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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 composition 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 study found evidence of high levels (80%) of surface fat even on particles of food industry grade (92.5%) sodium caseinate containing only 1% fat.

Keywords: sodium caseinate, maltodextrin, soya oil, emulsion, X-ray photoelectron spectroscopy

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 reveal that surface compositions are significantly different to the bulk composition of the powder (e.g., Kim et al., 2002 and 2009a,b,c). There is also evidence that spray drying of emulsions causes coalescence of fat globules (Ye et al., 2007) and release of free fat to the surface (Kim et al, ibid).

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) and storage stability (from fat oxidation). 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 crisp ("chip" in the USA) 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 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.

Mechanisms have been proposed recently for milk powders by Kim et al. (2009a, 2009b and 2009c). In these papers, the surface composition 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 the lack of detection due to the small amount applied, 0.1-0.4%, and that it is applied as spray dissolved in anhydrous milk fat. They also found that fat is present at the surfaces of the powders in far greater proportion than present in the bulk, confirming observations of Fäldt and Bergenståhl (1996a). Over long storage times they found no effective change in the surface composition by ESCA (Electron Spectroscopy for Chemcial Analysis) measurement. This is because the lactose remained in amorphous form due to the presence of a dessicant; however, after washing with organic solvents, some release of the low melting triglycerides was detected. Humid conditions were investigated by Fäldt and Bergenståhl (1996b) who observed the release of free fat to the surface.

Kim et al. (2009b) proposed mechanisms for the formation of the surface composition. 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 becomes segregated depending on their molecular weight. The emulsified oil and protein micelles are also carried along in the convective flux of water moving toward the surface. This movement occurs until the continuous phase becomes immobile, probably in the rubbery state, and thereafter the remaining continuous phase shrinks as the water leaves as vapour. Kim et al. do warn that the concentration gradients may not be observed if the drying gradient is greater than the transport velocities of the different species. 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 investigate 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.

MATERIALS AND METHODS

Emulsions were prepared from three ingredients, soya oil (sourced from a local supermarket), sodium 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). Sodium caseinate is known to be a better encapsulant than whey protein (Faldt and Bergenstahl, 1996b) and therefore provides a realistic model food system with which to observe surface composition.

The ingredients were mixed in parts according to Table 1 where 1 part represents 100 grams. The composition map is shown in Figure 1. The ingredients were stored in airtight containers and weighed to within 0.1 g into a 4 or 8 L container, depending on the dilution required. The sodium caseinate content dominates the emulsion viscosity and so water was generally added to each mixture in the ratio of 6 parts water to 1 part of sodium caseinate, except occasionally when maltodextrin levels were high.
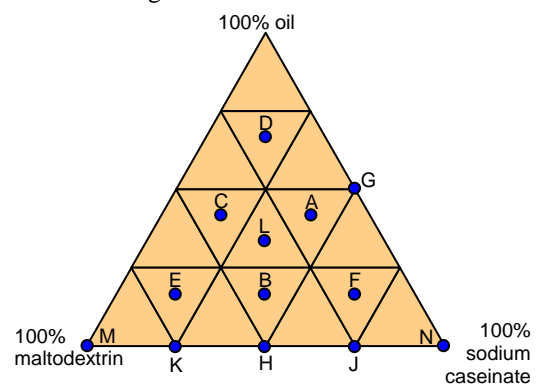

Fig. 1. Diagram showing dry basis compositions of samples tested.

Feed solution	Sodium Caseinate	Maltodextrin	Soya Oil	Water
A	5	2	5	30
B	5	5	2	30
C	2	5	5	12
D	2	2	8	12
E	2	8	2	12
F	8	2	2	54
G	6	-	6	36
H	6	6	-	42
J	9	3	-	54
K	3	9	-	18
L	4	4	4	36
M	-	12	-	12
N	12	-	-	72

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 minute at 3000 rpm, followed by 1 minute at 7000 rpm, then 8 minutes 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 forms at the walls. After blending, the free surface of the resulting emulsion had sheen, indicating it was well homogenised. The temperature of the this mixture could exceed 55°C. 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 minutes. This gently rotated the emulsion with the purpose of separating air bubbles that had become entrained during benchtop homogenisation.

