



# The structural modification and rehydration behaviours of milk protein isolate powders: The effect of granule growth in the high shear granulation process



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## ABSTRACT

The effects of granule growth in high shear granulation on the structures and rehydration abilities of milk protein powders were investigated. In this study, milk protein isolate, as a model powder, was agglomerated in a high shear granulator. The formed granules with different sizes were used to compare the densities, granule shapes and subsequently the wettability, dispersibility and solubility. It is found that the small nuclei showed the most compacted structures. Then the primary agglomerates coalesced to create irregular secondary structures with lower density and higher porosity until the final agglomerates formed. The densely packed structures allowed the granules to be more easily wetted by water. The large granules showed quicker release of materials into water until reaching a critical size, where more mechanical energy is potentially required for further granule break down. All the agglomerated MPI granules solubilised much more slowly than the standard MPI powder.

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## 1. Introduction

Milk protein isolate is a widely developed functional ingredient in the production of cheese, beverages, yoghurt and other food products. As a powder, it plays an important role in industry, due to its convenience for process, preservation and transportation (Ann Augustin and Clarke, 2011). Milk protein isolate powders are usually produced from skimmed milk by ultrafiltration to remove lactose and minerals and then dehydrated by spray drying (Chandan, 2011). The obtained products after spray drying are normally fine particles with dense structures, thus they may bring many problems, e.g. heterogeneity of the native structures (size, shape and porosity) (Cuq et al., 2013; Knight, 2001), and difficult-to-rehydrate (poor wettability and dispersibility) (Gaiani et al., 2007; Selomulya et al., 2013). These issues potentially restrict the applications of milk protein powders, as powders are required to have good handling properties, as well as quick and complete

rehydration behaviours to express their functionality. Granulation is a particle size enlargement process to form monodisperse granules and to optimise structural and physical properties (Cuq et al., 2013; Salman et al., 2007). Subsequently, the structures modified by the granulation process are also believed to strongly influence the rehydration properties (Ji et al., 2015; Knight, 2001).

Many different granulation processes using a variety of equipment have been widely developed in the applications of food and pharmaceutical materials (Barkouti et al., 2013; Litster and Ennis, 2013; Palzer, 2011; Rajniak et al., 2007). These processes result in different granule structures, due to the main differences in the mechanisms of particle growth and intensity of solidification (Barrera-Medrano et al., 2007). For example, fluidised bed wet granulation is used to atomize binding liquids into small droplets on the free-flowing solids without agitation (Turchiuli et al., 2013). Thus, the created granules usually show porous “raspberry” structures, which include large inter-particle void volume and internal pore volume, as the binding droplets play the role of bridges to coalesce the primary particles (Jacob, 2007; Ji et al., 2015). Another common used wet agglomeration equipment is the high shear granulator, which uses an impeller to vigorously agitate the

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powders during the addition of binding liquid, to produce the densely packed granules (Reynolds et al., 2006). These granules have not only comparatively higher density, but also a spherical shape and smooth surface, due to the effect of consolidation by agitation (Cuq et al., 2013). Although some studies have showed the advantages of agglomerated milk protein powders that were produced from a fluidised bed granulator (Ji et al., 2015), it is also necessary to find out if the high shear granulation process displays different beneficial roles on the milk protein powder due to its unique and special effects on the structural modification.

High shear granulation is a complex process and commonly consists of different groups of rate processes: 1) wetting and nucleation; 2) coalescence and consolidation; 3) attrition and breakage (Iveson et al., 2001; Mort, 2007). These competing physical phenomena occur in the granulator and control the granule size, shape and porosity, as well as many other important physical properties (Cuq et al., 2013). Wetting and nucleation is the first stage of granulation that distributes the binding liquid through the powders and then forms the nuclei aggregates, which are loosely packed (Litster and Ennis, 2013). When two or several particles collide during the liquid addition, they may stick together to create the new secondary agglomerates, and thus modify the structures. By the condition of high shear agitation, granules are consolidated through collisions with the granulator or other particles due to the force of agitation (Ennis, 2010). Plastic deformation may occur and that will squeeze out entrapped air and increase the internal pore saturation so as to reduce the granule size and porosity, which significantly influences the final structures of formed granules (Barrera-Medrano et al., 2007). Consequently, it is necessary to investigate how the different granule growth processes affect the structural formation of milk protein powders during the high shear granulation. However, as the growth processes always happen simultaneously and there is no clear definition to distinguish them, it is difficult to characterise the granules by the individual growth process (Hapgood et al., 2007). In that case, the granules with different particle sizes, which are caused by these growth rate processes, will be used to compare the structural and physical properties in this study.

