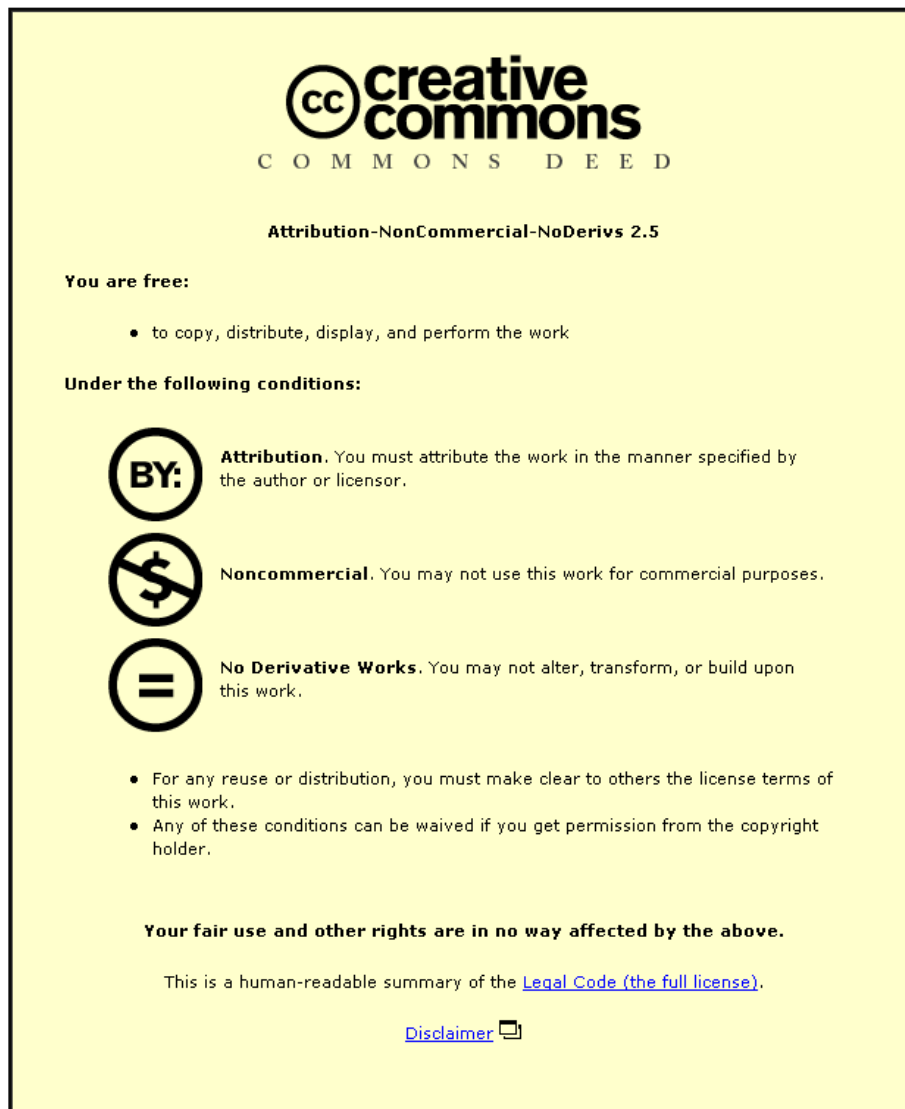


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CAKING BEHAVIOUR OF SPRAY-DRIED POWDERS – USING SCANNING PROBE MICROSCOPY TO STUDY NANOSCALE SURFACE PROPERTIES

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Abstract: Spray drying is widely used to manufacture many powdered products, with the drying process parameters having significant influence over the final powder's surface properties and propensity for unwanted caking. In most cases caking experiments are performed on bulk powders, but especially in multi-component powders, it is often difficult to interpret these results, where interaction effects between particles can be complex. Here we use the technique of scanning probe microscopy to characterise the nanoscale properties of spray dried model milk powders in order to investigate the surface properties of the powders.

