



## Effect of processing variables and bulk composition on the surface composition of spray dried powders of a model food system



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### ABSTRACT

The surface compositions of food powders created from spray drying solutions containing various ratios of sodium caseinate, maltodextrin and soya oil have been analysed by Electron Spectroscopy for Chemical Analysis. The results show significant enrichment of oil at the surface of particles compared to the bulk phase and, when the non-oil components only are considered, a significant surface enrichment of sodium caseinate also. The degree of surface enrichment of both oil and sodium caseinate was found to increase with decreasing bulk levels of the respective components. Surface enrichment of oil was also affected by processing conditions (emulsion drop size and drying temperature), but surface enrichment of sodium caseinate was relatively insensitive to these. The presence of “pock marks” on the particle surfaces strongly suggests that the surface oil was caused by rupturing of emulsion droplets at the surface as the surrounding matrix contracts and hardens.

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### 1. Introduction

Food powders are typically prepared from solutions, suspensions or emulsions by spray drying. Spray drying is a rapid rate process, yet observations of particle surfaces have revealed that surface compositions are significantly different to the bulk composition of the powder (Adhikari et al., 2009; Fäldt et al., 1993; Fäldt and Bergenstahl, 1996a; Jayasundera et al., 2009; Kim et al., 2002, 2009a,b,c; Vignolles et al., 2007). There is also evidence that spray drying of emulsions causes coalescence of fat globules (Ye et al., 2007).

The surface of a powder is arguably the most important part of a food particle, because it is the surface that interacts with the external environment. Surface character may affect dissolution, reactivity, diffusivity, or the relative importance of the various surface forces. These have process implications such as better powder handling, powder storage, wettability, environmental equilibrium and shelf life. The presence of fat at the surface is particularly known to markedly compromise wettability (a key parameter for most powder applications), flowability and storage stability (from fat oxidation) (Vignolles et al., 2007). There are also product quality

factors that influence the delivery mechanism or have sales advantages. These include improved appearance, hydrophobicity, swelling, taste, controlled release kinetics, sensitivity to release environment, or human response factors such as optimal digestive uptake, satiety, probiotic viability, enteric coatings and making substances hypo-allergenic. These might involve scenarios, such as fried potato snack flavourings, where the material is ingested in its dry powdered form.

Surfaces are described by their character and integrity, where character is the composition and morphology of the topmost visible surface, and integrity is the mechanical strength and resistive capacity of the surface and near surface regions. Particle performance is acutely dependent on its surface character and integrity, in a myriad of ways. Surface composition defines physiochemical behaviours such as adsorption, glass transition, polarity, reactivity, dissolution, swelling or charge carrying capacity. The morphology defines shape and size which directly affects flowability and dispersibility. When considering integrity, the mechanical strength may be adequate to survive the processing conditions but, in its development, may cause rupture of encapsulated fat globules releasing free fat or, alternately, the resistive properties may be poor if the particle is porous.

Various industries wish to develop products that have both discernible benefit and attract premium prices, which is particularly

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true for commodity food powders because of the huge volumes involved (dairy as an example), but the margins do not allow additional processing steps to be entertained. It is thus useful to investigate avenues for tailoring surface character and integrity using only the means that could readily be employed by industry: namely, by manipulating the formulation, the process equipment design and the drying environment.

While stickiness is the principle processing issue, there is a growing awareness of the need to quantify and manipulate the surface composition of food emulsions when spray dried. The review of Jayasundera et al. (2009) concluded that, while there is a rich and growing literature on quantifying surface and bulk compositions, there is a dearth of information on the mechanisms responsible for the differences between bulk and surface compositions. Mechanisms have been proposed recently for milk powders by Kim et al. (2009a,b,c). In these papers, the surface compositions of spray dried milk powders were studied for a range of milk compositions (whole milk, skim milk, instant whole milk, cream), the spray drying conditions (air inlet and outlet temperatures) and the changes that occur with storage. They found that the surface composition is determined during spray drying rather than in any of the other processing steps (e.g. conditioning fluid bed dryers or packaging). Interestingly, for instant whole milk powder, the soy lecithin (added as a natural surfactant) could not be detected at the powder surface. They explained this lack of detection as partly due to the small amount applied, 0.1–0.4%, and also that the lecithin was sprayed onto the powder dissolved in anhydrous milk fat. They also found that fat was present at the surfaces of the powders in far greater proportion than present in the bulk, confirming observations by Fäldt and Bergenstahl (1996a). Over long storage times they found no effective change in the surface composition as measured by Electron Spectroscopy for Chemical Analysis (ESCA). This is because the lactose remained in the amorphous form due to the presence of a desiccant; however, after washing with organic solvents, some release of the low melting triglycerides was detected. Humid conditions were investigated by Fäldt and Bergenstahl (1996b) who observed the release of free fat to the surface.

Kim et al. (2009b) proposed mechanisms for the formation of the surface composition as follows. Citing earlier work (Dombrowski and Fraser, 1954; Zakarlan and King, 1982), they proposed that the instabilities that form droplets begin at the interface between the oil and the continuous aqueous phase. This then results in the surfaces of the newly formed spray droplets being well represented by emulsified oil, even before drying commences. Subsequent drying and the associated mass transfer kinetics promote further segregation. In the continuous phase, water moves along a concentration gradient towards the surface. Being a small molecule, water moves relatively quickly and carries with it large molecules which cannot diffuse as quickly in the opposite direction. Thus molecules may become segregated depending on their molecular weight. The emulsified oil and protein micelles could also be carried along in the convective flux of water moving toward the surface. This movement occurs until the continuous phase becomes relatively immobile, and thereafter the remaining continuous phase shrinks as the water leaves as vapour. Kim et al. (2009b) warn that the concentration gradients may not be observed if the drying temperature is high and the droplets rapidly form a crust. In this case, the system may be quenched, where the components are relatively evenly distributed.

To further investigate this phenomenon, a series of experiments were performed to examine the surface compositions when spray drying a model food aqueous emulsion containing a protein (sodium caseinate), a carbohydrate (maltodextrin) and a fat (soya oil) in a matrix of compositions, so that the effect of different components on surface enrichment can be studied over a wide range of compositions.

The powders used here are not milk powders as used by Kim et al. (2009a,b,c); rather, they are more similar to those of Fäldt and Bergenstahl (1996a,b). Instead of lactose, maltodextrin DE10 is used as the carbohydrate, which has a higher glass transition temperature. Soya oil is used here instead of milk fat, which has a wide range of triacylglycerol chain lengths. Rather than using the whole range of milk proteins, this work selects the food grade refined form of the most significant protein, sodium caseinate. It is also known to be a better encapsulant than whey protein (Fäldt and Bergenstahl, 1996b) although is known to form interfaces that are more rigid and less elastic (Jayasundera et al., 2009). Therefore, sodium caseinate will provide a realistic model food system with which to observe surface composition and the surface release of oil. Thus, these differences mean the system used here is compositionally simple. It also allows flexibility to vary the emulsion composition.

## 2. Materials and methods

Emulsions were prepared from three ingredients: soya oil (Soyola, Kore S.A., Koropi, Greece), maltodextrin DE10 (Maltrin M100, Paroxite Ltd., Macclesfield, UK) and sodium caseinate. Two grades of sodium caseinate were compared – food industry (92.5% protein) grade (Adpro S, Adams Food Ingredients, Leek, UK), and a purer (99% sodium caseinate) grade (Sigma, Poole, UK).

The ingredients were mixed according to Table 1, which yielded the simple water-free composition map shown in Fig. 1. The ingredients were stored in airtight containers and weighed to within 0.1 g into either a 4 or 8 L container without baffles, depending on the dilution required. The total water-free mass of the ingredients was 1200 g. The sodium caseinate content dominates the emulsion viscosity and so water was generally added to each mixture in the ratio of six parts water to one part of sodium caseinate, except occasionally when maltodextrin levels were high, which had a secondary effect on emulsion viscosity. These dilutions were performed to ensure that the emulsions could be delivered by the peristaltic pump to the top of the spray dryer.

