Food Hydrocolloids 48 (2015) 8–16

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Mechanical properties of milk protein skin layers after drying: Understanding the mechanisms of particle formation from whey protein isolate and native phosphocaseinate

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ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form
13 January 2015
Accepted 15 January 2015
Available online 7 February 2015

Keywords:
Mechanical properties
Milk proteins
Phase transition
Particle shape
Drying behaviour

ABSTRACT

The spray drying of milk proteins usually leads to dry particles of which the final shape can influences physical and functional properties of powders. The aim of this study was to understand the mechanisms of particle formation by considering the mechanical properties of materials making up the two main classes of milk proteins: whey proteins and casein micelles. The progressive solidification of the interface of the droplet during drying time was studied by high speed camera and fluorescence microscopy, in different experimental conditions. The mechanical properties of the final protein materials were then characterized by micro indentation testing. The drying dynamics of whey protein and casein micelle droplets showed different timescales and mechanical lengths, whatever the drying conditions and the droplet configurations, leading to typical mechanical instability at the surface i.e. buckling and fracture. The interface of casein micelles reached sol–gel transition earlier estimated at around 156 $g.L^{-1}$ following by elastic and plastic regimes in which the shell distorted and buckled to form a final wrinkled particle. In contrast, the interface of whey proteins became elastic at only half the drying time estimated at around 414 $g.L^{-1}$, retaining a spherical shape, which finally fractured at the end of drying. The mechanical difference between the two plastic shells might be explained by the behaviour of proteins in jamming conditions. Analogous behaviour could be discussed between the casein micelles and soft and deformable colloids on the one hand, and between whey proteins and hard spheres on the other.

1. Introduction

The evaporation of a droplet, whether free falling in the air, suspended from a thin filament, or deposited on a substrate, has been extensively studied in the past and is still a significant subject for scientific and industrial research (Sadek, Schuck, et al., 2014). The evaporation of solute dispersions involves important physicochemical phenomena such as solute and solvent transport, adsorption and interactions between solutes and phase transitions. As the solutes concentrate at the interface during evaporation of the water, important rheological changes occur within the droplet, inducing its progressive transition to a solid state with a specific particle structure (Pauchard & Allain, 2003b). Thus the final shape of the particle depends on the physicochemical properties of the matter and the drying parameters. However, understanding precisely how the final shape is formed and how it can be controlled still represent a challenge.

Indeed, the final shape of film formed from biological solutions and protein dispersions has recently become an area of interest for many applications. For medical diagnostic purposes, some researchers have focused on the final pattern of human fluids such as synovial fluid (Shabalin & Shatokhina, 2007), whole blood (Sobac & Brutin, 2014) and DNA (Dugas, Broutin, & Souteyrand, 2005). This has mainly consisted of studying the evaporation of defined proteins, particularly lysozyme and bovine serum albumin (BSA)

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http://dx.doi.org/10.1016/j.foodhyd.2015.01.014
0268-005X/

(Accardo et al., 2010; Annarelli, Fornazero, Bert, & Colombani, 2001; Gorr, Zueger, & Barnard, 2012; Tarasevich & Pravoslavnova, 2007; Yakhno, 2008). Moreover, many studies have investigated the potential of proteins such as whey proteins and sodium caseinates to form delivery systems for probiotics and active substances in the pharmaceutical and food industries (Burgain, Gaiani, Cailliez-Grimal, Jeandel, & Scher, 2013; Hogan, McNamee, O'Riordan, & O'Sullivan, 2001; Sadeghi, Madadlou, & Yarmand, 2014; Serfert et al., 2013; Zhang & Zhong, 2013).

According to the literature available on spray drying, different proteins may result in various types of particle morphology (Ameri & Maa, 2006; Faldt & Bergenstahl, 1996; Kim, Chen, & Pearce, 2009). For example, Maa, Costantino, Nguyen, and Hsu (1997) reported distinct particle shapes (spherical, donut-like and wrinkled particles) after the drying of three model proteins (rhDNase, rhuMAbE25 and BSA, respectively). Sadek, Li, et al. (2014) previously focused on the spray drying of two main milk proteins, i.e. whey proteins and casein micelles. A specific monodispersed droplet spray drier (MDSD) was used in order to produce identical droplets though the same drying trajectory inside the drier. Two different types of morphology were clearly identified under controlled spray drying conditions; dense, wrinkled particles for casein micelles and hollow, spherical particles for whey proteins.

Each of these distinct morphologies resulted in the occurrence of different types of surface instability during evaporation. Pauchard & Allain (2003c) studied such physical phenomena on single droplets of colloid and polymer dispersions. They reported that the first instability is due to the formation of a permeable solid skin at the surface which bends under the pressure of solvent evaporation. Then, according to the mechanical properties of the skin, a large number of deformations, including invagination or fracture instability, may occur and finally shape the dried particle. The mechanical skin responses may be strongly linked to the internal properties of the material such as its porosity, thickness, viscoelasticity and microstructure.

