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Microstructure and lactose crystallization properties in spray dried nanoemulsions

P.G. Maher [a,b], M.A.E. Auty [a,*], Y.H. Roos [b], L.M. Zychowski [a,b], M.A. Fenelon [a]

[a] Food Chemistry & Technology Department, Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland
[b] Food Technology, School of Food and Nutritional Sciences, University College Cork, Cork, Ireland

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ABSTRACT

The objective of this study was to characterize lactose crystallization behaviour and microstructure of spray dried nanoemulsions with different fat globule sizes (FGS). Powders of the same composition (57.7% w/w lactose, 12.3% w/w sodium caseinate, 27.7% w/w sunflower oil, and 2.3% w/w water) but different FGS (mean diameters 1100 nm and 155 nm) prior to spray drying were manufactured. Differences in lactose crystallization were studied using dynamic vapour sorption (DVS) and polarized light microscopy (PLM). Crystallization kinetics was modelled using the Avrami and Yang equations. Results showed that lactose crystallized in three dimensions and more rapidly in powders with a smaller FGS. PLM images showed a higher rate of lactose crystal formation for smaller FGS powders when stored for 4 days at 55% relative humidity. Confocal laser scanning microscopy (CLSM) and cryo-scanning electron microscopy (Cryo-SEM) images indicated the more evenly distributed small fat globules inside powder particles prepared from spraydried nanoemulsions. The surface of powder particles was uneven and ruptured post lactose crystallization. Crystals appeared after humidification and were assumed to be anhydrous α- and β-lactose in a 5:3 molar ratio. Results showed powder particles of the same composition were altered in lactose crystallization characteristics by changing the FGS of emulsions pre spray drying.

1. Introduction

In dairy products, the degree of lactose crystallization has a significant effect on ingredient and food properties, such as texture and flavour. Crystallization of lactose in milk powders results in lumping and caking which has a negative impact on powder reconstitution (Lai & Schmidt, 1990). Component crystallization also causes the release of entrapped lipids in powders (Fäldt & Bergenståhl, 1996; Shimada, Roos, & Karel, 1991) making them more susceptible to oxidation.

Various methods can be used to quantify crystallization of amorphous sugars. Isothermal differential scanning calorimetry (DSC) was used by Kedward, MacNaughtan, Blanshard, and Mitchell (1998) and Roos and Karel (1990) to determine the crystallization of freeze dried lactose and sucrose at low water contents (<5%) and high temperatures (365–400 K). X-ray diffraction (XRD) was used by Jouppila, Kansikas, and Roos (1997) and Miao and Roos (2005) to monitor crystallization kinetics of lactose, trehalose and lactose/trehalose mixtures. Mahlin, Berggren, Alderborn, and Engstrom (2004) used atomic force microscopy (AFM) to quantify crystallization.

* *Corresponding author*. Tel.: +353 2542442.
E-mail address: mark.auty@teagasc.ie (M.A.E. Auty).
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Lactose crystallization can be measured by gravimetric means, by monitoring changes in mass of powder samples upon humidification (Iglesias & Chirife, 1978; Jouppila & Roos, 1994; Lai & Schmidt, 1990). Crystallization results in sorbed water release, which is measured from mass decrease in a humidified powder (Burnett, Thielmann, & Booth, 2004; Burnett, Thielmann, Sokoloski, & Brum, 2006). This method is most successfully used at ambient temperatures where the crystallization rate is quite slow and can be easily monitored (Kedward, MacNaughtan, & Mitchell, 2000).

Crystallization kinetics can be modelled using various relationships. The Avrami equation (Avrami, 1939, 1940) has been used by several researchers (Arvanitoyannis & Blanshard, 1994; Haque & Roos, 2005; Kedward et al., 2000; Mazzobre, Aguilera, & Buera, 2003). Derivative models from the Avrami equation include the Yang equation (Yang, Grey, & Doney, 2010) and Urbanovici–Segal equation (Urbanovici & Segal, 1990). The Urbanovici–Segal equation includes a parameter r ($r > 0$) that determines how far the model deviates from the Avrami equation (Soutari, Buanz, Gul, Tuleu, & Gaisford, 2012). Other kinetic models used to determine lactose crystallization are the Williams-Landel and Ferry (WLF) equation (Roos & Karel, 1991) and the Hoffman equation (Arvanitoyannis & Blanshard, 1994). The Arrhenius equation can be used to determine the activation energy (E_A) required for crystallization (Schmidt, Law, & Zhang, 1999). The Avrami equation determines the rate constant (k) and exponent (n) that, respectively, determine how fast the material crystallizes and in how many dimensions. Powders stored at increasing temperatures and humidities crystallize at faster rates (Soutari et al., 2012).