For some experiments a secondary homogenisation was performed. In these cases, the emulsion was passed through an pressure homogeniser (APV Model 15MR-8TBA, APV Gaulin Inc, Wilmington, MA). First, 2.4 litres of the emulsion was poured into the fill vessel and circulated through the homogeniser without pressure for approximately 4 minutes. The fill vessel is not agitated and as the emulsion is relatively viscous, one can approximate plug flow. Then 8000 psig of pressure was applied using the procedures in the operating manual. The emulsion was circulated through the homogeniser for a further 4 minutes. Then the valve downstream of the homogeniser was switched from circulate to discharge and the emulsion was discharged to a clean container. This procedure ensured that the entire emulsion experienced at least two passes through the pressure homogeniser. The remainder of the emulsion mixture was filled 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"

Emulsion characterisation

Before spray drying each solution was viewed under a microscope (Leica ATC 2000, magnification x200) to confirm that emulsification was satisfactorily achieved.

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. This is a tall-form co-current spray drier of 12 ft height x 4 ft 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 as the atomising gas. Ambient air was directly heated in a burner using natural gas, allowing control of the inlet air temperature. The operation was started by feeding distilled water and the inlet and outlet temperatures were set by adjusting the liquid feed and air flow rate. Once the required outlet temperature was reached, the solution was fed into the drying chamber. The outlet temperature was effectively regulated by variation of the liquid feed flow rate. Two spray drying conditions were employed. In LOW mode inlet and outlet air temperatures were 170°C and 80°C respectively, whereas in HIGH mode the inlet and outlet temperatures were 245°C and 100°C respectively (using a lower air flowrate). The particles were separated by a cyclone and collected in a receiving vessel. The final products were sealed immediately in 1 litre open containers which were placed in a drying cabinet for 1 hour. The containers were then sealed and stored at room temperature.

For cost reasons, feed solutions/emulsions prepared using high grade (99%) sodium caseinate, spray drying were dried using a benchtop spray 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 x 420 mm height. The same inlet and outlet temperature modes were used as for the pilot plant experiments.

An overview of the experimental programme is presented in Table 2. "1st trials" refers to experiments performed using the pilot scale spray dryer and using food grade sodium caseinate. "2nd trials" refer to experiments 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.

Table 2. Overview of experimental programme

Experimental conditions	1st trials	2nd trials
Low drop size + high drying temp	All samples	All samples
Low drop size + low drying temp	D, E, F	All samples
High drop size + high drying temp	D, E, F	D, E, F

Scanning Electron Microscopy

All powders were vacuum gold coated, released from vacuum, then and mounted in the SEM (Cambridge Stereoscan 360, UK) at the Department of materials, Loughborough University. Coating and scanning vacuums were both 10^{-4} Torr. The vacuum was applied over a period of approximately 2 minutes in all cases. Three views were sought; a wide view of a collection of particles, a close up view of a single particle surface and a close up cross section of a shell edge.

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 was, agglomeration would still be a concern in ambient air conditions. Instead, qualitative comparisons of size are made from the SEM images.

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 10^{-6} Torr. 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 ~5×5 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).

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 by Fäldt and Bergenståhl (1993), as used by Kim et al. (2009a,b). It is assumed that the calculated surface coverage can be regarded as a mass fraction. The elemental ratios of sodium caseinate, maltodextrin and soya oil were independently determined by separate ESCA experiments on the as received ingredients (sodium caseinate values are based on results for the pure grade sample), and are presented in Table 3.