### 2.1. Homogenisation

Emulsification/homogenisation was performed in a benchtop homogeniser (Ultra Turrax T-50, Ika-Werke GmbH, Staufen, Germany). This is a blade-in-cage assembly. The emulsion was formed by blending for 1 min at 3000 rpm, followed by 1 min at 7000 rpm, then 8 min at 10,000 rpm. At the lower speeds, a spatula was used to ensure lumps were circulated towards the contact zone and that no protein gel formed at the walls. The container used was a cylindrical bucket, without baffles. After blending, the free surface of the resulting emulsion had sheen, indicating it was well homogenised. Due to the high energy input of the high-shear homogeniser, the temperature of this mixture could exceed 55 °C. The mixture was

**Table 1**  
Compositions of feed solutions tested (wt.%).

Feed solution	Sodium caseinate	Maltodextrin	Soya oil	Water
A	11.9	4.8	11.9	71.4
B	11.9	11.9	4.8	71.4
C	8.3	20.8	20.8	50.0
D	8.3	8.3	33.3	50.0
E	8.3	33.3	8.3	50.0
F	12.1	3.0	3.0	81.8
G	12.5	0.0	12.5	75.0
H	11.1	11.1	0.0	77.8
J	13.6	4.5	0.0	81.8
K	10.0	30.0	0.0	60.0
L	8.3	8.3	8.3	75.0
M	0.0	50.0	0.0	50.0
N	14.3	0.0	0.0	85.7

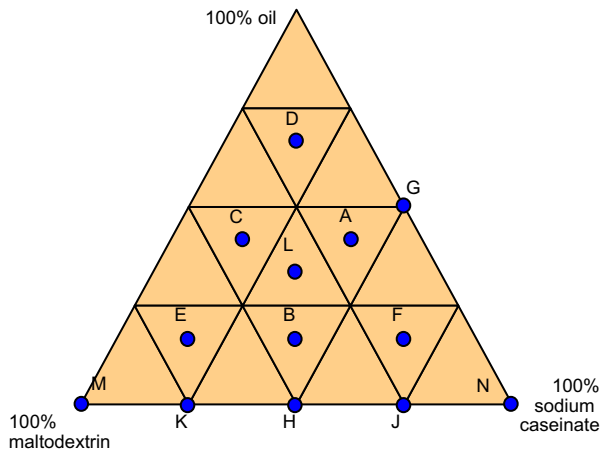


Fig. 1. Diagram showing water-free basis compositions of samples tested.

not actively cooled during this stage of preparation, partly because the trials contained between 2.4 and 6.0 L, in which the high-shear impeller was suspended. The container was moved to another workstation and a small two bladed paddle impeller was inserted. The impeller was set to approximately 300 rpm for at least 30 min. This gently rotated the emulsion with the purpose of separating air bubbles that had become entrained during benchtop homogenisation.

For all experiments listed as having “Low” oil droplet size within their emulsions (see Table 2), a second homogenisation was also performed. In these cases, the emulsion was passed through a pressure homogeniser (APV Model 15MR-8TBA, APV Gaulin Inc, Wilmington, MA). First, 2.4 L of the emulsion was poured into the fill vessel and circulated through the (single stage) homogeniser without pressure for approximately 4 min. The fill vessel was not agitated and as the emulsion was relatively viscous, there was approximately plug flow. Then 55 MPa of pressure was applied using the procedures in the operating manual. The emulsion was circulated through the homogeniser for a further 4 min. In both modes the homogeniser pumping rate was  $\sim 0.83$  L/min and so this ensured the contents of the fill vessel had received one pass through the homogeniser nozzle without pressure and one pass at pressure before finally being discharged at pressure via the nozzle to a clean container. Thus, overall, the emulsion experienced one pass through the nozzle at low-pressure and two passes at high-pressure. The remainder of the emulsion mixture was transferred into the fill vessel and homogenised where the circulation times were calculated according to remaining volume. Samples undergoing homogenisation in the benchtop homogeniser are referred to as “high” emulsion drop size and samples which were additionally passed through the APV homogeniser are referred to as “low” emulsion drop size.

## 2.2. Emulsion characterisation

Before spray drying each solution was viewed under a microscope (Leica ATC 2000, magnification 200 $\times$ ) to confirm that

Table 2

Overview of experimental programme. The drop size refers to the homogenised oil droplet size where “high” was obtained in a benchtop blade-in-cage homogeniser and “low” was obtained by additional treatment in a high-pressure homogeniser.

Experimental conditions		Pilot-scale dryer trials	Benchtop dryer trials
Homogeniser droplet size	Inlet/outlet drying air temperature ( $^{\circ}$ C)		
Low	245/100 (High)	All samples	All samples
Low	170/80 (Low)	D, E, F	All samples
High	245/100 (High)	D, E, F	D, E, F

emulsification was satisfactorily achieved, i.e., that droplets were less than 10  $\mu$ m. Solution viscosities (at 100  $s^{-1}$ ) after homogenisation were measured by Couette viscometer (ThermoHaake VT550 using an MVII bob, Thermo Fisher Scientific, Waltham, MA.) and were generally in the range 0.05–0.1 Pa s.

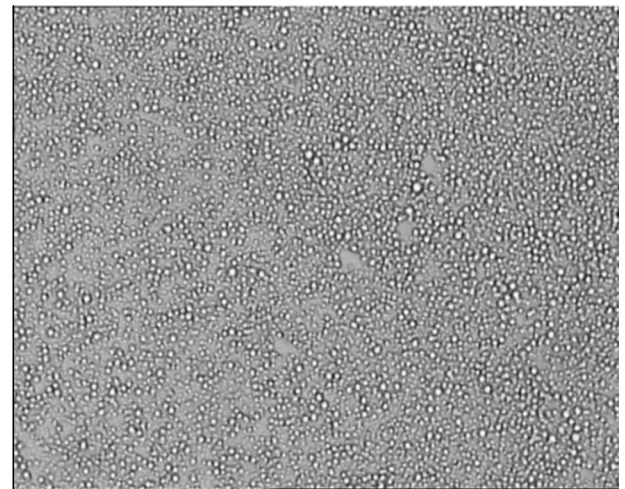
## 2.3. Spray drying

Two methods of spray drying were employed. For feed solutions/emulsions prepared using food grade sodium caseinate a pilot scale spray dryer was used and for feed emulsions prepared using high grade sodium caseinate a benchtop spray dryer was

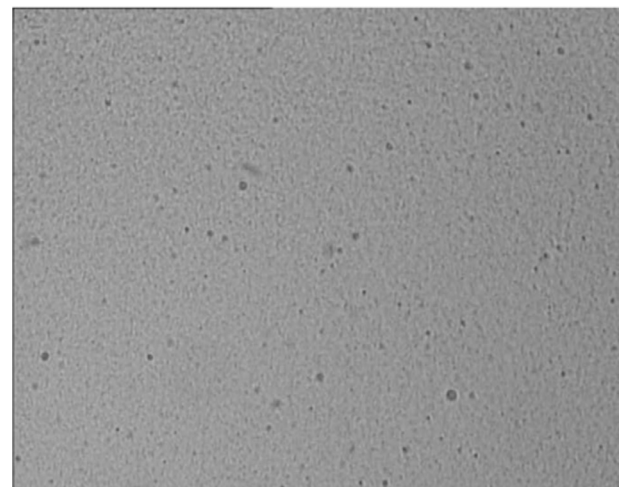
Table 3

Elemental ratios of ingredients used in compositional analysis as determined by ESCA.

Ingredient	% C	% O	% N	% Na
Sodium caseinate (99%)	66.1	18.1	15.1	0.5
Maltodextrin	57.7	42.3	0.0	0.0
Soya oil	90.5	9.5	0.0	0.0



(a)



(b)

Fig. 2. Light microscopy images of emulsions prior to spray drying to illustrate the difference between the two methods of homogenisation. The samples shown are of formulation L [0.333 NaCas:0.333 oil:0.333 maltodextrin] with (a) high emulsion oil drop size (after benchtop homogenisation) and (b) low emulsion oil drop size (after further high pressure homogenisation). The width of images corresponds to 0.336 mm.

