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Physicochemical properties of spray dried nanoemulsions with varying final water and sugar contents

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ABSTRACT

The objective of this study was to investigate the physicochemical properties of spray dried nanoemulsions having different final water and sugar contents. Formulations consisting of lactose or a 70:30 mixture of lactose: sucrose (23.9%), sodium caseinate (5.1%) and sunflower oil (11.5%) in water were heat treated (100 °C, 30 s), homogenized (17 MPa) or microfluidized (100 MPa) and spray dried at two different outlet temperatures (80 or 90 °C). Nanoemulsions produced by microfluidization were more stable and less viscous than control emulsions and had lower solvent extractable free fat. Increasing dryer outlet temperature reduced water content, water activity, particle size, tapped bulk density, with a consequent increase of onset temperature of glass transition (T_g) and crystallization (T_{cr}) of lactose in powders. Reduction of fat globule size by microfluidization lowered T_{cr} of lactose, an effect attributed to the lower level of protein in the continuous phase. Partial replacement of lactose with sucrose decreased T_g and delayed crystallisation. The study demonstrated that the physical properties of powders can be altered by reducing the fat globule size of emulsions pre spray drying.

1. Introduction

Spray drying is a method of food preservation based on dehydration to final water contents of <3% to reduce physical, chemical or biological deteriorative changes (Gharsallaoui et al., 2007). In many cases foods are dried in the form of an emulsion (Fäldt and Bergensåthl, 1996a,b), examples of which include: whole milk powder and milk based nutritional powders (e.g., infant formula), medical and therapeutic beverages. Protein is the main emulsifier in these emulsion systems and the amount of protein required to emulsify the fat phase depends on a number of factors including the amphiphilic nature of the protein, the concentration of both fat and protein phases, and mechanical forces used to disrupt the fat into smaller particles (Floury et al., 2000; Hogan et al., 2001b; Vega et al., 2007; Vega and Roos, 2006). High mechanical forces used during the process of microfluidization can be used to produce nanoemulsions (20–200 nm) which are more stable to creaming and sedimentation than conventional emulsions (1–100 μm); this has been attributed to the greater influence of Brownian motion in systems where gravity induced creaming or sedimentation (Huang et al., 2010; Solans et al., 2005) can occur. Moreover, lipid droplets with decreasing particle size are less likely to flocculate and coalesce due to a reduction in attractive forces between them (McClements, 2005). Consequently, nanoemulsions are increasingly being used in the food industry as delivery systems for non-polar bioactive lipids. Bioavailability of lipids in these systems is increased compared to conventional emulsions due to the smaller fat globule size and higher surface-to-volume ratio (Acosta, 2009; McClements, 2011); nanoemulsions are therefore useful for improving the bioactivity of lipophilic ingredients that are normally poorly absorbed.

The composition of the continuous phase of emulsions has a significant impact on viscosity, stability, and glass transition temperature as reported by Maher et al. (2011). Nanoemulsions have a greater interface area for protein to adsorb to, leaving less protein in the continuous phase. Other constituents of the continuous phase of dairy based beverages often include low molecular weight sugars, such as lactose and sucrose. The molecular and physicochemical properties of sugars, when superimposed on the properties of the dispersed phase, affect subsequent dried ingredient functionality both during and after reconstitution. For instance, sucrose will crystallize readily when exposed to high temperatures and relative humidities (Yu et al., 2007) and thus can be used to modulate certain glass forming structures in food. However, there is a critical humidity at a given temperature at which crystallization may occur (RH_c) (Burnett et al., 2004) and it is important to identify this humidity as it will determine the humidity range the powders can be stored at. Sugars (lactose and sucrose) are

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often combined with dairy solids to meet nutritional and structural requirements in the diet. They have the advantage of availability at low cost, low viscosity in concentrated solutions, and ability to produce a good glass upon spray drying. They are often combined with milk proteins such as casein, which have the advantage of being amphiphilic and having good heat stability and emulsifying properties (Hogan et al., 2001a; Huck-Iriart et al., 2011). Sodium caseinate readily adsorbs at the fat surface in emulsion systems which increases fat encapsulation, causing decreased free fat. This reduces the hydrophobicity on the surface of powders making them more wettable, flowable, dispersible, and reduces lipid oxidation (Fäldt and Bergensåthl, 1996a; Hardas et al., 2000; Kim et al., 2005).

The effect of reducing the fat globule size (FGS) in emulsions has been investigated previously (Mongenot et al., 2000; Sheu and Rosenberg, 1995; Soottitantawat et al., 2003). These studies looked at volatile retention whereas the current study investigated the physicochemical properties of spray dried conventional and nanoemulsions with different sugar and water contents. Powders were analysed for differences in free fat, glass transition, crystallization, and water sorption characteristics. The objective of this study was to investigate the functionality of spray dried nanoemulsions and show how their physical characteristics differ from powders made from conventional emulsions.

