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Influence of protein concentration on surface composition and physico-chemical properties of spray-dried milk protein concentrate powders

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ABSTRACT

Surface composition, moisture sorption behaviour and glass–rubber transition temperature (T_{gr}) were determined for spray-dried milk protein concentrate (MPC) powders over a range of protein contents (35–86 g 100 g^{-1}). Surface characterisation of MPC powders indicated that fat and protein were preferentially located on the surface of the powder particles, whereas lactose was located predominantly in the bulk. Moisture sorption analysis at 25 °C showed that MPC35 exhibited lactose crystallisation, whereas powders with higher protein contents did not and continually absorbed moisture upon humidification up to 90% RH. The GAB equation, fitted to sorption isotherms of MPCs, gave increases in monolayer moisture value (m_m) with protein content. T_{gr}, measured with a rheometer, decreased significantly ($P < 0.05$) with increasing water content and increased with increasing protein content ($P < 0.05$). In conclusion, increasing protein concentration of MPCs resulted in altered surface composition and increased m_m value and T_{gr} values.

1. Introduction

Milk protein concentrates (MPCs) are high-protein spray-dried powders derived from defatted milk by means of membrane separation (Chandan, 2011). Ultrafiltration (UF) and diafiltration (DF) are applied to skimmed milk, followed by evaporation and spray-drying (Mistry & Hassan, 1991), resulting in powders with protein concentrations ranging from 35 to 86 g 100 g^{-1}, with a concomitant reduction in lactose levels as protein content increases (Havea, 2006).

In recent years, MPCs of different protein contents have been produced and incorporated into a wide range of products. For example, MPC powders are often used to standardise the protein content of milk for cheese-making, and are also used in recombined cheese, infant milk formula (IMF), dairy-based beverages and sports and nutritional foods.

There are issues in the handling and storage of dried milk protein ingredients, e.g., powder blockage in spray dryers, powder silos and hoppers, and shelf-life issues involving caking. These issues can be related to surface composition and moisture levels, which affect key functional properties, e.g., stickiness, wettability, bulk density and flowability of powders (Kim, Chen, & Pearce, 2002; Nijdam & Langrish, 2006). Non-uniform distribution of components, e.g., on particle surfaces versus their interior, can occur through various mechanisms. Spray-drying involves the rapid removal of water from a concentrated dispersion, during which milk components are concentrated, as moisture evaporates from the droplet surface (Kim, Chen, & Pearce, 2009), causing concentration gradients of solutes. Osmotic forces cause dissolved milk components to migrate toward the surface, partially replenishing the aqueous phase (Birchal, Huang, Mujumdar, & Passos, 2006). Another influence is hydrophobicity, whereby hydrophobic molecules, such as fat, will preferentially take up position on the surface. One effect of this migration is that concentrations of lactose, fat, and protein at the surface of spray-dried dairy powders have been found to be different from the bulk composition (Fäldt & Bergenståhl, 1996; Kim et al., 2002; Nijdam & Langrish, 2006). Powders with high

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levels of surface fat are less wettable, less flowable, and more prone to lipid oxidation compared with those with lower levels of free fat (Vignolles, Jeantet, Lopez, & Schuck, 2007).

Moisture sorption behaviour and glass–rubber transition data provide information that is useful in selecting processing conditions for spray-dried milk powders, and that influence physical characteristics (such as stickiness, hygroscopicity and caking behaviour) and stability (storing and handling) of the final product. Moisture sorption isotherms show the quantity of water absorbed by powders and the relative humidity (RH) at which lactose crystallises in powders. Crystallisation of non-fat powders is undesirable as it causes sticking, caking and cohesion (Jouppila & Roos, 1994). Sorption isotherms can be modelled using equations such as Guggenheim–Anderson–de Boer (GAB) to determine factors such as the monolayer value of powders (Foster, Bronlund, & Paterson, 2005). Glass–rubber transition temperatures (T_{gr}) of powders influences their storage stability, as, at higher T_{gr} values, powder is less likely to crystallise during storage.

X-ray photoelectron spectroscopy (XPS) is an established method for elemental analysis of a variety of materials, including dairy powders (Kim et al., 2009; Nijdam & Langrish, 2006). The analysis provides relative atomic percentages of elements present at the surface of milk powder particles using measurements within ~5 nm of the surface (Gaiani et al., 2006). Surface composition of powder is of importance in understanding functional properties.

The physico-chemical properties of spray-dried dairy powders of different composition, such as milk powders with various fat levels, skimmed milk powder (SMP) with added lactose, and SMP with hydrolysed lactose or whey protein/lactose blends have been studied (Hogan & O'Callaghan, 2013; Nijdam & Langrish, 2006; Shrestha, Howes, Adhikari, & Bhandari, 2007a, 2007b). However, the effect of increasing protein content of MPCs on their physico-chemical properties, such as surface composition, moisture sorption behaviour and T_{gr}, has not yet been studied.