Keywords: skimmed milk powder, caking, scanning probe microscopy, atomic force microscopy, surface properties.

INTRODUCTION

Caking in powdered and granulated materials is an area of concern, both in manufacturing processes and in the quality of the final product. Caking problems are often worse for powders as they have large surface area to volume ratios, with the problem exacerbated for finer powders. Spray drying is widely used to manufacture many powdered products, with the drying process parameters (such as feed composition and drying temperature) having significant influence over the dried powder properties and their susceptibility to caking.

Many factors can affect caking behaviour and it is often difficult to interpret the results from bulk caking experiments, where interaction effects between particles can be complex (Leaper, Bradley et al. 2002; Leaper, Berry et al. 2003; Billings and Paterson 2008). It can also be difficult to control moisture content and temperature reliably and uniformly throughout the powder bulk, hence new techniques investigating properties at a particulate level need to be employed.

Previous studies have used scanning electron microscopy (SEM) (Al Mahdi, Nasirpour et al. 2006; Nijdam and Langrish 2006; Vehring 2008) to particle

interaction understanding. However, there are disadvantages with this method. Firstly, SEM requires the surface to be pre-treated, (i.e. coating in gold or carbon) which prevents further experiments on the powder particles and makes it difficult to see how a particle and its properties change under varying environmental conditions. Secondly, SEM is predominantly an imaging technique, with surface analysis only possible if used in conjunction with other analytical methods, such as Energy Dispersive X-ray Spectroscopy (EDS). However, only elemental analysis is possible, hence, information can be limited.

Here we demonstrate the use of atomic force microscopy (AFM) techniques, specifically, nanoindentation, force modulation microscopy (FMM) and phase imaging to characterize the topography, hardness and material properties of single particles in a spray dried powder down to the nanoscale. As the technique is based on measuring physical interactions between the probe and sample, it also allows surface property information to be collected such as changes in viscoelastic properties, which can be related to surface composition changes. Furthermore, samples can be imaged 'as is', without sample coating, enabling them to be rescanned at

intervals following controlled variations in humidity and/or temperature.

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 food grade sodium caseinate (Adams Food Ingredients, Leek, UK).

The ingredients were stored in airtight containers and weighed to within 0.1 g into a 4 or 8 litre container, depending on the dilution required. Ingredients were then mixed in different ratios along with water.

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.

Spray drying

Spray drying was performed using a pilot scale spray dryer. 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 outlet temperature was 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 different feed concentrations of whey protein solution were spray dried with the inlet and outlet temperatures set to 245 °C and 100 °C. 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.

Atomic Force Microscopy

A Park Systems XE-100 AFM was used throughout, with topography and phase images captured using intermittent contact mode.

RESULTS AND DISCUSSION

A typical powder particle topography and phase image for particles prepared from an initial feed emulsion with a composition of maltodextrin, protein and oil in a ratio of 4:1:1 is shown Figure 1. AFM phase imaging is sensitive to viscoelastic changes and hence is sensitive to material composition changes.

