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The impact of HPMC structure in the modulation of in vitro lipolysis: The role of bile salts

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ABSTRACT

The behaviour of two hydroxypropylmethylcelluloses (HPMC), with different molecular structures: E5LV and E4M, has been analysed in the presence of the bile salts, both at the oil-water interface (emulsion behaviour, interfacial properties and ζ-potential) and in the aqueous medium (particle size distribution analysis, cloud point temperature and electrical conductivity).

HPMCs emulsions experienced different degrees and rate of lipolysis (E4M emulsions experienced a higher lipid digestion than emulsions stabilized by E5LV) that were not related to differences in the molecular weight/viscosity.

Differences in the kinetics of lipolysis can be attributed to the interaction with BS according to methyl/hydroxypropyl ratio of these HPMCs. The self-assembly of the E4M cellulose, being the more hydrophilic cellulose (with a lower methyl/hydroxypropyl ratio than E5LV) was more hindered by the bile salts adsorption, thus developing a higher untangling at the interface that would increase the available sites for the lipase.

These results allow a better understanding of the mechanisms that affect food emulsions digestion and it could allow to design polysaccharides stabilized emulsions with better functional properties.

1. Introduction

Fat digestion is a complex colloidal process that requires the adsorption of lipase to the o/w interface of the emulsified droplets, in the presence of colipase and bile salts (BS), in the small intestine (Scholten, Moschakis, & Biliaderis, 2014; Singh & Sarkar, 2011; Zhu, Ye, Verrier, & Singh, 2013), where the absorption of fat digestion products occur, although partial digestion also takes place in the stomach (Klinkesorn & McClements, 2010). Lipids are hydrolysed (lipolysis) resulting in the release of two free fatty acids and one 2-monoacylglycerol (Gallier, Ye, & Singh, 2012). The BS play a key role in the digestion of lipids by stabilizing oil droplets (BS adsorb at the o/w interface and prepare the interface for the enzymatic breakdown due to the action of the lipase-colipase complex) and by forming micelles which are the transport vehicles of the lipolysis products to the enterocytes (Abrahamse et al., 2012; Bellesi, Pizones Ruiz-Henestrosa, & Pilosof, 2014; Bläckberg, Hernell, & Olivecrona, 1981; Sarkar, Ye, & Singh, 2016b; Singh & Gallier, 2014; Torcello-Gómez & Foster, 2014). BS molecules, that are secreted from the liver and stored in the gall bladder, present a high surface activity that makes them very efficient in displacing the adsorbed emulsifiers (complete or partial displacement) from the o/w interface (Bellesi et al., 2014; Maldonado-Valderrama & Patino, 2010; Mun, Decker, Park, Weiss, & McClements, 2006; Sarkar, Horne, & Singh, 2010a; Singh & Ye, 2013; Torcello-Gómez & Foster, 2014; Torcello-Gómez, Maldonado-Valderrama, Jódar-Reyes, & Foster, 2013). The effect of the conformation that they adopt at the o/w interface is very important, as they tend to lay flat at the interface, by maximizing the interfacial area (Chu et al., 2010; Maldonado-Valderrama & Patino, 2010, 2008).

It is very interesting the possibility of manipulating the lipid digestion that could improve health by modifying serum lipid levels (Maldonado-Valderrama, Gunning, Ridout, Wilde & Morris, 2009), in order to produce novel foods that could permit the control of appetite, of the digestion and/or the control of nutrients delivery (Dickinson, 2008; Hur, Lee, Lee, Bahk, & Kim, 2015;

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Scholten et al., 2014; Zimet & Livney, 2009). This fact could allow to decrease the existing growing obesity crisis, associated to a negative impact in the health of the population (Bellesi et al., 2014; Marciani et al., 2009).

The characteristics of the interfacial layers surrounding the fat droplets have been reported to play a significant role in the extent of lipid digestion, using different surface active components, as well as the release rate of any entrapped components (Bellesi et al., 2014; Li & McClements, 2011; Malaki Nik, Wright, & Corredig, 2011; McClements & Li, 2010; Mun, Decker, & McClements, 2007; Sarkar et al., 2016a; Torcello-Gómez & Foster, 2014; Tzoumaki, Moschakis, Scholten, & Biliaderis, 2012; Ye, Cui, Zhu, & Singh, 2013).

Polysaccharides are natural biopolymers that are commonly employed in many food dispersed systems, such as emulsions and foams, and they are normally used to control the texture and stability of these products (Dickinson, 2003; Hanazawa & Murray, 2014). Most of these molecules do not tend to adsorb at fluid interfaces because of their high hydrophilic character (Camino, Pérez, & Pilosof, 2009a; Rodríguez Patino and Pilosof, 2011). However, there exist a group of surface active polysaccharides, such as cellulose derivatives, that have received a great interest recently because of their physico-chemical properties and many technological applications (Arboleya & Wilde, 2005; Pérez, Sánchez, Pilosof, & Rodríguez Patino, 2009; Rodríguez Patino and Pilosof, 2011). Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) are considered the principal cellulose derivatives and they are used in a broad range of applications in pharmaceutical and food formulations (Pérez, Carrera Sánchez, Pilosof, & Rodríguez Patino, 2015).