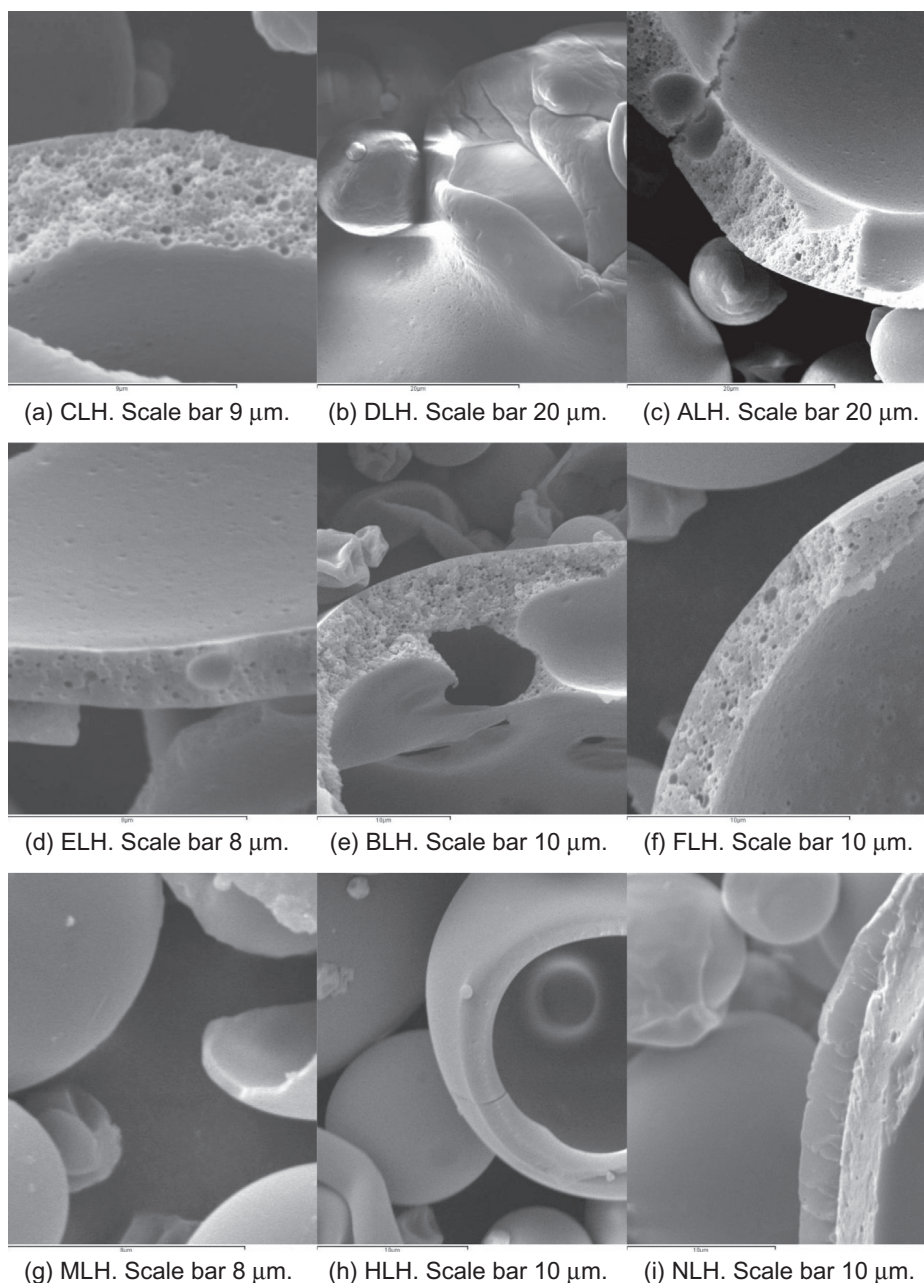


used for cost reasons. The operation of each spray dryer is discussed below.

The pilot scale spray dryer is a tall-form co-current spray drier of 3 m height  $\times$  0.9 m diameter (Spray Processes, Bedford UK). A peristaltic pump (Watson-Marlow 510U) was used to deliver the feed solution to the atomiser. The atomisation was performed by a twin-fluid nozzle, using compressed air at 2.7 bar as the atomising gas. Ambient air was directly heated in a natural gas burner and drawn through the dryer by a fan at the dryer outlet. The operation was started by feeding distilled water, and the inlet and outlet temperatures were set by adjusting the natural gas and liquid feed flowrates respectively. Once the required outlet temperature was reached the feed solution (at ambient temperature) was fed into the drying chamber and the flow adjusted again to the desired outlet temperature. Air flow rates were estimated from velocity measurements using a rotary vane anemometer (Airflow LCA 6000VT,

Airflow Developments Ltd., High Wycombe, UK). Two spray drying conditions were employed. In “low” mode, inlet and outlet air temperatures were 170 °C and 80 °C respectively with an air flow rate of  $\sim 3.8 \text{ kg min}^{-1}$ , whereas in “high” mode the inlet and outlet temperatures were 245 °C and 100 °C respectively with a lower air flowrate of  $\sim 3.2 \text{ kg min}^{-1}$ . The lower air flowrate was achieved by passing the outlet air through an additional filter system and was needed to achieve the high inlet temperature. The low and high conditions respectively represent typical and maximum spray drying conditions that are used in the spray drying of foods. The dried particles were separated by a cyclone and collected in a receiving vessel. The final products were immediately placed in 1 L open containers and put in a drying cabinet at 60 °C for 1 h. The containers were then sealed and stored at room temperature.

For cost reasons, feed solutions/emulsions prepared using high grade (99%) sodium caseinate were dried using a benchtop spray



**Fig. 3.** SEM images of the shell walls of spray dried powders at fixed process conditions of low emulsion oil droplet size and high drying temperature; (a) CLH, (b) DLH, (c) ALH, (d) ELH, (e) BLH, (f) FLH, (g) MLH (maltodextrin), (h) HLH, and (i) NLH (sodium caseinate). Scale bars vary as indicated. Trials are labelled (A, B, C, etc.) as per the composition diagram in Fig. 1, emulsion droplet size (low L or high H), drying temperature (low L or high H).

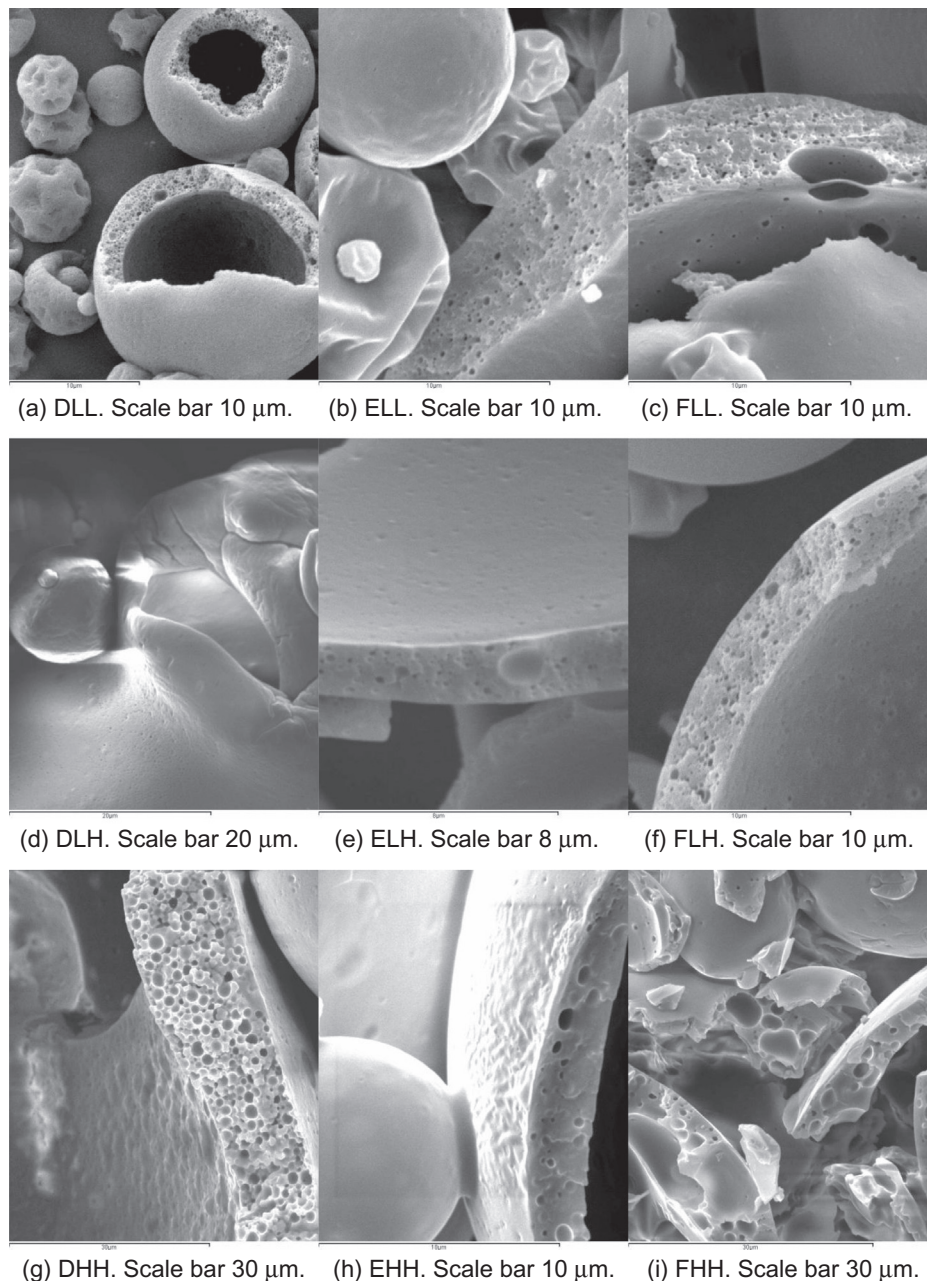
dryer (Lab-Plant SD-06, Lab-Plant UK Ltd., Filey, UK), which is a co-current dryer with pneumatic atomiser and a cylindrical drying chamber of dimensions 215 mm OD  $\times$  420 mm height. The same inlet and outlet temperature modes were used as for the pilot plant experiments, but the airflow rate was approximately 0.27 kg/min.

