Effect of homogenization conditions on physicochemical properties of chitosan-based film-forming dispersions and films

María Vargas*, Ángela Perdones, Amparo Chiralt, Maite Cháfer, Chelo González-Martínez

Department of Food Technology, Institute of Food Engineering for Development, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain

ABSTRACT

Film-forming dispersions (FFD) based on high molecular weight chitosan (CH) alone or in combination with oleic acid (OA) were prepared under different homogenization conditions (rotor-stator or rotor stator together with microfluidization at different pressures). Film-forming dispersions (FFD) were characterized in terms of particle size distribution, rheological properties, distribution and ζ-potential. In order to study the impact of the properties of the FFD on the casted films, the water vapour permeability, mechanical properties and microstructure of the dry films were evaluated. Results showed that microfluidization promoted significant changes in the size and surface charge of the FFD particles, which in turn had an impact on the rheological properties of the FFD. The changes were more marked with the increase in microfluidization pressure. As regards film properties, the higher the microfluidization pressure in the FFD, the lower the water vapour permeability values and the stiffer the CH-OA composite films. These results were explained by film microstructure, which was observed by SEM.

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1. Introduction

Polysaccharides and lipids are commonly mixed in order to obtain composite films or coatings to take advantage of the special functional characteristics of each group, thus diminishing their drawbacks (Greener & Fennema, 1994). Lipids contribute to the improvement of the water vapour resistance of the films, whereas hydrocolloids confer selective permeability to O_2 and CO_2, durability, structural cohesion and integrity (Krochta & De-Mulder-Johnston, 1997). The way in which lipids are emulsified (emulsion structure) and the emulsion stability directly affects the film structure and thus, its properties. During film drying, the solvent is evaporated and the effective lipid concentration increases, in line with flocculation phenomena, coalescence and creaming, depending on the physical state of the lipid, the composition of the continuous phase and the drying conditions. Small particles and a high emulsion stability (exhibited during the film drying) will give rise to a homogeneous distribution of the lipid particles in the film, which in turn contributes to a more efficient control of water transfer (Debeaufort, Martin-Polo, & Voilley, 1993).

Emulsion stability depends on the complex mechanisms, but it is well known that some of the key aspects are the average fat globule size and their size distribution pattern which, in turn, affect the stability, colour, and rheological properties of the FFD, among other factors (Becher, 2001). Rotor-stator systems are also often used in the food industry to homogenize different media and high viscosity immiscible liquids (Schubert, 1997), reaching particle sizes in the range of 1 μm (Urban, Wagner, Schaffner, Roglin, & Ulrich, 2006). To reduce the size of the lipid particles, homogenizers that use pressures of up to 500 bar have been commonly used, giving rise to particles much smaller than 1 μm. Nowadays, high pressure homogenizers such as microfluidizers can produce pressures in the range of 1000 bar or higher. Although the use of such pressures leads to finer emulsions, the average particle size only reduces slightly (Perrier-Cornet, Marie, & Gervais, 2005). The greatest effect is observed on the particle size distribution, which becomes narrower when compared with that obtained by low pressure homogenization (Paquin, 1999). Microfluidization can provide dispersions and emulsions with narrower particle size distributions due to the high shear stresses developed in the microchannels of the interaction chamber, and has been used in the pharmaceutical industry (Pinnamaneni, Das, & Das, 2003; Strawbridge, Ray, Hallett, Tosh, & Dalgleish, 1995). However, there are few studies into the effect of microfluidization on the properties of the film-forming dispersions used to obtain edible films and coatings.

On the other hand, some studies have also pointed out that high homogenization pressures can affect not only fat globules but also other food constituents, such as proteins (Lee, Lefèvre, Subirade, & Paquin, 2009) and polysaccharides (Kasaai, Charlet, Paquin, & Arul,

* Corresponding author. Tel.: +34 96 387 70 00x73642; fax: +34 96 387 73 69.
E-mail address: mavarco@tal.upv.es (M. Vargas).

2003; Paquin, 1999), modifying their functional properties. This modification may not only lead to a change in the degree of aggregation but also to irreversible disruption of the biopolymer conformation.

The aim of this work is to analyse the effect of homogenization treatments on the physicochemical properties of chitosan-oleic acid film-forming dispersions such as the particle size, zeta potential and rheological properties. Some relevant properties of the films obtained with such FFD, like water vapour permeability, microstructure and mechanical properties, were also characterized and related with the characteristics of the FFD.

2. Materials and methods

2.1. Materials

Film-forming dispersions (FFD) were prepared with high molecular weight chitosan (CH) with a deacetylation degree of 75.6% (CAS Number 9012-76-4, Batch 10305DD, Sigma–Aldrich, USA, viscosity in 1 wt% glacial acetic acid solution: 1.406 Pa s), 98% glacial acetic acid (CAS Number 64-19-7, Panreac, Spain) and oleic acid (OA) (CAS Number 112-80-1, Panreac, Spain).

