Effect of oil content and surfactant addition on color and mechanical properties of hydroxypropyl methylcellulose emulsion-based edible films

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ABSTRACT

The rearrangement of the oil droplets in the film matrix during film drying, which defines its internal and surface structure, has an important role in the optical and mechanical properties of the emulsion-based films. The objective of this work was to study the effect of oil concentration and the use of surfactant sodium dodecyl sulfate (SDS) over color and mechanical properties of hydroxypropyl methylcellulose (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. Emulsions were formed using an ultrasonic homogenizer. Edible films were obtained by drying the emulsions at 40 °C for 24 h and then equilibrate the films for 48 h at 22% RH. Transparency (T) of films was measured at a wavelength of 600 nm using a spectrophotometer. White index (WI) and total color change (ΔE) of films were calculated from measurements done in L*a*b* scale by a colorimeter. Tensile measurements were carried out for films of 30 mm wide and 100 mm long. Tensile stress (σB) and percentage of elongation at break (Eg) were calculated. The incorporation of oil produced a decrease in T and an increase in WI and ΔE of the emulsion-based films with respect to the pure HPMC film. The decrease in T and the increase in WI and ΔE were related to the light-scattering effect of oil, which was dependent of the microstructure of the emulsion-based films. Addition of oil and SDS decreased the σB 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 addition oil and SDS into edible films had no significant effect (p>0.05) over Eg. Microstructure formation during drying of emulsion-based edible films had an enormous influence over the optical properties of films, transparency and color was dependant on the way that oil droplets were structured into the film.

Keywords: Emulsion; edible films; microstructure; optical properties; tensile properties

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 is 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. The barrier (water, O2, CO2, etc), mechanical and optical properties of a film are relevant when defining its suitability for a specific target application. Polysaccharides and proteins create a network responsible for the mechanical properties, but their inherent hydrophilic nature makes them a poor barrier for water vapor transfer. On the contrary, because of their hydrophobic character, lipids are good water vapor barriers, but films made from lipids alone are usually brittle from the mechanical point of view. Generally, films composed of one substance have either good barrier or good mechanical properties but not both [2]. Therefore, 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]. 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. Hence, the objective of this work was to study the effect of oil concentration and the use of surfactant sodium dodecyl sulfate (SDS) over color and mechanical properties of hydroxypropyl methylcellulose (HPMC) emulsion-based edible films.

MATERIALS & METHODS

Raw materials
Hydroxypropyl methylcellulose (HPMC, Methocel E19, Dow Wolff Cellulosics, Germany) was used as the structural material in all the formulations due to their excellent film-forming properties, 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 used as plasticizer and 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.

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 as plasticizer 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, 8]. For film-forming emulsion preparation sunflower oil was added dropwise to 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. All formulations were done at the same amount of total solids.

Film formation
Edible films were obtained by casting 12 g of the film forming dispersions on leveled acrylic plates (length 10 cm, width 10 cm). Film forming dispersions were dried by convection in an oven at 40 °C and 23% relative humidity for 24 h. The films were removed from the oven and immediately placed in a desiccator (25 °C) over a saturated solution of potassium acetate (22% RH) (Sigma-Aldrich Corp., St. Louis, MO, USA) and held for 48 h before testing. Measurements of film thickness were made at 8 positions on each film sample using a digital micrometer, average values were calculated with an accuracy of 0.002 mm.

Light absorbance of the films
The light barrier properties of films were measured by exposing the films to light at wavelengths ranging from 200 to 900 nm, using a spectrophotometer (Shimadzu, UV-160, Kyoto, Japan). The film sample was cut into a rectangular shape and placed on the internal side of a spectrophotometer cell. The transparency of the films was calculated by Eq. (1):

\[
T = \frac{\text{Transmittance}_{600}}{x} \quad (1)
\]

where Transmittance_{600} is the transmittance of light through the film at 600 nm and x is the film thickness (µm).
Instrumental color of the films
Color measurements were done using a tristimulus colorimeter (HunterLab ColorFlex, Hunter Associates Laboratory Inc., Reston, VA, USA), applying the CIELab scale. The instrument was standardized each time with white and black ceramic plates. Measurements of film color were done in triplicate over the white ceramic plate used for calibration. The whiteness index ($WI$) was defined as:

$$WI = 100 - \sqrt{100 - L_*}^2 + a_*^2 + b_*^2$$

where $L_*$ (black 0 to light 100), $a_*$ (red 120 to green -120) and $b_*$ (yellow 120 to blue -120) values correspond to whiteness, redness and yellowness, respectively.

Total color difference ($\Delta E$) between control HPMC film ($L_0^*, a_0^*, b_0^*$) and emulsion-based films ($L^*, a^*, b^*$) was defined as:

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2}$$

Microscopic structure of emulsion-based films
The microscopic structure of emulsion-based films was observed under 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).

