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Coating particles using liquids and foams based on viscous formulations with industrial mixers: Batch operation

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Abstract

Particle or powder coating with viscous liquids has been essential in industry for surface modification purposes to induce and enhance specific functionalities. This paper evaluates the performance of using foams (of different bubble diameters) versus liquids as a means of coating powder beds based on viscous liquid formulations. Coating with viscous liquids present numerous industrial challenges and therefore preparing foam equivalents can render the liquid component weak enough (through pre shearing to form the foam), to allow it to break up and coat particles under the shear forces exerted in a mixing device.

In this study, two shear mixers are used; the first type consists of paddles in different configurations attached to a single rotating shaft, whilst the second type is a commercial twin screw mixer (**TSM**). The quality of coating achieved on the bulk powder bed using liquids and foams (stained with a dye) is assessed by image analysis to determine the homogeneity of the colour distribution. In addition, Scanning Electron Microscopy provides a tool to further investigate the coating quality of individual particles from the bulk product.

The results show that large bubble foams (centimetre size) are much more effective at distributing within the fluidised powder bed compared to the starting viscous liquid and small bubble foams (sub-millimeter size). Furthermore, there is a maximum ratio of foam to powder beyond which agglomeration occurs and is insufficient to fully coat the particles. Coating of individual particles is achieved in the case of the TSM, whereas SEM proves that the single shaft paddle mixer crushes the particles and subsequently granulates them together to form granules of a size comparable to the size of coated particles seen after coating with the TSM.

Keywords: Powder coating; viscous liquid; foam; image analysis; foam rheology; surface modification

1. Introduction

The ability to coat individual particles existing in powder form is an important unit operation within the pharmaceutical, food, personal care and agrochemical industries. It is a process wherein a thin film of liquid coats or shells individual solid particles to provide properties and value that the base product does not offer. Coatings are added to serve numerous applications including; physical and chemical protection, improving aesthetics, taste masking, controlled and targeted release, improving powder flowability, dust reduction and density modification etc.[1-4] Often a complete coating of the particle is not needed to provide the desired effect however, all such processes require a good even distribution of the coating material.

Numerous techniques can be employed to coat the particulates including; fluidised bed, panning and dipping. The choice of technique used is mostly governed by the characteristics of the powders to be coated and the properties of the coating material. Fluidised bed coating, and in particular the Wurster process[5], utilises an atomised bottom spray to coat and a hot fluidised air flow to fluidise and dry the wetted particles is the most extensively used technique in industry. It offers increased control over residence time distribution and homogeneity of coating compared to other methods,[6] however it is an expensive and slow process.[7] Part of the reason for this is that a high level of solvent (often water) is needed to achieve the low viscosities needed to atomise and spread over the particle surface, sometimes as much as 85% by weight of the solution.[8] This drives up the drying cost required and reduces the product throughput.

An alternative is to use agitator mixers/blenders that comprise of a fixed static shell with mechanical mixing arising only from paddles (other designs utilise plow and ribbon designs) attached on either a single or twin shaft system. The paddles are orientated to impart lateral and/or axial mixing.[9] The mixer can be operated both in batch and continuous modes (with cycle times of 10 seconds to a few minutes). The twin shaft paddle mixer (often referred to as a twin screw mixer (TSM)) is based on a screw conveyor (auger) design which conveys the material from the inlet zone to the outlet. The paddle blades are fitted such that they mimic the auger screw design that not only conveys the material but also eliminates potential dead spaces during the mixing process within the vessel, by overlapping the screw paths. The paddle blades in a counter-rotating TSM, lift the particles up from the bottom of the trough to the middle of the mixer vessel known as the fluidised zone, this is where the mixing process takes place in a weightless state due to the centrifugal force generated by the paddles. This zone allows the particles to move in all directions which cause them to mix as random as possible. The blades operating at high speeds (200 – 3500 rpm)[10] create the force needed to crush any soft lumps that may form in the product.[11, 12]

The fundamental processes involved in coating/mixing particles and in wet granulation (particle size enlargement process) using aqueous liquid formulations are inter-related and are well described by regime maps.[13] Clearly, for coating there is usually a desire to avoid the agglomeration regime. In wet granulation processes, recent studies investigating aqueous foam binders found that the granules and tablets produced, exhibited similar properties to those created with the conventional liquid spray granulation method and could be scaled up reproducibly.[14-16] These studies conclude that using foam binders provide numerous advantages over liquid binders such as improved binder dispersion, wetting throughout the powder, need for less binder, and simpler addition methods as there is no need for nozzles.[17, 18]

The benefits of using foams over aqueous liquids have also been realised in other industrial processes. In textiles, foams are used as they lead to a reduction in the amount of liquid present on the fabric thus reducing the drying time needed. Furthermore foams offer versatility in how they can be added within different unit operations and are not material dependent with regards to coating.[19] In the paper industry, foams are used due to reduced water consumption and energy costs to add insulation, fireproof and pigment coatings onto the surface.[20-22]

The interaction penetration time comparing liquids and foams into a loosely packed powder bed was studied by Tan et al.[23]. The viscosity of the liquid was modified using hydroxylpropyl cellulose (HPC) and hydroxylpropyl methylcellulose (HPMC), to achieve a viscosity range of ~5 – 83 mPa.s. Since the foams were dispensed using a foam dispenser, the amount of foam varied with each stroke. In order to compare the penetration times of both liquid and foam binders, the times were normalised with mass of binder added. It was found that that the penetration time of foams is generally slower than liquid droplets, particularly if the foam drainage rate is slow due to the foam drainage cycle. This is further affected by the foam bubble size, its interstitial viscosity and volume ratio of air vs. total volume of foam.

When a liquid droplet sits on a powder bed it becomes absorbed as a whole into the powder pores. In contrast, in foams (air bubbles connected by a series of interconnected thin films of liquid) the liquid has to drain in a tortuous manner before it reaches the powder surface and penetrates the powder through the pores. This tortuous path is further complicated as the bubbles undergo rupture, growth and rearrangement as the liquid drains. This is likely the rate limiting step in foam penetration time.[23-25]

In 2011, Tan and Hapgood confirmed their initial observations of foam-powder interactions by adding small amounts of foam (using a relatively low viscosity liquid, ~20 mPa.s) on a moving powder bed with a lab scale granulator.[17] When using foams with a low air fraction, wide granule size distributions were obtained due to rapid drainage of the foam. In the case of when foams with high air fraction were used they wetted the powder slowly as the foam remained stable. The wetting was dictated by high intensity mixing to get efficient dispersion of the foam within the powder bed.[17] These tests were performed with small amounts of foam binder and was later tested with larger volumes of the binder.[26] Bubble size and size distribution data for the foams studied were not highlighted, instead they were expressed as foam quality (referred to as the gas volume fraction vs. total foam volume).

To date the majority of studies investigating the interaction between liquids (and their subsequent foams) and powders are based on liquids with relatively low viscosities (below 1 Pa.s).[14, 23, 26, 27] There are numerous studies which investigated liquids with higher viscosities (up to 10 Pa.s.),[28-31] and ultra-high viscosities (~800 Pa.s.),[32, 33] but in all these cases the liquid was distributed onto the powder by simply pouring. The reasons being the following: liquids above 1 Pa.s can be a) difficult to atomise using conventional nozzles as they are resistant to the deformation process[34], b) lead to blockages within the nozzles and c) often difficult to pump.

The present work examines, for the first time the coating of powders within industrial mixers, comparing the coating performance using highly viscous liquids and their subsequent foams. A mechanically agitated powder bed was generated for this work using a) a paddle mixer and b) a commercial TSM.[35] This study looks at factors which impact the mixing/coating efficiency such as liquid viscosity, comparison of foams vs. liquids, influence of foam bubble size produced from these liquids and the Liquid/Powder ratio. The influence of particle type, shaft rotational speed and mixing time were also studied.

2. Materials and Methodology

2.1 Materials

Granular Sodium Sulphate (Grupo Crimedesa, Spain) (median size = 250 µm), Granular Sodium Carbonate (Tata Chemicals Ltd., U.K.) (median size = 280 µm) and Blown Powder (P&G, U.K.) (median size = 150 µm) were used as model particle systems. The particle median size was calculated via sieve analysis.

Granulated sugar (Tate & Lyle) and green food grade dye (Langdale) was purchased from a local supermarket (Leeds, U.K.). Whey protein concentrate (unflavoured Whey protein 80) was purchased from The Protein Works. Distilled water was used in the preparation of all solutions.