An overview of the experimental programme is presented in Table 2. A first set of trials was performed using the pilot scale spray dryer and using food grade sodium caseinate. A second set of trials was performed using the benchtop spray dryer and the purer grade sodium caseinate. More extensive investigations (varying drop size and drying temperature) were performed for compositions D, E, and F than other samples. Replicates were not performed. Experiments are not reported for the conditions of low drying temperature and high emulsion oil drop size, because these powders did not dry sufficiently quickly and caked in the dryer outlet. These conditions were therefore not pursued in this work.

The compositions studied are intended to represent a wide spectrum of food grade emulsions with substantial quantities of carbohydrate, oil and protein. This work is not intended to investigate small protein concentrations in and around the critical micellar concentration. Here, the protein concentrations are much larger.

#### 2.4. Scanning Electron Microscopy

All powders were vacuum gold coated, released from vacuum, and mounted in the SEM (Cambridge Stereoscan 360, UK) at the Department of Materials, Loughborough University. Coating and scanning vacuums were both 13 mPa. The vacuum was applied over a period of approximately 2 min in all cases. Three views were sought: a close up cross section of a shell edge, a close up view of a particle surface, and a wide view (lower magnification) of a collection of particles.



**Fig. 4.** SEM images of the shell walls of the three emulsion compositions (D, E and F, first character) after processing with high (H) and low emulsion (L) drop sizes (second character) and high (H) and low (L) spray drying outlet air temperature (third character). Scale bars vary as indicated. The compositions of emulsions D, E and F are shown in Fig. 1.

Size distribution measurements by laser diffraction were not made, because early attempts in a Coulter laser diffraction particle sizer (Coulter LS130) gave distributions that were clearly larger than seen by SEM, indicating that agglomeration occurred during dispersion with the carrier fluids (ethanol and acetone were trialled). A powder feeder system was not available to make dry measurements but, even if it were, agglomeration would still be a concern under ambient air conditions. Instead, qualitative comparisons of size are made from the SEM images.

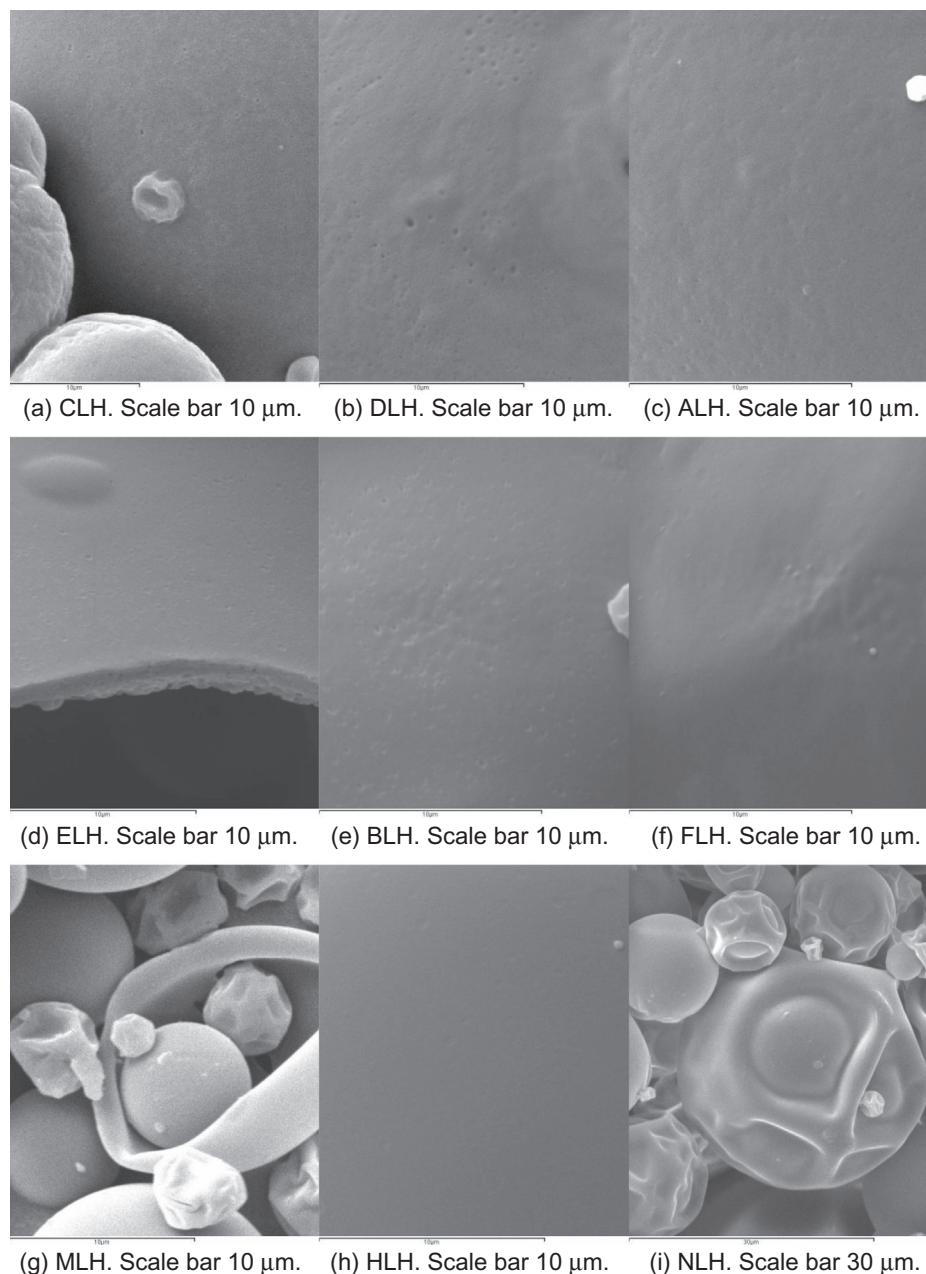
### 2.5. Electron Spectroscopy for Chemical Analysis

All powders were analysed for elemental ratios of carbon, oxygen, nitrogen and sodium by ESCA (ESCALAB 5, V.G. Scientific, East Grinstead, UK) at the Department of Materials, Loughborough University. The ESCA used a non-monochromatic Al K X-ray source.

The working chamber pressure was below 0.13 mPa. The pass energy was 85 eV and the scanning step size was 0.4 eV. Powder samples were mounted into aluminium dishes and levelled off. The analysis area was  $\sim 5 \times 5$  mm. Dwell times were 80 ms with 15 scans for the whole spectrum measurements (total 1.20 s) and 500 ms with 25 repeats for those measurements limited to detecting nitrogen (total 12 500 ms).

### 2.6. Determination of surface composition

The fractional coverages of sodium caseinate, maltodextrin and oil on the powder surfaces were then calculated from the elemental ratios of carbon, oxygen and nitrogen using the inverse matrix method of Fäldt et al. (1993), as also used by Kim et al. (2009a, 2009b). It is assumed that the calculated surface coverage can be regarded as a mass fraction. The elemental ratios for sodium



**Fig. 5.** SEM images of the particle surfaces of spray dried powders at fixed process conditions of LOW emulsion oil droplet size and HIGH drying temperature for: (a) CLH, (b) DLH, (c) ALH, (d) ELH, (e) BLH, (f) FLH, (g) MLH (maltodextrin), (h) HLH, and (i) NLH (sodium caseinate). Scale bars are 10  $\mu\text{m}$ , except for 5(i) which is 30  $\mu\text{m}$ . The compositions of emulsions C, A, E, B, F, M, H and N are shown in Fig. 1.



caseinate, maltodextrin and soya oil were independently determined by separate ESCA experiments on the individual ingredients (sodium caseinate values are based on results for the pure grade sample), and are presented in Table 3.

