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Microstructure evolution of micellar casein powder upon ageing: Consequences on rehydration dynamics

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ABSTRACT

Micellar casein (MC) powder must be completely dispersed and dissolved in water to fully exhibit their functional properties. However, the rehydration properties of these powders decline strongly during storage, leading to loss of solubility and longer rehydration time. In this work, controlled ageing was applied to a MC powder in order to better understand the mechanisms responsible for the deterioration of rehydration properties in the course of storage. The objective was to investigate evolutions of powder surface structure and composition as well as the link between these changes and the decline in rehydration properties, which were evaluated through characteristic times of different steps constituting the full rehydration process. Lipid migration (towards the particle surface) and increase of interactions between surface micellar particles during storage were proven to be responsible for major changes in different rehydration stages. First, the delay in water penetration into particles was quantified; then, the increase of particle fragmentation time was determined and finally, an extended total rehydration time was evidenced. Analysis of the characteristic times of different rehydration stages shows unambiguously that the main step increasing the total rehydration time of aged powder is not lipid migration but the crosslink formation during storage, which can thus be considered as the rate-limiting stage for rehydration of aged powder.

1. Introduction

During the latest years, high-protein dairy powders such as Milk Protein Concentrates (MPC) have been increasingly used as ingredients by food manufacturers because of their nutritional and functional qualities (Gaiani et al., 2007b; Kelly et al., 2016; Selomulya and Fang, 2013). In MPC, casein/whey protein ratio is the same as in skimmed milk. For that reason, MPC is often used to standardize the protein content in normal milk and in many dairy products including cheese and yoghurt.

For these applications, instant dissolution, or at least good rehydration ability is a desired property, while wettability, sinkability, dispersibility and solubility are the essential prerequisite features for the dairy solution to display its underlying functionalities at the end of the reconstitution operation (Crowley et al., 2015; Mimouni et al, 2010b).

However, it has been reported in several studies that high-protein dairy powders have poor rehydration properties (Fyfe et al., 2011; Gaiani et al., 2007b; Gaiani et al., 2009; Schuck et al.,

Abbreviations: MPC, Milk protein concentrate; MC, Micellar casein; SEM, Scanning Electron Microscopy; NMR, Nuclear magnetic resonance; XPS, X-ray photoelectron spectroscopy; Tof-SIMS, Time-of-Flight Secondary Ion Mass Spectrometry; PSD, Particle size distribution.

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2007), especially for MPC with increased protein content and casein-dominant powders (Crowley et al., 2015).

Moreover, it has also been observed that rehydration properties alter significantly during storage (Anema et al., 2006; Gazi and Huppertz, 2015; Le et al., 2011; Thomas et al., 2004), particularly under severe conditions (e.g., high temperature and humidity).

The decline in rehydration properties of a given powder during its storage is the key issue to be addressed when setting up reliable reconstitution processes on an industrial scale. Storage-induced ageing effects should be taken into consideration in the development of upstream processing routes in order to increase powder rehydration ability in reconstitution operations. Consequently, it is necessary to investigate in depth the underlying mechanisms governing the decrease of rehydration ability during storage and to evaluate their consequences on the three theoretical phases of the rehydration process (Davenel et al., 1997; Gaiani et al., 2007b; Ji et al., 2016):

i) wetting and immersion of particles, including the penetration of the liquid into the pore matrix due to capillary forces
ii) dissolution of the solid bridges between casein micelles constituting the particles, leading to particle fragmentation and release of casein micelles within the liquid volume
iii) dissolution of fragmented particles and consequent reduction in size

At the present state of the art, the understanding of powder reconstitution is insufficient to provide clear guidelines regarding which steps are more drastically impacted by storage conditions. But some researchers tried to approach the problem by illustrating the surface microstructure evolution of hydrated high-protein dairy powder particles under different storage conditions, Mimouni et al. (2010a; 2010b) have shown that an evolution of the particle surface microstructure occurred upon ageing. The monolayer skin (composed of casein micelles) formed on the particle surface during storage exerts a stabilizing effect on particle integrity by making its release of individual micelles difficult and slowing down the complete dissolution of the particle. Burgain et al. (2016) recently confirmed this point as they observed a particle surface hardening phenomenon during storage. It is often mentioned that this skin formation at the surface of primary particles prevents powder to fully reconstitute, even after extended periods of rehydration, due to inhibited transfer of water into powder particles and/or slowed release of cross-linked casein micelles (Mimouni et al., 2010b).