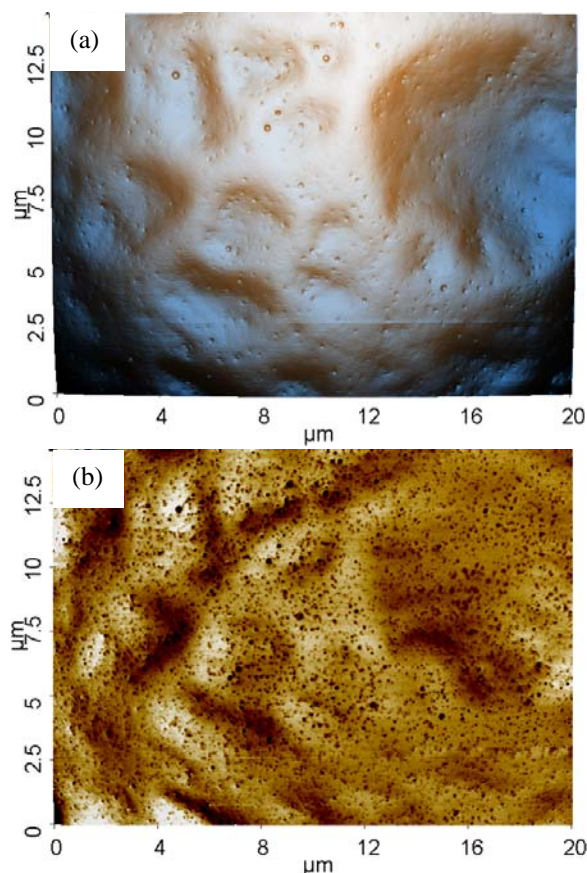


Fig. 1(a). Topography image of a model powder. (b) Corresponding phase image.

From the AFM images it is evident that the surface is characterized by a uniform distribution of small circular features less than 200 nm in size (small dark spots in Figure 1(b)). It is known that for certain ratios of constituents and under certain drying conditions, that the concentration of oil at the surface of the particle is increased compared to the bulk composition. It is possible that the areas evident in the phase image are regions of higher oil concentration. However, phase imaging only gives a quantitative analysis of the surface, showing that these regions have differing material properties, but not how those properties change.

In order to elucidate the surface composition of the particles other AFM based analytical methods were

used. Using nanoindentation, force-distance (F-D) curves were measured in a regular grid across the surface in order to construct a map of the surface hardness. A second technique of force modulation microscopy was also used to map the surface hardness. In this mode an oscillating voltage is applied to the AFM probe in order to measure the surface hardness continuously. This constructs a high resolution plot of the material properties, but is at the expense of not having individual F-D curves to study. However, a combination of the two methods can give much information about the composition of the particles. The surface topography of a particle along with the corresponding FMM map is shown in Figure 2(a) and (b) respectively.

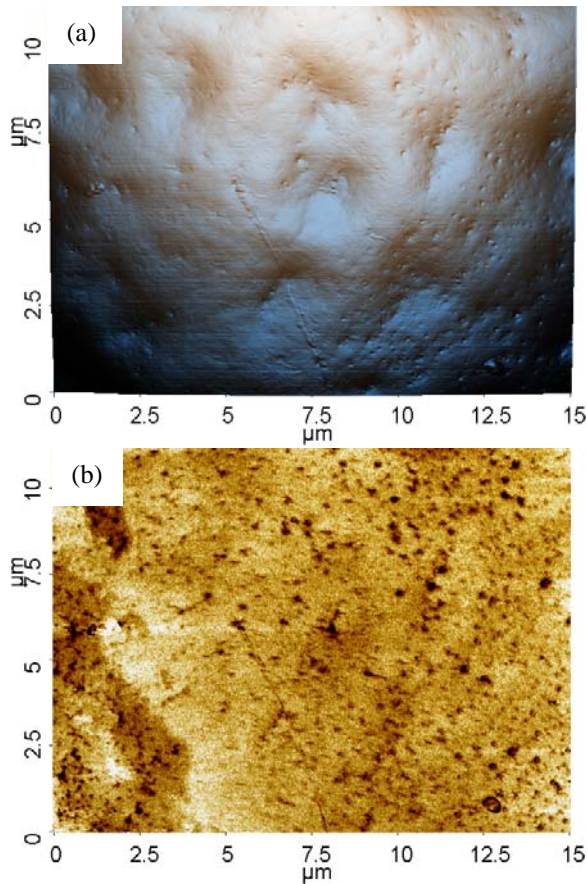


Fig. 2(a). Topography image of a model powder. (b) Corresponding FMM image

In the FMM map of the particle, darker areas correspond to softer regions of the particle. These soft areas showing a high correlation with the circular features that are proposed to be regions with a high concentration of oil.