While much research has been conducted into the fundamentals of granulation (Litster and Ennis, 2013; Salman et al., 2007), less attention has been given to the subsequent influence on functionality of powders. However, the agglomerated granules with modified structures are believed to potentially influence the rehydration behaviours, which include wetting, dispersing and dissolving phases (Hogekamp and Schubert, 2003; Richard et al., 2013). Each of them is closely related to the powders' physical and structural properties. Good wettability and dispersibility are both favoured by large particles with high inter-particle porosity and high particle density (Forny et al., 2011; Goalard et al., 2006), while the dissolving behaviour is prone to the presence of small hydrophilic particles on the surface (Lillford and Fryer, 1998). Some studies showed that, agglomerated milk protein powders produced from fluidised bed display better wettability due to liquid being more easily penetrate into solids with porous structures (Ji et al., 2015). But for the high shear granulation, which has completely different granule growth mechanism from fluidised bed (Jacob, 2007), the similar studies haven't been reported so far. Consequently, it is essential to investigate the effect of its granule growth processes, on the individual wetting, dispersing and dissolving behaviours of milk protein powders.

In summary, the objective of this study is to investigate the effect of granule growth during the high shear granulation, on the rehydration abilities (wettability, dispersibility and solubility) of milk protein isolate powders. As part of this work, granules' structural modifications, including densities and morphology, were

also examined.

## 2. Materials and methods

### 2.1. Materials

Milk protein isolate powders (MPI) were supplied by Kerry Ingredients (Kerry, Ireland). The composition is 86% milk protein, 1.5% fat, 6% ash, 5.2% moisture and less than 1% lactose. The lactose used in the high shear granulation, was purchased from Arla Food Ingredients (Viby J, Aarhus, Denmark).

### 2.2. High shear granulation

The MPI powders were agglomerated by a high shear granulator (4M8, Procept, Zelzate, Belgium). 200 g batch sizes of MPI standard powders were fed into the glass bowl and then were agitated by an impeller at a speed of 300 rpm and a chopper at a speed of 500 rpm during the granules formation stage. 100 mL 15% w/v lactose solution used as the binding solution was added into the bowl by droplets at the dosing speed of 4 mL min<sup>-1</sup>. When the binding solution had been used up, the product continued to be consolidated by the impeller and chopper at the same speed for another 10 min, which made sure the total granule size distribution was properly mono-dispersed. After that, a fluidised bed (VFC-Lab Micro flo-coater, Vector Corporation, Iowa, USA), which provided the air with a temperature of 50 °C and the flow velocity of 200 L min<sup>-1</sup>, was used to dry the granules until the moisture content was lower than 10%. Three batches of MPI granules were prepared respectively for the repeated measurements.

### 2.3. Powder characterisation

The granules were subjected to a sieve analysis using a nest formed from 75, 106, 180, 425, 850 and 1000 µm sieves (Endecotts, London, UK) to obtain five agglomerate size fractions (S1: -1000/+850 µm; S2: -850/+425 µm; S3: -425/+180 µm; S4: -180/+106 µm and S5: -106/+75 µm). The particles of size larger than 1000 µm or the smaller size than 75 µm were removed. Therefore, including the standard MPI powder, six samples in total were investigated in this study. All the powders based on the different sizes were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 60 °C temperature for 24 h and then kept in the desiccators to reach ambient temperature. The final moisture contents of samples before measurement were about 2–3%.

### 2.4. Physical properties

#### 2.4.1. Granule size, density and porosity

The particle sizes of granules were measured by laser light scattering using Malvern Mastersizer 3000 (Malvern Instruments Ltd, Worcestershire, UK). At least three measurements were made and the average D (50) value was taken. The loose and tapped bulk densities were measured by a tapping machine with a graduated cylinder (Funke Gerber, Berlin, Germany). The volume occupied by 30 g powder was used to calculate the loose density while the tapped density was obtained by the volume after 100 taps. In addition, the apparent density of powder was measured by Gas Pycnometer (AccuPyc II 1340, Micromeritics Instrument Corporation, Georgia, USA). Sample was placed in the cell and purged with a flow of helium to degas the cell by ten pressurisation cycles. All the density measurements were repeated at least three times. Finally, the porosity was calculated using the tapped density and the apparent density.

#### 2.4.2. Granule shape

The shape of a granule is usually quantified by three parameters, which are circularity, convexity and elongation. In this study, they were measured by Malvern Morphology G3 (Malvern Instruments Ltd, Worcestershire, UK). The detailed method was described by Ji et al. (2015). Briefly, a volume of sample was dispersed uniformly into a single layer on the glass plate. Then, the microscope was used to observe these particles and give out the average values of circularity, convexity and elongation. All the measurements were repeated at least five times.

#### 2.5. Wettability

##### 2.5.1. Wetting time

Wetting time is used to quantify the wettability of powders. The method was based on GEA Niro method (GEA Niro, 2005), which recorded the time needed for powders to achieve complete wetting without agitation. In this study, 6 g samples were put into a 400 mL beaker containing 100 mL distilled water at 20 °C temperature. All the measurements were repeated three times.

##### 2.5.2. Capillary rise wetting

Powder wettability can also be quantified by the Washburn method (Washburn, 1921), which is based on the powder capillary rise wetting behaviour. It measured the liquid that penetrated into powders by recording its penetration length or absorbed weight. In this study, 2 g of powder was loaded into a cylindrical glass tube with an open base bottom, which was covered by filter paper and gauze. The tube with powders on the bottom was fixed to just touch the distilled water at 25 °C temperature. After that, the additional mass of wetted powder was recorded in 10 min. The measurements for each powder were repeated three times.