HPMCs are non-ionic cellulose derivatives with methyl (hydrophobic) and hydroxypropyl (hydrophilic) groups added to the anhydroglucose backbone and include a family of cellulose ethers that differ principally in molecular weight, viscosity, degree of substitution (DS). DS is the average number of hydroxyl groups per anhydroglucose unit where hydrogen is replaced by methyl and molar substitution (MS) is the average number of propylene oxide groups per anhydroglucose unit. The higher the degree of total substitution is, the higher the hydrophobicity of the polysaccharide will be, thus their surface/interfacial activity will also increase (Camino et al., 2009a; Chang & Gray, 1978; Daniels & Barta, 1994; Wollenweber, Makievski, Miller, & Daniels, 2000). Furthermore, it is also known that HPMCs provide health effects, such as the hypocholesterolemic effects (Kim et al., 2011; Maki et al., 2000, 2009; Reppas, Swidan, Tobey, Turowski, & Dressman, 2009; Torcello-Gómez & Foster, 2014; Yokoyama et al., 2011), as well as their promissory usage as vehicles for encapsulation of active food ingredients (Fathi, Martín, & McClements, 2014; Mun, Kim, Shin, & McClements, 2015) in order to get a controlled release in the gastrointestinal tract. Due to all these interesting properties and because of the necessary reduction in the fat consumed by the populations, their use in food systems could be a good strategy to diminish the effective caloric content of the foods, to control the lipid digestion or to control the satiety (Beysseriat, Decker, & McClements, 2006; Mudgil & Barak, 2013; Torcello-Gómez & Foster, 2014).

The behaviour of one of these HPMC emulsions has been recently evaluated (Bellesi, Martinez, Pizones Ruiz-Henestrosa, & Pilosof, 2016) when exposing it to the complex simulated human gastrointestinal conditions to mimic their transit through the human digestive tract (exposition to the stomach juices and the pancreatic fluid (small intestine), containing enzymes such as trypsin, chymotrypsin, lipases, etc., and the biliary fluid, containing different bio-surfactants, such as the BS, phospholipids, cholesterol and the products obtained from the lipid digestion) (Mackie & Macierzanka, 2010; Nik, Corredig, & Wright, 2010). A much lower extent and rate of lipolysis was observed when using HPMC as emulsifier as compared to β-lactoglobulin. Thus HPMC seems to be a good emulsifier to reduce the extent of the lipolysis in the emulsions.

Torcello and Foster (Torcello-Gómez & Foster, 2014) have recently analysed the competitive adsorption of different modified celluloses and BS. They observed that the adsorption of the mixed systems (polysaccharides (10^{-3}% (w/w)) + BS) was controlled by the BS when using BS concentrations from 10^{-3} to 10^{-1} M. When analysing the behaviour of these systems in the aqueous phase (micro-DSC measurements) they observed the existence of interactions between these molecules that affected their adsorption to the o/w interface.

The objective of present work was to study the lipid digestion (free fatty acid release (FFA)) of the o/w HPMCs stabilized emulsions as affected by the molecular weight or hydrophobicity of HPMC and to understand the involved mechanism, mediated by the BS. Furthermore, the physico-chemical changes occurring in the emulsions and interfaces, when in contact with the BS (important physiological components for the lipase to develop the hydrolysis), as well as HPMCs-BS interactions in the bulk phase, have been assessed in order to explain the observed differences in the kinetics of the free fatty acid release.

2. Materials and methods

2.1. Materials

Commercial HPMCs: E5LV and E4M (food grade) from The Dow Chemical Company were kindly supplied by Colorcon (Argentina) and used without purification. Their properties (Table 1) have already been indicated by Camino and Pilosof (Camino, Sánchez, Rodríguez Patino, & Pilosof, 2011). HPMC solutions were prepared in hot water at 90 °C by dispersing the powder in Trizma [$(CH_2OH)_3CNH_2$/$(CH_2OH)_3CNH_3Cl$] buffer at pH 7. The solutions were prepared at 2% (w/w) and stored at 4 °C for 24 h in order to achieve their complete hydration (Camino et al., 2009a). Methocel E5LV was used due to its low molecular weight and high hydrophobicity (Camino & Pilosof, 2011), and Methocel E4M, was used because of its higher viscosity and molecular weight and lower hydrophobicity than E5LV (Table 1). The interfacial behaviour of HPMCs have been extensively studied in previous studies (Camino et al., 2009a, 2009b, 2011; Arboleya & Wilde, 2005; Camino & Pilosof, 2011; Wollenweber et al., 2000).

Commercial sunflower oil was purified, to eliminate the possible surface-active contaminants, with Florisil 60-100 Mesh (Fluka) as described by Bellesi et al. (Bellesi et al., 2014).

All the glassware was cleaned using ammonium persulfate-sulfuric acid to eliminate all the possible surface-active contaminants that could interfere in the measurements and rinsed with bi-distilled water.

Table 1
E4M and E5LV properties.

Properties	E4M	E5LV
% methyl	28.0	29.5
% hydroxypropyl	10.2	9.7
Methyl/hydroxypropyl ratio	2.3	3.0
Methyl substitution (DS)	1.90	1.90
Hydroxypropyl substitution (MS)	0.23	0.23
Total substitution (DS + MS)	2.13	2.13
Viscosity (cp), 2% wt solution (20 °C)	4965	5.4
Molecular weight (kDa)	90	2