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Physical properties and lipid bioavailability of nanoemulsion-based matrices with different thickening agents

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ABSTRACT

This work studies the influence of two thickening agents, starch and carboxymethyl cellulose (CMC) with different structural characteristics on physical properties and lipid bioavailability of avocado oil-based nanoemulsions. Eight nanoemulsions were prepared varying oil content (5 and 15%) and thickener type and concentration (CMC: 0.5–0.75%; Starch: 6–8%). Particle size (PS) and zeta potential (ZPot) depended mainly on the thickener type; starch-based nanoemulsions showed a lower PS and ZPot values near to zero. Nanoemulsions containing the highest oil (15%) and thickener concentrations (0.75% CMC or 8% starch) were more viscous and pseudoplastic than those with 5% oil. With respect to physical stability, the CMC-thickened nanoemulsions exhibited a better stability than starch-based samples. Starch-based nanoemulsions with 15% oil showed the highest creaming index values (40–45%) after 21 days of storage. In turn, the hydrocolloid type had a significant ($p < 0.05$) effect on lipid bioavailability of O/W nanoemulsions. Nanoemulsions with 5% and 15% oil did not show significant differences on the digestion rate due to thickener type. However, nanoemulsions with 15% oil presented lower digestion rates and final extent of free fatty acids released, with a lag time increased. At 15% oil, CMC-based nanoemulsions showed a lower release of free fatty acids after lipolysis than starch-thickened samples, indicating that CMC caused physical retention of oil droplets in the matrix structure, delaying lipid digestion.

1. Introduction

In recent years, there has been a growing interest in the design of novel food structures in order to develop functional foods that prevent diseases and promote health. Nanotechnology applied to food involves the design, creation, development, and use of material structures and systems in the nanometer scale (<100 nm) (Fathi, Martin, & McClements 2014; Robles-García et al., 2016; Salvia-Trujillo, Martin-Belloso, & McClements, 2016). Indeed, nanotechnology can modify the physical properties of foods, and improve the bioavailability of functional components incorporated within these structures (He & Hwang, 2016; Mason, Wilking, Meleson, Chang, & Graves, 2006; Salvia-Trujillo, Qian, Martín-Belloso, & McClements, 2013).

Nanoemulsions consist of small oil droplets dispersed (diameter < 100 nm) in a continuous phase, where each droplet is surrounded by emulsifier molecules. They have a considerable potential for encapsulating, protecting and delivering lipophilic bioactive agents. They can also be designed to have different optical (transparent or slightly turbid), rheological and stability characteristics when controlling their composition and structure (Silva, Cerqueira, & Vicente, 2011; McClements, 2013; Odriozola-Serrano, Oms-Oliu, & Martin-Belloso, 2014). Additionally, the very small size of oil droplets in nanoemulsions can increase the digestion rate and the total amount of free fatty acids released during digestion, in comparison with conventional emulsions (Li & McClements, 2010; Salvia-Trujillo et al., 2013; Troncoso, Aguilera, & McClements, 2012a), but this increase depends on the type of component encapsulated, and the composition and structure of the nanoemulsions (McClements, 2013).

Food products based on emulsions are complex food structures consisting of mixtures of different kinds of colloidal particles, which have been reassembled and transformed through different processing operations. Hence, many of the nutrient and

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physiologically present and active compounds within these complex structures must be liberated and converted into an absorbable form during digestion (Singh, Ye, & Ferrua, 2015). For this reason, the role of food structure in nutrient bioavailability is a key factor to consider in the development of new products with enhanced properties.

The incorporation of biopolymers represents one of the most common strategies used to stabilize emulsions, since one of the greatest problems of food emulsions is that they are unstable and tend to break during certain processing operations or during storage. A large number of hydrocolloids are used as structuring, thickening or gelling agents in the aqueous phase; in addition some of them with surface activity can also act as emulsifiers in oil-in-water (O/W) emulsions (Dickinson, 2009; McClements, 2005). Its influence on the stability and physical properties of emulsions depends on its molecular characteristics and on its impact on bulk physicochemical properties (Chung, Degner, & McClements, 2013a).

Starch is the most widely used thickener in the food industry. It is present in many emulsion-based foods as sauces, dressings, soups, and desserts. Generally, the use of starch as thickener in emulsion leads to a large increase in viscosity, improving its stability to phase separation (Chung, Degner, & McClements, 2013b, 2014; Arancibia, Jublot, Costell, & Bayarri, 2011; Bortnowska, Balejko, Tokarczyk, Romanowska-Osuch, & Krzemi, 2014). However, it has been reported that the textural characteristics of emulsion-based sauces are highly sensitive to the aggregation state of the fat droplets in the spaces between the starch granules (Chung, Degner, & McClements, 2014). On the other hand, carboxymethyl cellulose (CMC) has been used as fat replacer and thickener in semi-solid matrices due to its technological, sensory and nutritional advantages (Bayarri & Costell, 2011; Bayarri, González-Tomás, & Costell, 2009; Mirhosseini et al., 2008). Nevertheless, some authors have informed that the structural differences between cellulose- and starch-based matrices result in different rheological and sensory properties (Arancibia et al., 2011; Ferry et al., 2006).