##### 2.5.3. Contact angle

Contact angle is the tangent angle at the contact point of three phases (liquid, solid and air) and it is a widely used parameter to describe the wettability of powders. As the wetting behaviour is believed to be a dynamic process, the contact angle and how it varies with time was used to quantify the wetting process directly (Yuan and Lee, 2013). An optical tensiometer (Attension Theta, Biolin Scientific Ltd., Espoo, Finland) was used to observe the penetration of a 12 mL water droplet into powder beds and to record contact angles over time. Before that, powders were firstly loaded into an aluminium pan with a diameter of 100 mm. Then a leveller was used to form a smooth surface, which is necessary for determining the right contact points and for calculating the angles. The contact angle was recorded as a function of time. All the measurements were repeated at least five times.

#### 2.6. Granule dispersibility

The dispersibility of granules was quantified by the change of particle size during the solubilisation process (Mimouni et al., 2009). The sizes of dispersed granules were measured by Malvern Mastersizer 3000 based on laser light scattering technique (Malvern Instruments Ltd, Worcestershire, UK). Details of the method were described by the study of Ji et al. (2015). Approximately 5 mg samples were fed into 120 mL dispersion unit with 2000 rpm agitation and the measurements were carried out every 2 min for a total of 140 min and at 25 °C ± 2 °C temperature ranges. The results of D (50) and D (10) were presented as a function of mixing time.

#### 2.7. Dissolution

The dissolved solids kinetics was used to describe the solubility

of granules in this study. 1 g sample was added into 50 mL water in a standard 200 mL beaker, which was preheated in a 25 °C water bath. Then it was stirred by a 3-pitched-blade impeller with a diameter of 4 cm at an agitation speed of 300 rpm. After different mixing times (15, 30, 60, 90, 120, 150, 180, 240 and 300 min), each suspension was centrifuged at 3000 g and 25 °C for 10 min (Eppendorf Centrifuge 5810R, Hamburg, Germany). Approximately 2 mL supernatant was taken and a solids analyser machine (Smart System 5, CEM, North Carolina, USA) was used to measure the dissolved MPI in the supernatant, expressed as the percentage of overall MPI solids (%). Triplicate measurements for each sample were presented.

#### 2.8. Granule microstructure by SEM

A field emission scanning electron microscope (Zeiss Supra, Carl Zeiss Microscopy GmbH, Jena, Germany) was used to observe the MPI granules. They were placed on a double-sided adhesive tape and fixed to SEM stubs before imaging at 1.35 kV. Two magnifications (80× and 150×) were performed respectively, based on the different granule sizes.

#### 2.9. Statistical analysis

Results were expressed as mean ± standard deviations (SD). SPSS software (PASW, Statistics 1.8) was used to carry out One-way analysis of variance (ANOVA). Statistical differences of particle size, density and morphology descriptors were compared by the least significant difference (LSD) test, in relation to the applied variable using F-test. Differences were considered to be significant at  $P < 0.05$ .