2.2. Methodology:

2.2.1. Preparation of sugar-protein solutions:

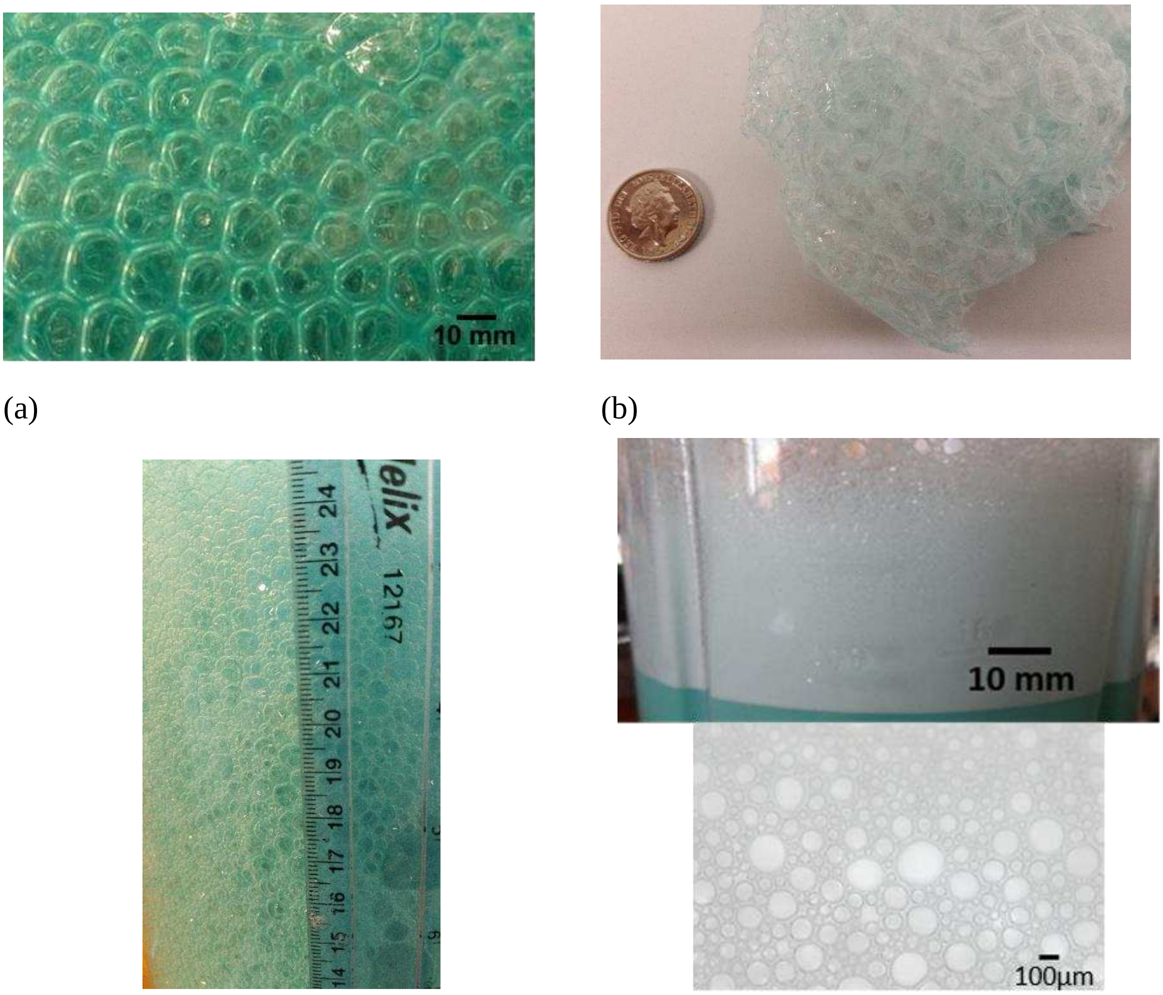
Liquid viscosity was controlled by changing the ratio of added sugar to distilled water. The viscosities of these liquids were measured using a Bohlin Gemini Rheometer (Malvern Instruments, U.K) with a cup and bob geometry. The gap size used was 150 microns at all experiments were conducted at 25°C. To prepare the solutions, typically, 400 g of water was heated in a beaker to 80 °C using a magnetic hot-plate stirrer. Afterwards, the required amount of sugar was added slowly and allowed to mix using a magnetic stirrer until the sugar fully dissolved (full formulation details outlined in Table 1). This sugar solution was left to cool at room temperature before adding it to a 1.5 L Kenwood blender (FDM781BA model). To this 80 g of whey protein powder and 2 mL of food dye was added and blended at maximum blender speed for 20 minutes. The resulting sugar-protein solution was allowed to rest after mixing to remove any entrained air.

Table 1: Details of the formulations used in this study to control the liquid viscosity

Formulation	Sugar (g)	Water (g)	Protein (g)	Dye added (mL)	Density (g/mL)	Viscosity (Pa.s)
1	400	400	80	2	1.21	0.06
2	600	400	80	2	1.26	0.17
3	800	400	80	2	1.31	0.32
4	1000	400	80	2	1.38	4.80

2.2.2. Preparation of foam:

For large bubble sized foams the sugar-protein solutions were placed in a 10 L beaker and were foamed using a 20 micron porous ceramic sparger at an air flowrate of 1 L min^{-1}. This was typically done for around 20 – 60 mins to achieve a beaker full of foam. This foaming process was affected by room temperature and although the quality of the foam did not change at different temperatures, the time needed for foaming was affected. A higher room temperature resulted in faster rate of foam generation. For small bubble sized foam, the Kenwood blender was used to foam the initial sugar-protein solutions. Digital images of the large bubble and small bubble foams are presented in Figure 1 highlighting the large difference in bubble size.



(a) (b)

(c) (d)

Figure 1: Comparison of the size of the two foams. (a)-(c) is the big bubble foam and (d) is the small bubble foam.

2.2.3. Liquid/Foam coating of powders:

In this study two mixers were used; a) single shaft paddle mixer and b) a commercial TSM. The custom made single shaft paddle mixer was fabricated with the internal dimensions of 150 mm (l) × 62 mm (w) × 90 mm (h) (Figure 2a) with four different paddle designs as illustrated in Figure 2b. The paddles were attached to a central shaft (6 mm) and this shaft was rotated using an overhead mixer (Heidolph RZR 2041). The speed range tested was from ~30 to 70 rpm. The TSM supplied by Ajax, U.K. was set up in batch mode such that the screw like paddles conveyed all the material towards the middle of the mixer and then back to the edges (like a fountain flow) to encourage ample back mixing (Figure 3). The speed range of the motor driving the shaft was investigated from 10 to 70 Hz, since there is no reduction gearbox the corresponding rpm's are 600 to 4200 (corresponding to tip speeds of 0.2 to 1.2 m/s). In both mixers the powder fill level was recorded in relation to the total paddle height and then liquid (poured) and foam (scooped) was introduced into the middle section of the mixer. The mixing time was varied from 5 to 120 mins.

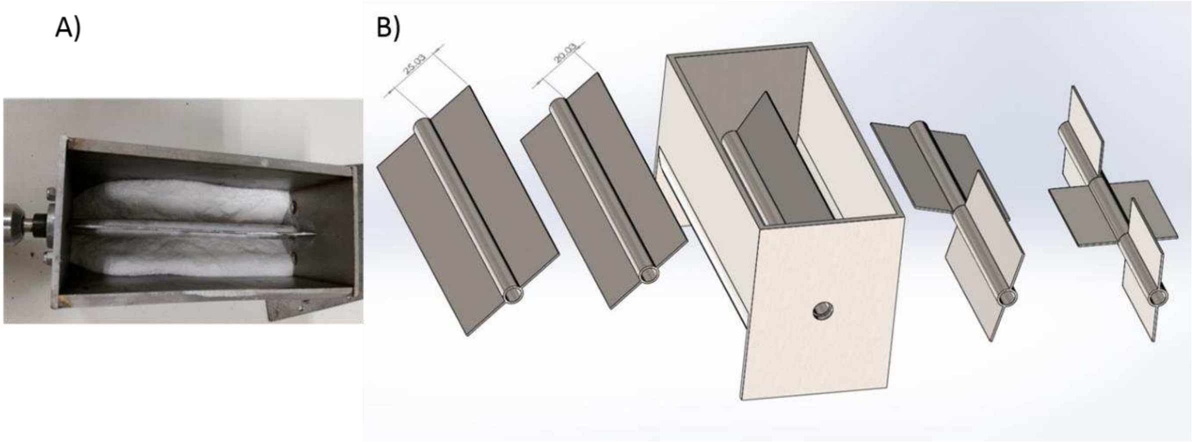


Figure 2: Custom built single shaft paddle illustrating (A) System in operation and (B) schematic of mixer and the four different paddle configurations used in the present study. The

large flat paddle (left) has a radius of 25 mm on top of a 5mm shaft radius and is 5 mm larger in width compared to the other paddles resulting in a low paddle to wall clearance (1mm).

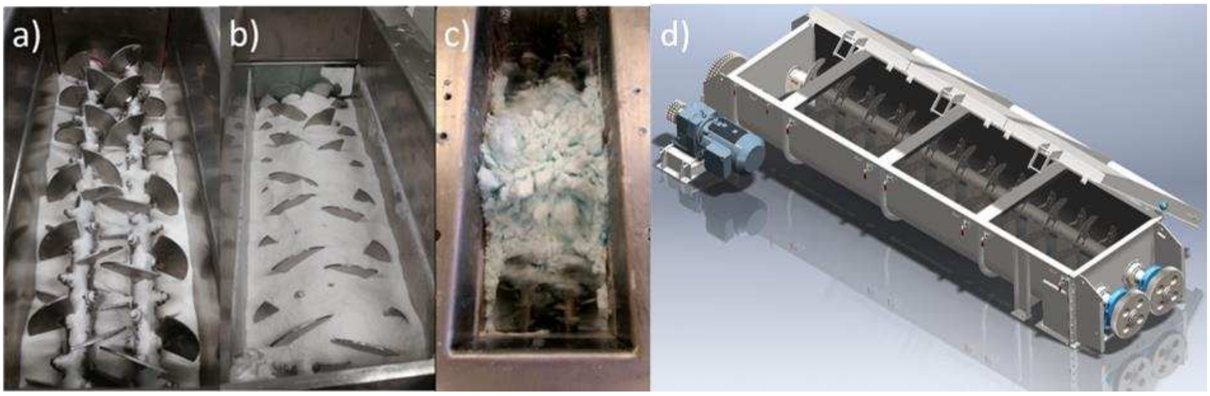
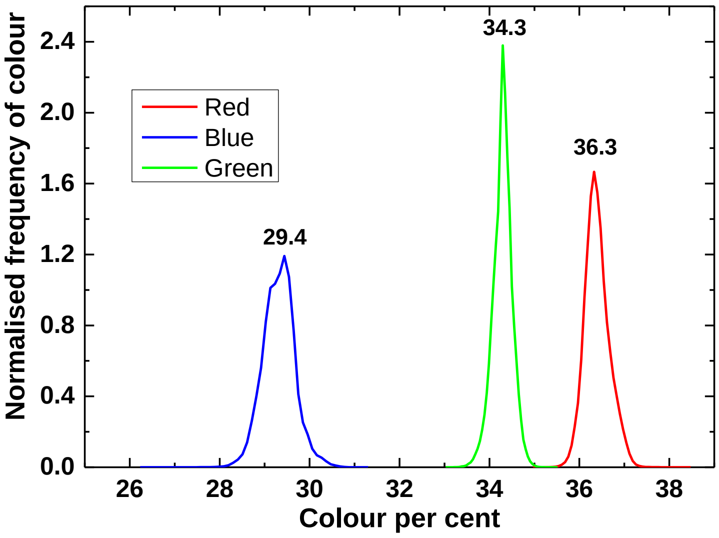


