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Influence of chitosan concentration on the stability, microstructure and rheological properties of O/W emulsions formulated with high-oleic sunflower oil and potato protein

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Relatively concentrated (40 wt%) O/W emulsions formulated with high-oleic sunflower oil as disperse phase, potato protein isolate as emulsifier and chitosan as stabiliser were prepared by rotor–stator/high-pressure valve/rotor–stator homogenization. The influence of chitosan concentration on the physical stability of emulsions was studied in (0.25–1) wt% range by visual inspection, rheological and microstructural techniques. Steady shear flow curves were sensitive to the occurrence of creaming upon the rise of zero-shear viscosity values. The effect of increasing concentration of chitosan on the zero-shear viscosity turned out to be dependent on emulsion ageing and always resulted in a stepwise increase of the critical shear rate for the onset of shear thinning flow. The critical oscillatory shear stress for the onset of non-linear viscoelastic behaviour was more sensitive than the critical shear rate to detect creaming in emulsions. Mechanical spectra are definitely demonstrated to be the most powerful tool to detect not only creaming but also oil droplet flocculation on account of changes in the plateau relaxation zone. CSLM micrographs supported the interpretation of dynamic viscoelastic results, especially when flocculation as well as coalescence took place. Cryo-SEM micrographs evidenced the formation of increasingly denser protein–polysaccharide networks with chitosan concentration and the fact that the latter governs the microstructure of the emulsion when reaches 1 wt% concentration promoting enhanced physical stability.

1. Introduction

The shelf-life of food emulsions is principally determined by their physical stability, given that emulsions are thermodynamically unstable systems which will breakdown over time due to one or several physicochemical mechanisms such as creaming, flocculation, coalescence, phase inversion and Ostwald ripening. In addition, the chemical stability of some ingredients, such as polyunsaturated oils, must be also taken into consideration (McClements, 2005).

Proteins and small-molecule surfactants are the emulsifying agents most commonly used for food processing (Dickinson, 2003). They do not only promote the formation of emulsions but also improve their physical stability since they reduce the oil–water interfacial tension and form a protective membrane around the oil droplets, which prevent them from aggregating. Nevertheless, a number of other factors, such as changing the interfacial rheological properties of emulsion droplets or the kinetics of adsorption to the interface, also determine the efficiency of emulsifier molecules (Sánchez, Berjano, Guerrero, & Gallegos, 2001).

Polysaccharides are often added to the oil-in-water emulsions in order to provide texture and to improve emulsion stability (McClements, 2005). The ability of polysaccharides to stabilise emulsion droplets is attributed to their ability to increase the viscosity of the continuous phase or their ability to promote formation of a gel network in the aqueous medium. However, the surface activity of some specific polysaccharides may also be taken into account (Dickinson, 2003). Actually, polysaccharides can be even more effective than surfactants and proteins in regards to emulsion stability. This is a consequence of polysaccharides' ability to enhance the formation of a thicker and stronger secondary layer favouring electrostatic and mainly steric stabilisation. The use of polysaccharides to enhance the stability of emulsions that contain proteins has been previously reported in many studies as illustrated by the recent reviews by Dickinson (2011), Murray (2011) and Schmitt and Turgeon (2011).

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Proteins tend to be better than polysaccharides at producing small emulsion droplets when used at low concentrations, whereas polysaccharides tend to be better than proteins at producing emulsions that are stable to a wider range of conditions (McClements, 2005). Therefore, exploiting the uses of proteins and polysaccharides is of increasing interest since the combination of the attributes of these two kinds of biopolymers tends to produce small emulsion droplets with good physical stability. Linkages of protein and polysaccharide components may occur by either covalent bonding or electrostatic interactions (Dickinson, 2008, 2009; McClements, 2006). Thus, protein–polysaccharide complexes may have better functional properties than individual biopolymers on their own; this offers opportunities for the design of new ingredients with applications in the food industries.

In recent years, the link between diet and health has received increasing public attention, especially in the popular media. More and more, medical specialists agree that a good diet can be helpful in preventing many diseases. Concurrently, the recent perception of an obesity epidemic has the potential to promote consumption of low-fat food commodities and functional food products. These recent trends contribute to the increasing popularity of incorporating healthy ingredients into one's diet.

High-oleic sunflower oil is known for its high content of monounsaturated fatty acids (MUFA) since it has at least 82 percent oleic acid. A relationship between diets high in saturated fat and risk of heart disease has been demonstrated, which has resulted in nutrition recommendations to decrease dietary with saturated fat and to replace by dietary carbohydrate or unsaturated fat (Krauss et al., 2000).