### 3. Results and discussion

#### 3.1. Effect of different granule sizes on the physical and structural properties of MPI

##### 3.1.1. Density and porosity

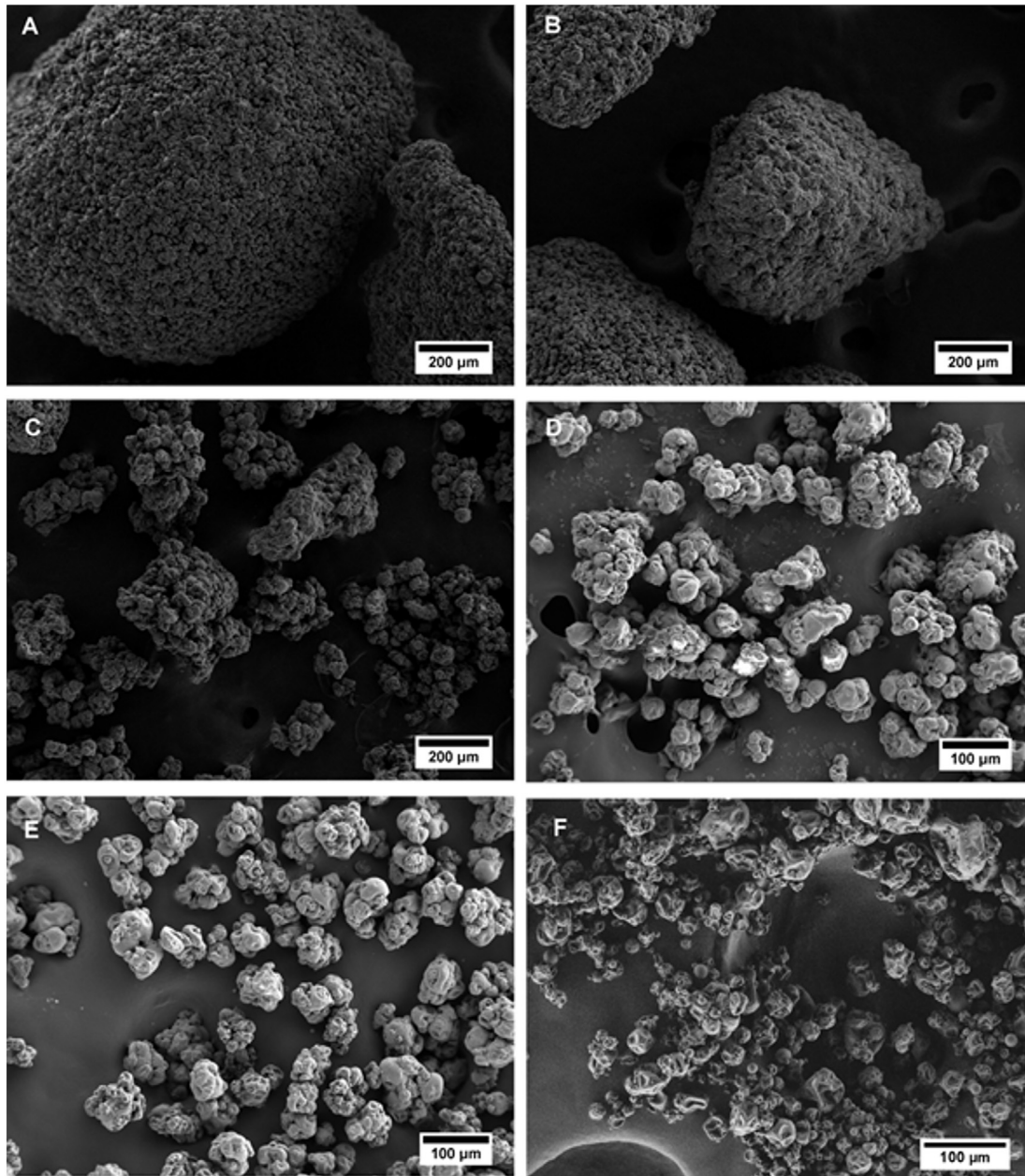
In Table 1, it is obviously to see that the agglomerated MPI showed significantly higher loose and tapped bulk densities than the unagglomerated powder, which means high shear granulation creates denser structures. It is due to the densification of high shear agitation which compressed the particle volume, squeezed out entrapped air to remove the internal pores, and thus decreased the total volume that granules occupied, which can be observed from Fig. 1. The SEM images show the granules were coalesced by single primary particles and also their structures were densely packed and highly compacted compared to the standard MPI powders. In addition, from looking at the granules with different sizes in Table 1, the smallest granules S5 had the highest apparent density and the larger granules had progressively lower apparent densities. For bulk densities, it is interesting to find that largest granules S1 with 1075 µm size, present the highest loose density of 0.538 g/mL, while the smallest granules S5 showed the highest tapped density of 0.561 g/mL. S3 and S4, which were in the range of 106 µm–425 µm, had the lowest loose and tapped densities of all the granules. The porosity values of all the samples are also presented in Table 1. Similarly, the MPI granules generally had significantly lower porosities than the standard MPI, as the porosity is mainly dependent on bulk density and apparent density. Thus, S1, S2 and S5 had relatively low porosity values, which were all below 54%, while the porosities of S3 and S4 were more than 60%.

At the beginning of process, when MPI particles were wetted by liquid, the nuclei granules were formed as the primary aggregates fused by the standard particles. At the same time, they were

**Table 1**  
Bulk density, apparent density and porosity of powders.\*

Sample	Characterisation	Particle size D(50) ( $\mu\text{m}$ )	Loose density (g/mL)	Tapped density (g/mL)	Apparent density (g/mL)	Porosity (%)
S1	>850 $\mu\text{m}$	1075 $\pm$ 15 <sup>a</sup>	0.538 $\pm$ 0.006 <sup>a</sup>	0.543 $\pm$ 0.002 <sup>a</sup>	1.127 $\pm$ 0.010 <sup>a</sup>	51.8 $\pm$ 0.2 <sup>a</sup>
S2	425 $\mu\text{m}$ – 850 $\mu\text{m}$	681 $\pm$ 9 <sup>b</sup>	0.500 $\pm$ 0.006 <sup>b</sup>	0.538 $\pm$ 0.002 <sup>a</sup>	1.145 $\pm$ 0.008 <sup>ae</sup>	53.0 $\pm$ 0.2 <sup>b</sup>
S3	180 $\mu\text{m}$ – 425 $\mu\text{m}$	263 $\pm$ 5 <sup>c</sup>	0.431 $\pm$ 0.003 <sup>c</sup>	0.463 $\pm$ 0.000 <sup>b</sup>	1.188 $\pm$ 0.005 <sup>b</sup>	61.0 $\pm$ 0.1 <sup>c</sup>
S4	106 $\mu\text{m}$ – 180 $\mu\text{m}$	111 $\pm$ 2 <sup>d</sup>	0.450 $\pm$ 0.000 <sup>d</sup>	0.478 $\pm$ 0.000 <sup>c</sup>	1.203 $\pm$ 0.004 <sup>c</sup>	60.3 $\pm$ 0.1 <sup>d</sup>
S5	<106 $\mu\text{m}$	75 $\pm$ 1 <sup>e</sup>	0.526 $\pm$ 0.000 <sup>e</sup>	0.561 $\pm$ 0.000 <sup>d</sup>	1.214 $\pm$ 0.005 <sup>d</sup>	53.8 $\pm$ 0.1 <sup>e</sup>
Standard		33 $\pm$ 1 <sup>f</sup>	0.303 $\pm$ 0.000 <sup>f</sup>	0.345 $\pm$ 0.000 <sup>e</sup>	1.163 $\pm$ 0.011 <sup>e</sup>	70.3 $\pm$ 0.2 <sup>f</sup>

\*Data are expressed as mean  $\pm$  standard deviation; values followed by a different superscript letter in the same line are significantly different at  $P < 0.05$ .



