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# Comparative study of deteriorative changes in the ageing of milk powder

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ABSTRACT

Skim milk powders produced by spray drying (mostly amorphous) are commonly used in downstream food industries and have to be stored for long times after production before final use. However, their physicochemical qualities and properties decline during long-term storage due to the hygroscopicity of amorphous lactose. Surface modification of particles by crystallisation of the outer layer, giving so called "egg-shell" particles, has shown significant improvements in the physical properties of the powder in their fresh state. In this study, the raw powder and processed powder (with modified surface) were stored at around 33% relative humidity and 25–30 °C for 30 weeks to investigate the effect of ageing on these two types of powders. Agglomeration, large lactose crystal formation on the surface, surface composition changes and protein modifications were studied. The changes between the raw powder and process powder were compared after ageing. The non-hygroscopic crystalline surface layer showed significant benefits in maintaining the physicochemical qualities of the powders over long storage times. The aged raw powder showed a 24% change in the crystallinity, a 3% change in the lactose/protein ratio on the surface and 6% protein denaturation compared with the aged processed powder with a 4% change in the crystallinity, a 1.5% change in the lactose/protein ratio on the surface and 2% protein denaturation, respectively, after 30 weeks storage.



## 1. Introduction

Milk powders are widely used in food processing industries or for re-constituting and often must be stored for months. The shelf life for a food product is marked by an increase in undesirable physicochemical qualities or microbial levels. Spray-dried milk powders, in amorphous states, are very unstable. They have a tendency to sorb moisture and form caked powders that are not free flowing. The increase in moisture content, due to the elevated water activity, causes bridge formation between particles, protein denaturation and modification (Haque et al., 2010; Liu and Chaudhary, 2011), the progress of Maillard reactions and decolouration (Bell, 2008), bacteria growth (Tapia et al., 2008) and quality loss (Sablani et al., 2007). These deteriorative changes start by sorbing moisture form environment, leading to a decrease in the glass-transition temperature of amorphous components to below ambient conditions, which initiates crystallisation and an increase in the stickiness of the powders. The expelled water from crystallisation further increases the water activity and enhances the changes. In addition, crystallisation of lactose from the matrix rearranges the protein–lactose bonds and de-stabilizes the proteins, meaning that less amorphous lactose is available around the proteins to be attached to the H-bond active sites of the proteins (Buera et al., 2005; López-Díez and Bone, 2000). Amorphous component of powders readily sorb moisture from the environment, which leads to high moisture-content gradients near the surface, initiating moisture migration into the particles.

There are different methods that are commonly used to prevent the powders from sorbing moisture, such as keeping them in cool and dry conditions and using sealed impermeable packaging. Crystallisation of lactose in milk powders in pre-crystallisation or post-crystallisation facilities has been suggested (Hynd, 1980; Yazdanpanah and Langrish, 2011b) to improve the powder stability against moisture sorption and enhancing the physical properties. Yazdanpanah and Langrish (2011b) showed the improvement (decrease) in moisture sorption for the crystallised lactose and milk powders that were crystallised in a fluidized-bed dryer/crystallizer. The mostly crystalline powders that were produced by that technique have a very much reduced tendency to sorb moisture from the environment (even under very humid conditions for a long time).

Amorphous materials have greater solubility, porosity (Trivedi and Axe, 2001) and bioavailability (Yang et al., 2010), compared with crystalline materials. The lower solubility and higher stability of the milk powders with crystallised lactose (mostly crystalline particles) could be disadvantages when the powders are needed to be reconstituted or dispersed in dairy processing industries. Sandiness and rough texture in ice-cream and chocolate that is made from this kind of crystallised milk powder are not desirable in sensory analysis (McSweeney and Fox, 2009).

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The destabilisation effect of lactose crystallisation during storage and the elevated water activity also cause protein denaturation, releasing encapsulated ingredients, such as fat, and decreasing the nutritional value of the stored powder (Augustin et al., 2007; Fyfe et al., 2011). Proteins are stable in their low-energy, native (folded) state. Denaturation or unfolding, which are changes in the secondary structures of proteins, increase the hydrophobicity of the proteins (Haque et al., 2010) and promote aggregation and destabilisation (Allison et al., 1999). Most dairy powders have shelf-lives of around 36 months in cool and dry conditions when packed in sealed moisture-proof containers. The moisture sorption and diffusion rate, and consequential lactose crystallisation and protein modification, increase the rate of quality loss in the powders.