Unfortunately, a lot of questions are still not elucidated concerning this skin formation during storage and its influence on the successive steps constituting the powder rehydration process:

- Could the slowed water penetration due to the presence of the formed skin around the particle (explain alone the rehydration property decline of casein-dominant powders)?
- If not, which is the rate-limiting stage of rehydration, namely the diffusion of water into the particle or the final release of surface cross-linked casein micelles into the surrounding liquid?
- Is the retarded release of casein micelles due to cross-linking the only cause for the extended rehydration time after storage, or other rearrangements at the molecular scale (such as migration of lipid components) could also contribute to an additional delay?

To answer these questions and fill the gap, a high-protein micellar casein (MC) powder was elaborated by membrane filtration of skimmed milk followed by spray-drying to obtain a casein-dominant powder (>90% casein). Such MC powders, initially used in cheese making (Maubois and Brulé, 1982), are nowadays added to foodstuffs to enhance certain techno-functionalities (heat stability, viscosity, gelation, emulsifying and foaming properties) (Broyard and Gaucheron, 2015). As a second step, different controlled storage conditions (various temperatures at a fixed level of relative humidity) were applied to the MC powder for increasing time period. The evolution of rehydration properties with storage time were assessed through ultrasound attenuation tests, granulomorphometry and static light scattering to determine the three characteristic rehydration times: relaxation, fragmentation and total rehydration time.

Then, Scanning Electron Microscopy (SEM) imaging was carried out for aged and non-aged powder particles during the course of rehydration. The evolution of MC powder bulk/surface/extreme surface composition during storage at dry state was followed using a set of techniques (Iatroscan, Nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (Tof-SIMS)). Finally, these experimental data were analysed in order to:

i) find out the link between the rehydration property decline and the storage-condition dependent microstructure evolution of the MC powder particle surface;
ii) identify which step(s) is/are more drastically impacted by the storage condition, constituting thus the rate limiting stage in rehydration.

2. Materials and methods

2.1. Dairy powder manufacture and controlled storage conditions

Micellar Casein (MC - Promilk 872 B1) concentrate was obtained from microfiltration (pore size = 0.1 μm) of skimmed milk at Ingredia (Arras, France). The retentate was spray-dried as previously described in Pierre et al. (1992) and Schuck et al. (1994) in Bionov (Rennes, France) pilot plant (GEA, Niro Atomizer, St Quentin en Yvelines, France). Inlet air temperature was 180 ± 10 °C, fluid bed air temperature was 70 ± 1 °C and outlet air temperature was 65 ± 5 °C. MC powder was packaged in individual cans of 380 g directly after manufacture (Water activity: 25%). Cans were stored under a controlled temperature of 4 °C, 20, 40 or 60 °C until 12 months. It will be shown later that for a storage temperature of 4 °C, few evolutions of the rehydration properties could be observed even for the longest storage time (12 months). Therefore, this storage condition will be considered in the following as the reference condition and powder stored at this temperature will be named “reference powder”. Although 40 °C and 60 °C may seem extreme temperatures, it has been shown that these temperatures could be achieved in course of powder shipment (Leinberger, 2006), and were thus considered in this study. Another reason for the choice of bigger temperatures is that there exists a correspondence between storage at ambient temperature for longer time period and at these two higher temperatures for a shorter time, as shown by Nasser et al. (2017) and Norwood (2016).

2.2. Analysis of structure and composition of casein powder surface

2.2.1. Iatroscan analysis

Iatroscan apparatus was used to quantify polar lipid and triglycerides in the core and on the surface of the powder.

Lipid extraction and analysis were performed as described by Gaiani et al. (2007a). Briefly, lipids were extracted according to the Folch method and collected in chloroform (5 mg mL^{-1}). Lipids of different classes were separated on chromarods-SIII and quantified using a thin layer flame ionization detection Iatroscan apparatus