**Fig. 1.** SEM images of MPI granules with different particle sizes by granule growth processes. (A: S1; B: S2; C: S3; D: S4; E: S5; F: standard MPI).

solidified by the force of agitation, which resulted in the less air entrapped and the small interstitial spaces in the matrix (Cuq et al., 2013; Knight, 2001). Therefore, the bulk and apparent volumes of S5 decreased and its porosity also became lower. As the nuclei

granules continued to grow, they coalesced together to create the bigger secondary agglomerates based on the bridges that produced by the binding liquid (Hapgood et al., 2007). This process produced the more irregular particles, which increased the void volumes

among these particles (Iveson et al., 2001). It may be the reason why S3 and S4 have the comparatively lower bulk densities and higher porosities than other granules. When the secondary agglomerates reached the critical size, the bonds were not strong enough to connect other particles. In that case, the granules stopped growing and they were highly deformed again by the mechanical solidification (Reynolds et al., 2005). Hence, as it showed in Fig. 1 A&B, the more compacted large granules S1 and S2 formed and the particles were closely arranged on the surface. However, it is difficult to conclude the effect of granule growth precisely due to the formed granules may break into fragments by breakages. That will also influence the structures of obtained granules, which need further studies in the future.

### 3.1.2. Granule morphology

Three parameters (Circularity, Convexity and Elongation) are used to describe the granules with different particle sizes. Examining Table 2, S5 had both highest circularity and convexity values of 0.891 and 0.965 respectively, which were the most spheroidal shape and smoothest surface of all the samples including the standard MPI. As explained previously, the initial formed nuclei granules were consolidated through collisions with other granules and granulator. Therefore, the formed shapes were rather spheroidal and smooth by the uniformly force from ploughshares and chopper (Litster and Ennis, 2013). As the granule size increased, it is found that granules formed with significantly lower circularity and convexity values. Especially for S3, it had only 0.767 for circularity and 0.866 for convexity, which was even lower than that of unagglomerated MPI. In Fig. 1 C&D, it is also clear to see that S3 and S4 had less rounded shapes. It is commonly considered that the agglomerated secondary granules may cause irregular shaped particles and also rougher surfaces, due to the bridges formed between particles which modified the shapes (Barrera-Medrano et al., 2007; Hapgood et al., 2007; Reynolds et al., 2006). Furthermore, when granule size reached S1 or S2, the coalescence stage was no longer the dominant growth process. Their shapes again became more rounded and smoother than S3 or S4, by the influence of further densification (Fig. 1 A&B). But for elongation, which is used to quantify the ratio of particle length and width, there is no significant difference among these granules with different particle size, because single granule was homogenised based on the force from high shear agitation. Thus, their elongation values were all about 0.26, while the standard MPI had a comparatively longer shape.

## 3.2. Effect of different granule sizes on the wettability of MPI

### 3.2.1. Wetting time by immersional wetting procedure

According to the results in Table 3, the agglomerated granules, regardless of the particle size, took significantly less time to be wetted by water than that of standard powders. The wettability seemed to correspond to the particle size of samples with larger

granules showing better wettability. S1 and S2 displayed the best wettability taking less than 10 s to be fully wetted. The other granules all had shorter wetting times than 60 s, which can be considered as the easy wetting powders. However, the standard powders took more than 20 min to completely immerse below the water surface, due to an impermeable hydrophobic layer formed to separate the water surface and dry powder (Ji et al., 2016). This was not a problem for the agglomerated granules after high shear granulation process. The surface tensile strength of the assembly of granules is reduced by the size enlargement when contacting with water. Hence, the granules separated during wetting process rather than adhering together as fine particles (Knight, 2001). However, particle size is not the only factor that influences the wetting behaviours. Ji et al. (2016) demonstrated that the agglomerated MPI produced by fluidised bed granulation, which had a median particle size of about 180  $\mu\text{m}$ , still floated on the water surface for more than 8 min. Therefore, the densely packed granules with higher density also significantly improve the wettability of MPI due to there being fewer pores in the matrix (Hogekamp and Schubert, 2003).

