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Drying-induced mechanisms of skin formation in mixtures of high protein dairy powders

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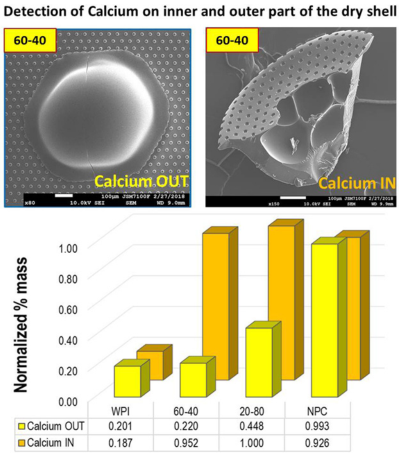
GRAPHICAL ABSTRACT



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ABSTRACT

Spray drying of dairy products consists of spraying droplets of feed solution into a hot air flow to quickly evaporate water and finally to form dried particles. In order to understand the role of the two-major milk protein (whey proteins and micellar caseins) in the mechanisms of particle formation the evaporation of mixtures containing different whey protein to casein ratios the obtained milk protein concentrates was investigated at single droplet and jet monodispersed stages. The results obtained suggest that the evolution of skin mechanical properties with time strongly depends on the composition of the mix and most of all on both size and mechanical characteristics of the colloidal components. Interestingly, the remarkable shape analogies observed in spray dried particles compared to the single droplets suggest that, despite the significant difference in terms of experimental conditions and process characteristic time scale, the ongoing evaporation dynamics are almost equivalent. Moreover, our results showed an overrepresentation of the smaller size whey proteins at the particle surface of dairy colloidal mixes, in agreement with reported results on model colloids.

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1. Introduction

Spray drying is widely used in liquid food processing to extend the stability of biological and physicochemical properties of products during long-term storage and to improve their handling and transport [1–3]. It consists of spraying droplets of feed solution into a hot air flow to quickly evaporate water and finally to form dried particles whose morphology (e.g., particle size, shape, internal structure and surface properties) confers specific aerodynamic behaviors that have a direct impact on their final application [4,5].

This process is yet mostly empirically controlled on an industrial scale, emphasizing the need to overlap interdisciplinary fields of knowledge, particularly in terms of product quality and process performance. However, the polydispersity of the droplets, the fast-drying kinetics, the complexity and the large scale of the drying equipment make the experimental ability to monitor and sample the process in real equipment even more challenging [6,7].

To overcome these difficulties, many experimental studies based on the drying of a single droplet have been developed, but only a few concern protein solutions [8–14]. In previous works [15–18], we developed a multi-scale approach to investigate the shape dynamics and final structure of pure milk protein droplet in a dry environment (low relative humidity) on a nonwetting surface by using a hydrophobic substrate in a pendant configuration. This approach was successfully applied to the single droplet drying of 10% w/w solutions either of whey protein, which represents 20% of the proteins in bovine milk, or of casein micelle dispersion, which represents 80% of the proteins in bovine milk. Throughout this experimental strategy, we highlighted distinct drying behaviors of whey proteins and casein micelles in terms of drying kinetics and droplet dynamics, whatever the experimental conditions. It was shown that a skin formed at the sol-gel transition, regardless of the protein material. After the sol-gel transition, the droplets underwent different types of skin/surface instabilities which may be related to specific mechanical properties of the protein materials: brittle plastic skin layer for whey proteins and ductile elastic skin layer for casein micelles.

However, since milk is a complex colloidal system, it is necessary to investigate the influence of mixtures of these two kinds of proteins to obtain a model system closer to a real formula composition. Moreover, studying ternary mixtures of whey proteins and casein micelles would help in determining the skin formation mechanisms apart from sol-gel transition of binary mixtures. In a recent article published by our group [16], the properties of particles of dairy colloid mixes obtained by monodisperse spray drying (MDSD) have been characterized as a function of whey protein to casein ratio. However, although the experimental conditions similar to the industrial ones, the MDSD technique does not allow an on-line observation of drying mechanisms and, consequently, of skin formation. Thus, in this work the pendant configuration has been used to shed light on the stages of the drying process in droplets of mixtures containing different whey protein to casein ratios. In particular, we investigated the evaporation of sample with protein composition similar to human milk and infant formula on the one hand and bovine milk on the other hand due to their both nutritional and industrial significance. The single droplet approach, coupled to a qualitative comparison with dry particles obtained by spray-drying from the same samples, contributed to improve the understanding of the role of each protein in the particle-forming mechanisms. We highlighted the impact of the component characteristics, in particular the mechanical properties of the dairy colloids, on the particle formation.