Table 3. Elemental ratios of ingredients used in compositional analysis as determined by ESCA.
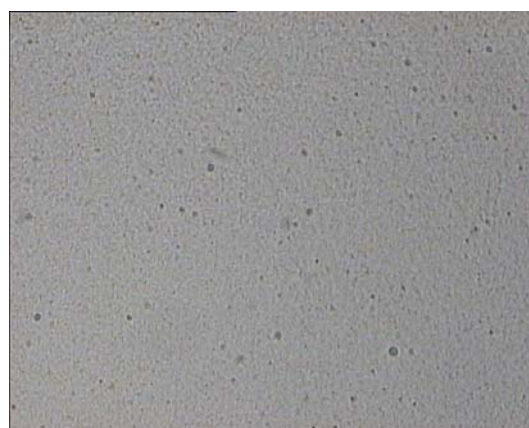
Ingredient	% C	% O	% N	% Na
Sodium caseinate (99%)	66.1	18.1	15.1	0.5
Maltodextrin	57.7	42.3	0	0
Soya oil	90.5	9.5	0	0

RESULTS AND DISCUSSION

Emulsion drop sizes

(a)

(b)

Fig. 2. Light microsopy images of emulsions prior to spray drying. The samples shown are of formulation L with (a) high drop size (after benchtop homogenisation) and (b) low drop size (after further high pressure homogenisation). The width of images corresponds to 0.336 mm.

Fig. 2 clearly shows the presence of emulsion droplets in samples of formulation L before and after high pressure homogenization. Drop sizes are typically 2.5-5 microns for the "large drop size" sample (after homogenization with the benchtop homogenizer), which falls to less than 1 micron for the "low drop size sample" (after further homogenization with the APV high pressure homogenizer).

Scanning Electron Microscopy

SEM images were taken of all samples and by necessity only a very small sample can be shown here.

We first turn our attention to Fig. 3. which shows close up images from (occasional) broken particles. These clearly show the classical spherical shell structure of spray dried particles. The "craters" seen in the cross sections of the broken shells provide confirmation that the oil droplet phase survives spray drying (although the oil is likely to have evaporated by the time the SEM image is taken). Evidence that these "craters" are not simply the result of air bubbles can be drawn from he observation that larger emulsion "craters" are present in the powder formed from the emulsion with the larger drop sizes.

The droplets are much more visible in the cross section of the shell than when viewing the particle surface, and it appears that relatively few of the oil droplets protrude to the surface of the particles (where they cause a "pock-marked" appearance).

Images of spray dried sodium caseinate (N) and maltodextrin (M) are shown in Fig. 4 for comparison with a series of SEM images showing the effect of emulsion drop size and drying temperature on the three compositions D, E and F shown in Fig. 5. These images are all at the same scale 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 greater solution viscosity of the emulsions or a greater tendency to undergo droplet expansion during drying.

Observations from Fig 5 include:

Particles produced using a low drying temperature are generally smaller and more shriveled than those produced at higher temperatures (which presumably inflate more due to internal boiling).

The D powders (containing the most soya oil) produce particles that are less spherical and more agglomerated than the E and F trials, but this effect is less apparent at low temperatures.

The E powders (containing the most maltodextrin) seem to produce the most brittle powders possibly due to the high glass transition temperature of maltodextrin.
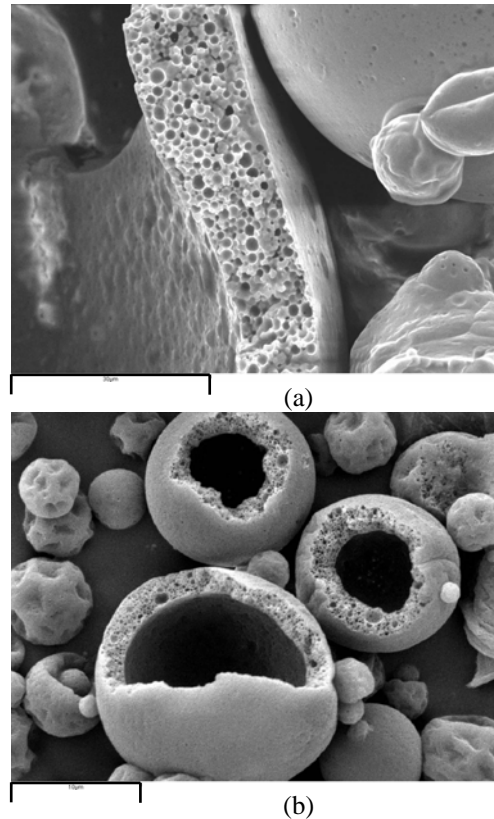