Lately, several studies have been carried out to understand the relationship between composition and nutrient bioavailability. Sanz and Luyten (2007) evaluated the suitability of custards as food matrices to promote the bioaccessibility of genistein as lipid bioactive compound. They found that the use of CMC instead of starch as thickening agent significantly reduced the genistein bioaccessibility. In a recent study, Espert, Salvador, and Sanz (2016) evaluated the *in vitro* digestibility of highly concentrated O/W emulsions (50% oil) thickened by methylcellulose. They reported that there was a 12% reduction in free fatty acids formation in comparison with the control without thickener. However, less information exists about how the hydrocolloids affect lipid release from nanoemulsions during *in vitro* digestion. A few studies have reported the use of biopolymers as emulsifiers on nanoemulsions and its relationship on lipid bioavailability (Liang, Shoemaker, Yang, Zhong, & Huang, 2013; Pinheiro, Coimbra, & Vicente, 2016). They have found that the digestibility of emulsified oil droplets by hydrocolloids can be retarded or inhibited depending on the interfacial layer composition. Moreover, the presence of hydrocolloids in nanoemulsions may influence their gastrointestinal fate, which may impact the nutritional properties of any encapsulated lipid bioactive compounds (Dickinson & Leser, 2013; Gidley, 2013; Salvia-Trujillo et al., 2016).

Based on this context, the aim of this work was to study the effect of two thickening agents with different structural characteristics, starch (globular structure) and CMC (polymeric structure), on physical properties and lipid bioavailability of avocado oil-based nanoemulsions, in order to understand the complex relation among composition, physical properties and lipid bioavailability.

2. Materials and methods

2.1. Fabrication of O/W nanoemulsions

Thickened O/W nanoemulsions were prepared with avocado oil (Casta de Peteroa, Terramater S.A., Chile) as dispersed phase and purified water from an inverse osmosis system (Vigaflow S.A., Chile) as dispersant phase. Tween 80 (Sigma-Aldrich S.A., France) was used as emulsifier. Carboxymethyl cellulose (CMC) with a molecular weight of 30,000 Da and degree of substitution ranging from 0.75 to 0.85 (CEKOL 30000, Quimatic S.A., Chile), and pregelatinized waxy corn starch (ST) (Snow-Flake G-2141, Inducorn S.A., Chile) were used as thickening agents.

Eight formulations were prepared varying avocado oil concentration (5 and 15% wt/wt), thickener type (CMC and ST) and thickener concentration (low: 0.5% wt/wt CMC or 6% wt/wt ST; high: 0.75% wt/wt CMC or 8% wt/wt ST). The corresponding effective concentrations of thickeners on the aqueous phase used are shown in Table 1. The thickener levels were selected according to previous experience based on comparable rheological properties (Arancibia, Bayarri, & Costell, 2013; Arancibia, Navarro-Lisboa, Zúñiga, & Matiacevich, 2016). A fixed concentration of Tween 80 (emulsifier-to-oil mass ratio 6:5) was used in each nanoemulsion, previously determined by the optimization of sonication-processing conditions (surfactant-to-oil-ratio and sonication time) by Surface Response Methodology.

The nanoemulsion-base was prepared by the following procedure: first, Tween 80 was dispersed in purified water using a magnetic stirrer (Arex, VelpScientifica, Italy) at 200 rpm for 10 min at room temperature. Then, oil was added slowly to the aqueous phase and the mixture was stirred using a high-performance dispersing homogenizer (Wiggen Hauser D130, Germany) at 21200 or 16800 rpm (for samples with 5% or 15% oil, respectively) for 10 min in a water bath at 5 ± 1 °C. In order to obtain nanoemulsions, the coarse emulsions were then homogenized using a sonicator (VCX500, SONICS & Materiales, USA) with a stainless steel ultrasound probe (13 mm of diameter). Sonication was performed at 80% amplitude and 20 KHz of frequency, during 21 and 16 min for samples with 5 and 15% wt/wt oil, respectively.

After that, CMC or ST was added to the O/W nanoemulsions. CMC was added slowly to nanoemulsions and dispersed using an overhead stirrer at 1500 rpm (BS, Velp Scientifica, Italy) for approximately 40 min (until complete dispersion of CMC). Starch-based nanoemulsions were prepared as follows: starch and nanoemulsion were weighed in a beaker and mixed at 250–350 rpm (samples with 5 and 15% wt/wt oil, respectively) and 40 °C for 10 min with the help of a magnetic stirrer and a hot plate (Ared,

Table 1
Thickener concentrations in the nanoemulsions and aqueous phases for samples containing 5 and 15% oil.

Oil concentration (% wt/wt)	Thickener concentration in nanoemulsions (% wt/wt)	Thickener concentration in aqueous phase (% wt/wt)
5	0.5% CMC	0.53% CMC
	0.75% CMC	0.79% CMC
	6% Starch	6.32% Starch
	8% Starch	8.42% Starch
15	0.5% CMC	0.59% CMC
	0.75% CMC	0.88% CMC
	6% Starch	7.06% Starch
	8% Starch	9.41% Starch