Physicochemical characterization of hydroxypropyl methylcellulose based oil-in-water emulsions for edible film formation

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ABSTRACT

Initial characteristics of emulsions would lead to different structures during drying of emulsion-based films, which in turn will affect the behavior of the film. The objective of this work was to study the effect of oil concentration and the use of surfactant over bubble sizes, interfacial tension, rheological properties and stability of oil-in-water emulsions stabilized by hydroxypropyl methylcellulose (HPMC) alone or by HPMC with sodium dodecyl sulfate (SDS). HPMC was used to prepare sunflower oil-in-water emulsions containing 0.3 or 1.0% (w/w) of oil, with or without SDS, using an ultrasonic homogenizer. Microstructure of emulsions was evaluated in terms of droplet sizes by means of image analysis. Interfacial tension measurements were carried out by the pendant drop method. Rheological properties were evaluated using the flow curve test. Stability of emulsions (creaming) was measured using a spectrophotometer at 850 nm. Image analysis did not show differences between 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 containing 0.3 and 1.0% oil showed a Newtonian behavior with viscosity values of 6.61×10⁻² and 3.28×10⁻² Pa s for emulsions formulated without surfactant and values of 6.23×10⁻² and 5.60×10⁻² Pa s when SDS was incorporated. Emulsions formulated with 1.0% of oil presented higher stability, with almost no change in normalized transmittance during 5 and 3 days of storage, for emulsions with and without SDS, respectively. Emulsions with an oil content of 0.3% showed an exponential decay of normalized transmittance with time. The oil content and the surfactant addition had an effect over the microstructure and physicochemical properties of HPMC-based emulsions which could lead to different microstructures during film formation.

Keywords: Emulsion; microstructure; droplet diameter; interfacial tension; creaming

INTRODUCTION

An edible film is defined as a thin layer of material, which can be consumed, providing a barrier to mass transfer in the food itself or between the food and the surrounding environment [1]. 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. However, most of the works in this area are focused on the formulation point of view and only few works deals with the effect of the film structure on their physical properties. Nowadays, considerable attention has been focused on the development of composite edible films, which take advantage of the distinct functional properties of each class of film-formers: the moisture barrier properties of lipids and the ability to form a resistant matrix of the hydrocolloids [1, 2, 3]. One approach is to design composite films is dispersing a lipid compound into a hydrocolloid film-forming dispersion to make an emulsion, which is then cast and dried to prepare an emulsified-film.

Many of the most important properties of emulsion are determined by the size of the droplets they contain [4, 5]. 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 destabilization phenomena like creaming, aggregation and/or coalescence [6]. Controlling the initial structure and some properties of the
film-forming emulsion can contribute to the understanding and tailoring of film properties. Therefore, the objective of this work was to study the effect of oil concentration and the use of surfactant over bubble sizes, interfacial tension, rheological properties and stability of oil-in-water emulsions stabilized by hydroxypropyl methylcellulose (HPMC) alone or by HPMC with SDS.

**MATERIALS & METHODS**

**Raw materials**

Hydroxypropyl methylcellulose (HPMC, Methocel E19, Dow Wolff Cellulosics, Germany) was used in all formulations due to their excellent film-forming properties [1], also the presence of hydroxypropyl and methyl groups in HPMC renders the cellulose molecule hydrophobic and thus HPMC acquires surface active properties [7]. Propylene glycol (Sigma-Aldrich Corp., St. Louis, MO, USA) was incorporated to the formulations because acts as plasticizer in edible films [1]. A commercial brand of sunflower oil (Natura™, Argentina) was used as the hydrophobic dispersed phase. Sodium dodecyl sulfate (Sigma-Aldrich Corp., St. Louis, MO, USA) was used as surfactant in some formulations.

**Interfacial tension measurements**

Interfacial tension measurements were carried out by the pendant drop method previously reported [8]. A small solution drop (about 10–20 µl) attached to the tip of a stainless-steel needle (outer diameter of 1.25 ± 0.005 mm) was hung into 10 ml of the oil under a constant temperature (with the accuracy ± 0.1 °C). The drop was formed by a controlled syringe pump (Model 1000, New Era Pump System Inc., Farmingdale, NY, USA). Images of the drop were taken with a CCD camera (Pulnix TM-6740GE, Pulnix Inc., San José, CA, USA) with a pixel resolution of 640 × 480 equipped with a zoom objective. The shape of the drop at equilibrium, determined by the balance of gravity and interfacial tension, was determined from the fundamental Laplace equation:

\[
\frac{d \sin \theta}{dx} = \frac{2}{b} \frac{g \Delta P}{\gamma} - \frac{z}{x} \sin \theta
\]  

(1)

The origin of the coordinate system was at the drop apex; \(x\) and \(z\) are the Cartesian coordinates at any point of the droplet, \(b\) is the radius curvature at the apex; \(\theta\) is the angle between the drop axis and the normal to the drop interface. To validate the results it was corroborated experimentally that the interfacial tension of the pure water/air system was 72 ± 0.3 mN/m.