The aim of the present study was to investigate the effect of protein concentration (35–86 g 100 g^{-1}) on physico-chemical properties of a series of MPC powders made from the same milk source. Hence, differences in milk composition were not a factor, as would be the case if powders were collected from industrial sources. Powder particle surface composition of MPC powders was analysed using XPS, and moisture sorption isotherms and T_{gr} of the powders were also measured.

2. Materials and methods

2.1. Sample preparation

Seven non-agglomerated MPC powders were produced from skimmed milk by ultrafiltration, diafiltration and spray-drying, as reported by Crowley, Gazi, Kelly, Huppertz, and O'Mahony (2014b). The powders, referred to as MPC35, MPC50, MPC60, MPC70, MPC80, MPC85, MPC90, in order of increasing protein content, had measured protein levels in the range 35–86 g 100 g^{-1} (Table 1). Chemical composition of the powders was determined by NIZO food research (Ede, The Netherlands), using the Kjeldahl method for protein, furnace method for ash and HPLC for lactose content, as detailed by Crowley et al. (2014b).

2.2. Powder particle size

Powder particle size was determined by laser-light-scattering using a Malvern Mastersizer 3000 with an Aero S unit (Malvern Instruments Ltd., Malvern, Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 4 mm and then fed into the dispersion system. The feed rate was 18–25% to keep the laser obscuration level at 1–6%. Compressed air at 0.5 bar was used to transport and suspend the powder particles through the optical cell, a measurement time of 10 s was used, and background measurements were made using air for 20 s. Volume mean diameter, $D_{4,3}$, was used to characterise the particle size of powders.

2.3. Surface structural analysis by scanning electron microscopy

Surface structure was observed using scanning electron microscopy (SEM). Samples were imaged using a field emission scanning electron microscope (FE-SEM; Zeiss Supra Gemini, Darmstadt, Germany) at 2.00 kV. Samples were mounted on double-sided carbon tape, attached to SEM stubs, and then sputter-coated with chromium (Emitech K550X, Ashford, UK). Representative micrographs were taken at 1000× and 5000× magnification to visualise surface characteristics.

2.4. Surface composition of powders

Surface composition of powders was determined as described by McCarthy et al. (2013). In brief, a Kratos Axis 165 X-ray photoelectron spectrophotometer (XPS; Kratos Analytical, Manchester, UK), using a monochromatic Al Kα X-ray source (1486.58 eV) at 150 W (15 kV, 10 mA) was used. The powder samples were attached to the sample holder prior to analysis using double-sided conductive tape. Using theoretical elemental compositions, a matrix formula was used to determine relative amounts of protein, fat and lactose on the powder surface, as described by Fäldt, Bergenståhl, and Carlsson (1993).

2.5. Glass–rubber transition temperature

Powders were dried overnight at 70 °C in a vacuum oven, followed by further drying in a desiccator over P_2O_5 for two days. Samples were placed in vacuum desiccators over saturated salt solutions of LiCl, CH_3COOH, $MgCl_2$ or K_2CO_3, to give respective RH of 11.4%, 23.1%, 33.2%, and 44.1%, at room temperature, giving a_w values of 0.01 × RH (Labuza, Kaanane, & Chen, 1985). The samples were stored under these conditions for up to 15 d before analysis of T_{gr} values of powders by a thermo-mechanical technique, as described by Hogan, Famelart, O'Callaghan, and Schuck (2010), using a standard laboratory rheometer (AR2000, TA Instruments Ltd., Crawley, UK). Powder samples (~1 g) were compressed (30 N) between a Peltier base plate and a 40-mm diameter steel parallel plate, and heated via the Peltier plate from 20 to 100 °C at a constant rate (2 °C min^{-1}). The T_{gr} was identified as the point of inflection on the normal force versus temperature curve. All T_{gr} measurements were carried out in duplicate.

2.6. Sorption isotherm studies

Water sorption isotherms were determined gravimetrically using a dynamic vapour sorption (DVS) technique (DVS Advantage 1 Surface Measurement Systems Ltd., London, UK). The DVS apparatus monitors the moisture sorption capacities of powders during storage by recording changes in sample weight over time at a constant temperature (25 °C) and varying RH (between 0 and 90%). Samples (30 mg) dried as described in Section 2.4 were loaded into the sample pan. Accurate RH settings were obtained by mixing dry nitrogen gas with saturated water vapour in defined proportions. Samples were humidified from 0 to 90% RH in increments of 10% RH. For each step, equilibrium was considered to be reached when change in mass with time (dm dt^{-1}) was <0.001 mg min^{-1} for at least 10 min. Graphs of water uptake over time (isotherms) for each