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Effects of ultrasound treatment on lipid self-association and properties of methylcellulose/stearic acid blending films

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ABSTRACT

The effects of ultrasound treatment (UT) on the properties of methylcellulose (MC)/stearic acid (SA) blending films were studied. Film-forming emulsions were prepared with different UT conditions and characterized with respect to viscosity. The lipid aggregation and distribution in the blending dispersions were studied by the micrographs of Transmission Electron Microscopy (TEM). The micrographs of both surface and cross-section of the films were observed by scanning electron microscope (SEM) and the tensile strength (TS), elongation at break (E), water vapor permeability (WVP) and contact angles of the resulting films were determined as well. The intensification of the UT condition led to a decrease of viscosity of the MC-SA blending emulsions, a more homogeneous lipid distribution and a denser internal microstructure of the resulting films. UT exposure affected the mechanical, moisture barrier and surface hydrophobic properties. The optimal values of both TS and E was obtained from the sample treated for 10 min and 180 W power, while the sample treated for 10 min and 270 W presented the lowest value of WVP. However, an excessive exposure of UT led to a decrease of the mechanical and moisture barrier performance. By observing and analyzing the SEM graphs and the contact angles of the film surfaces, it was found that UT within the appropriate bounds had a notably positive effect on improving the surface hydrophobic property of the MC-SA blending films.

1. Introduction

Generally, edible films are prepared from polysaccharides, proteins, lipids or a blend of these macromolecules (Atarés, De Jesús, Talens, & Chiralt, 2010). Among these raw materials, methylcellulose (MC) is one of the derivatives of cellulose which can be produced from cotton cellulose, wood and annual plant pulps with an excellent film-forming property. MC-based films present good mechanical and gas barrier properties, which can contribute to increasing the shelf-life of products (Baldwin, Nisperos-Carriedo, & Baker, 1995a,b; Debeaufort & Voilley, 1997). However, the weak water resistance of the MC films, because of the hydrophilic nature of cellulose derivatives, is one of its main disadvantages that need to be improved to meet the requirements of food packaging (Turhan & Sahbaz, 2004; Zuo, Song, & Zheng, 2009).

In contrast, lipids have excellent moisture barrier efficiency due to their hydrophobicity, but most solid lipid-based films are brittle and unstable when used alone because of their poor film-forming property (Fabra, Pérez-Masiá, Talens, & Chiralt, 2011). In the last decade, many works have been done on the application of fatty acids as lipid components to be incorporated in hydrophilic films to modulate their water vapor barrier properties (Fabra, Jiménez, Atarés, Talens, & Chiralt, 2009; Fernández, de Apodaca, Cebrián, Villarán, & Maté, 2007; Jimenez, Fabra, Talens, & Chiralt, 2010; Zahedi, 2010). Generally, lipids are dispersed into the hydrocolloid aqueous solution (emulsion technique) and dried to obtain emulsified films. These composite films can take advantage of

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the functional properties of each component of the film to provide both barrier and mechanical properties (Hagenmaier & Shaw, 1990; Koelsch & Labuza, 1992a,b; Yang & Paulson, 2000). Moreover, several studies pointed out that the mechanical and barrier properties mainly depend on the chain length and degree of unsaturation of the fatty acids, and the internal structure of the dried emulsion which constitutes the films (Fabra et al., 2011; Fernández et al., 2007; Hagenmaier & Shaw, 1990; Koelsch & Labuza, 1992b). The tendency to self-associate in polysaccharide hydrocolloids is a particular feature of lipids, which gives rise to different micelles structures (Krog, 1997). During the drying process of film-forming emulsions, the aggregations in the aqueous system develop and crystallize with the reduction of the solvent availability. The micelles form different size of microphase separation in the dried polysaccharide matrix, depending on the affinity with their aqueous environment and the hydrophobic forces. A recent work on hydroxylpropyl-methylcellulose films containing fatty acids showed that the formation of layers of the crystallized lipid in the dried films plays a relevant role in the water barrier properties, and the film which formed the biggest lipid microphase separation showed the minimum value of WVP (Jimenez et al., 2010).

Ultrasound treatment (UT) is described as acoustic waves with frequencies higher than human earshot (20–100 kHz). The application of UT on the polysaccharide has been performed as early as 1933 (Kardos & Luche, 2001). Ultrasound waves generate intense pressure, shear and heat inside the materials treated, which can physically disrupt the structure of the polymers, or promote certain chemical reactions between components (Marcuzzo, Peressini, Debeaufort, & Sensidoni, 2010). In the application of UT on film preparation, a number of researches have shown that UT has an obviously effect on changing the behavior of film-forming emulsions and the distribution of the components, then improving the properties of the final films (Ahmadi, Sareminezhad, & Azizi, 2011; Cheng, Chen, Liu, Ye, & Ke, 2010; Marcuzzo et al., 2010; Rodriguez-Turienzo, Cobos, & Diaz, 2012).