(a)

(b)

Fig. 3. SEM images of spray dried particles of solution D (1st trial) processed using (a) high drop size and high drying temperature, and (b) low drop size and low drying temperature. The scale bars are 30 µm and 10 µm for Figs. 3 a. and b. respectively.
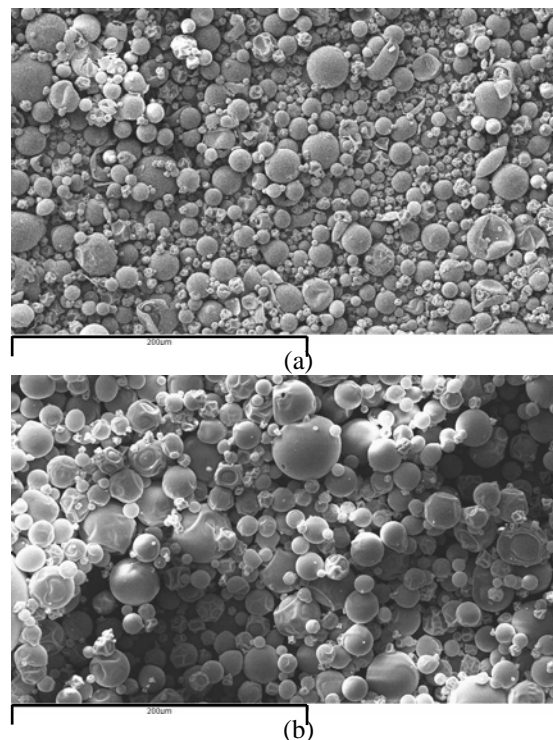

(a)

(b)