Figure 3: Commercial TSM setup in Batch mode. The image illustrates a) configuration of the paddle orientation in the central zone between the two shafts to allow material to be conveyed in the middle of the mixer and back out again, b) Mixer filled with test powder and c) 'fountain' like mixing of the powder, d) Schematic of the TSM (illustration courtesy of AJAX Equipment Ltd).

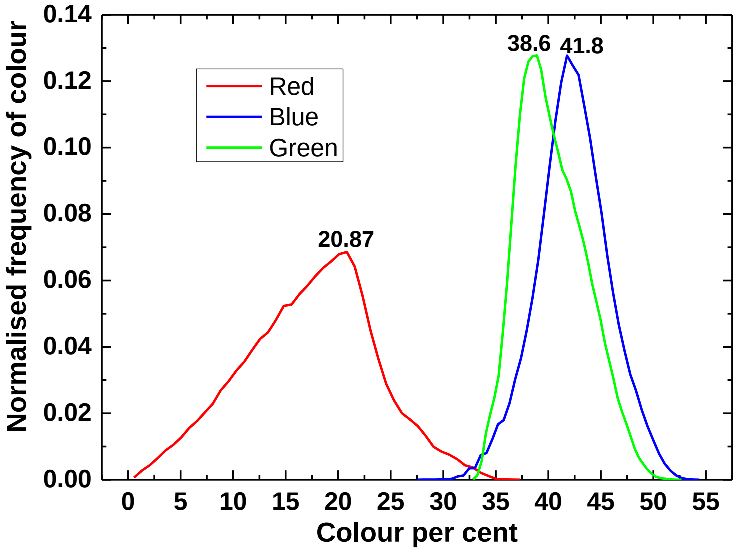
2.2.4. Image analysis methodology

After each subsequent run, samples were taken and spread onto flat trays for colour imaging, using a Nikon D3200 digital SLR camera mounted on a tripod. Imaging of the powders were done in the laboratory under a controlled environment. The colour was represented in the sRGB (standard Red Green Blue) colour space and had a resolution of 300 dpi. Prior to image analysis the images were normalised to avoid shadow issues by using a colour threshold between the values of 4 and 200. The images were analysed using a custom-made software developed within MATLAB®, which plots the histograms of red, green and blue intensities. After a second normalisation, differences in colour distribution were highlighted. For each test condition studied, at least 3 different powder samples were subjected to image analysis and the typical error encountered during processing was within 3 - 5%.

To determine which component of RGB could be used for colour distribution analysis, images of the white sulphate powder as well as the green dye were analysed. RGB data for both materials are illustrated in Figure 4. It is evident from these plots that for this particular particle (Figure 4a) and dye (Figure 4b), the green histogram produced both the sharpest and narrowest peak compared to the red and blue components. For this reason, all further analysis was conducted with the green colour component only.



(a)



(b)

Figure 4 (a) Normalised histograms of red, green and blue light components for the sodium sulphate particles used for this study. Notice green peak as it appears to be much sharper (and taller) than the others. Intensity of red and green has a slight difference (2%). (b) Normalised histograms of red, green and blue light component of the dye used for this study. Notice that green and blue show similar peak heights (3% difference) and similar distribution widths.

2.2.5. SEM/EDX Measurements

Scanning electron microscopy (SEM, Hitachi SU8230 equipped with a 1-30 kV cold field emission gun) was used to investigate the size and shape of the coated and uncoated particles. The microscope was equipped with an Oxford Instruments 80 mm^2 SD detector for energy dispersive X-ray (EDX) spectrometry with Aztec processing software to enable compositional analysis of the particles to determine the quality of the coating (distribution of coating on particle surface). For better spatial resolution the samples were vacuum cleaned for 10 min (Quorom Technologies sputter coater and vacuum cleaner), so that the electrostatic charging during SEM analysis would be minimised.

3. Results and Discussion

3.1 Effect of material parameters

In order to understand the mechanism and performance of coating particles using foams prepared from viscous liquids, there are several material parameters that can be examined. For this study the following parameters were considered; i) effect of using viscous liquids vs. equivalent foams consisting of either large (cm) or small (sub mm) sized bubbles, ii) influence of initial liquid viscosity and c) amount of foam added (i.e. influence of liquid content). The coating performance of these was evaluated by examining the colour distribution within the bulk powder.

Sugar-protein solutions were used as a model liquid system to investigate, as the viscosities of sugar syrups are very sensitive to the sugar content especially at high content values[36]. In these solutions the purpose of the protein was to act as a stabiliser for the generation of foams of different bubble sizes only and thus was kept fixed. It should be highlighted that the protein would also play a role in liquid viscosity, but since it was fixed the effect would apply across all the formulations investigated.

3.1.1 Paddle mixer

To evaluate the influence of material properties within the paddle mixer, the large flat paddle (i.e. low paddle to wall clearance) was used as the default paddle setup. This was to allow the low paddle-wall clearance to force agitation of the whole powder whilst minimising any potential make-up at the walls. In addition the shaft speed was kept constant at 34 rpm and operated for 30 minutes, with a powder fill level that covered half of the paddle (i.e. up to the central shaft).

To compare the effect of viscous liquid vs. small and large bubble foam, formulation 2 was used as the default formulation. The total mass of liquid/foam added was kept constant at 16 g to 200 g powder equating to a liquid to solid ratio of around 8%. The effect of liquid viscosity and amount of foam added were also subsequently investigated. Figure 5 shows resulting histograms of the green distribution on the coated particles, when using; a) a viscous liquid, a small bubble foam and a big bubble foam (both fabricated from the same liquid), b) foams comprised of similar bubble size (in this case cm sized) produced from liquids with increased viscosities and c) the effect of foam mass added (corresponding to an increase in the liquid content inside the mixer).

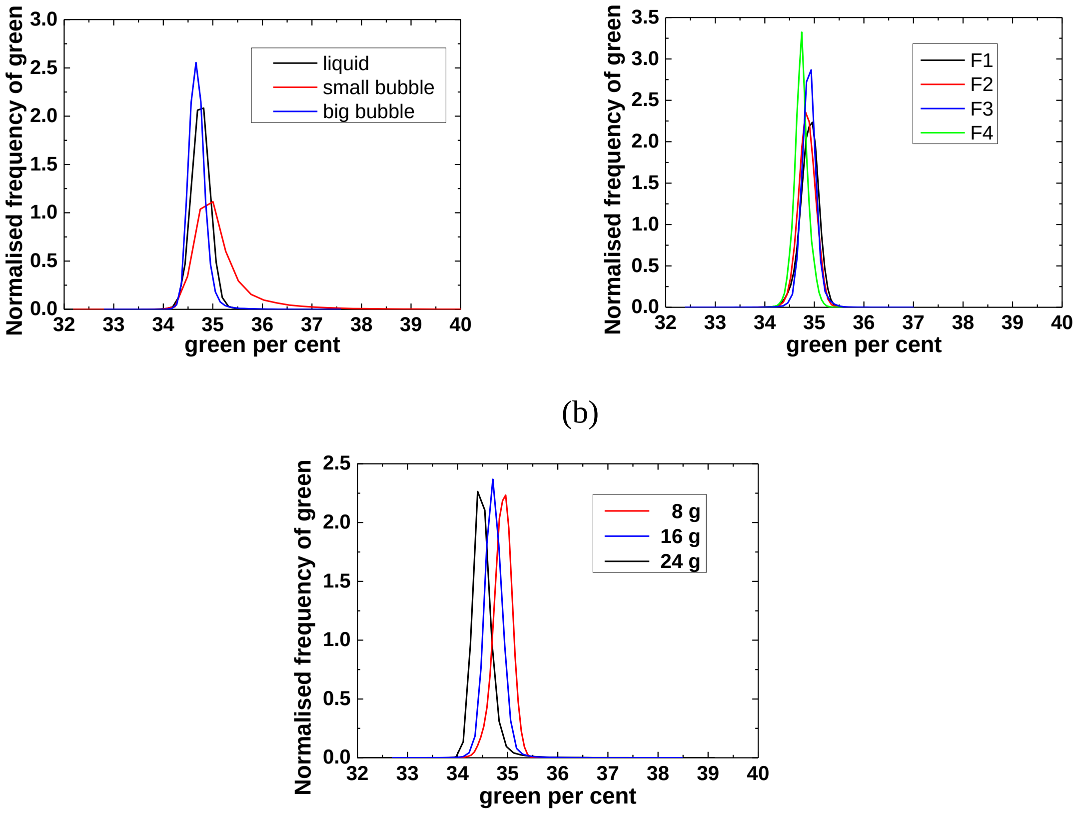
In Figure 5a it can be seen that the quality of the final coated particles (evenness of colour distribution on bulk powder) is increased when a big bubble foam is used in comparison to the viscous liquid. The resultant peak yields a narrower distribution and has a sharper taller peak indicating improved colour distribution. When the viscous liquid is poured onto the moving powder bed it is unable to move laterally initially, instead it penetrates in a vertical direction[17] forming a narrow band in the centre of the mixer. As the mixing time progresses this narrow band begins to grow laterally due to the cascading effect of the wetted particle tumbling on the downward strike of the paddle blade. As a result, over time this continual lateral movement will lead to an improved colour distribution within the whole powder bed.