2. Materials and methods

2.1. Materials

The materials used were lactose (Glanbia, Kilkenny, Ireland), sucrose (purchased from local market), sodium caseinate (Kerry Ingredients, Listowel, Ireland) and sunflower oil (Trilby Trading, Drogheda, Ireland). Analytical grade petroleum ether (BP 40–60 °C) was purchased from Sigma to Aldrich (Sigma–Aldrich, Wicklow, Ireland). The protein content of the sodium caseinate was 89.8%, as determined by the Kjeldahl method (IDF, 2001) and using a nitrogen-protein ratio of 6.38.

2.2. Methods

2.2.1. Emulsion preparation

Batches (30 kg) of oil-in-water emulsions were formulated with lactose or a 70:30 lactose: sucrose mixture (23.9%), sodium caseinate (5.1%) and sunflower oil (11.5%). A coarse emulsion was made by mixing these ingredients with a high shear mixer (Silverson Machines Ltd., UK) at 60 °C. The mixture was then subjected to high-temperature short-time pasteurization (100 °C, 30 s) using a Microthermics tubular heat exchanger (Model 25HV; North Carolina, USA). Control emulsions were produced using an in-line 2-stage homogenizer (model NS20006H, GEA Niro, Soavi, Parma, Italy) at a first stage pressure of 13.79 MPa and a second stage pressure of 3.45 MPa. Nanoemulsions were produced using a Microfluidizer (model M-110EH, Microfluidics, Newton, Mass., USA) at 100 MPa and 60 °C in a Y-shaped interaction chamber with one pass. Control and nanoemulsions were spray dried using a single stage pilot-scale spray dryer (Anhydro F1 Lab, Copenhagen, Denmark) equipped with a two-fluid nozzle atomization system (Type 1/8 JAC 316ss) and counter-flow drying. The inlet temperature of the dryer was set at 185 °C and the outlet temperature was set at either 80 °C or 90 °C with a water evaporation rate of ~20 kg/h to give high and low moisture powders, respectively. An experimental design is given in Table 1 showing the 8 different powder types that were produced. The first letter represents the sugar used (L or S), the second letter the emulsion type (C or N), and the number represents the air outlet temperature from the dryer in degrees Celsius (80 or 90).

Table 1
2^3 factorial experimental design and coding system of powders.

Powder	Sugar	Emulsion type	Dryer outlet temp (°C)
LC80	Lactose	Control	80
LC90	Lactose	Control	90
LN80	Lactose	Nanoemulsion	80
LN90	Lactose	Nanoemulsion	90
SC80	Lactose/sucrose	Control	80
SC90	Lactose/sucrose	Control	90
SN80	Lactose/sucrose	Nanoemulsion	80
SN90	Lactose/sucrose	Nanoemulsion	90

2.2.2. Particle size analysis

Mean fat globule size (FGS), D[4,3] (De Brouckere mean), of each control emulsion was determined using a laser-light diffraction unit (Mastersizer S, Malvern Instruments Ltd., Worcestershire, UK) equipped with 300 RF lens. The optical parameters chosen were a particle and dispersant refractive index of 1.46 (oil) and 1.33 (water), respectively. Samples were measured post homogenization and post reconstitution. Mean powder particle size, D[4,3] was determined by laser diffraction with the dry powder feeder (Malvern Mastersizer).

Mean (z-average) FGS of nanoemulsions was measured using an intensity distribution by a Zetasizer Nano system (Malvern Instruments, Inc., Worcester, UK). Measurements were carried out at 25 °C and at a scattering angle of 173°. Samples taken post homogenization were compared to reconstituted powder samples after dilution to a solids content of 0.5% (w/w) using distilled water to avoid the effects of multiple scattering.

2.2.3. Apparent viscosity measurements

Apparent viscosity measurements of control and nanoemulsions pre and post homogenization (40% solids) were carried out using a controlled stress rheometer (AR G2 rheometer, TA Instruments, Crawley, UK), equipped with a concentric cylinder geometry. The temperature was controlled by a Peltier apparatus (±0.1 °C). Samples (17 mL) were pre-sheared at 500 s^{-1} for 1 min, followed by equilibration for 2 min. Samples were then sheared from 5 to 500 s^{-1} over 3 min, held at 500 s^{-1} for 1 min, and then sheared from 500 to 5 s^{-1} over 3 min. Measurements were carried out at 55 °C to replicate the temperature of the emulsions pre drying. The apparent viscosity was taken at 500 s^{-1}.

Powders, reconstituted at 12.5% solids, were analysed using an AR G2 rheometer equipped with a 60 mm stainless steel parallel plate. Samples (~2 mL) were measured according to the above procedure at 25 °C and a shear rate of 300 s^{-1}.

2.2.4. Emulsion stability

A LumiFuge 116 stability analyzer (L.U.M. GmbH, Berlin, Germany) was used to measure the separation rate of conventional emulsions and nanoemulsions at 25 °C. The Lumifuge is an analytical centrifuge that continually measures the light transmitted through a sample over the total length of a measurement cell. The samples (0.4 mL aliquots) were placed in polycarbonate sample cells and centrifuged (285*g*) for approximately 7.2 h, simulating approximately 3 months of separation under normal gravity. Separation rates were determined using the software package SepView 4.1 (L.U.M GmbH). The velocities of the separation of individual particles (mm/d) were measured from the measurement results.