Fig. 4. SEM images of spray dried (a) maltodextrin and (b) sodium caseinate (1st trial). Scale bars are 200 µm in both cases.
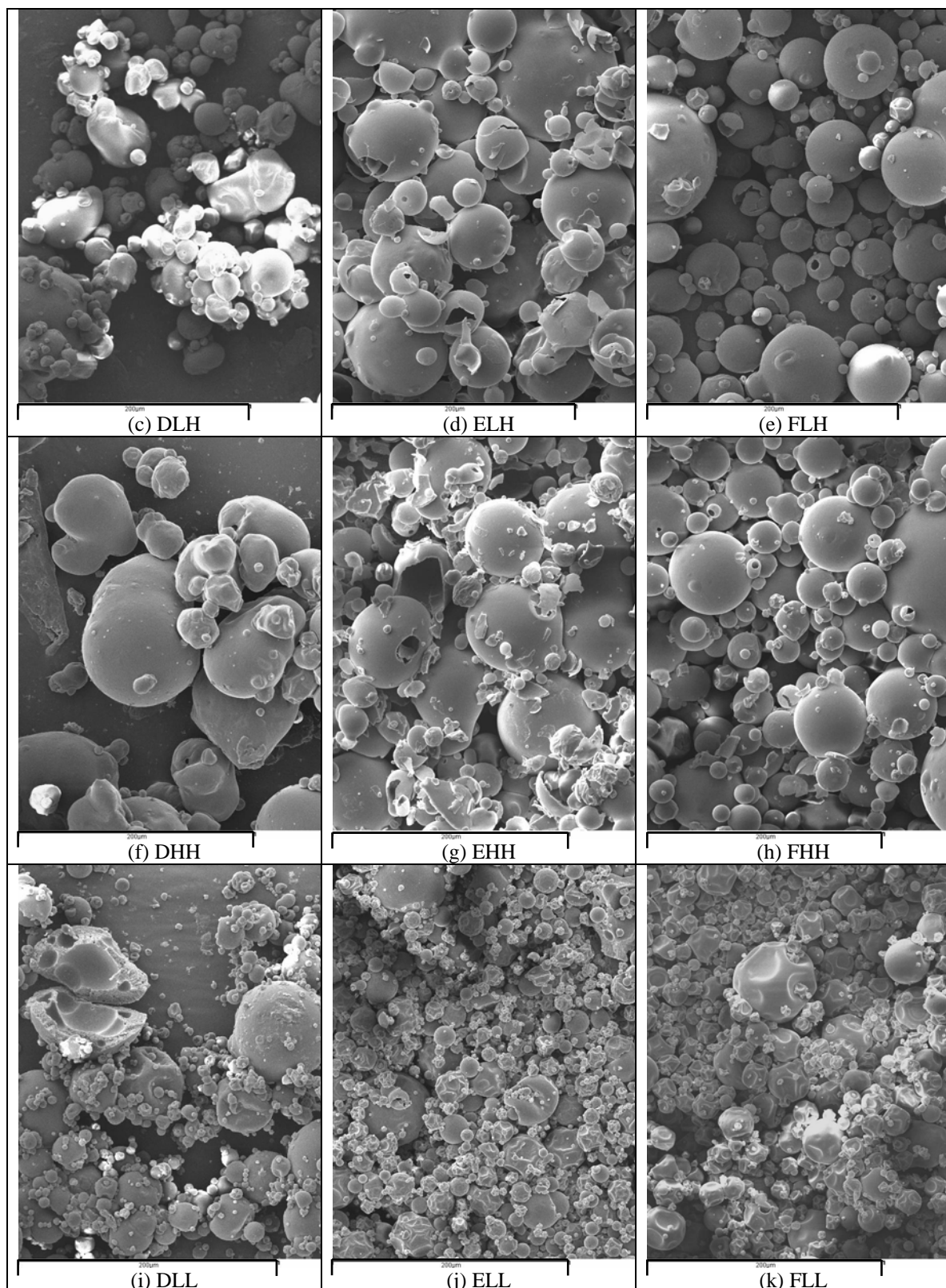
Fig. 5. Scanning Electron Micrograph images of three emulsion compositions (D, E and F, first character) after processing with high (H) and low emulsion (L) drop sizes (second character) and high (H) and low (L) spray drying outlet air temperature (third character). Scale bars are 200 microns in all cases. All samples are from the 1st trial.
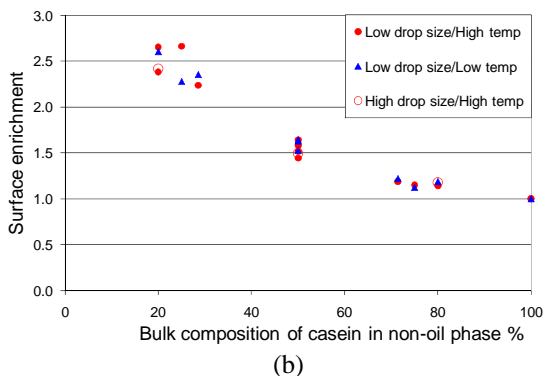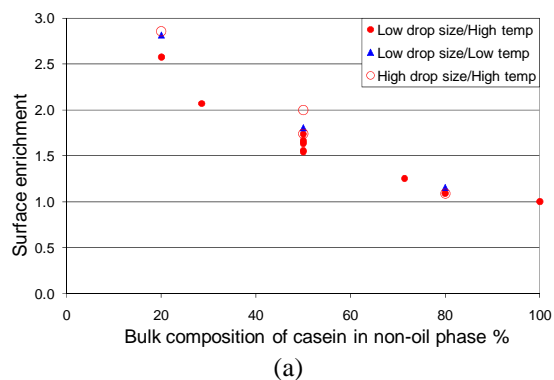
Fig. 6 Surface enrichment of sodium caseinate in the the non-oil phase compared to the bulk phase, plotted against bulk sodium caseinate content for (a) 1st trials using food grade sodium caseinate and (b) 2nd trials using higher purity sodium caseinate.

Fig. 7 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.

Electron Spectroscopy for Chemical Analysis

The ESCA data was processed by assuming a two phase system, i.e. an oil phase which is 100% fat, and a non-oil phase which is 0% fat. 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 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.