When using large bubble foams, the foam deforms and elongates laterally across the powder bed. This deformation is most likely due to the low elastic shear modulus that is also seen in detergent foams.[37] Deformation of the foam leads to an in increased contact area between the foam and the interacting powder bed. The agitation of the paddle causes the foam to get roped into the powder and become mechanically dispersed.[38] Furthermore coating distribution within the powder bed will occur via wetted particles contacting and transferring liquid onto non-wetting particles. This has been alluded to by Smith and co-workers as the ‘contact spreading’ mechanism that occurs within a tumbling drum. [39, 40] This mechanism was also confirmed in the paddle mixer by mixing spray dyed spheronised beads with non-dyed beads as shown in Figure S1 in the supplementary information.

Small bubble foam results in poor distribution of the colour within the powder bed. This is likely due to its high shear modulus and therefore behaves more like a solid (in comparison to the viscous liquid). This means it is much more difficult to break down from the shear forces generated by the agitation of the paddles. This corresponds well with the viscosity measurements illustrated in Figure S2 in the supplementary information, where small bubble foam has an increased viscosity and behaves like a non-Newtonian liquid compared to the initial liquid.

To get representative information on the rheological properties of foams with the large bubble sizes is more challenging. The instrumentation needs to have a large geometry in order to get representative rheological information of the bulk foam. In addition, transferring the foams from a beaker after formation into a rheometer geometry is difficult, as the foam structure is affected prior to any rheological measurements being carried out. It was assumed that the apparent viscosity of big bubble foams was lower than the small bubble foam indicated by the ease to deform them.[41, 42] Obtaining information on the rheology of big bubble foams is the subject of current on-going work within the group.

When the liquid viscosity is increased the resulting big bubble foam leads to an improvement in the colour coating distribution of the particle as shown in Figure 5b. Although the rheological properties of these foams are unknown, it is hypothesised that this will also lead to an increase in the viscosity of the liquid films that interconnect the bubbles to create the foam, whilst the overall viscosity of the bulk foam will be lower than that of the initial liquid. As a result, the foam will have an increased residence time within the powder bed as the deformation and elongation process will take longer. Furthermore, increasing the initial liquid viscosity will lead to an increase in thin liquid film viscosity within the foam. This increases the viscous component of the adhesion force acting between the film and the particle leading to increased contact time between the thin films and the powder bed, resulting in improvements in colour distribution.[43-46] The influence of added foam mass on colour coating distribution is presented in Figure 5c. It shows minimum difference (<5%) in both axes so it can be considered that the amount of foam inserted into the paddle mixer does not affect the final coating quality (evenness of coating on bulk powder).



(a) (b)

(c)

Figure 5. Histograms showing the quality of coating using the paddle described in section 2.2.3. (a) Comparison of the use of liquid, small bubble foam and big bubble foam (b) effect of viscosity, where F1, F2, F3, F4 are foams produced from liquids of increasing viscosities (c) effect of the increase of liquid content.

Further increase in the amount of foam (foam to powder mass ratio = 15%) leads to excessive agglomeration (Figure 6a) and over-wetting. This results in dough-type (foam to powder ratio = 20%, Figure 6b) or paste like samples (excess of foam to powder ratio >25%, Figure 6c). This behaviour has limited the ability to investigate any effect on the increase of the liquid content (i.e. foam mass). To be able to research this effect further, an intermediate step of drying between two additions of foam mass, should be introduced. This study is beyond the scope of the specific paper and is not described in this study.

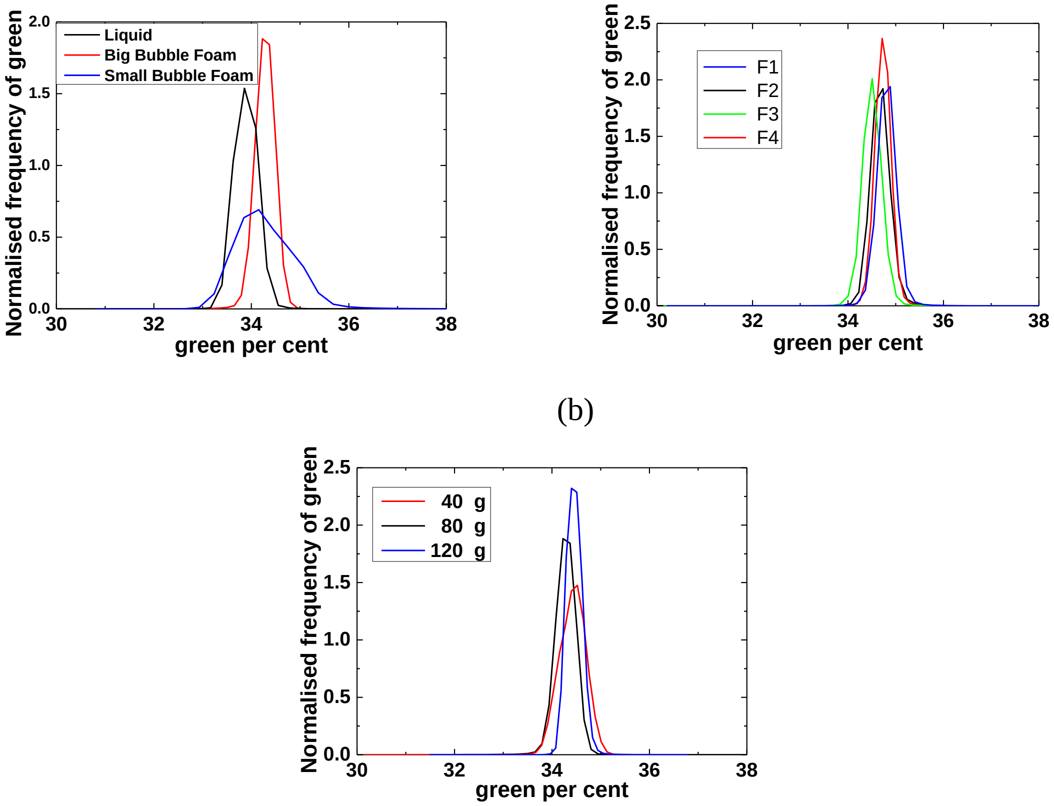
Figure 6. Effect of increased amount of foam added on agitated powder bed; A) formation of large aggregates when foam to solid ratio = 15%, B) formation of dough-like sample at foam to solid ratio = 20% and C) paste formation at foam to solid ratios in excess of 25%.

The influence of particle type was also investigated and it was found that **sodium carbonate** and the **blown powder** easily agglomerated (even at low liquid contents) when using both viscous liquids and foams. As a result, the rest of the study was conducted with sodium sulphate only.

To conclude, the best material parameters for achieving the optimum coating quality when using the paddle mixer are i) use of the large bubble sized foam, ii) use Sodium Sulfate (i.e. materials that do not hydrate easily), and iii) selecting the highest viscosity liquid to produce the subsequent foam.

3.1.2 TSM

The TSM was configured into a batch setup, such that the quadrant paddles conveyed the powder (which was filled up to the shaft) into the centre of the mixer. To compare the performance of the TSM vs. the paddle mixer, the effect of; i) liquid vs. different sized bubble foam based on formulation 2 using identical liquid/foam mass (liquid/foam to powder ratio = 6%) (Figure 7a), ii) initial viscosity of liquid (Figure 7b) and iii) added foam mass (Figure 7c) on the green colour distribution of coated particles were again investigated. The shaft speed was kept constant at 10 Hz.



(a) (b)

(c)

Figure 7. Histograms showing the quality of coating on sodium sulphate particles using the TSM. (a) Comparison of the use of liquid, small bubble foam and big bubble foam (b) effect of viscosity, where F1, F2, F3, F4 are foams produced from liquids of increasing viscosities (c) effect of the increase of liquid content.