### 3. Results and discussion

#### 3.1. Emulsion drop sizes

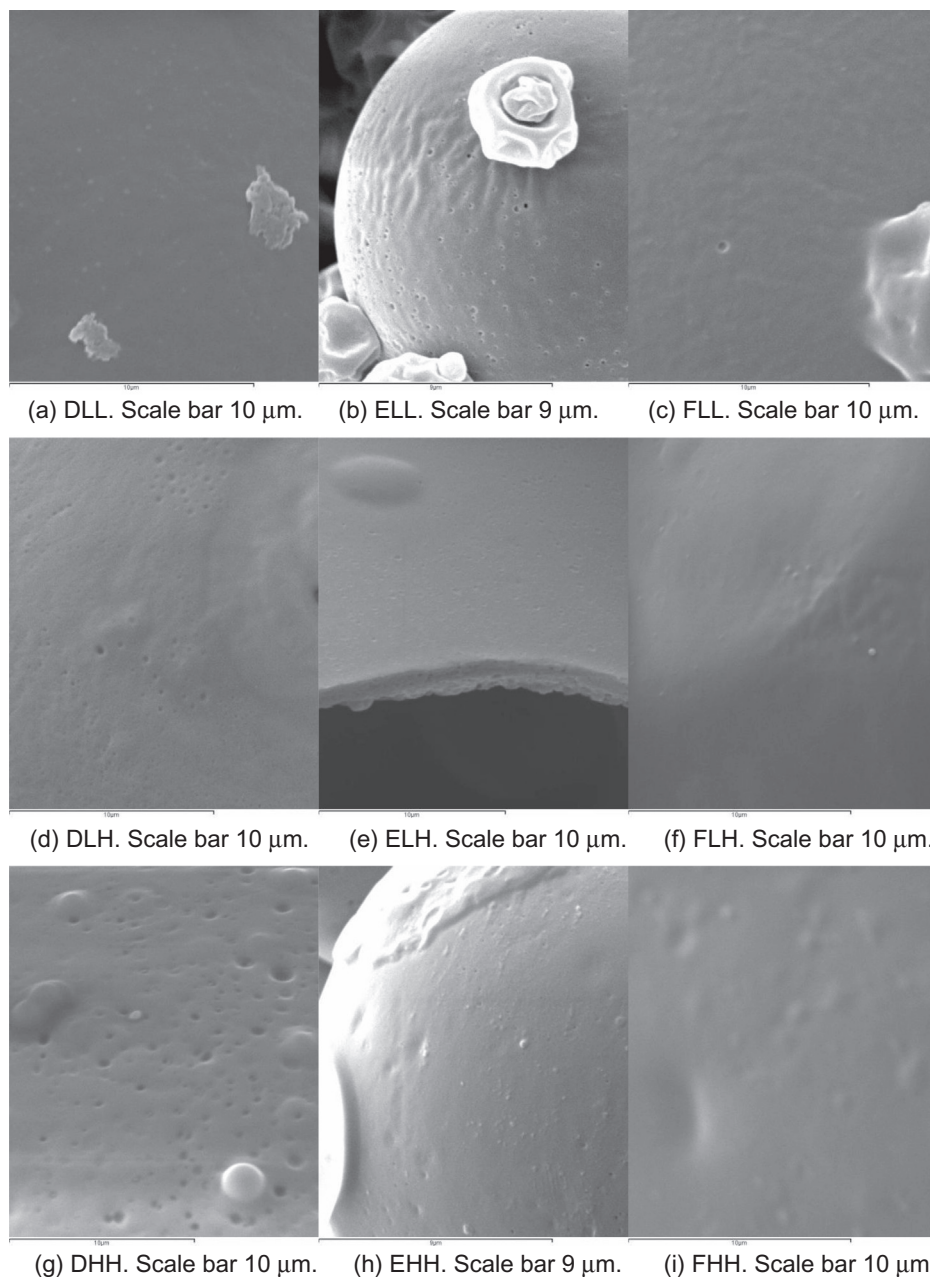
The emulsion oil droplet sizes were similar across all formulations for each homogeniser type. Fig. 2 clearly shows (for formulation L) the presence of emulsion droplets before (Fig. 2a) and after (Fig. 2b) high pressure homogenisation. Light microscope imaging revealed them to be typically 2.5–5  $\mu\text{m}$  for the “high” drop size sample (after homogenisation with the benchtop homogeniser),

which falls to less than 1  $\mu\text{m}$  for the “low” drop size sample (after further homogenisation with the APV high pressure homogeniser).

#### 3.2. Scanning Electron Microscopy

SEM images were taken of all samples. Figures shown here are taken from the pilot scale dryer trials (1st trials), but no significant differences were found between these equivalent samples from the benchtop dryer trials (2nd trials).

Fig. 3. shows close up images from (occasional) broken particles. These clearly show the classical spherical shell structure of spray dried particles. The tiny “craters” seen in the cross sections of the broken shells result from oil droplets that may have evaporated during the sample preparation for SEM images as the vacuum was applied for gold coating (soya oil has a saturation vapour



**Fig. 6.** SEM images of the particle surfaces of three emulsion compositions (D, E and F, first character) after processing with high (H) and low emulsion (L) drop sizes (second character) and high (H) and low (L) spray drying temperature (third character). The compositions of emulsions D, E and F are shown in Fig. 1.

pressure of  $\sim 4$  Pa), or were dispersed when the particle walls broke by brittle fracture. Evidence that this was due to oil droplets comes from the fact that the SEMs of the three samples that do not contain any oil (maltodextrin, sodium caseinate and the 50:50 mixture – all on the bottom row of images on Fig. 3.), do not show evidence of these droplets. Interestingly, the cavities appear to be uniformly distributed across the thickness of the wall, which suggests that the drying kinetics are fast compared to the transport velocities of the emulsion droplets.

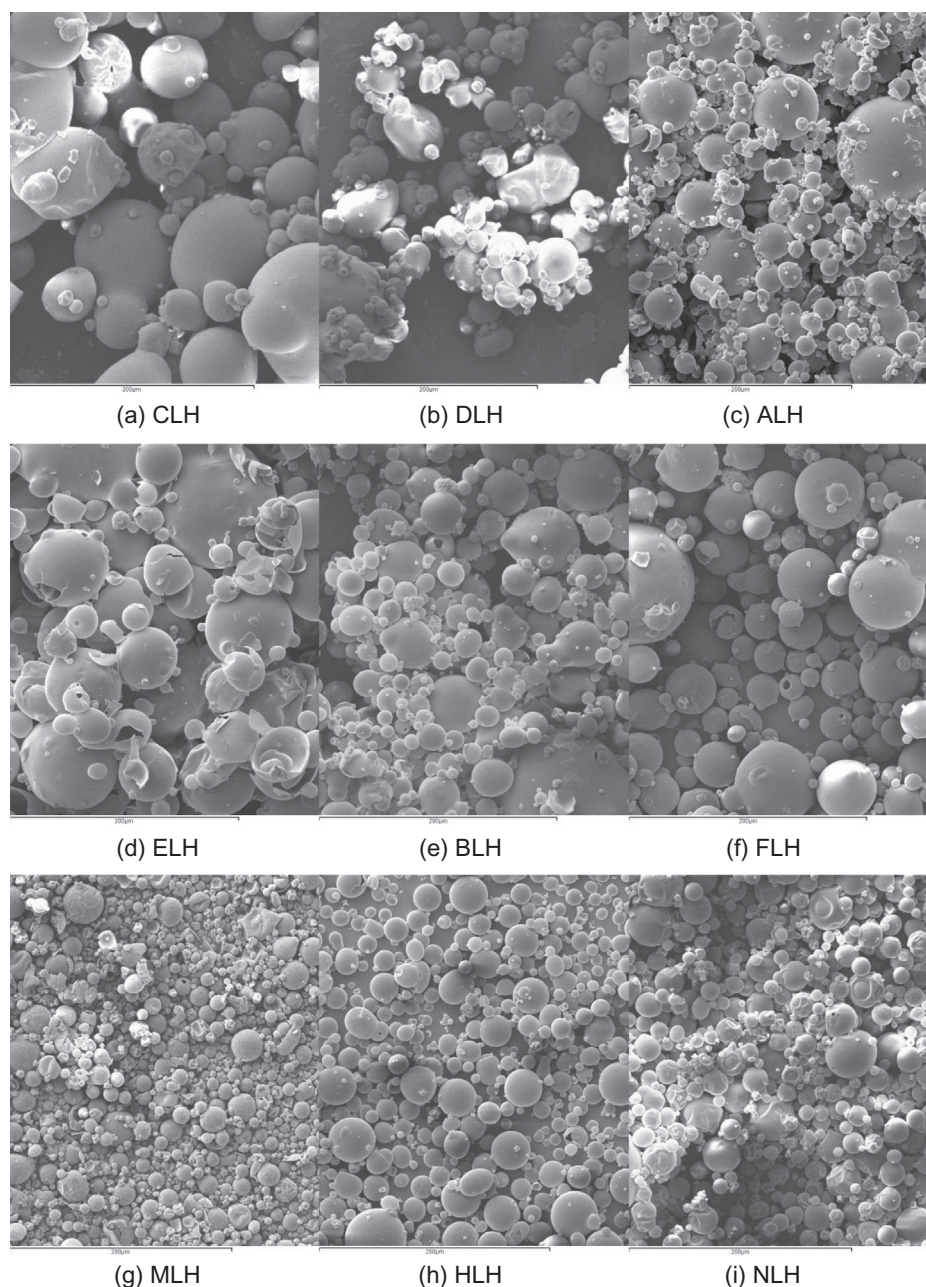
A number of the particles shown contain larger wall cavities (e.g. in Fig. 3c). These are most likely to be from air bubbles originally entrained during homogenisation or atomisation, or a result of foaming during vacuole formation.