**Emulsions formation**

Different compositions of the film-forming dispersions were formulated (Table 1). HPMC powder was dispersed in distilled water at 60°C for 2 h under moderate stirring avoiding foam formation, then propylene glycol was added and, depending on the formulation, SDS was incorporated as surfactant, the solution was stirred for 30 min more and left at 4°C for at least 12 h to allow complete hydration of the polymer. At the SDS concentrations used no interactions occurs between the surfactant and the HPMC [7, 9]. For emulsion preparation sunflower oil was added dropwise to HPMC dispersions while mixing at 30°C using a stirring plate at 300 rpm for 1 min, forming a coarse emulsion. The oil-to-surfactant mass ratio was 10-to-1 for the surfactant stabilized emulsions. For fine emulsion formation 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.

**Flow properties of film-forming dispersions**

The rheological behavior of the emulsions was determined using a coaxial cylinder geometry in a controlled shear rate rheometer (model DV-III, Brookfield Engineering Laboratories, Stoughton, MA, USA) at 25°C applying the flow curve method. Shear rate (\(\dot{\gamma}\)) was increased linearly from 0 to 100 s⁻¹ in 30 min (upward ramp) and then decreased in a similar way to 0 s⁻¹ over 30 min (downward ramp). Experiments were done in triplicate.
Quantification of droplet sizes and size distributions of emulsions by image analysis

Droplet sizes were determined from images of the emulsions obtained with a light microscope (Olympus BX50, Optical Co. Ltd., Tokyo, Japan) and recorded with a digital CCD camera (CoolSnap-Pro Color Photometrics Roper Division, Inc., Tucson, AZ, USA). Each image (1392×1040 pixels) was saved as a 24 bits TIFF image file of approximately 1.38 MB, without compression.

Image processing for droplet size analysis was carried out automatically using a segmentation algorithm developed under Matlab environment (Matlab 7.6 (R2009a), The MathWorks Inc, MA, USA), mainly based on mathematical morphology. Briefly, the data processing of the digitalized images consisted of different steps, including contrast enhancement, different filter operations followed by an automatic segmentation. This procedure allowed considerable reduction of the data analysis time without losing accuracy.

A substantial number of droplets (N = 1000) were counted to obtain statistical estimates of the droplet size distribution in each sample. Droplet size distributions were generated by grouping the droplets into classes belonging to a common interval. Frequency distribution of droplet sizes was computed using MS-Excel (Microsoft™ Excel 2007). The volume frequency of any class interval was calculated as the number of droplets in that class (class frequency) divided by the total number of droplets, and expressed as a percentage. The volume-surface mean diameter ($D_{3,2}$) was calculated using Eq. 2.

$$D_{3,2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where $n_i$ is the number of droplets with diameter $d_i$ (µm).

Creaming of emulsions

The destabilization of the emulsions produced by gravitational separation (creaming) was evaluated by means of spectrophotometric measurements. Light transmittance was measured at 850 nm using a spectrophotometer (Shimadzu, UV-160, Kyoto, Japan). Emulsions were contained in plastic cuvettes with a 1 cm path length. Transmittance measurements were made using a standard double-beam arrangement, with the transmittance of the sample being measured relative to that of a reference cell containing distilled water [10].

RESULTS & DISCUSSION

Rheological behavior of film-forming dispersions

All the film-forming dispersions showed Newtonian behavior. The incorporation of oil to HPMC dispersions did not change their rheological behavior, probably because at low volume fraction of oil the colloidal interactions between droplets are too weak to induce a change in the ideal liquid behavior [4]. Viscosity of HPMC dispersion was 8.2×10−2, being higher than the film-forming emulsions (Table 1). Emulsions containing 0.3 and 1.0% oil showed viscosity values of 6.6×10−2 and 3.3×10−2 Pa s for emulsions formulated without SDS, respectively, and values of 6.2×10−2 and 5.6×10−2 Pa s when SDS was incorporated. The decrease in viscosity values, for film-forming emulsions, with an increase in oil content was due to replacing part of the polymer for oil and/or surfactant.