When using the TSM, the behaviour in the colour distribution profiles is similar to that observed with the paddle mixer as illustrated in Figure 7 when comparing the use of liquid, small and big bubble foam, and when increasing the viscosity of the initial liquid. In Figure 7a we can clearly see that the quality of the final coated particles is increased when a big bubble foam is used. This again is due to its ability to elongate, deform, and as well as due to the high surface contact area. Furthermore, in the TSM, since the paddle configuration is such that the powder is conveyed into the middle of the mixer, addition of the foam here causes it to ‘bump’ or float on top of the powder bed.[38] The foam bumps along towards the edge of the mixer, where the powder level progressively decreases, and it is there that it gets ‘roped’ within the bed and becomes mechanically dispersed.[38] This leads to a homogeneous colour distribution of the powder bed. Small bubble foam again performs the worst (due to the high shear modulus meaning it is difficult to break up the foam to coat the particles within the powder bed), whilst using the liquid results in a middling coating distribution. In Figure 7b it is evident that increasing the viscosity of initial liquid when using the large bubble foams, leads to improvement in the coating distribution. This is due to an increase in the adhesive force via the viscous component, and subsequently leads to an increased contact time between the particles and the thin liquid films. When increasing the amount of foam added (Figure 7c) (i.e. changing the foam to solid ratio), the quality of the final product (in terms of colour distribution) improves, a fact that is indicated by a narrower distribution and a taller peak. The reason for this improvement is because the mechanical dispersion in the TSM is much more efficient, as the paddles are able to chop the foam into smaller segments within the powder bed. This means that the localised liquid-solid ratio is maintained at a low level, preventing the formation of large aggregates and over-wetting of the powder into a paste. This mechanism allows for the use of increased foam to solid ratio providing more coating material to the coating process.

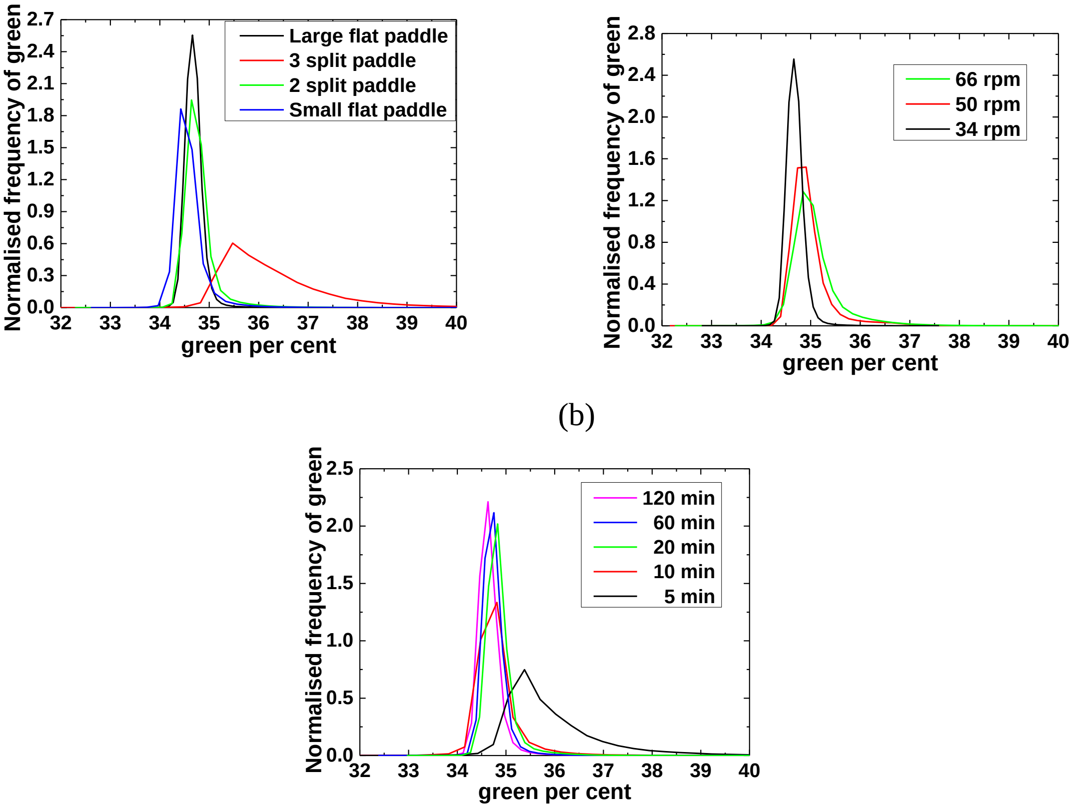
To conclude, the best material parameters for achieving the optimum coating quality when using the TSM mixer are i) use of the large bubble sized foam, ii) increased foam to solid ratio (to allow more coating material to be present) without reaching the agglomeration regime, and iii) selecting the highest viscosity liquid to produce the subsequent foam.

3.2. Effect of process parameters on the coating of particles using foams

In order to determine the feasibility of coating powder beds with big bubble foams prepared from viscous liquids, there is a need to understand the effect of the process parameters of the mixers on the coating distribution. Therefore in this study, the influence of the following factors were considered; i) paddle configuration, ii) mixing time, iii) mixer speed and iv) powder fill-level. Formulation 2 was used as the default starting liquid and the foam to solid ratio was maintained at 7% (although this was altered in the TSM when investigating the powder-fill level).

3.2.1. Paddle mixer

The influence of paddle geometry, mixer speed and mixing time on the powder colour distribution (green component of RGB) using the paddle mixer is presented in Figure 8.



(a)

(b)

(c)

Figure 8. Histograms showing the effect of different process parameters on the quality of coating using the paddle mixer. Influence of; (a) paddle geometry (b) paddle agitation speed and (c) residence time (total mixer operation time). Plots b and c were conducted with the large flat paddle configuration.

Four paddle configurations were designed to develop understanding of how the paddle design affects the mixing and coating operation. The large flat paddle (paddle to wall clearance ~0.5 mm) ensured that the entire powder was picked up and moved with every paddle stroke. This however sometimes caused particles to get caught in the clearance between the end of the paddle and the wall (largest particle size = 300 µm), and jam the mixer. The small flat paddle had a large clearance (~5.5 mm) that was designed to reduce potential jamming issues, and subsequently was made more complex by adding 2 and 3 splits along the paddle length (see Figure 2b).

The plot in figure 8a shows the histograms after the analysis of the final product comparing the performance of the four paddles operating at a default mixer speed of 34 rpm (slowest speed feasible with the Heidolph drive) for 30 minutes. It is shown that the best coating distribution is achieved with the large flat paddle, indicated by the sharpest and tallest distribution.

The small flat paddle and the 2-split paddle perform comparatively showing very similar profiles with the minor difference attributed to experimental error. The lower peak values as well as a broader distribution width indicate that an increased wall clearance acts as a hindrance in achieving homogeneous coating. The histogram for the 3 split paddle shows a very wide and poor distribution attributed to bad coating distribution in the final product. The paddle is constructed such that along the length there are 3 paddles that are 90° to each other. As the paddles rotate, this sudden change in paddle orientation allows the particles to simply drop through in between the gap. This means that the foam and the powder bed does not mix efficiently and leads to an environment of over-wetting, resulting in the formation of large aggregates and in extreme cases, the formation of a dough or paste.

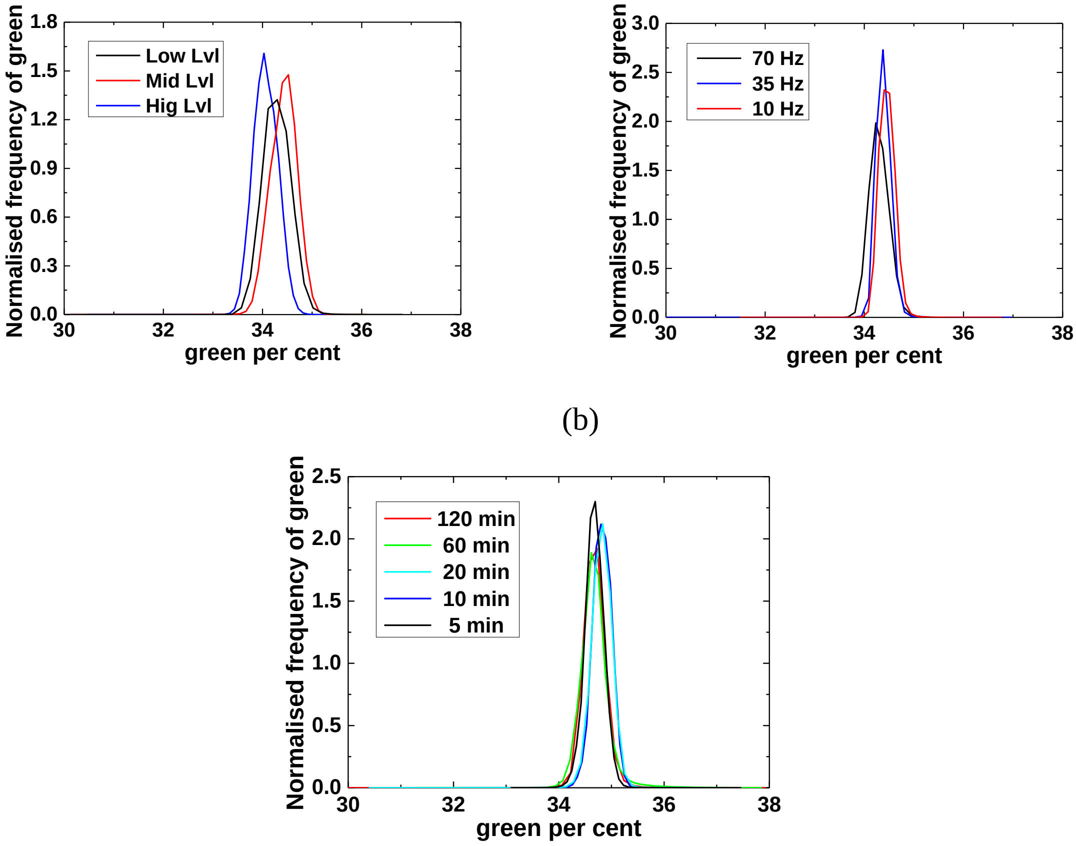
Since the large flat paddle results in the most homogeneous and even colour distribution, it is used as the default paddle throughout the rest of the processing parameters study. The mixer speed regulates the shear forces that the paddle imposes on the powder bed. Investigating the effect of speed (Figure 8b) shows that the best quality of coating (in terms of colour distribution) is achieved when the paddle mixer operates at lowest speed. It is postulated that this can be attributed with the time that the foam spends deforming and breaking up within the powder bed. A lower mixer speed allows the foam to stretch and deform over a much larger area (especially laterally) before getting roped into the bed which causes subsequent breakage into thin films. This increases the contact time with the particles leading to improved mechanical dispersion and thus providing a homogeneous coating. When the mixer speed is increased the shear induced on the foam also increases, limiting the lateral movement of the foam. Instead it is deformed radially giving rise to a high local liquid to powder ratio and prevents contact spreading. This results in a poor coating distribution.