Fig. 4 shows the effect of changing emulsion oil drop size and drying temperature on the sample wall structures. It can be seen that the high emulsion droplet sizes (bottom row of Fig. 4) produce

the largest craters (as expected). The inner and outer surfaces adjacent to these edge cross sections show protruding bumps which are most likely emulsion oil droplets that are still covered and have not ruptured. Other surfaces have a more pockmarked appearance which may have been caused by droplet rupture. Understanding how these rupture events occur is important for controlling oil release onto the surface.

The drying temperature does not appear to affect the structure of the wall, because respective images at high and low drying temperatures are indistinguishable. The only exception is the DLH sample (Fig. 4d) which appears to have lost structure and has a surface that could be described as warped and folded, but with residual evidence of pock marks. Sample DLH will be discussed again later.

The pock marks are examined more closely in Figs. 5 and 6. Fig. 5 shows the different formulations at fixed process conditions of low (L) emulsion oil droplet size and high (H) drying



**Fig. 7.** SEM images of spray dried powders at fixed process conditions of LOW emulsion oil droplet size and HIGH drying temperature for: (a) CLH, (b) DLH, (c) ALH, (d) ELH, (e) BLH, (f) FLH, (g) MLH (maltodextrin), (h) HLH, and (i) NLH (sodium caseinate). Scale bars are 200  $\mu$ m in all cases. The compositions of emulsions C, A, E, B, F, M, H and N are shown in Fig. 1.



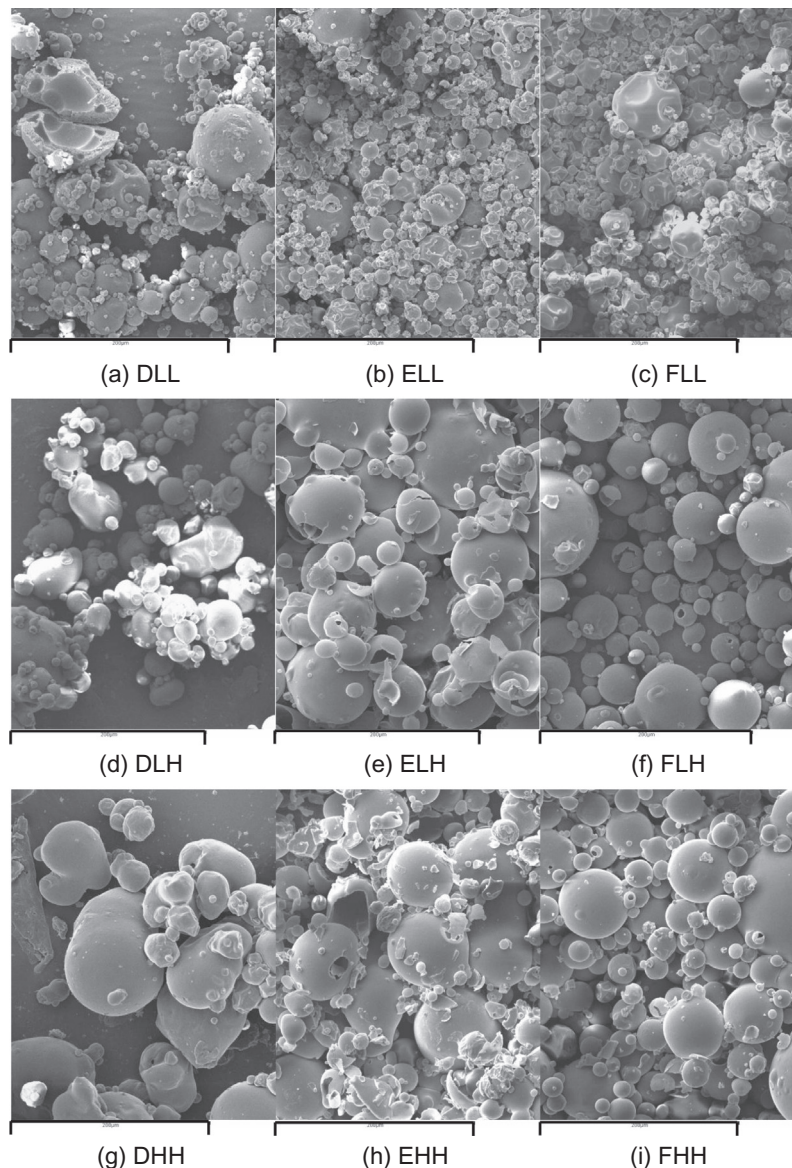
temperature. Fig. 6 shows only formulations D, E and F at the various combinations of process conditions HH, HL, LH for the emulsion oil drop size and the drying temperature. Evidence that the pock marks are due to oil content can be seen from the bottom row of Fig. 5. These samples have zero oil content and also show completely smooth surfaces. As the oil content increases to the maximum value of 33.3% (F → A → D and E → C → D), the size and spatial density of the pock marks decreases, once again indicating that they originate from oil droplets rupturing at the surface. Also, as the sodium caseinate content increases from 8.3% to 12.1% (D → A → F and E → B → F), the surface becomes softer in appearance, indicating that the surface is more plasticised.

As the maltodextrin content decreases from 33.3%, the surface definition changes from well-defined to soft (E → C → D, E → B → F and E → A). The soft appearance of D, A and F obscures much of the structure present during formation of the surface. However, despite its soft appearance, trial DHH had such large pock markings due to the high oil content that the evidence still remains. DLH in contrast appeared soft, warped and folded, which is likely to be due to the combination of small emulsion oil droplets

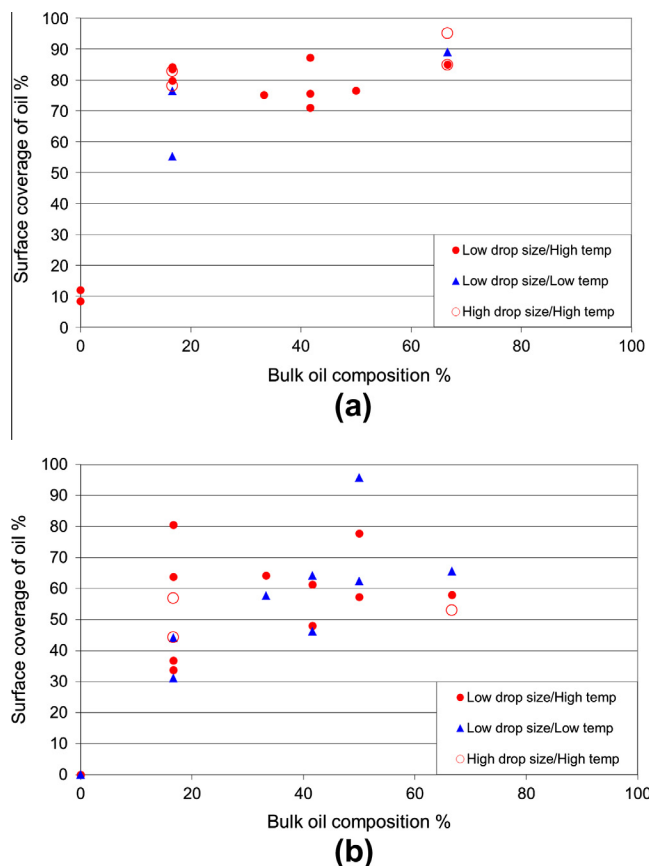
and a low maltodextrin concentration (8.3%), which meant the surface became plasticised and rubbery.