<table>
<thead>
<tr>
<th>Film forming dispersion</th>
<th>HPMC</th>
<th>PEG</th>
<th>Oil</th>
<th>SDS</th>
<th>$\gamma$ (mN/m)</th>
<th>$\mu \times 10^2$ (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPMC</td>
<td>3.50</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.23</td>
</tr>
<tr>
<td>HPMC-0.3</td>
<td>3.20</td>
<td>2.0</td>
<td>0.3</td>
<td>-</td>
<td>13.0</td>
<td>6.61</td>
</tr>
<tr>
<td>HPMC-0.3-SDS</td>
<td>3.17</td>
<td>2.0</td>
<td>0.3</td>
<td>0.03</td>
<td>5.9</td>
<td>6.23</td>
</tr>
<tr>
<td>HPMC-1.0</td>
<td>2.50</td>
<td>2.0</td>
<td>1.0</td>
<td>-</td>
<td>12.9</td>
<td>3.28</td>
</tr>
<tr>
<td>HPMC-1.0-SDS</td>
<td>2.40</td>
<td>2.0</td>
<td>1.0</td>
<td>0.1</td>
<td>5.7</td>
<td>5.60</td>
</tr>
</tbody>
</table>

Microstructure of emulsions

Polydisperse emulsions were produced using ultrasound as homogenizing medium (Fig. 1). Microscopy images showed a high similarity in droplet sizes of emulsions with and without SDS, showing only differences in the concentrations of droplets present in the micrographs at 0.3 and 1.0% of oil. Emulsions
formulated with SDS presented smaller droplet sizes and lower dispersions of sizes, independent of the oil concentration. Image analysis did not show differences between droplet size distributions of emulsions prepared at different oil contents (Fig. 2). However, by using SDS the droplet size distributions were shifted to lower values, probably because the addition of SDS decreased the interfacial tension between oil and HPMC with a value of ~5.8 mN/m, whereas a value of ~13.0 mN/m was measured for HPMC dispersions without surfactant. The volume-surface mean droplet diameters \( D_{3,2} \) did not present statistical differences \((p> 0.05)\) between the oil concentration used. The \( D_{3,2} \) values were 3.79 and 3.77 \( \mu m \) for emulsions containing 0.3 and 1.0% of oil without surfactant, respectively, and 2.72 and 2.71 \( \mu m \) for emulsions containing 0.3 and 1.0% of oil with SDS.

![Figure 1. Gallery of images obtained by optical microscopy of emulsions stabilized by HPMC alone or by HPMC with SDS. Micrographies are shown without image processing.](image)

**Destabilization of emulsions**

Scattering of light, which can be due to reflection, refraction, or diffraction, occurs at sites where the refractive index changes, for instance at the droplet interface. Hence, when a beam of light is directed through an emulsion, it is scattered by the droplets and only a part can be transmitted through the sample [4, 5]. The degree of scattering by an emulsion depends on the concentration, size and refractive index of any particles present [10]. For a spectrophotometer in which none of the light scattered by the turbid sample reaches the photodetector and for a sample which does not adsorb light, the transmittance can be directly related to the concentration of droplets and thus, to the creaming. As the droplets moved upwards due to gravity there was a decrease in the transmittance at the bottom of the emulsions (because the droplet concentration decreased). The curves shown in Fig. 3 indicate that the rate of creaming decreased appreciably when the oil concentration was increased from 0.3 to 1.0% of oil and, as expected, the creaming was faster in the emulsion containing the larger droplets. Emulsions formulated with 1.0% of oil presented higher stability, with almost no change in absorbance during 5 and 3 days of storage, for emulsions with and without SDS, respectively (Fig. 3). Emulsions oil content of 0.3% showed an exponential decay of absorbance with time.
CONCLUSION

The oil content and the surfactant addition had an effect over the microstructure and physicochemical properties of HPMC-based emulsions which could lead to different microstructures during film formation affecting the behavior of the film.

ACKNOWLEDGEMENTS

RN Zúñiga thanks to the financial support of the VRAID of the Pontificia Universidad Católica de Chile and the INNOVA CORFO project Preservation of Quality and Shelf-life Extension of Fresh Blueberries using Edible Films.

REFERENCES