For the residence time, and how it effects the quality of coating, histograms of the final coated particles from 5 to 120 mins are illustrated in Figure 8c. In the plot it is illustrated that for mixing times of 20 minutes and above, the quality of coating achieved remains consistent, i.e. appears to be optimised. The histograms show minimum difference in the peak height and distribution width (sharpness) indicating that 20 mins is the shortest time needed to achieve the best coating and thus colour distribution. Below this mixing time, there simply is not enough time for the foam to undergo breakage, and become mechanically dispersed, so the resultant samples exhibit poor coating distribution.

To conclude, the optimised conditions for achieving the best coating quality when using the paddle mixer are i) use of the large flat paddle, ii) mixing for a period of at least 20 mins, and iii) selecting the lowest shaft speed of 34 rpm.

3.2.2 TSM

In the TSM the paddle type could not be changed and thus the study was conducted with quadrant blades. It was deemed that the properties of the mixer that would cause the greatest impact on the coating distribution was different powder fill levels, shaft speed and the total mixing time.


(a) (b)

(c)

Figure 9. Histograms showing the effect of different process parameters on the quality of coating using the TSM; (a) influence of powder fill level (b) TSM shaft rotational speed and (c) residence time (total time of operation).

Powder fill level will dictate how the foam interacts with the agitated powder. Three fill levels were chosen; i) covering 50% of the paddle height based on the paddles below the shaft equating to ~1000 mL, ii) up to the shaft (1500 mL) and iii) covering 50% of the paddle height based on paddles above the shaft (2000 mL). Figure 9a shows the histograms after the analysis of the final product when the three different powder fill levels are used. The plot indicates that the sharpest and tallest distribution is observed using the highest fill-level, followed by mid and low levels consequently. Since the powder is conveyed into the centre of the mixer, increasing the fill level will result in more of the paddles being covered by the powder bed. When the foam is added on top of the powder bed in the centre of the mixer, it 'bumps' on the surface of the bed longer covering a larger lateral distance when the initial fill level is high. This results in a high contact time between the foam and powder bed before it finally gets 'chopped up' and 'roped' into the powder at the edge of the mixer where the fill level drastically decreases. This provides indication that the TSM operates better at high fill levels (shaft and above). Following this outcome the TSM was operated at the highest fill levels as the default set-up when investigating the effect of mixer shaft speed and residence time.

Regarding the effect of speed, Figure 9b shows that the best quality of coating (in terms of distribution) is achieved when the TSM operates at middle and low speeds. At these mixer speeds the foam has the ability to deform much slower and occupy a higher contact area axially over the powder bed. At the highest speed studied, this is no longer the case, as the increased speed rapidly chops up the foam limiting lateral (axial) movement, such that the bulk resides in the centre of the mixer. This equates to less homogeneity in the coating distribution, and as a result the peak height is much lower.

For the residence time, histograms of the final coated particles for a mixing time of 5 to 120 mins is presented in Figure 9c. In this plot the behaviour of the TSM is different than the one previously encountered with the paddle mixer. The quality of mixing in the TSM is already optimised in the first 5 minutes, with just minor changes in the histograms up until 20 minutes. As the mixing time increases further, the histograms start to exhibit a falling peak height up to 17% when comparing to the peak height observed at 5 mins. Since a good coating distribution is already achieved at 5 mins, we hypothesize that an increased mixing time causes increasing hydration of the particles, as the dye absorbs further into the pore network of the particles, reducing overall colour intensity. Furthermore, the friction between the powder bed and the paddles will give rise to the overall temperature, leading to some drying effects. This again will cause a reduction in the intensity of the colour coating observed.

To conclude, the optimised conditions for achieving the best coating quality when using the TSM in batch operation with the large bubble foams are i) high powder fill-level, for ii) a mixing period of 5 min, with iii) a shaft speed of 35 Hz.

3.3. SEM/EDX Analysis

Image colour analysis is a powerful tool when trying to characterise the quality of coating on a bulk powder bed, however it does not distinguish the quality of coating on individual particles. Therefore samples were characterised using SEM in backscatter mode to determine how the coating on individual particles differed when using the paddle mixer and TSM. The presence of coating on the particles was further confirmed using EDX.

Characteristic micrographs of coated particles produced using the paddle mixer with a large flat paddle are presented in Figure 10. These particles were coated with the large bubble foam made from an initial viscous liquid based on formulation 2. The images show a clear contrast between the coated and non-coated regions of the particle surface. The indication of non-coated and coated regions are further confirmed by the EDX spectroscopy data presented in Figure 11. Elemental analysis clearly defines and distinguishes the presence and locations of the carbon-based coating on the particle surface, in comparison to the base composition of the particle i.e. sodium, sulphur and oxygen.

The micrographs in Figure 10, also show that is not necessary for a full shell of coating on every individual particle to produce an apparent colour change in the bulk powder with a homogeneous coating distribution. Another key finding from the SEM analysis is that in the paddle mixer the resultant finished product are aggregates made up of particles of different sizes glued together by the coating in the size range of around 250μm. Since this size is comparable to the original sieved sodium sulphate powder used in this study, it indicates that the low clearance of the large paddle is breaking the initial particles into different smaller sizes, and subsequently binds them together.

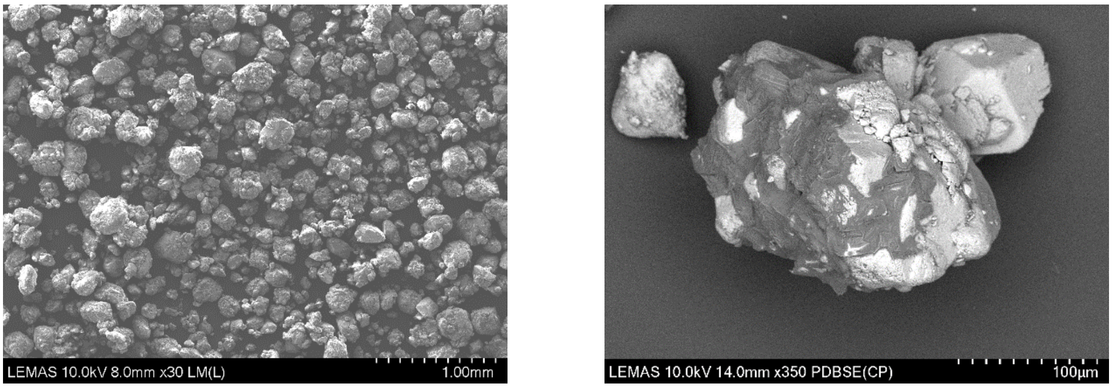


Figure 10. Scanning electron micrographs of particles coated using large bubble foams in the paddle mixer using the large flat paddle. Dark areas on the particle surface indicate coating sites.

