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The microstructure and component distribution in spray-dried emulsion particles

Marta Munoz-Ibanez[a], Marine Nuzzo[b,c], Christelle Turchiuli[a,d], Björn Bergenståhl[c], Elisabeth Dumoulin[a], Anna Millqvist-Fureby[b,*]

[a] UMR Ingénierie Procédés Aliments, AgroParisTech, Inra, Université Paris-Saclay, 1 avenue des olympiades, 91300 Massy, France
[b] SP Technical Research Institute of Sweden, Box 5607, SE-114 86 Stockholm, Sweden
[c] Lund University, Department of Food Technology, Engineering and Nutrition, P.O. Box 124, SE-221 00 Lund, Sweden
[d] Université Paris-Sud, IUT Orsay, Plateau de Moulon, F- 91400 Orsay, France

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ABSTRACT

Microencapsulation by spray drying of oil-in-water (o/w) emulsions provides a means to encapsulate functional lipophilic ingredients. The active ingredient is dispersed in continuous solid phase providing protection. However, the encapsulation efficiency depends on the microstructure and morphology of the dry particles influenced by several mechanisms occurring during processing such as oil droplet breakup during atomization, ingredient diffusivity, interfacial adsorption of surface active ingredients, and drying kinetics. In this work, sunflower oil (model for lipophilic compounds) was encapsulated in solid particles composed of acacia gum and maltodextrin DE12. Three powders with different initial emulsion size (e.g. about 0.1 and 1 μm) and atomized under high and low shear rate were analysed for the morphology and distribution of oil droplets and matrix constituents within the solid particle (20–100 μm). The microscopic (optical, SEM, LVSEM, confocal Raman), spectroscopic (XPS) and analytical (solvent extraction) techniques used were either qualitative or quantitative. Their combination made it possible to determine both the composition at the surface and inside the particle. The surface differs from the bulk in composition, confirming the constituent segregation during spray drying, and depended on the initial emulsion size and atomization conditions that must be controlled for an efficient encapsulation. Especially, the use of confocal Raman microscopy is promising for the study of processstructure-properties relationship.

1. Introduction

Spray-drying is a common technology to encapsulate fats and oils in solid matrices to create a powder product with improved shelf stability and new functionality compared to a liquid emulsion. The functional properties of the powder, such as wetting, flowability, oxidation stability, etc. are strongly linked to the structure of the particles on different levels and the oil encapsulation efficiency (Kim, Chen, & Pearce, 2002; Nijdam & Langrish, 2006). Encapsulation of oil in powders is an area that has been researched over many years, and the encapsulation efficiency and stability of the encapsulated oil are two important parameters of practical relevance. There are several different aspects that influence the properties and microstructure of the powder, including formulation and processing conditions.

The emulsion droplet size as well as particle size influence the oil encapsulation and surface oil (Jafari, Assadpoor, Bhandari, & He, 2008; Sarkar, Arfsten, Golay, Acquistapace, & Heinrich, 2016; Soottitantawat, Yoshii, Furuta, Ohkawara, & Linko, 2003; Soottitantawat et al., 2005). However, the optimum emulsion droplet size to minimise surface oil depended on the oil type, emulsion processing technology and particle size. The increase in surface oil at larger oil droplet size has also been observed by several other authors (Jafari et al., 2008; Millqvist Fureby, 2003; Soottitantawat et al., 2003, 2005). The instability of emulsion droplets during spray-drying was explained by the fast dehydration, leading to close contact between droplets, resulting in coalescence and weak stabilising surface layers on the droplets (Taneja, Ye, Jones, Archer, & Singh, 2013). This may contribute to the common explanation of high surface oil based on rupture of oil droplets at the particle surface (Fäldt & Bergenståhl, 1995; Kim, Chen, & Pearce, 2009;

* Corresponding author.
E-mail address: anna.fureby@sp.se (A. Millqvist-Fureby).

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Nijdam & Langrish, 2006). The processing conditions during spray-drying were also linked to the oil encapsulation efficiency, where effects of shear have been put forward by Risch and Reineccius (1988) and Soottitantawat et al. (2005). This is further supported by Munoz-Ibanez, Azagoh, Dubey, Dumoulin, and Turchiuli (2015), who showed that the droplet breakup during the atomisation step of spray drying is influenced by the shear exerted on the droplets. This leads to decrease in droplet size, but it is not clear whether it is the droplet size per se, or other effects that cause the increase in surface fat for large initial emulsion droplet sizes.

To extend the understanding of the complex mechanisms leading to oil encapsulation and the final microstructure of spray-dried particles different analytical tools for detailed characterisation are necessary. The effects of composition and processing for spray-dried dairy-like emulsions (Kim et al., 2002, 2009; Millqvist-Fureby, Elofsson, & Bergenståhl, 2001; Murrieta-Pazos, Gaiani, Galet, & Scher, 2012; Wu et al., 2014) as well as other food protein and biopolymer formulations (e.g., Fäldt, Bergenståhl, & Carlsson, 1993; Fäldt & Bergenståhl, 1994, 1995; Nuzzo, Millqvist-Fureby, Sloth, & Bergenståhl, 2015) on the surface composition have been studied rather extensively. These studies show that the surface active components are over-represented at the dry particle surface, since these adsorb to the surface of the drying drop. The surface oil coverage, as determined by XPS in a surface layer of approximately 2–5 nm, can still be very high due to spreading of oil originating from ruptured oil droplets (Chew, Fu, Gengenbach, Chen, & Selomulya, 2015; Keogh et al., 2001; Millqvist-Fureby et al., 2001; Nikolova et al., 2015). The morphology of the particles is influenced by several parameters, such as the solids content in the feed, the drying rate (Walton & Mumford, 1999), and the composition and viscoelastic properties of the adsorbed surface film of the drying drop (Elversson & Millqvist-Fureby, 2006; Nuzzo, Millqvist-Fureby et al., 2015).