2.2. Preparation of the film-forming dispersions

Chitosan (0.5% w/w) was dispersed in an aqueous solution of glacial acetic acid (0.25% v/w). After 12 h of stirring, this dispersion was homogenized by means of a rotor-stator homogenizer (DI25 Yellow Line, IKA®, Germany) at 20500 rpm for 4 min. To prepare CH-OA FFD, chitosan (0.5% w/w) was dispersed in an aqueous solution of glacial acetic acid (0.25% v/w) and, after 12 h of stirring, oleic acid was added to reach a final concentration of 0.5% (w/w). The mixture was emulsified using the rotor-stator homogenizer (DI25 Yellow Line, IKA®, Germany) at 20500 rpm for 4 min. Subsequently, FFD were submitted to a second homogenization at high pressure in a single pass by using a Microfluidizer® (M110-P, Microfluidics, Newton, MA, USA) at different pressures: 9000, 12000, 18000 and 24000 psi (62, 83, 124 and 165 MPa, respectively). Pure CH dispersions were also submitted to different pressures (83 and 165 MPa) in the microfluidizer after the rotor-stator homogenization. Table 1 shows the composition and homogenization conditions for each FFD.

2.3. Characterization of the film-forming dispersions

2.3.1. Particle size and ζ-potential measurements

The analysis of the particle size of CH-OA FFD was carried out by using a laser diffractometer (MasterSizer 2000, Malvern Instruments, UK). The samples were diluted in a sodium acetate buffer solution (175 mM) under the appropriate solvent conditions

(pH = 4.8) at 2000 rpm until an obscuration rate of 10% was obtained. The Mie theory was applied by considering the following optical properties for OA droplets: a refractive index of 1.46 and absorption of 0.00. Three samples of each FFD were measured in triplicate. In order to carry out ζ-potential measurements, FFD were diluted to a droplet concentration of 0.02% using a sodium acetate buffer solution (175 mM) at pH 4.8. ζ-potential was determined by using a ZetaSizer (Nano-Z, Malvern Instruments, UK). The Smoluchowsky mathematical model was used to convert the electrophoretic mobility measurements into ζ-potential values.

2.3.2. Rheological behaviour

The rheological behaviour of film-forming dispersions was analysed in triplicate after one day of storage at 25 °C by means of a rotational rheometer (Haake Rheostress1, Thermo Electric Corporation, Germany) with a type Z34DIN Ti sensor system of coaxial cylinders. Rheological curves were obtained after a stabilization time of 5 min at 25 °C. The shear stress (σ) was measured as a function of shear rate ($\dot{\gamma}$) from 0 to 512 s^{-1} in the following way: 5 min to reach the maximum shear rate and 5 min to attain zero shear rate. The power law model (Eq. (1)) was applied to determine the consistency index (K) and the flow behaviour index (n) of the FFD. Apparent viscosities were calculated at 100 s^{-1}.

$$\sigma = K\dot{\gamma}^{n} \tag{1}$$

2.4. Preparation of films

Films were obtained by casting. FFD were poured onto a framed and leveled polytetrafluoroethylene (PTFE) plate ($\varphi = 15$ cm) and were dried at room temperature for 48 h. Films were prepared by pouring the amount of FFD that will provide a polymer surface density in the dry films of 56 g/m^2. Dry films were peeled off from the casting surface and preconditioned in desiccators at 20 °C and 58% relative humidity (RH) during one week prior to performing all the tests. Film thickness was measured using a hand-held digital micrometer (Palmer–Comecta, Spain, ±0.001 mm). The thickness of each film was measured five times and the mean values were used in water vapour permeability calculations.

2.5. Characterization of the films

2.5.1. Water vapour permeability

Samples of dry films ($\varphi = 4$ cm) were stored in desiccators at 58.5% RH and 20 °C for at least 15 days prior to the evaluation of the water vapour transmission rate. Water vapour permeability (WVP) was measured, in quintuplicate, according to the "water method" of the ASTM E–96-95 (ASTM, 1995), using Payne permeability cups (Elcometer SPRL, Hermelle/s Argenteau, Belgium). De-ionised water was used inside the testing cup to achieve 100% RH on one side of the film, while an oversaturated magnesium nitrate solution was used to control the relative humidity on the other side of the film: 58.5%. During WVP testing, the side of the film in contact with the PTFE plate was placed in contact with the part of the test cup having the highest RH. A fan placed on the top of the cup was used to promote convection. Water vapour transmission rate (WVTR) measurements were taken at 20 °C. To calculate WVTR (Eq. (2)), the slopes of the steady state period of the curves of weight loss as a function of time were determined by linear regression. For each type of film, WVP measurements (Eq. (3)) were carried out in triplicate.

$$WVTR = J/A \tag{2}$$

$$WVP = \frac{WVTR}{P_{w1} - P_{w2}} \cdot L \tag{3}$$

Table 1
Composition of the FFD and homogenization conditions.

FFD	Chitosan (%w/w)	Oleic acid (%w/w)	Homogenization conditions
CH	0.5	–	RS
	0.5	–	RS + 12 (MF at 93 MPa)
	0.5	–	RS + 24 (MF at 165 MPa)
CH:OA	0.5	0.5	RS
	0.5	0.5	RS + 9 (MF at 62 MPa)
	0.5	0.5	RS + 12 (MF at 83 MPa)
	0.5	0.5	RS + 18 (MF at 124 MPa)
	0.5	0.5	RS + 24 (MF at 165 MPa)

RS: Rotor-stator homogenization; MF: Microfluidization.