Data for the surface enrichment of sodium caseinate in the non-oil phase are presented in Fig. 6. The main observation is that significant enrichment of sodium caseinate occurs within the non-oil phase, and the effect becomes stronger as the bulk composition of sodium caseinate decreases. There appears to be relatively little variation with other variables (such as drop size, drying temperature and overall oil content). It is also apparent that very similar results were observed between the two series of trials.
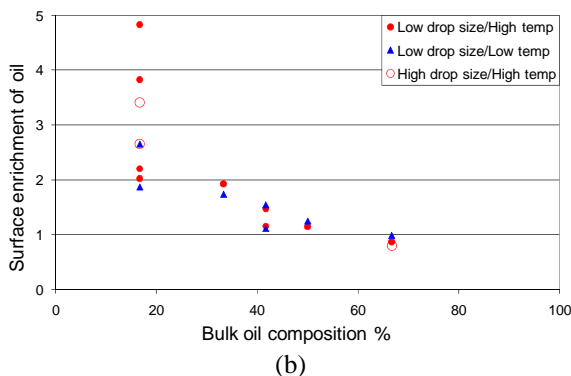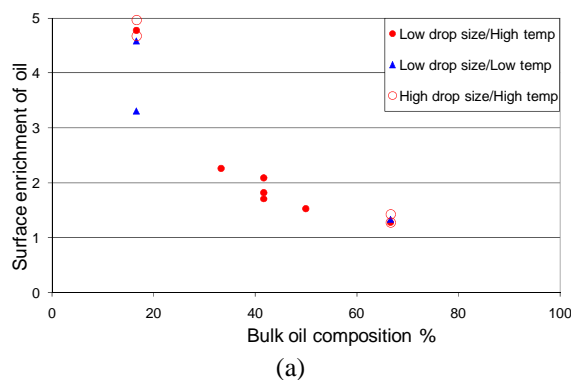
Fig. 7 shows equivalent data for the overall surface enrichment of oil. A significant surface enrichment effect is also observed, and again the effect is more pronounced as the bulk composition of oil is lowered. This agrees with results from Kim et al., (2009b) who found much higher enrichment ratios of fat with skimmed milk (where bulk levels of fat are very low) than with full fat milk. Comparing the two series of trials (Figs. 7a and b) it can be seen that higher values of surface fat (particularly at low oil compositions) are present in the first series of trials which used food grade sodium caseinate and the pilot scale dryer. 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 manufacturers 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) is spray dried and the powder analysed by ESCA, much lower levels of nitrogen are 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 is tested as received). When these elemental values are subjected to the matrix analysis used for the other 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 of a fat-like composition) is able to coat the particle surface extremely effectively. This obviously has implications for the behaviour (such as caking) of such powders.

The surface enrichment of fat for the 2nd trials is variable suggesting that factors in addition to bulk oil content are important.

CONCLUSIONS

The surface composition of food powders created from spray drying solutions and emulsions containing a wide range of different compositions of sodium caseinate, maltodextrin and soya oil have been successfully analysed using Electron Spectroscopy for Chemical Analysis. The results show significant enrichment of oil at the surface of particles compared to the bulk phase (as found in studies of milk based systems), and (when the non-oil components only are considered), a significant surface enrichment of sodium caseinate also. The study 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. However, this contrasts with SEM images of the particles which show a much greater presence of droplets inside of the particle shells than at the particle surface. A possible conclusion is thus that the surface fat may be present in a very thin layer rather than within the usual size emulsion droplets.

The mechanism for surface enrichment is still however unclear. The two main rival mechanisms are:
(i) that species enrich at the surface during droplet disintegration when forming the spray, and
(ii) that species enrich at the surface by not being able to diffuse fast enough away from the surface.

As both the oil droplets and sodium caseinate molecules can be said to have an affinity for the surface, and as they are both also larger than the maltodextrin and water molecules that also make up the system, this study does not fully resolve this question, although the variability of the enrichment of the oil phase with processing parameters suggests this may be a fruitful avenue for future investigation.

ACKNOWLEDGEMENTS

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