Polarized light microscopy (PLM) is a useful technique in distinguishing crystalline from non-crystalline material (Hartel, 2001) and can be used to directly measure the rate of crystal growth. Mazzobre et al. (2003) used polarized light videomicroscopy (PLV), in conjunction with DSC, to determine the isothermal crystallization kinetics of lactose and lactose–trehalose mixtures. The PLV method proved a useful way of directly observing individual crystal growth and morphological aspects that were undetectable by DSC.

The distribution of fat globules has a significant effect on functional properties of dairy powders (Pisecky, 1997). Techniques such as CLSM and cryo-SEM are useful in highlighting microstructural differences which help explain why dairy powders have various functional properties. CLSM is widely used for studying the microstructure of cheese, milk powder and chocolate (Auty, Twomey, Guinee, & Mulvihill, 2001). McKenna (1997) examined whole milk powder using CLSM. Kelly, O'Mahony, Kelly, and O'Callaghan (2014) used CLSM to analyze the distribution of fat droplets in powder samples where different fat blends were stabilized by sodium caseinate. These authors were dual-labelled with Nile Red/Fast Green FCF to show the distribution of fat and protein, respectively, throughout the powder particles. Air vacuoles were also visible in powders in images produced by CLSM. SEM techniques have been developed to examine the outer and inner structures of foods (Soottitantawat, Yoshi, Furata, Ohkawara, & Linko, 2003). SEM has been used in studies of microencapsulation properties of powder structures stabilized by sodium caseinate (Fäldt & Bergenståhl, 1996; Hogan, McNamee, O'Riordan, & O'Sullivan, 2001a,b). Cryo-SEM is a useful technique in analyzing nano-sized particles embedded in food matrices (Dudkiewicz et al., 2011).

The objectives of the present study were (1) to investigate the effects of reducing the FGS of emulsions prior to spray drying on water-induced lactose crystallization during storage; and (2) to characterize powder microstructure using correlative microscopy techniques (PLM, CLSM and cryo-SEM) to help explain differences of the physical properties of the powders.

2. Materials and methods

2.1. Materials

Two powders, containing 57.7% w/w lactose, 12.3% w/w sodium caseinate, 27.7% w/w sunflower oil and 2.3% w/w were used (Maher, Roos, & Fenelon, 2014). The powders differed in their mean FGS as they were both homogenized (60 °C with a single pass) at different pressures prior to spray drying. Conventional emulsions were produced using in-line two-stage homogenization (model NS20006H, GEA Niro, Soavi, Parma, Italy) at first- and second-stage pressures of 13.79 MPa and 3.45 MPa, respectively, giving a FGS of ~1100 nm. Nanoemulsions were produced by microfluidization with a microfluidizer (model M-110EH, Microfluidics, Newton, MA, USA) at 100 MPa, giving a FGS of ~155 nm. All emulsions were spray dried at the same conditions (inlet/outlet dryer temperatures of 185 °C/80 °C) with 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. Resulting powders were labelled C and N for conventional emulsion powders (FGS ~ 1100 nm) and nanoemulsions powders (155 nm), respectively.

2.2. Methods

2.2.1. Dynamic vapour sorption

Water sorption isotherms of powders were obtained from the DVS Data Analysis Suite in Microsoft Excel using a DVS-1 analyser (Surface Measurement Systems, London, UK) equipped with a Cahn microbalance. Powder samples (~30 mg) were placed in the sample pan with an empty pan used as a reference. Samples were humidified at 55% relative humidity (RH) on the DVS for two days (48 h) for C and N at 25 °C. Mixing dry nitrogen gas (200 mL/min) with saturated water vapour in the correct proportion using mass flow controllers was used to get accurate RH readings. Samples were measured from three replicate spray drying trials.

2.2.2. Polarized light microscopy

Samples were examined using an Olympus BX51 light microscope (Olympus BX-51, Olympus Corporation, Tokyo, Japan) with a 10× dry objective lens using polarized light. Digital images (TIFF, 8-bit) were taken using a Jenoptik C14 Imagic camera, and captured. Powders were analyzed pre- and post-lactose crystallization following storage over a saturated solution of $Mg(NO_3)_2$ (55% RH) for 4 days at 20 °C. Crystalline regions appeared as bright areas on the micrographs.