### 3.2.2. Capillary rise wetting

From Fig. 2, it can be seen that the agglomerated MPI granules absorbed significantly more water by capillary force than the standard powders in 10 min. The results are consistent with the wetting time measurements, the granules with large size also have the better wettability based on the capillary rise wetting procedure. The standard MPI only adsorbed 0.244 g water while S1 and S2 adsorbed most, exceeding 8.5 g water. This is due to the larger void spaces between each granule, which causes a higher pore radius that results in a positive correlation with the depth of liquid intrusion (Lazghab et al., 2005; Palzer et al., 2003; Yuan and Lee, 2013). This is shown by the Washburn model as Eq. (1) (Washburn, 1921):

$$l^2 = \frac{\cos\theta \cdot r \cdot \gamma \cdot t}{2 \cdot \eta} \quad (1)$$

where  $l$  is the penetration depth of the liquid,  $\eta$  is liquid viscosity,  $\gamma$  is the liquid surface tension,  $r$  is radius of pores,  $\theta$  is the contact angle and  $t$  is time for penetration. Hence, it indicates that the large pores between the particles result in greater penetration depth or the greater mass of liquid by spontaneous intrusion, which is also used to explain the better wettability of the big granules. However, it is interesting to find that, though the particle size of S5 was only 75  $\mu\text{m}$ , it exhibited much better wetting behaviour than the standard MPI. If compared to the results presented by Ji et al. (2015), S5 still adsorbed more water than the agglomerated MPI produced by fluidised bed with a median size of 180  $\mu\text{m}$ . Similar to immersional wetting procedure, special water bonding capacity of whey protein also limited the behaviours of capillary rise wetting (Gaiani et al., 2007; Schubert, 1993).

### 3.2.3. Contact angles by spreading wetting procedure

For the droplet spreading wetting procedure, the wettability of powdered samples was compared based on the changes of contact angle as a function of time (Gao and McCarthy, 2006). In Fig. 3, firstly, the contact angle of standard MPI powder decreased from 160° to 40° in about 300 s, which was much longer than that of the agglomerated MPI granules with different sizes. These granules took less than 10 s to allow the water droplet penetrate into the powder bed. Again, the bigger granules seemed to cause quicker disappearance of water droplets. For example, S1 and S2 not only had the lowest initial wetting angles of 130°, but also required only about 2.8 s for the contact angle to decrease to 40°. This is not simply due to the granules' high porosities, as the standard

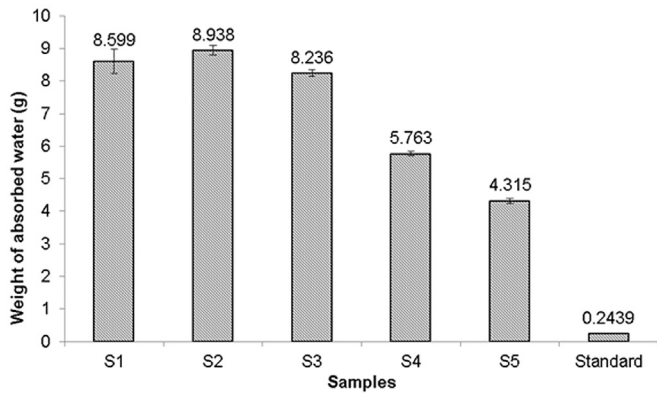
**Table 2**  
Morphological descriptors of powders.\*

Sample	Circularity (0.5)	Convexity (0.5)	Elongation (0.5)
S1	0.862 ± 0.018 <sup>a</sup>	0.931 ± 0.015 <sup>a</sup>	0.262 ± 0.000 <sup>a</sup>
S2	0.870 ± 0.004 <sup>a</sup>	0.933 ± 0.001 <sup>a</sup>	0.258 ± 0.004 <sup>d</sup>
S3	0.767 ± 0.015 <sup>b</sup>	0.866 ± 0.013 <sup>b</sup>	0.262 ± 0.010 <sup>a</sup>
S4	0.820 ± 0.006 <sup>c</sup>	0.908 ± 0.005 <sup>c</sup>	0.263 ± 0.002 <sup>a</sup>
S5	0.891 ± 0.001 <sup>d</sup>	0.965 ± 0.001 <sup>d</sup>	0.263 ± 0.006 <sup>a</sup>
Standard	0.816 ± 0.023 <sup>c</sup>	0.931 ± 0.009 <sup>a</sup>	0.301 ± 0.012 <sup>b</sup>

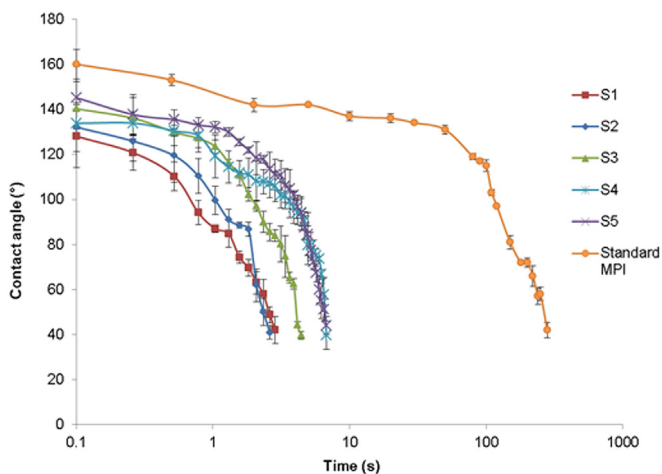
\*Data are expressed as mean ± standard deviation; values followed by a different superscript letter in the same line are significantly different at  $P < 0.05$ .