In examining Fig. 6 in the same way, the surface features of the E trials (most maltodextrin) are also the sharpest and most defined, indicating that the maltodextrin assists the rapid formation of a glassy surface. The edges of the pock marks are also well defined indicating that cavity rupture occurs around the same time that the surface glass is forming. This suggests that rupture is caused by brittle fracture of the layer of the continuous phase covering the emulsion droplets. In contrast, the F trials (most sodium caseinate) appear softer indicating that the glass transition of the edges of ruptured cavities does not occur as quickly, and that further flow has occurred to soften the surface appearance. The D trials (mostly oil) are generally rubbery in appearance, indicating that the oil is an effective plasticiser.

Particles that have undergone drying at the higher temperature appear to show a more defined surface than those at the lower temperature. This may be because the lower drying temperature allows longer drying times and thus more time for surfaces to smooth out before they harden.



**Fig. 8.** SEM images of spray dried powders for three emulsion compositions (D, E and F, first character) after processing with high (H) and low emulsion (L) drop sizes (second character) and high (H) and low (L) spray drying temperature (third character). Scale bars are 200  $\mu$ m in all cases. The compositions of emulsions D, E and F are shown in Fig. 1.



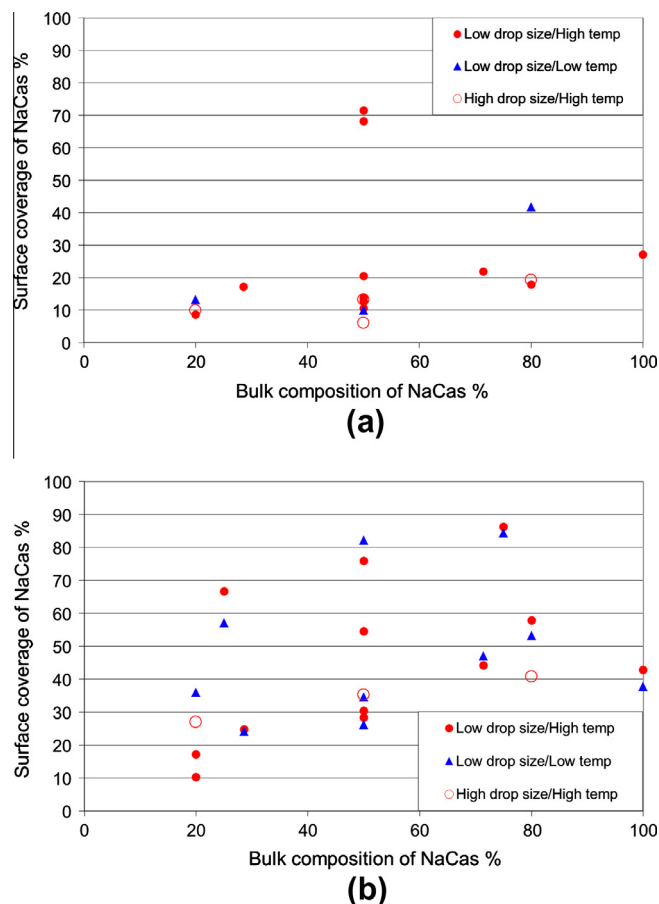
**Fig. 9.** Surface coverage of the oil phase plotted against bulk oil content for (a) 1st trials using food grade sodium caseinate and (b) 2nd trials using higher purity sodium caseinate. The legend refers to the emulsion oil drop size (low or high) and the temperature of spray drying (low or high).

Fig. 7. shows the particles at lower magnification and it can be immediately noticed that the particle sizes of the maltodextrin and sodium caseinate particles are much smaller than for the emulsions. This may reflect a reduced tendency to undergo droplet expansion during drying due to internal boiling (which is very likely to have occurred given the thin walls found on particles shown in Figs. 3 and 4). The two pure samples are the only samples that show signs of dimples, but otherwise the sphericity of the particles tends to increase as the oil content is lowered. Compositions with the lowest protein content (D, C, E) appear to show the most signs of agglomeration or fusing of particles. Sample E also has the most broken particles.

Fig. 8 shows the effect of varying processing conditions on particle morphology. On this occasion there appears to be little effect of emulsion drop size, but particles produced using the low drying temperature were generally smaller and more shrivelled than those produced at the higher temperature (which presumably inflate more due to internal boiling). Therefore, it is likely that mass and heat transfer rate processes affect the development of mechanical strength of the shell matrix so that, when the drying temperature is low, the wall does not acquire the strength to resist collapse as a vapour vacuoles form in the middle of the drying droplet. The phenomenon appears to affect small particles more than large particles.

### 3.3. Electron Spectroscopy for Chemical Analysis

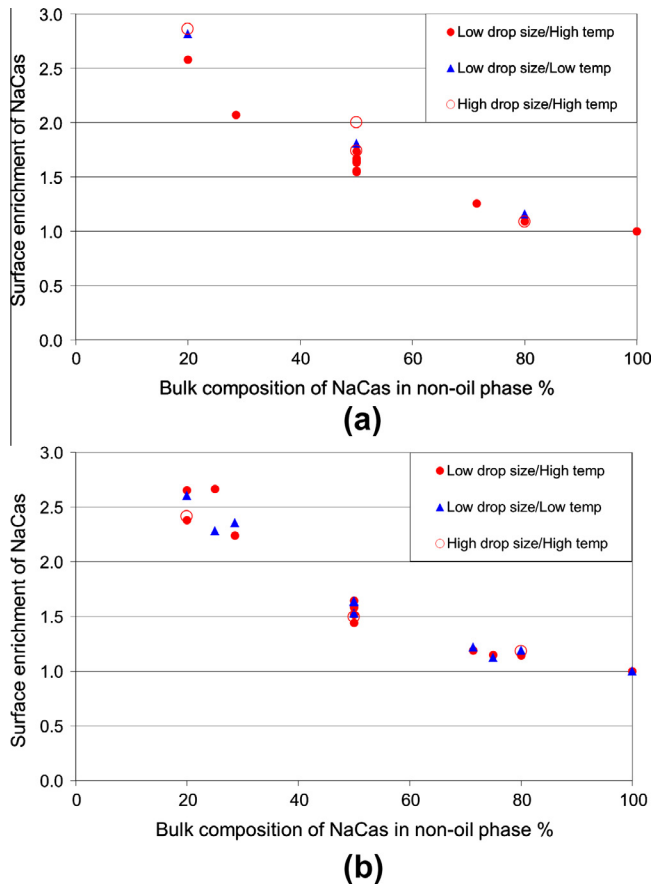
The ESCA data for oil coverage and sodium caseinate coverage are presented in Figs. 9 and 10, respectively. Fig. 9 shows much higher levels of surface fat than bulk fat across virtually all samples. This has been reported in most studies on systems containing



**Fig. 10.** Surface coverage of sodium caseinate plotted against bulk sodium caseinate content for (a) 1st trials using food grade sodium caseinate and (b) 2nd trials using higher purity sodium caseinate. The legend refers to the emulsion oil drop size (low or high) and the temperature of spray drying (low or high).

oil emulsions such as Kim et al. (2002 and 2009b) and Millqvist-Fureby (2003). An exception is the study by Fäldt and Bergenstahl (1996c) on the ternary system of lactose, sodium caseinate and soya oil in which the surface of spray dried particles was almost entirely covered by protein. This was explained by the special action of the lactose which was able to keep the protein “solubilised” (surface active) during drying (see also the review by Jayasundera et al. (2009)). When the lactose was allowed to crystallise by humidifying the sample over 4 days this was accompanied by an increase in fat coverage. The study reported in this paper used a similar system which differed only in the replacement of lactose by maltodextrin. However, it is clear that the maltodextrin does not have a similar “solubilising” effect.

