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Physical properties of emulsion-based hydroxypropyl methylcellulose films: Effect of their microstructure

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ABSTRACT

The initial characteristics of emulsions and the rearrangement of the oil droplets in the film matrix during film drying, which defines its microstructure, has an important role in the physical properties of the emulsion-based films. The objective of this work was to study the effect of the microstructure (two droplet size distributions) and stability (with or without surfactant) of HPMC oil-in-water emulsions over physical properties of HPMC emulsion-based edible films. HPMC was used to prepare sunflower oil-in-water emulsions containing 0.3 or 1.0% (w/w) of oil with or without SDS, as surfactant, using an ultrasonic homogenizer. Microstructure, rheological properties and stability of emulsions (creaming) were measured. In addition, microstructure, coalescence of oil droplets, surface free energy, optical and mechanical properties and water vapor transfer of HPMC films were evaluated. Image analysis did not show differences among droplet size distributions of emulsions prepared at different oil contents; however, by using SDS the droplet size distributions were shifted to lower values. Volume mean diameters were 3.79 and 3.77 μm for emulsions containing 0.3 and 1.0% without surfactant, respectively, and 2.72 and 2.71 μm for emulsions with SDS. Emulsions formulated with 1.0% of oil presented higher stability, with almost no change during 5 and 3 days of storage, for emulsions with and without SDS, respectively. Internal and surface microstructure of emulsion-based films was influenced by the degree of coalescence and creaming of the oil droplets. No effect of microstructure over the surface free energy of films was found. The incorporation of oil impaired the optical properties of films due to light scattering of light. Addition of oil and SDS decreased the stress at break of the emulsion-based films. The replace of HPMC by oil and SDS produce a lower "amount" of network structure in the films, leading to a weakening of their structure. The oil content and SDS addition had an effect over the microstructure and physical properties of HPMC-based emulsions which lead to different microstructures during film formation. The way that oil droplets were structured into the film had an enormous influence over the physical properties of HPMC films.

1. Introduction

An edible film is defined as a thin layer of material, which can be eaten as part of the whole product, providing a barrier to mass transfer (moisture, gas, flavors, *etc.*) between the food and the surrounding environment or in the food itself, for instance between compartments of different water activities in the same food (Borlieu, Guillard, Vallès-Pamiès, & Gontard, 2007; Borlieu, Guillard, Vallès-Pamiès, Guilbert, & Gontard, 2009). For the past 10 years, research on edible films and coatings in foods was driven by food engineers due to the high demand of consumers for longer shelf-life and better quality of fresh foods as well as of environmentally friendly packaging. In addition, edible films and coatings can be used as a vehicle for incorporating natural or chemical antimicrobial agents, antioxidants, enzymes or functional ingredients such as probiotics, minerals and vitamins (Skurtys et al., 2010). Excellent reviews on film-forming food biomaterials and their properties can be found in the recent published literature (Borlieu et al., 2007, 2009; Nussinovitch, 2003; Skurtys et al., 2010). Although the potential of edible films to improve food quality and extend shelf life has been proved, most of the works in this area are focused on the formulation point of view and few studies deals with the effect of the film microstructure on their physical properties.

The barrier (water vapor, O_2, CO_2, *etc.*), mechanical and optical properties of a film are the upmost importance when defining its suitability for a specific target application. Generally, films composed of one substance have either good barrier or good mechanical properties but not both (Borlieu et al., 2009; Callegarin, Quezada

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Gallo, Debeaufort, & Voilley, 1997). Polysaccharides and proteins create a network responsible for good mechanical properties, but their inherent hydrophilic nature makes them a poor barrier for water vapor transfer. On the contrary, lipids have excellent water vapor barriers because of their hydrophobic character, but films made from lipids alone are usually brittle, opaque, unstable and waxy tasting (Callegarin et al., 1997). Therefore, considerable attention has been focused on the development of composite edible films, which combine the advantages associated of each class of film-formers: the moisture barrier properties of lipids and the ability to form a resistant matrix of the hydrocolloids (Borlieu et al., 2007, 2009; Callegarin et al., 1997; Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002). One approach to design composite films is dispersing a lipid compound into a hydrocolloid film-forming dispersion making an emulsion, which is then cast and dried to prepare an emulsified-film. Emulsified-films are less efficient than bilayers films due to the non-homogeneous distribution of lipids, but they have received more interest because they need only one drying step instead of the two necessary for create bilayer films (Quezada Gallo, Debeaufort, Callegarin, & Voilley, 2000). Goods reviews on lipid-based films can also be found in the recent literature (Callegarin et al., 1997; Morillon et al., 2002).

Many of the most important properties of emulsions are determined by the size of the droplets they contain (Walstra, 2003). Initial characteristics of emulsions (particle size and size distribution) would lead to different microstructures during drying of emulsion-based films, which in turn affects to a greater extent the physical properties of the film. Hence, the emulsion structure has to be controlled during the preparation and formation (drying) of the film. Heat and solvent evaporation during drying of the hydrocolloid-based emulsion induces changes in the initial emulsion structure, particularly driven by destabilization phenomena like creaming, aggregation and/or coalescence (Phan The, Debeaufort, et al., 2002; Phan The, Péroval, et al., 2002). The rearrangement of the oil droplets in the film matrix during the film drying, which defines its internal and surface structure, has an important role in the optical, mechanical and barrier properties of the emulsion-based films.