**Table 3**  
Wetting time of dairy powders by immersional wetting procedure.

	S1	S2	S3	S4	S5	Standard
Wetting time	5 s ± 1 s	7 s ± 1 s	15 s ± 2 s	25 s ± 4 s	41 s ± 7 s	>20 min



**Fig. 2.** Mean weight of absorbed water for samples (the agglomerated MPI granules S1, S2, S3, S4, S5 and standard MPI) after 10 min.



**Fig. 3.** The change of contact angle (°) as a function of time using the sessile drop technique in approx.20 °C temperature.

powders have an even higher value, as shown in Table 1. Thus, it is believed that the granules having larger voids between the particles result in the easy-wetting behaviours (Yuan and Lee, 2013). Meanwhile, as explained previously, standard MPI powders with poor wettability are usually due to the formation of impermeable hydrophobic gel-like layers (Ji et al., 2016). However, it appears that this did not happen for the agglomerated granules. Overall, all the applied wetting procedures showed that the MPI granules formed in high shear granulation exhibited much better wettability than the standard MPI powders.

### 3.3. Effect of different granule sizes on the dispersibility and solubility of MPI

#### 3.3.1. Particle size changes during MPI granules solubilisation

As it is seen from Fig. 4 A&B, 50% of the standard MPI particles were completely rehydrated into water in about 32 min, while the most of the agglomerated granules were found to be more difficult

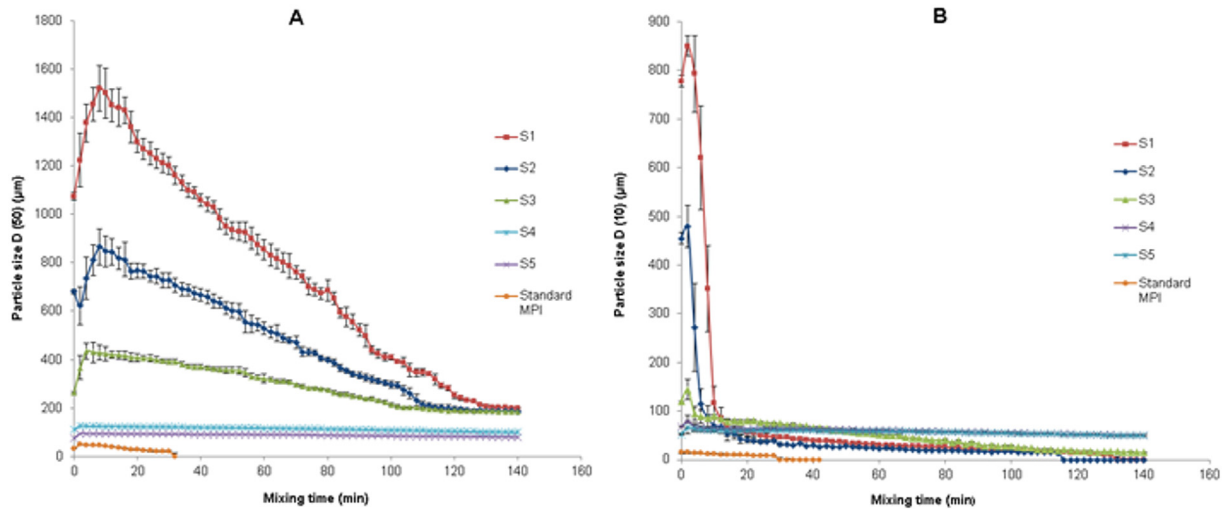
to disperse based on the slower decrease of particle size. Particularly, there were almost no size changes for S4 and S5 for the whole 140 min, which indicated that they both had the extremely poor dispersibility at the condition of 2000 rpm agitation. In addition, S1, S2 and S3 were found to slowly release the materials into the surrounding aqueous phase by the different releasing rates. In Fig. 4A, the largest granules S1 took the longest time of 130 min to reach 200 μm particle size, although its dissolution rate was quickest of all. S2 and S3 also required more than 100 min achieving a relatively stable particle size. It is surprising to see that these three granules all finally decreased to a constant size, which was about 200 μm. However for S4 and S5, which had smaller sizes initially (111 μm and 75 μm respectively), their particle sizes were maintained at about their initial values. At the same time, in Fig. 4B, 10% of S1 and S2 particles displayed totally different dispersing behaviours, as their sizes decreased dramatically during the first 20 min and the materials were solubilised in about 120 min. S3 also showed similar dispersion process but it began with smaller size and still was not totally dissolved at 120 min.