Further information on the composition of the regions can be gained from analyzing the F-D curves taken across the particle. Figure 3(a) shows the phase image after a grid of 16x16 force-distance curves were taken. The grid of nanoindentations is clearly visible, along with the darker regions showing differing material composition. Figure 3(b) shows the hardness values for each of the F-D curves, which

provides a map of surface properties. It is however, difficult to correlate the softer (brighter) areas to the circular features, due to the lower number of data points. This is an inherent disadvantage to using F-D curves, as a greater number of data points would result in the indentations interfering with each other and producing unreliable data.

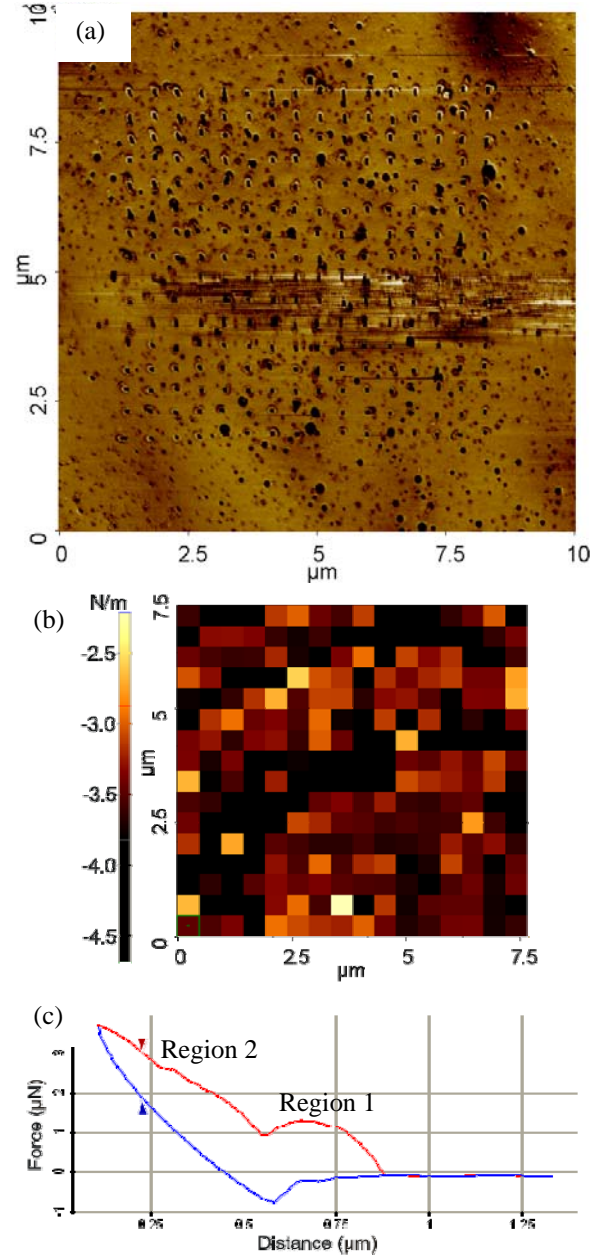


Fig. 3(a). Phase image showing the grid of nanoindentations. (b) Map of surface hardness. (c) Force-distance curve from a softer area of the particle.

However, if one of the F-D curves is chosen, corresponding to a softer area of the sample, it can be seen from Figure 3(c) that there are two distinct regions to the curve. In region 1 there are large non-linearities, with the data suggesting that as the probe is pushed into the particle it first encounters some resistance, which then drops as the probe continues.

Region 2 follows a linear trend, suggesting the material properties at this depth are more uniform. These two regions can be seen as evidence for a softer surface, where the oil concentration is higher, followed by a harder layer underneath the particle surface, with the softer layer extending $\sim 0.5 \mu\text{m}$ in this case.