Controlling the initial structure and some properties of the film-forming emulsion can contributes to the understanding of film properties. The ability of food manufacturers to formulate emulsion-based products with tailored properties depends on knowledge of the relationship between their physical properties and their composition and microstructure (Chanamai & McClements, 2001). Therefore, the objective of this work was to study the effect of the microstructure of oil-in-water emulsions stabilized by hydroxypropyl methylcellulose (HPMC) alone or by HPMC with sodium dodecyl sulfate (SDS) over physical properties of HPMC emulsion-based edible films. This study is an attempt to relate the microstructure of the films with their barrier, mechanical and optical properties. To compare in a more realistic way the treatments, emulsions with two equal droplet size and size distributions were produced, independent of concentration of the dispersed phase used.

2. Materials and methods

2.1. Materials

Hydroxypropyl methylcellulose (HPMC, METHOCEL E19, Dow Wolff Cellulosics, Bomlitz, Germany) was used as the structural material in all formulations due to their excellent film-forming properties (Borlieu et al., 2007; Skurtys et al., 2010). HPMC is a white, odorless and tasteless powder of a water-soluble cellulose derivative. The presence of hydroxypropyl and methyl groups in HPMC renders the cellulose molecule hydrophobic and thus HPMC acquires surface active properties (Petrovic, Sovilj, Katona, & Milanovic, 2010). According to the manufacturer HPMC has a nominal viscosity of 19 mPa s and a number average molecular weight of 16,000. The methoxyl degree of substitution was 1.9 and the hydroxypropyl molar substitution was 8.5. These factors affect the thermal gelation temperature of the aqueous dispersions and the strength of the films formed (Cash & Caputo, 2010). Propylene glycol (PG, LyondellBasell Industries Holdings, Rotterdam, The Netherlands) was incorporated to the formulations because behaves as plasticizer in edible films, giving to the material flexibility and tear resistance (Borlieu et al., 2007). A commercial brand of sunflower oil (Natura™, Argentina) was used as the hydrophobic dispersed phase. Sodium dodecyl sulfate (SDS, Sigma–Aldrich Corp., St. Louis, MO, USA) was used as surfactant in some formulations. All reagents were used as received without further purification.

2.2. Emulsion formation

Different compositions of the film-forming dispersions were formulated according to Table 1. HPMC powder was dispersed in distilled water at 60 °C for 2 h under moderate stirring avoiding foam formation, then PG was incorporated and, finally, depending on the formulation, SDS was added. The dispersion was stirred for 30 min more and left at 4 °C for at least 12 h to allow complete hydration of the polymer. Previous studies has been shown that inter/intra-molecular interactions occur between HPMC and SDS above certain surfactant concentration, *i.e.* critical aggregation concentration (CAC), leading to modification in some physical properties of the system, such as viscosity and surface tension (Katona, Sovilj, Petrovic, Mucic, 2010; Nilsson, 1995; Petrovic et al., 2010). At the SDS concentrations used in this work, probably no interactions occur between the surfactant and the HPMC. Values for CAC were found about 1.0% (w/w) of SDS, below this concentration no interactions occur, independent of the polymer concentration (Nilsson, 1995; Katona et al., 2010). For film-forming emulsions, sunflower oil was added dropwise to dispersions while mixing using a stirring plate at 300 rpm for 1 min at 30 °C, thus forming a coarse emulsion. The oil-to-surfactant mass ratio was 10-to-1 for the SDS stabilized emulsions. In order to decrease the droplet sizes an ultrasonic processor (Branson Sonifier 450, Branson Ultrasonics, Danbury, CT, USA) with a 19 mm (0.75 in.) stainless steel ultrasound probe was used to sonicate 60 g of the coarse emulsion in a 120 ml beaker. The tip horn was adjusted 1 cm below the surface of the sample. Sonication was carried out in the pulsed mode (frequency of one pulse per second, duration of the pulse 0.3 s) at a nominal power level of 250 W for 180 s. Film-forming dispersions were degassed at room temperature with a vacuum pump. All formulations were done in triplicate at the same level of total solids and were named HPMC, HPMC-0.3, HPMC-1.0, HPMC-0.3-SDS and HPMC-1.0-SDS, according to the levels of oil and SDS used (Table 1).

Table 1
Compositions of the film-forming dispersions (%, w/w) for 100 g of dispersion. All dispersions were formulated at the same level of solids.

Film forming dispersion notation	HPMC	PG	Oil	SDS
HPMC	3.50	2.0	–	–
HPMC-0.3	3.20	2.0	0.3	–
HPMC-0.3-SDS	3.17	2.0	0.3	0.03
HPMC-1.0	2.50	2.0	1.0	–
HPMC-1.0-SDS	2.40	2.0	1.0	0.10

HPMC, hydroxypropyl methyl cellulose; PG, propylene glycol; SDS, sodium dodecyl sulfate.