Mechanical properties of the films
Tensile measurements were carried out for films cut in rectangular sections (30 mm wide, 100 mm long). Samples were mounted and clamped with grips in a TAXT2i Texture Analyzer (Stable Micro Systems, Godalming, UK). Grip separation was set at 50 mm and samples were stretched at a constant speed of 0.1 mm/s at 25 ºC until break. Tensile properties, tensile strength ($\sigma_B$) and percent of elongation at break ($E_B$), were calculated from stress-strain and force-distance curves, respectively. Measurements were done in triplicate.

RESULTS & DISCUSSION
Formation of edible films
Both HPMC and emulsion-based films based on HPMC were flexible and easy to handle, while the former was transparent the latter were opaque in a degree dependant on the formulation. No statistical differences ($p>0.05$) were found between the thickness of edible films (Table 1), so the effect of thickness over color and mechanical properties can be avoided.

<table>
<thead>
<tr>
<th>Table 1. Composition (% w/w) of the film forming dispersions and thickness of the emulsion-based films</th>
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<tbody>
<tr>
<td><strong>Emulsion-based film</strong></td>
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<tr>
<td>HPMC</td>
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<tr>
<td>HPMC-0.3</td>
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<tr>
<td>HPMC-0.3-SDS</td>
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<tr>
<td>HPMC-1.0</td>
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<td>HPMC-1.0-SDS</td>
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Microscopic structure of emulsion-based films
Many of the structural components in food emulsions are in the micron-size range and therefore cannot be observed directly by the eye (e.g., emulsion droplets, surfactant micelles, fat crystals) [5], also this is true for emulsion-based edible films. So, the study of the microstructure of this kind of films is crucial to understand and design their physical properties. The effects of oil concentration and the use of SDS on the microstructure of emulsion-based edible films are shown in the micrographs presented in Figure 1. Different microstructures were obtained for emulsion-based edible films, almost intact oil droplets can be seen for HPMC-0.3, HPMC-0.3-SDS and HPMC-1.0-SDS films, which appear as dark grey circles with a white center. However for HPMC-1.0 films only “oil plates” with an irregular form can be seen, which also appear
in the other films, these “oil plates” are coalesced oil droplets produced during formation of films. For emulsion-based films without SDS the micrographs show larger “oil plates” than for SDS stabilized emulsions. During drying of emulsions water evaporates and instability phenomena occurred (i.e. creaming, aggregation and coalescence) being dependent on the concentration of the oil phase and the use of surfactant. The evaporation of water lead to an increase in the viscosity of the continuous phase and a decrease in the initial thickness of the emulsion layer, then the solidification and shrinking of the continuous phase produces a pressure over the droplets increasing the coalescence. At higher oil concentrations and in the absence of SDS the degree of coalescence was higher as observed in Fig. 1.

![Figure 1. Gallery of images obtained by optical microscopy of emulsion-based films stabilized by HPMC alone or by HPMC with SDS.](image)

**Color and transparency of film-forming dispersions**

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 interphase [4, 5]. Therefore, the transmittance of light through emulsion-based films can be related to the concentration of droplets and also to the microstructure of the films. The decrease in transparency ($T$) of emulsion-based films without SDS, in comparison with the control, was 38% and 70% for films formulated with 0.3 and 1.0% of oil. In turn, diminution in $T$ for emulsion-based films with SDS was 13% and 14% for oil contents of 0.3 and 1.0%, respectively. The incorporation of oil produced an increase in the white index ($WI$) of the emulsion-based films with respect to the control HPMC film, consequently leading to a change in the color ($\Delta E$) of emulsion-based films (Fig. 2). The effect of oil content and incorporation of SDS showed the same trend for both $WI$ and $\Delta E$, the increasing order of change, for $WI$ and $\Delta E$, among the formulations evaluated was: HPMC-0.3-SDS > HPMC-1.0-SDS > HPMC-1.0 > HPMC-1.0. The decreasing in transparency and the increasing in $WI$ and $\Delta E$ are clearly related to the light-scattering effect of oil. The “oil plates” formed during drying produced a higher scattering of light, decreasing its transmittance and hence diminishing the transparency of the emulsion-based films and also changing their color.
Mechanical properties of the films

The addition of oil had a significant effect (p<0.05) on $\sigma_B$ decreasing its value when comparing with pure HPMC films (Fig 3). The replace of HPMC by oil produce a lower “amount” of network structure in the films, leading to a weakening of their structure. In addition, the oil may act as structural defects decreasing the strength of films. Crack propagation in a complex structure is highly dependent on interfacial properties and defects, and the heterogeneity of the structure [10]. Differences between $\sigma_B$ values for films with and without SDS are attributed to the same effect already explained for the differences found between pure HPMC films and films with oil. The addition oil and SDS into edible films had no significant effect (p>0.05) over the percent of elongation at break ($E_B$) as seen in Figure 3, the average value obtained for $E_B$ was 167%. According to Foegeding [11], the strain at break of a gel material is determined by the type of network structure and not by the concentration of the hydrocolloid.
CONCLUSION

Microstructure formation during drying of emulsion-based edible films had an enormous influence over the optical properties of films, transparency and color was dependant on the way that oil droplets were structured into the film. The decrease in strength at break of HMPC-based films was function of the oil content and the addition of surfactant.

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