In many particles studied it was also found that the particles showed a high degree of surface wrinkling. However, when the powders were humidity and temperature cycled between 40% RH, 25 °C and 75% RH, 40 °C the particles swelled. This had the effect of both resulting in smoother particles, which did not return to their original shape, and causing nearby particles to 'flow' into larger ones. This effect can be seen in Figure 4, with spray dried particles of the maltodextrin constituent material.

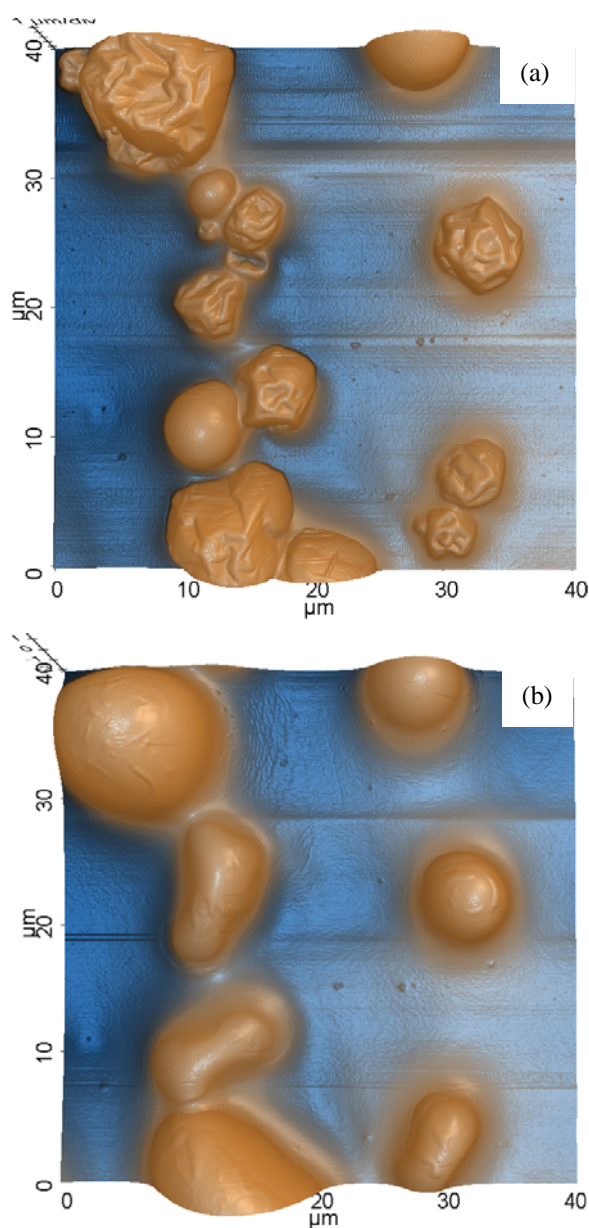


Fig. 4(a). Spray dried maltodextrin uncycled. (b) After cycling to 75% RH, 40 °C, then returning to 40% RH, 25 °C.

CONCLUSIONS

By using a combination of AFM based techniques, including: phase imaging, force modulation microscopy and nanoindentation we have shown that the material properties at the surface of a model milk powder system are not uniform. The surfaces are characterized by many small circular features, less than 200 nm in size, which are softer than the surrounding areas. The larger of these features are also seen in the topography images, however, the smaller features are only visible from phase imaging, meaning other techniques, such as SEM would be unlikely to detect their presence. It is likely that these areas contain a higher concentration of oil compared to their surroundings. It was also found that significant surface changes occur in particles when humidity and temperature are cycled, with significant degradation of particles and plastic flow occurring. When considering caking mechanisms in these multi-component systems the mechanisms can be considerably complicated by the surface properties reported here, with surface oil concentrations, surface wrinkles and topography and particle swelling all playing crucial roles in the caking behavior of the powder.

ACKNOWLEDGEMENTS

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