Generally, the micellar casein that exists in milk protein powder has slow dispersion behaviour, due to its complex structures of inter-linked network of casein micelles (Mimouni et al., 2010; Schuck et al., 2007). However, the poor dispersibility of the agglomerated granules is determined by other more important factors. It can be explained as the strong interactions for the granule structures, caused by solidification in the high shear granulation (Reynolds et al., 2006). According to the results, the agglomerated granules were very difficult to break down and collapse into small solids, which can be defined as poor dispersibility, at the 2000 rpm agitation condition. Furthermore, it is concluded that the primary aggregates of granules were the most compacted, which led to the slowest release rate of materials (Hapgood et al., 2007). It is conceivable that the size of remaining particles corresponds closely to the granule strength that can resist the agitation force, as higher mechanical energy is required to separate the primary aggregates and disperse them into the medium. That is also the reason why S1, S2 and S3 have the different dispersibility during the process. It is believed that the strength of formed granules was weaker than that of primary nuclei structures, because of the final granules consisting of several nuclei granules, layering and filling by the primary particles and the particles that broke down from other granules by attrition (Barrera-Medrano et al., 2007). Consequently, these materials were less bounded to the large granules and easier to disperse and dissolve into water than that in the small nuclei, which is demonstrated by the changes of D (10) particle sizes in Fig. 4B.

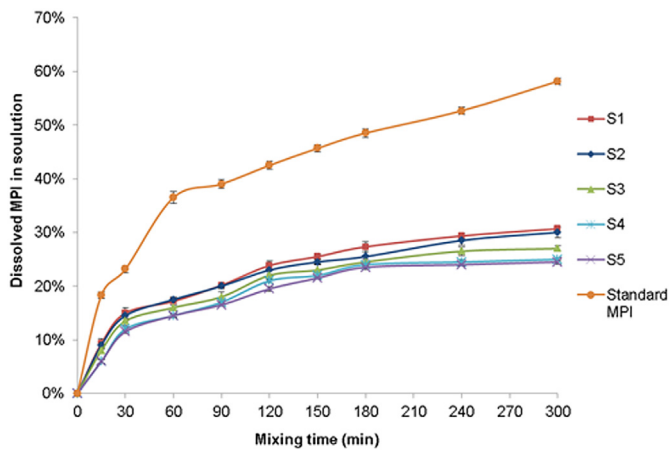
On the other hand, before the powders started to solubilise into water, their particle sizes increased over the first several minutes, as they swelled up by absorbing water following the wetting stage (Gaiani et al., 2009). It can be found that standard MPI and small granules S4 and S5 stopped swelling by 4 min, while the large granules took longer time to reach a peak in particle size. For example, the size of S1 can increase to about 1500 μm in 8 min. It is indicated that water needed more time to completely penetrate into the large granules with the longer diameter (Palzer, 2007).

#### 3.3.2. Dissolution of MPI granules

Fig. 5 shows the dissolved MPI solids percentage in solution as a



**Fig. 4.** Particle size measurements of dispersed particles of the agglomerated granules S1, S2, S3, S4, S5 and standard MPI, as a function of mixing time (every 2 min) **A:** D (50); **B:** D (10).



**Fig. 5.** Solubilisation as measured by dissolved MPI percentage (%) versus different mixing time.

function of mixing time. The standard MPI displays the best dissolution behaviour compared with others, as nearly 60% of its solids dissolved after 5 h mixing time. The agglomerated granules displayed much lower dissolution ability with only 30% solids being solubilised in the supernatant after 5 h mixing; S4 and S5 with the smallest granule sizes showed the least dissolved solids of only about 25%. It is very similar to the results of dispersibility of the different granules where small granules also had the poorest dispersing behaviours. It is commonly considered that good dispersibility is a prerequisite for particles to dissolve into liquid quickly (Forny et al., 2011). Therefore, when the release of materials into water was prolonged by the dense structures and the dissolution ability was thus also limited.

In addition, the solid percentage of all the samples increased comparatively quickly over the first 30 min and was then followed by slower dissolution behaviour for the next 300 min. It is believed that the first dissolved solids were mainly contributed by the easy-dissolving components, e.g. whey protein and some minerals, when water began to penetrate into the structures of granules (Mimouni et al., 2010). However, the agglomerated granules retarded the release of these materials, as those easy-dissolved components did not solubilise as much as those in standard MPI powders. This may

be due to slower water penetration of water inside the granule matrix (Palzer, 2007), which may cause the partial dissolution of whey protein and minerals. This phenomenon was more obvious for the small granules, because of their more compacted structures (Iveson et al., 2001).

#### 4. Conclusion

The MPI granules produced by high shear granulation process were found to have modified physical and structural properties that influenced their rehydration behaviours in water. The high agitation condition in the process consolidated the granules and caused high deformation and densely packed structures. Therefore, they usually had the higher bulk density and lower porosity. The different granule growth processes created the granules with complex “hierarchical” structures. The small nuclei firstly formed by fusing standard MPI together and displayed the more compacted structures after solidification. Then they coalesced to form irregular secondary agglomerates with lower density and higher porosity until they were deformed by agitation again.

These modifications made powders that were more easily wetted by water, especially for the large granules. At the same time, they also resulted in poorer dissolution due to prolonged water penetration into the denser structures. Comparatively, the large granules exhibited quicker release of materials into water until reaching a critical size, below which may require more mechanical energy to further break down the particles. Overall for MPI powder, high shear granulation produced granules with superior wetting characteristics in comparison to both standard MPI powder and granules produced by fluid bed granulation. However these granules proved more difficult to dissolve. Considering this, high shear granulation may have potential to improve the rehydration ability of poor wetting powders that dissolve easily.

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