopolymer concentration of 2% w/w and $WR_{3/1}$. The requisite amount of primary emulsion was added drop-wise with continuous agitation to aqueous dispersions of W + C (1.5 g W + 0.5 g C/68 g of distilled water) for ME_{PF}, and to aqueous dispersions of W (1.5 g W per 40 g of distilled water) for ME_{LL}. In both cases the aqueous dispersions were adjusted to the different pH_i values mentioned above, and homogenization was done a high shear homogenizer operated at 4000 rpm during 5 min.

The third stage for ME_{LL} consisted in pouring the protein covered preliminary ME into a C aqueous dispersion (0.5 g C per 28 g of distilled water) with a homogenizer at 4000 rpm for 5 min.

All of the $ME_{x,y}$ were prepared by triplicate using completely randomized experimental design.

2.5. Mean droplet size and optical micrographs of ME

The mean surface-volume droplet size ($d_{3,2}$) of the $ME_{x,y}$ was determined with a Malvern Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK), using deionized water (refractive index 1.333) as dispersant within 1 h of initial preparation and at different intervals during 21 days of storage at 4 ± 1 °C.

Micrographs of the $ME_{x,y}$ were taken after 1 h of preparation and after 21 days of storage using an optical microscope (Olympus BX45, Olympus Optical Co., Tokyo, Japan) coupled to an image analyser system (digital Olympus camera C3030, Olympus Imaging Americas Inc., Center Valley, PA, USA). Selected micrographs taken at a magnification of 100× are presented. An estimation of the W_1/

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