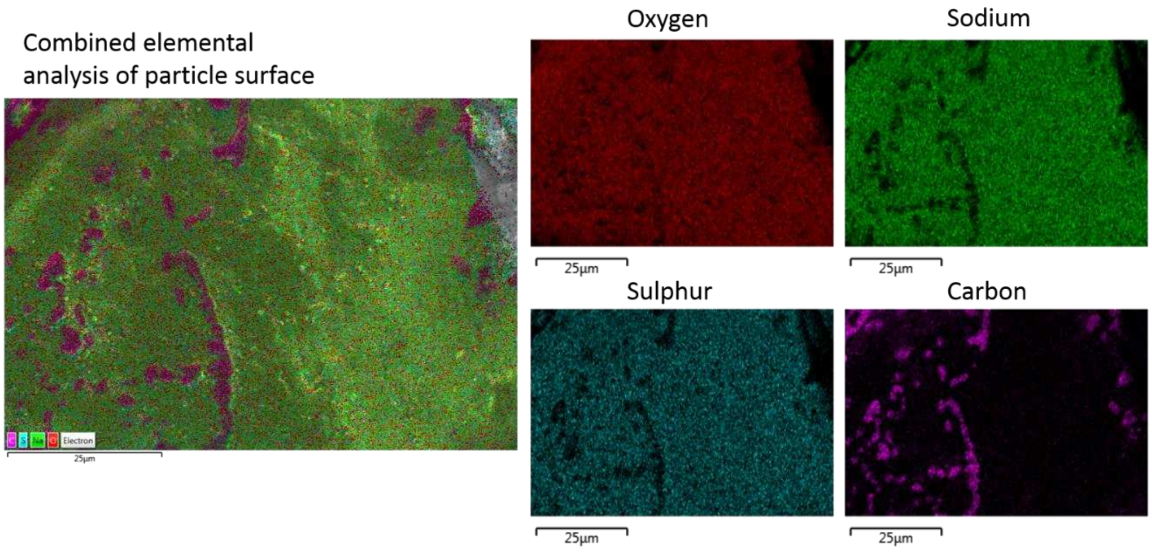
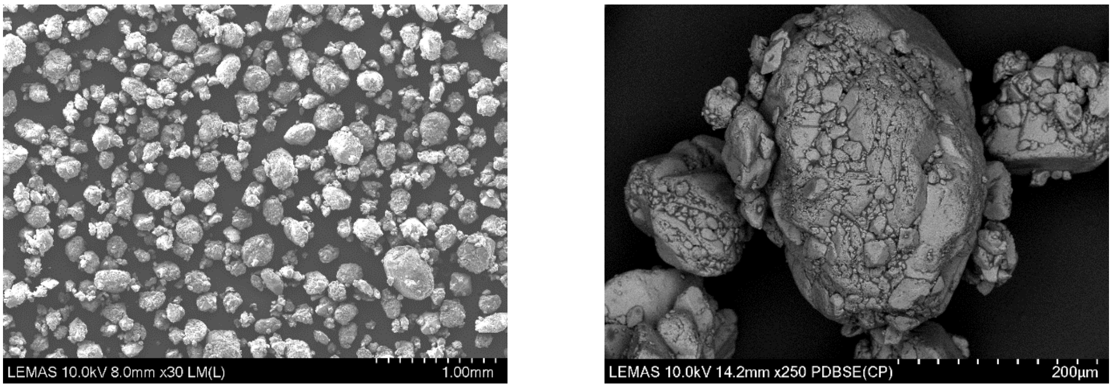
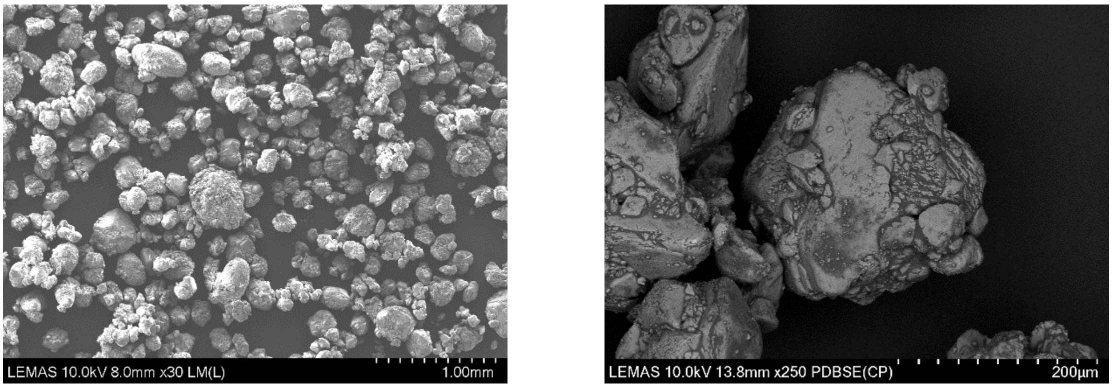


Figure 11. Energy dispersive X-ray spectroscopy of a particle partially coated within the paddle mixer. The elemental analysis shows clear difference in the coated and non-coated regions determined by analysis of the carbon content across the particle surface.

For the TSM, the SEM micrographs of particles that have been coated with the large bubble foam made from an initial viscous liquid based on formulation 2, are presented in Figure 12. The snapshots are taken of particles at different mixing times, and all of them indicate a partial coating on the particle surface. It is evident that the bulk of the coating resides in the cracks and surface defects of the particle. This observation points towards a capillary force phenomenon, as a possible mechanism, which anchors the coating much more at these rough surfaces, rather than at the smoother ones. The presence of coating within these particle surface cracks, is again confirmed by EDX spectra presented in Figure 13.



TSM 10min time



TSM 120 min

Figure 12. Scanning electron micrographs of particles coated using large bubble foams in the TSM mixer. Dark areas on the particle surface indicate coating sites with clear concentration of the coating material in the particle surface cracks.

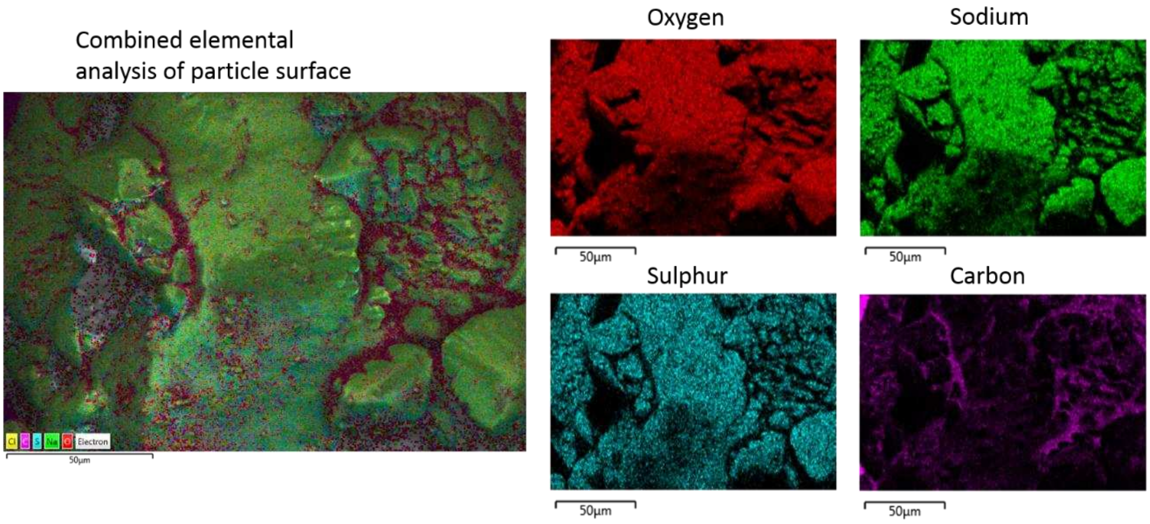


Figure 13. Energy dispersive X-ray spectroscopy of a particle partially coated within the TSM. The elemental analysis shows clear difference in the coated and non-coated regions determined by analysis of the carbon content across the particle surface.

When samples coated using large bubble foams based on formulation 4 (highest viscosity tested in this study) within the TSM were investigated, the resultant SEM and EDX analysis showed interesting features (Figure 14). Although the sodium sulphate powder had been sieved, the end product still contained a large amount of small particles. Due to their irregular shape it is postulated that some of these fines were retained. The SEM micrographs show a large percentage of these smaller particles to have a full shell of coating around them. This indicates that the adhesion force between the viscous thin films of the foam and particle is such that they undergo a large contact time with each other, allowing the smaller particles to become fully enveloped by the thin film. This may also indicate why powders coated with large bubble foams based on the highest liquid viscosity gave the best colour distribution i.e. coating distribution.

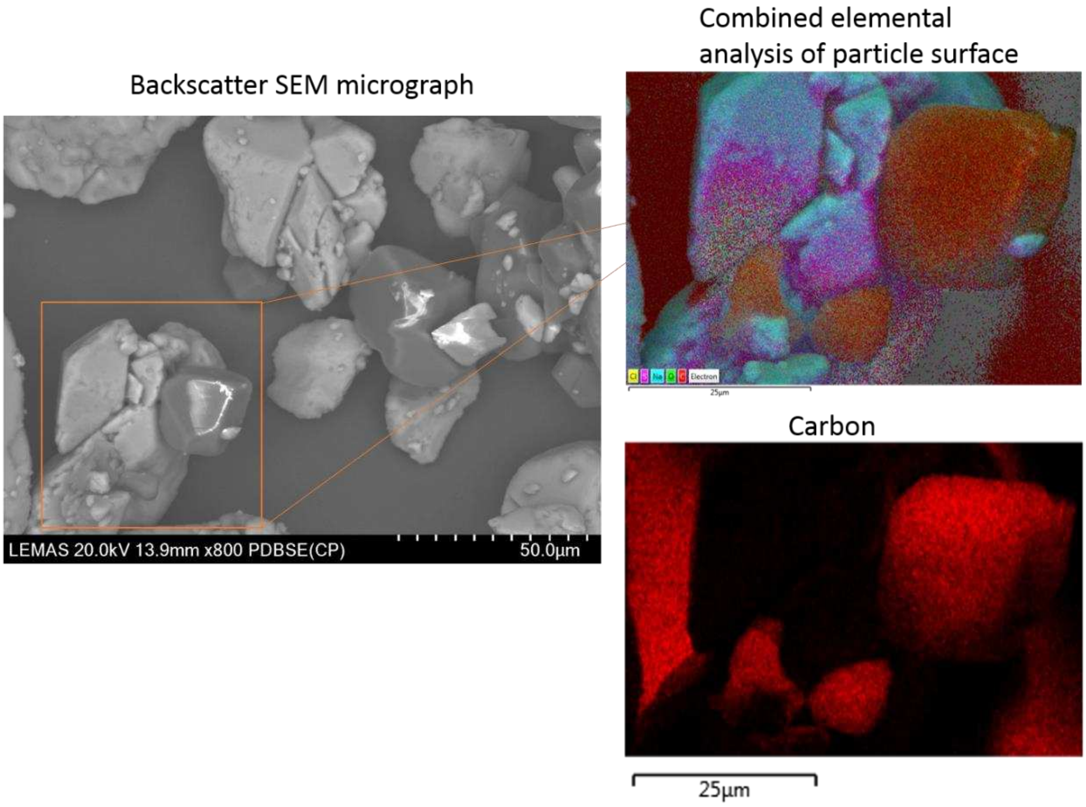


Figure 14. Energy dispersive X-ray spectroscopy of particles coated with foams made from the highest viscosity liquid studied using the TSM. The elemental analysis shows clearly that some particles are fully coated as determined by analysis of the carbon content across the particle surface.