2. Materials and methods

2.1. Sample preparation

Solutions of mixes of whey protein isolates (WPI) and native phosphocaseinates (NPC) with concentration equal to 12% w/w were prepared varying the WPI/NPC ratio from 100/0 to 60/40 (ratio similar to human milk and infant formula), 20/80 (ratio similar to bovine milk) and 0/100. For this purpose, WPI and NPC powders, obtained from industrial sources and characterized by a protein content of 86% and 82%, respectively, were reconstituted in adequate proportions in osmosed water supplemented with 0.02% w/w sodium azide as bacteriostatic agent (Sigma-Aldrich) at 50 °C and then continuously stirred for 48 h at room temperature to ensure full dissolution. Protein particle size, measured by dynamic light scattering using a Zetasizer NanoZS apparatus (Malvern Instruments, Malvern, United Kingdom), ranged from 8 to 30 nm and from 108 to 300 nm for WPI and NPC proteins, respectively.

2.2. Single droplet experiment

The experiments were performed on the four WPI/NPC ratio kinds of concentrates. Droplets of 0.5 μl were gently deposited on a hydrophobic support with a microsyringe (Hamilton, 7000.5H 0.5 μl). The support consisted of a patterned PDMS surface prepared according to the protocol developed in a previous work by Sadek et al. [15] in order to produce a contact angle ≥100°. A pendant droplet configuration was adopted to maintain the spherical shape of the droplet and thus to minimize the effects of gravity normally observed in the sessile configuration. Such a setup mainly allowed to highlight the impact of drying kinetics on the different stages of the process. All the experimental observations were performed in a sealed cubic glass chamber ($80 \times 80 \times 80\,\mathrm{mm}^3$) at controlled temperature, $T = 20 \pm 1$ °C and relative humidity, RH = 2%. The significant mitigation of RH, due to the use of zeolites (HG2-DES-3, Rotronic), ensured a constant drying stress and enhanced a faster evaporation of the solvent in approximately 10 min.

The development of the skin at the liquid-air interface during the different stages of the evaporation was investigated coupling the direct visualization of droplet profile and mass measurements during drying, and scanning electron microscopy (SEM) on the dry particles obtained.

The evolution of droplet profile was observed with a high-speed camera (Fastcam MC2 10,000 NB, Photron) equipped with lenses for high magnification (Zoom 6000, Navitar). To produce a uniform background, a light source (Phlox 100/100 LLUB, Stemmer Imaging) was placed in the opposite direction with respect to the camera position. Images were acquired throughout the evaporation every 10 s and the sequences were subsequently analyzed by a custom image analysis software (ImageJ). The same pendant configuration was used to evaluate the mass loss (M) by an ultra-microbalance (XP2U, Mettler Toledo) with an accuracy of 0.1 μg.

The dry particles resulting from the complete evaporation of the droplets were observed by SEM (JEOL JSM 7100F) to investigate the impact of the different sample composition on their main morphological characteristics. Moreover, an elemental analysis (EDS) was performed on both external and internal parts of the dry shell to investigate the structure of the skin at the molecular scale. To this end, both samples and substrates were coated with carbon before the visualization at 10 kV.

2.3. Jet monodispersed droplet

Experiments of spray drying of the same blends were carried out using a Monodisperse Spray Dryer (MDSD-MarkII, Dong-Concept New Material Technology Co.). The solutions, kept in a pressurized reservoir, were flowed at a mass flow rate of $1.48\,\mathrm{g\,min}^{-1}$ through a piezoelectric ceramic nozzle, with an orifice of 100 μm diameter and a 7 kHz fixed frequency to induce periodic breakup of the liquid jet and thus form a well-defined droplet channel. The dispersion of droplets from the nozzle outlet was completed by a complementary air flow fixed ($3\,\mathrm{L^*min}^{-1}$) in order to avoid droplets merging. The inlet and outlet temperatures and drying air flow rate were kept constant at 193.5 ± 1.6 °C,