As introduced above, both methylcellulose and stearic acid are well researched raw materials to manufacture the edible films. Meanwhile, UT was employed commonly as a kind of typically treatment method in the food packaging industry. For a blending film containing lipid, the microstructure which determines the final properties is greatly influenced by the degree of lipid self-association. However, to the best of the author's knowledge, there were few reports on the application of UT in the polysaccharide-lipids blending system which refer to the significant effects on preventing lipid self-association and micro-phase separation. Implied by previous research on similar materials, the well studied UT technique can be expected to prevent the lipid self-association in the emulsion, and then to modify the microstructure of the blending matrix and improve the properties of the final films. And it can serve as a mature methodology to overcome the problems of phase separation in polysaccharide-lipids matrix and the subsequent impairments on film properties. Therefore, In order to investigate the influence of UT on MC-SA blending films, in this work, we prepared MC-SA blending dispersions and applied different conditions of UT to modify the film-forming dispersions. The effects of UT on the lipid self-association in the MC matrix were analyzed, as well as its influence on the microstructure and physical properties of the resulting films.

2. Materials and methods

2.1. Materials

Methylcellulose (M20, 17.0–23.0 mPa s of viscosity, 20 g L^{-1}, at 20 °C) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Stearic acid (SA, $C_{18:0}$) was supplied by Xilong Chemical Factory Co., Ltd. (Guangdong, China). Polyethylene glycol 400 (PEG-400), purchased from Guangfu Fine Chemical Research Institute (Tianjin, China), was used as plasticizer. All reagents involved were of analytical grade.

2.2. Film preparation

The film-forming aqueous dispersions were prepared by dissolving 4% (w/w) MC, dispersed in 25% (v/v) ethanol solution at 80 °C. SA (15% (w/w) of the total dry matter) and PEG-400 (30% (w/w) of the total dry matter), were added to the solution in turn. After stirring (600 rpm) for 15 min at 80 °C, the blend dispersions, except control, were modified using a SL-SM50 ultrasonic processor (Shunliu Instruments Co., Ltd, Nanjing, China) equipped with a sonotrode with 2 mm of tip diameter, at a frequency of 25 kHz. The temperature of samples was controlled in the range of 20–80 °C by a SLDHX-05 water cooling system (Shunliu Instruments Co., Ltd, Nanjing, China). The detailed modification conditions (different output powers and exposure times) are listed in Table 1. Each film was prepared by weighing 150 mL of the film-forming emulsions and spreading evenly on square Teflon casting plates (20 × 20 cm^2) using a thin-layer chromatography spreader. Then they were dried in a ventilated climatic box at 30 °C and 50% relative humidity (RH) for approximately 15 h. The dried films were peeled from the plates and equilibrated at 25 ± 1 °C and 53% RH in a desiccator for 48 h using saturated salt solutions of $Mg(NO_3)_2$ before testing.

2.3. Rheological behavior of film-forming emulsions

The rheological behavior of the film-forming emulsions was analyzed using a viscosity meter (DV-II, Qunchang Scientific Instrument, Shanghai, China) in triplicate at 25 °C.

2.4. Thickness measurements

Film thickness was measured using a manual digital micrometer (Mitutoyo Manufacturing, Tokyo, Japan) with an accuracy of 0.001 mm. Measurements were made at least ten random locations for each film. The mean thickness was used to calculate the values of WVP and mechanical properties.

Table 1
Different UT exposure conditions for MC-SA emulsions.

Sample	Temperature (°C)	Power (W)	Time (min)	Thickness (μm)
A (Control)	20	0	0	261 (2)^{a}
B1	20	90	5	226 (4)^{bcd}
B2	20	90	10	216 (3)^{defg}
B3	20	90	15	206 (4)^{gh}
B4	20	90	20	211 (4)^{fgh}
B5	20	90	25	226 (3)^{bcd}
B6	20	90	30	192 (5)^{i}
C1	20	180	5	235 (3)^{b}
C2	20	180	10	222 (1)^{cde}
C3	20	180	15	228 (1)^{bc}
C4	20	180	20	207 (2)^{fgh}
C5	20	180	25	196 (4)^{hi}
C6	20	180	30	194 (5)^{i}
D1	20	270	5	221 (4)^{cde}
D2	20	270	10	214 (2)^{efg}
D3	20	270	15	213 (6)^{efg}
D4	20	270	20	218 (2)^{cdef}
D5	20	270	25	211 (3)^{efg}
D6	20	270	30	199 (3)^{hi}

Data reported are mean values and standard deviation (in parenthesis).
$^{a–i}$ Different superscripts within a column indicate significant differences among samples ($p < 0.05$).