Most of the physical properties in spray-dried milk powders, such as flowablity, stickiness, agglomeration and caking, are surface-dominated properties (Fäldt and Bergenståhl, 1994; Yazdanpanah and Langrish, 2010). Surface amorphicity and composition of the powder particles may then be expected to play an important role in their flow behaviour, because flowability involves overcoming the surface attractions between the particles. Amorphous and hygroscopic materials on the surfaces have very significant effects on the agglomeration, stickiness and hygroscopicity of the particles. Moisture sorption by crystalline lactose is significantly lower than by amorphous lactose (Bronlund and Paterson, 2004), and this lower amount of moisture on the surface causes fewer moisture-induced changes inside particles. Also, particles with crystalline surfaces have weak tendencies to form bridges with other particles due to the high thermodynamic stability of the crystalline state. Yazdanpanah and Langrish (2010) have demonstrated that a thin layer of modified molecular structure on the surfaces of particles can greatly improve the physical properties of the powders. They created a new milk powder structure that was called an egg-shell structure, with a crystalline surface and an amorphous core, which has the good flowability and stability characteristics of crystalline powders, while preserving the desirable characteristics of the amorphous core. The previous report shows significant improvements in stability, flowability and physical properties of the freshly-processed powders with egg-shell structures compared with raw commercial powders, while maintaining the same functionality. There are few reports in the literature about long-term studies of processed powders, and this study addresses this issue.

The aim of this study was to investigate the water-induced changes in the skim milk powders during storage, comparing the raw commercial powder with the processed powders, with an egg-shell structure, during long storage. The effect of the crystalline outer layer on the physical properties of the fresh powder has been studied before (Yazdanpanah and Langrish, 2010); in this research, the effects of the crystalline surface layer on the moisture sorption rate and the deteriorative changes in milk powder have been investigated.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Raw skim milk powder

Skim milk powder (medium heat) has been supplied by Murray Goulburn Cooperative Co. Ltd. (Brunswick, VIC, Australia). The manufacturer's specification data sheet has showed that the composition on a dry weight basis was lactose (59% w.w$^{-1}$), protein (39% w.w$^{-1}$) and fat (0.9% w.w$^{-1}$). The moisture content of the raw milk powder has been measured to be 3.8% w.w$^{-1}$ from oven drying tests. This powder will be called raw powder hereafter.

#### 2.1.2. Processed powder

Processed powder with egg-shell structure particles has been made by a fluidized-bed crystallisation technique described before (Yazdanpanah and Langrish, 2010). The processing condition was 60 °C, 40% RH and 20 min processing time. After processing, the powder was transferred to a vacuum dryer and left under vacuum at room temperature for 4 h to slow down further crystallisation. The processed powder has been analysed by previously-described methods to confirm that it has an egg-shell type structure, and the amorphicity of the core of the particles has been checked.

### 2.2. Methods

#### 2.2.1. Experimental setup

The raw powder and processed powder have been stored under controlled humidity and temperature conditions at 25–30 °C and 32–35% RH for 30 weeks. Both raw and processed powders have been kept separately in the same sorption box at these constant temperature and humidity conditions for 30 weeks to age the powders. The powders have been left under vacuum for 4 h to remove the initial moisture content prior to placing them in the sorption box containing saturated $MgCl_2$ solutions giving ~33% relative humidity. A Tiny Tag Extra TGX3580 datalogger device from Gemini Data Loggers has been used for recording the temperature and the relative humidity during the storage period. The equilibrium moisture content of skim milk powder at 33% relative humidity is 7.3% (w.w$^{-1}$), and the glass-transition temperature was reported as 22 °C (Schuck et al., 2005). The samples have been examined when fresh and after 15 and 30 weeks of storage to assess any changes in crystallinity and protein modifications. The tests after 15 weeks storage time have showed that this time period was not adequate to develop the changes to an extent that was readily detectable with the sensitivity of the equipment used here, such as XRD. Therefore the 30 weeks aged powders were compared with the fresh state of the powders.

#### 2.2.2. Scanning electron microscopy

A scanning electron microscope was used to observe the surface morphology of the powders. The samples were prepared by placing a small amount of each sample on a carbon tape that was placed on an aluminium sample disc. The sample was coated by a standard 30 nm gold layer to produce the conductive surface (Emitech, K550X, Quorum Technologies, UK). The electron micrographs were produced using a Zeiss ULTRA plus (Carl Zeiss SMT AG, Germany) scanning electron microscope (SEM) in the In-Lens mode with an operating voltage of 2 keV. A range of 500–30,000 times magnification was used in the images.

#### 2.2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to investigate the bulk crystallinity of raw and processed powders by using a Siemens D5000 diffractometer. The scanning range was set to 5–30°, the step size was 0.02° with a scanning rate of 1 step/s, and the operating conditions were 40 kV and 30 mA. The EVA evaluation program (DIFFRAC Plus, Bruker analytical X-ray system, GmbH) was used for peak searching and calculating under-peak areas as part of the quantitative crystallinity analysis. Each scan has been repeated three times, and the average value and the standard deviation have been reported.

#### 2.2.4. Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflectance (ATR) spectra were acquired using a single bounce diamond ATR (Universal ATR) in a nitrogen purged Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific Inc) controlled by OMNIC 8.2.387. The FTIR spectra were collected at a resolution of 4 cm$^{-1}$ with 32 scans over a range of wavelengths from