Therefore, the aim of this study was to evaluate:

i) Are particular mechanical properties of a dry skin layer associated with specific protein nature?
ii) Do these mechanical properties explain the occurrence of surface instability during evaporation?

In other words, the aim of this study is to know if the nature of the protein may lead to a skin layer whose physical properties condition the way that a droplet or the shell responds to mechanical stress induced by the evaporation process. In order to investigate these questions, experiments were conducted with distinct proteins, i.e. whey protein isolates (WPI) and native phosphocaseinates (NPC) to form the dried material. Understanding the drying behaviour of the two different protein materials should therefore provide key information to be able to predict the final structure of milk powders and thus control their physical properties.

2. Materials and methods

In the first part, the drying process of a droplet has been reported according to two different configurations, i.e. a single, pendant droplet and a confined droplet. In the second part, the mechanical properties of the skins of different milk proteins have been characterized in order to establish the elastic and plastic behaviours of the protein materials. These results are then discussed to understand the occurrence of droplet deformation during the drying process.

2.1. Materials

Experiments were conducted with distinct proteins, i.e. whey protein isolates and native phosphocaseinates. These are the two main classes of proteins in milk according to the ratio 20:80 (WPI:NPC). They are distinct in size and structure. Whey proteins have a rigid, compact globular structure with well defined folding of the polypeptide chain. They are mainly constituted of 70% β-lactoglobulin, often in dimer form (molecular mass 36.6 kDa), with 20% α-lactalbumin (molecular mass 14.2 kDa) (Walstra, Wouters, & Geurts, 2005). Native phosphocaseinates, also called casein micelles, represent a complex association of caseins (α_{s1}-, α_{s2}-, β- and κ-caseins), phosphate and calcium ions organized into micellar structures. The casein micelles are dynamic structures interacting with the soluble phase and highly hydrated as they contain around 3.7 g of water per gram of casein (de Kruif, 1998). They can be considered as natural and colloidal microgels with diameters ranging from 30 to 300 nm, and thus very different from whey proteins. The feed solutions were prepared from two milk protein powders, whey protein isolates and native phosphocaseinates, obtained from industrial sources and presenting protein content around 89 and 82% (w/w), respectively. The two solutions were reconstituted at 100 $g.L^{-1}$ protein in osmosed water at 50 °C with continuous stirring for two days at 20 °C to ensure full dissolution. The pH for WPI and NPC concentrates was in the range of 6.59 ± 0.16 at 25 °C. Particle size was measured by dynamic light scattering using a Zetasizer NanoZS apparatus (Malvern Instruments, Malvern, United Kingdom). The different sizes of proteins ranged from 8 to 30 nm and from 108 to 300 nm for WPI and NPC proteins, respectively.

2.2. Methods

2.2.1. Observation of single, pendant droplet

The drying process of a single, pendant droplet and its final particle shape were studied according to Sadek et al. (2013). A pendant droplet was deposited on a hydrophobic surface (providing a contact angle of the single droplet > 100°) and placed in a dry environment (Fig. 1a). The impact of matter on droplet deformation in a suspended system might be more noticeable than in a sessile droplet which is known to collapse with gravity and pressure gradient (Chen et al., 2012). The temperature was kept constant at 20 °C whereas relative humidity (RH) was decreased to 2% in the presence of excess zeolites, in order to ensure a constant drying stress. A sealed glass chamber was used to reduce atmospheric disturbance. The hydrophobic surface was designed to ensure a small contact area with the droplet, making it possible to maintain the spherical shape of the droplet in order to limit its impact on droplet dynamics during drying. The external shape of the droplet was recorded with a high-speed camera (Fastcam MC2 10,000 NB, Photron, United States) equipped with suitable lenses (Zoom 6000, Navitar, United States). A light (Phlox 100/100 LLUB, Stemmer imaging, France) illuminated the droplet from behind to produce a uniform background. Drying took around 10 min, and data were recorded automatically every 10 s. Images from the camera were analysed with ImageJ software (U.S. National Institutes of Health). The final particle shape was also observed by scanning electron microscopy (SEM, model 6301, JEOL, Germany) at 7 kV and 100× after coating with gold/palladium.

2.2.2. Observation of confined droplet

The principle of a confined droplet is to sandwich a droplet between two circular, parallel horizontal glass slides, as a thin liquid film with $h << r_{(t)}$ and to allow it to evaporate in this confined system (Fig. 1b). This two dimensional (2D) configuration bypassed