4. Conclusions

This work proposes the use of foams with mm size bubbles for the coating of particles when high viscous liquids need to be used. To the best of the authors’ knowledge this is the first systematic study that investigates distributing of viscous liquids and their subsequent foams within fluidised powder beds as a means of coating particles. The proof of concept for this method is provided, and coating of particles in a high shear industrial mixer is performed and validated. The samples are analysed with the use of image analysis, and the coating quality is considered to be proportional to good colour distribution of the coating formulation. For validating the quality of the particle coating further, SEM analysis was performed on several different samples. There, the difference between the final outcomes of the use of the two different mixers was evident. Partial and full coating of the particles was achieved in the case of the TSM, whilst granulation was the mechanism of creating the final coloured particles for the case of the paddle mixer.

Milimeter bubble sized foams lead to improved coating performance when compared to the initial high viscosity liquids and micron sized foams (equivalent to those of a shaving foam). Surprisingly, the increase in initial liquid viscosity improves the coating performance of the millimetre sized foams, while as expected the increase in the foam mass and thus liquid content, increased the coating quality.

For the best results regarding coating, one should use the TSM, fill it up above the height of the shaft when operating at the specific configuration. Lower speed will favour better distribution of foam and 5 minutes is enough time for it to mix.

Additional drying steps in between the introduction of foam in the system might help to improve the coating of particles when using foams of high viscous liquids analogous to the Wurster fluidised bed coater. For further improvement of the proposed process, there should be an effort on understanding the mechanism of coating when foams are used especially relating the rheological behaviour (based on bubble size) to coating performance. This way, this process of coating powder beds could be used for a continuous operation in an industrial unit, where coating with viscous liquids is essential.

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Supplementary Information

Coating particles using liquids and foams based on viscous formulations with industrial mixers: Batch operation

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S1. Contact mechanism

The dyed beads were placed centrally in the mixer amongst the non-dyed beads and snapshots of the colour distribution was taken with respective to time. It was found that excess surface liquid on the dyed beads transferred onto the non-dyed beads such that the whole bed became homogenous in colour as the mixing progressed. This is illustrated in Figure S1 of the supplementary information.

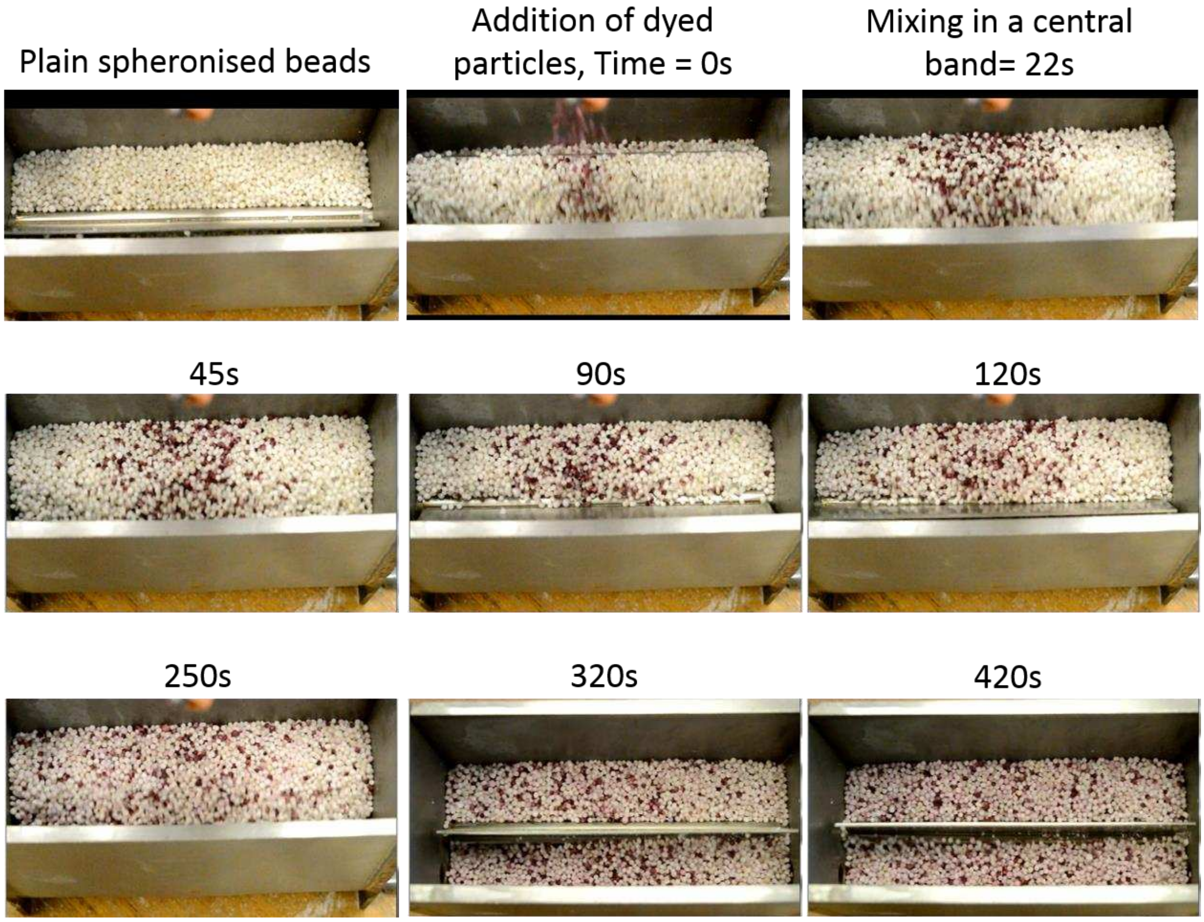

Figure S1. Illustrating the transfer of liquid from dyed beads placed centrally in the mixer onto plain beads and the distribution of colour laterally throughout the mixer with time. Suggests that this occurs via ‘contact mechanism’ as the dyed beads were dried so liquid transfer occurs from any excess dye bound to the surface of the beads after the drying process.

S2. Viscosity measurements

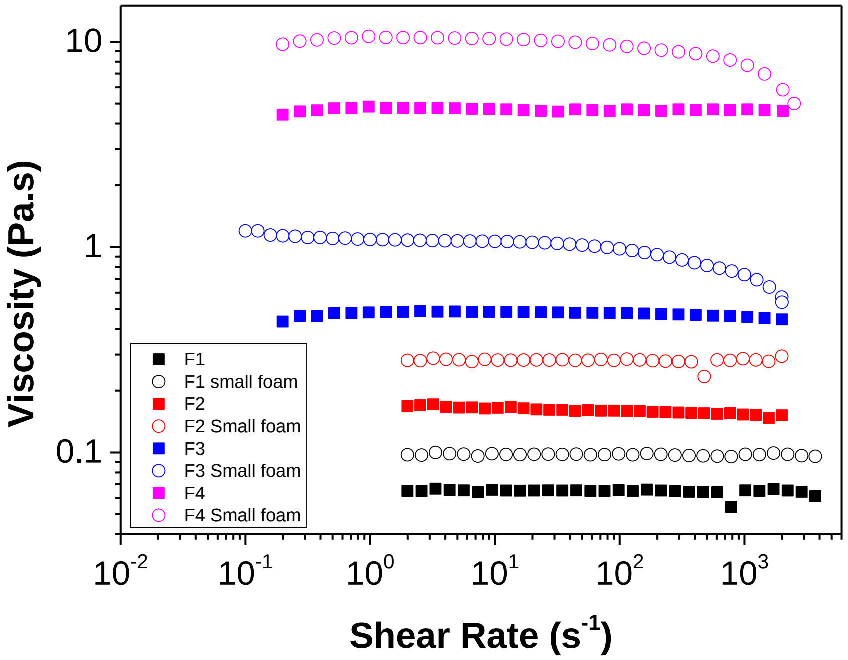

Figure S2. Effect of shear rate on apparent viscosity of small bubble foam compared to initial sugar-protein liquids (formulations 1-4). (Closed symbols represent liquid and open symbols represent the fine foam).

The data indicates that the viscosity of the liquid formulations at near zero-shear increases with increasing sugar content (F1 to F4) and all exhibit Newtonian behaviour (closed symbols). The apparent viscosity of small bubble sized foams (open symbols) prepared from these liquids using a food blender is significantly higher than the liquid. Furthermore small bubble foams of F3 and F4 exhibit shear-thinning behaviour due to the stick-slip motion of the bubbles as they rearrange and undergo structural changes with increasing shear. At around a shear rate of 2000 s^{-1} the viscosity matches that of the initial liquid as the shear causes complete breakdown of the foam structure. For small bubble foams of F1 and F2, a Newtonian behaviour is observed. This may be due to a) relatively lower gas volume fraction in the foams formed meaning a reduction in the stiffness of the foams i.e. do not shear thin or that b) much higher shear rates are needed to obtain significant changes in the foam structure to show non-Newtonian behaviour.