Comparing the two series of trials (Figs. 9a and 9b) it can be seen that higher values of surface fat (particularly at low oil compositions) were present in the first series of trials which used food grade sodium caseinate and the pilot scale dryer, even when nominally no fat was present. This effect is attributed to the small amounts of fat that are present in the food grade sodium caseinate ingredient used in these trials. The manufacturer's specification for the food grade sodium caseinate is (dry basis): sodium caseinate 92.5%, ash 3.9%, fat 0.8% (max 1.4%) and carbohydrate (lactose) 0.1%. However, when an aqueous solution of food grade sodium caseinate (solution N) was spray dried and the powder analysed by ESCA, much lower levels of nitrogen were observed than for the purer grade sodium caseinate (typically C:O:N:Na ratios of 85.3:11.6:3.0:0). (Similar values are observed when the food grade sodium caseinate was tested as received). When these elemental values were subjected to the matrix analysis used for the other

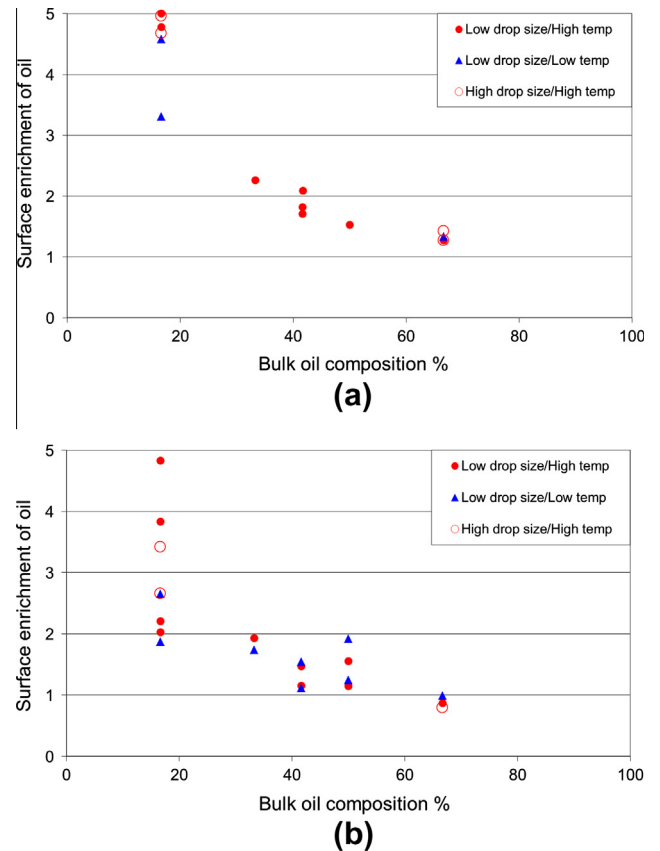


**Fig. 11.** Surface enrichment of sodium caseinate in the non-oil phase compared to the bulk phase, plotted against bulk sodium caseinate content for (a) 1st trials using food grade sodium caseinate and (b) 2nd trials using higher purity sodium caseinate. The legend refers to the emulsion oil drop size (low or high) and the temperature of spray drying (low or high).

samples, a composition of 19.9% protein, 1.2% “maltodextrin” and 78.9% fat emerges. This strongly suggests that a tiny amount of native fat left over from the manufacturing process (or at least a component with a fat-like composition) was able to coat the particle surface extremely effectively. This obviously has implications for the behaviour (such as caking and flowability) of such powders.

The data in Fig. 9 are subject to a fair degree of scatter and there is even more scatter when the data for sodium caseinate are plotted (Fig. 10). To make better sense of the data the results were further processed assuming a two phase system, i.e. an oil phase which is 100% fat, and a non-oil phase which is 0% fat. Given that these particles have formed from emulsions and the fat continues to exist as a separate phase (as evidenced from the SEM images), this seems a reasonable assumption. Within this scheme the surface can thus be characterised by two independent variables: (i) the overall fat coverage (fraction covered by the oil phase), and (ii) the composition of the non-oil phase (which depends on the relative amounts of sodium caseinate and maltodextrin). Within these definitions a surface enrichment factor can be calculated to express how these variables differ between the surface and the overall composition. It should be noted that interpretation of the data using this scheme does not necessarily depend on the existence of two phases, but it is at the very least a useful way to deconvolute the oil and non-oil data.

When plotted this way (Fig. 11) the sodium caseinate data now show much less scatter and the data from the two trials also agree much better with each other. It can be seen that significant surface enrichment of sodium caseinate occurs within the non-oil phase,



**Fig. 12.** Surface enrichment of the oil phase compared to the bulk phase, plotted against bulk oil content for (a) 1st trials using food grade sodium caseinate and (b) 2nd trials using higher purity sodium caseinate. The legend refers to the emulsion oil drop size (low or high) and the temperature of spray drying (low or high).

and the effect becomes stronger as the bulk composition of sodium caseinate decreases. This also agrees with results from lactose/sodium caseinate and sucrose/protein systems where the protein was over-represented at the air–water surface (Adhikari et al., 2009; Millqvist-Fureby, 2003; Shrestha et al., 2007). There appears to be relatively little variation with other variables (such as emulsion drop size, drying temperature, or overall oil content), except that the results from the benchtop dryer track lower than those of the pilot scale dryer. The difference is likely to relate to the effect of droplet size on the rate of drying: while droplet size was not measured in this study, it is likely to be smaller in the benchtop dryer, due to the limited design residence time in this type of dryer.

Fig. 12a shows equivalent data for the overall surface enrichment of oil from the 1st trials. A significant surface enrichment effect is also observed, and again the effect is more pronounced as the bulk composition of oil is lowered. The surface enrichment of oil can also be seen to be much higher at low bulk fat contents. This agrees with results from Kim et al. (2009b) who found much higher enrichment ratios of fat with skimmed milk (where bulk levels of fat are very low) than with full fat milk. There is some variation of data, particularly at low oil compositions suggesting that factors in addition to bulk oil content are important.

The surface enrichment of fat for the 2nd trials was more variable, which may be a consequence of smaller droplets and/or faster drying. Enrichments are also slightly lower than in the 1st trials, which may be due to the difference in atomisation conditions between the dryers, as explained above. However, the two samples that showed the most surface enrichment occurred with composition E which had the highest content of maltodextrin (i.e. lowest content of sodium caseinate). This could be because a lack of the



sodium caseinate emulsifier leads to less free oil on the surface, but it could also be because the higher glass transition temperatures likely with maltodextrin produce a harder shell with less elasticity which, as stress develops during drying, may more easily rupture fat globules. The rate at which stress develops and the viscoelastic character of the matrix will be formulation dependent. A further set of longer experiments were performed on sample ELL and EHH, which also showed that over the course of 100 min in the ESCA the level of surface fat rose substantially by 20% and 30% respectively. Increases were not observed when the same treatment was applied to the FLL sample. It may be that fat is being expelled to the surface under the influence of the vacuum, and the maltodextrin rich system is less able to prevent it for the reasons given above.

#### 4. Conclusions

When considering the SEM and ESCA evidence together, some potential explanations emerge regarding the factors driving the evolution of surface composition in emulsion systems undergoing spray drying. The SEMs clearly show evidence of emulsion droplets within the walls of the spray dried particles and that the system is clearly two phase. The SEM images also display “pock marks” at the surface of some of the samples which appear to be the result of droplets having burst at the surface. (The fat appears to have evaporated during SEM preparation.) Droplet bursting is quite plausible given that the particle surface dries to a hard crust during which it may contract, limiting the volume able to be occupied by the oil droplets. The buildup of stress then leads to rupture and the release of oil to the surface. The results showed a clear dependence of the surface enrichment of both oil and sodium caseinate on the formulation. There is some dependence of oil enrichment on process conditions, which may reflect the influence of process conditions on crust formation, and the pilot scale dryer surface enrichments (Fig. 11a, 12a) are consistently higher than those of the benchtop dryer. The sodium caseinate enrichment is presumably the result of its surface active nature and may occur earlier in the process as the droplet is forming.

Oil enrichment was found to decrease when samples were exposed to vacuum over 100 min in the ESCA equipment, which suggests environmental conditions are important (as was found by Fäldt and Bergenstahl (1996c) when they humidified samples containing lactose). This study also found evidence (albeit not 100% conclusive) of high levels (80%) of surface fat even on particles of food industry grade (92.5%) sodium caseinate containing only 1% fat. This obviously has implications for understanding the handling of such powders.

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