Nowadays, there is an increasing demand on protein ingredient for food applications as well as a trend to replace animal proteins by plant proteins. In addition, some of these proteins may be extracted from agro-material wastes or byproducts (i.e. from starch industry) and as a consequence may contribute high value-added products (Romero et al., 2011). Among them, potato may be regarded as a potential source to produce plant protein-based food products with high valorisation standards. Furthermore, potato proteins display a nutritional quality higher than most major plant proteins, being not far from that of egg proteins (Bartova & Barta, 2009; Van Gelder & Vonk, 1980). In spite of the aforementioned advantages derived from the use of potato proteins in food emulsions, there are some drawbacks related to protein denaturation induced by industrial processing (Knorr, 1980) that leads to poor solubility and limited emulsion stability (Van Koningsveld et al., 2006).

Chitosan (CH) is a cationic naturally occurring polysaccharide, which offers interesting properties to be used in food stuffs due to its multifaceted properties such as biocompatibility, biodegradability, non-toxic nature, anti-hypercholesterolemic activity, antimicrobial activity, and film-forming properties (Akbuga, 1995; Berger et al., 2004; Borderías, Sánchez-Alonso, & Pérez-Mateos, 2005; Felt et al., 1999; Muzzarelli, 2009; Patashnik, Rabinovich, & Golomb, 1997). In addition, Casettari, Gennari, Angelino, Ninfali, and Castagnino (2012) have pointed out in their recent paper that radical scavenger, anti-microbial and antioxidant properties of chitosan are quite interesting for its applications as food additive.

The use of chitosan is still restricted in some regions. However, a number of European countries as well as United States, Japan and South Korea have approved commercialisation of chitosan-based nutraceuticals (Muzzarelli, 2009). Therefore, chitosan's use in food emulsions contributes a value-added benefit to the food in which it is being used. In fact, the formulation of emulsions stabilised by chitosan has raised a significant interest in the literature on food science. Different types of emulsions formulated with lecithin as primary emulsifier and chitosan were widely studied by Ogawa, Decker, and McClements (2003a, 2003b, 2004), Klinkesorn and McClements (2009) and Chuah, Kuroiwa, Kobayashi, and Nakajima (2009). Others formulated with whey-proteins and chitosan were characterised by Laplante, Turgeon, and Paquin (2005, 2006) and Speiciene, Guilmineau, Kulozik, and Leskauskaite (2007). Chitosan has been also used in flavour–oil emulsions (Kaasgaard & Keller, 2010) and in the formulation of beef emulsions (Kurt, 2010).

The stabilising action of chitosan in oil-in-water emulsions occurs not only through either viscosity modification of the aqueous continuous phase or the promotion of a network of oil droplets, but also because of surface activity which is quite important in regards to its contribution to the emulsifying capacity when formulated with proteins (Calero, Muñoz, Ramírez, & Guerrero, 2010).

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This study focuses on emulsions formulated with a) high-oleic sunflower oil, whose dietary benefits have been supported above, b) vegetable protein (a potato protein isolate which may provide added value to byproducts associated with potato-based starch manufacturing), and c) chitosan, which can be useful to prepare emulsions by the so-called layer by layer technique (McClements, 2004; Schmitt & Turgeon, 2011) taking advantage of its cationic properties at pH below the isoelectric point of potato protein isolate. In addition, the use of chitosan as emulsion additive is interesting as a way to add value to cray-fish industry byproducts. To be more precise, the specific goals of this project were to study the effect of chitosan concentration on the stability, microstructural, and rheological properties of O/W potato protein-stabilised emulsions.

2. Materials and methods

2.1. Materials

Potato Protein Isolate (PPI) (ca. 80 wt%) was supplied by Protastar (Reus, Barcelona, Spain). The chemical composition of potato protein isolate was determined in a previous study (Romero et al., 2011), being as follows: 80 $\pm$ 2 wt% protein; 3.1 $\pm$ 0.4 wt% lipids; 5.9 $\pm$ 0.6 wt% carbohydrates; 0.8 $\pm$ 0.1 wt% ashes; 10 $\pm$ 2 wt% moisture.

Chitosan (CH) of medium molecular weight (MW 190,000–310,000 Da, 75–85% deacetylated), anhydrous sodium acetate and glacial acetic acid were used as supplied by Sigma Aldrich (St. Louis, USA).

2.2. Preparation of protein dispersion

The low solubility of the PPI studied has been put forward in a previous paper of this laboratory that showed the soluble fraction of protein as a function of pH (Romero et al., 2011).

Potato protein dispersion was prepared by dispersing 5.0 wt% potato protein powder in Milli-Q water. Protein dispersion was stirred for 10 min and was then adjusted to pH 11.5 with 1 M NaOH in order to improve protein solubility. Finally, the protein dispersion was sonicated for 7 min. No apparent changes in molecular weight distribution of PPI due to sonication was detected by electrophoresis (data not shown).