The composition of the internal structure on the other hand still remains largely theoretical. Drusch and Berg (2008) have studied how the emulsion droplets are located in spray-dried emulsion powders using confocal laser scanning microscopy (CLSM), and found that powders with higher oil content presented higher levels of surface oil and oil droplets close to the surface compared to powders with less oil content. CSLM has been used to provide information about particle internal structure in different types of milk powder (Auty, Twomey, Guinee, & Mulvihill, 2001). In this study the whole milk powder showed very low levels of surface fat, and an even distribution of oil droplets throughout the particles, while a high fat cream powder showed some surface fat and larger oil droplets. Recently, Sarkar et al. (2016) used CSLM to visualise the close packing of oil droplets in spray-dried emulsions with ultra-high oil content and cross-linked whey protein as the emulsifier and matrix material.

However, CLSM requires fluorescent labelling of the components to be visualized, and is thus limited to the determination of components of sufficiently different properties, i.e. oil, carbohydrate and protein, and does not distinguish between components of similar dyeing properties, such as different polysaccharides. Confocal Raman imaging, on the other hand, allows for internal particle investigations with the same level of resolution as CLSM, but no labelling is required as the full Raman spectrum in each pixel of the image is used to construct an image of the localisation of the different molecular components. Recently, Nuzzo, Sloth, Brandner, Bergenståhl, and Millqvist-Fureby (2015) showed phase segregation in spray-dried powder particles and in individually dried particles composed of maltodextrin and hydroxypropyl methyl cellulose using confocal Raman microscopy. The same technique was also used to investigate the internal structure of single particles composed of lactose and BSA, HPMC or Poloxamer 188 (Nuzzo, Sloth et al., 2015). In these investigations, the more surface active macromolecules were located at the surface, and a layer with a thickness in the micrometre range enriched in this component was found at the surface.

The aim of this paper is to elucidate how oil droplet breakup during atomization influences the localization of ingredients and the oil encapsulation in spray-dried powders composed of sunflower oil, maltodextrin and acacia gum. We address the distribution of dry emulsion components within the particles by means of confocal Raman microscopy coupled with traditional microscopic (optical, Scanning Electron Microscopy, Low Vacuum, Scanning Electron Microscopy), spectroscopic (X-ray photoelectron spectroscopy) and analytical (solvent extraction) techniques.

2. Materials and methods

2.1. Materials

Maltodextrin DE12 (Glucidex®, Roquette, France) was used as matrix material in combination with acacia gum (Instantgum AA, Nexira, France), also bringing emulsifying and film forming properties. Food grade sunflower oil (60 g/100 g poly-unsaturated fatty acids, 29 g/100 g mono-unsaturated fatty acids, 11 g/100 g saturated fatty acids) was used as a model for lipophilic compounds. Ultra-purified water (Elga option 3, U.S) was used as solvent.

2.2. Methods

2.2.1. Preparation of emulsion

The preparation at pilot scale was based on a previous study (Turchiuli, Lemarié, Cuvelier, & Dumoulin, 2013). All the emulsions were prepared with the same concentration and quantity (2500 g). They consisted of oil (4%w/w), acacia gum (14.4%w/w), maltodextrin (21.6%w/w), and water (60%w/w) leading to a total dry matter of 40%w/w where 10%w/w of the dry matter corresponded to oil and the remaining 90%w/w to maltodextrin and acacia gum with a weight ratio of 3/2.

Aqueous phases were prepared by first dissolving the acacia gum, and second, the maltodextrin powder, in water at 40 °C using a high speed blender with 3-blade axial flow impeller (Eurostar Ika, Labortechnik).

The large oil droplet size coarse emulsions (about 1 μm) were prepared by dispersing the oil into the aqueous solution by rotor-stator homogenization (AXR, Silverson Machines Ltd, UK) at 3500 rpm for 20 min. To obtain the small oil droplet size emulsion (average droplet size about 0.1 μm), the coarse emulsion was further emulsified using a high pressure homogenizer (Rannie Slow 22–50, APV, UK) at 300 bar with re-circulation for 4 min (flow rate 7.7 kg min^{-1}, ~12 passes).

2.2.2. Spray drying

The emulsions were spray dried in a pilot dryer (Niro Minor, GEA Process Engineering, France). The dimensions of the cylindro-conical drying chamber were H 1.1 m × L 0.8 m. The initial liquid emulsion was atomized with a rotary atomizer with a diameter of 5 cm, 24 rectangular vanes of 3.5 × 6 mm and operated by compressed air.

In order to produce powders with and without change in oil droplet size distribution during atomization, coarse emulsions were atomized at two different rotational speeds chosen from a previous study (Munoz-Ibanez et al., 2015): a conventional speed used in spray drying (i.e. 33200 rpm) and found to lead to monomodal oil droplet breakup and a low rotational speed (i.e. 3270 rpm)., corresponding to a capillary number value below the critical value obtained (i.e. 0.7), in order to preserve the emulsion microstructure. For the small oil droplet size emulsion,