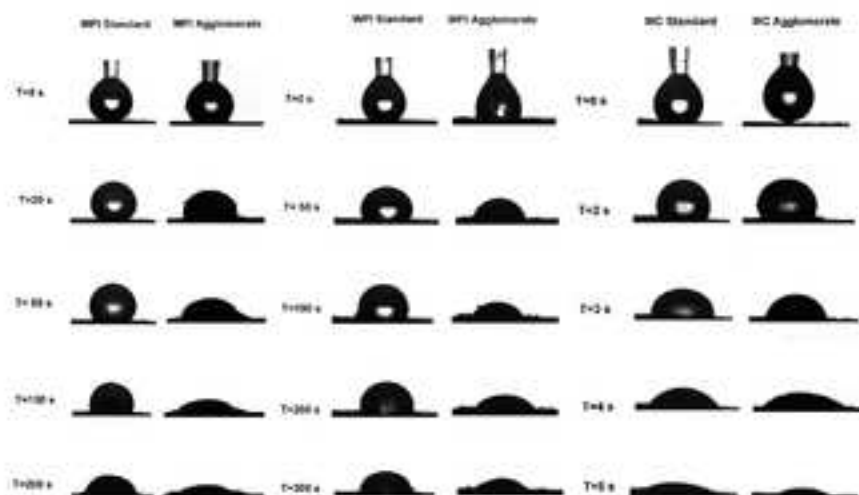
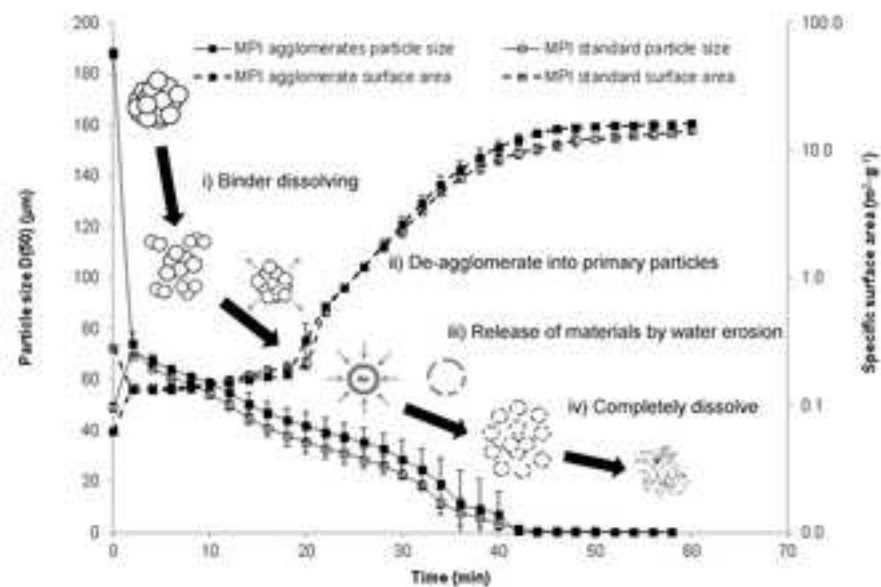


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The change of contact angles for wettability measurements



Schematic of MPI and its agglomerate rehydration in water, based on the change of particle size and SSA as a function of time.

Rehydration behaviours of high protein dairy powders: the influence of agglomeration on wettability, dispersibility and solubility

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Abstract

Five common high protein dairy powders and their agglomerates produced by fluidised bed granulation were evaluated and compared for their rehydration characteristics in this study. Wettability of powders was measured by immersion wetting time, capillary rise wetting and contact angles methods, while dispersion and solubilisation processes were quantified by the change of particle size and the sediment height after centrifugation. The results showed that these high protein dairy powders generally had poor wettability, especially for whey protein isolate and the caseinates, which formed an impermeable layer separating the water surface and powders just after they contacted the water. However, the casein-micellar dominant powders exhibited prolonged dispersion due to strong interactions inside the micellar structures. The agglomerates with large particle size and high porosity are expected to exhibit increased wettability. However, agglomeration only caused the external structural modification and thus is difficult to accelerate the dispersion process of micellar casein, which can be explained by the milk protein isolate rehydration mechanism. The micellar structure inhibits the release of materials into surrounding liquid phase, which is mainly responsible for the extended rehydration time.

Keywords: high protein dairy powders, agglomeration, rehydration, wettability, dispersibility

1. Introduction

The production of milk protein is growing rapidly worldwide due to its advantageous nutritional and functional properties. As milk protein consists of casein and whey protein, different milk protein materials can be produced using different manufacturing processes (Ofstedal, 2013). For example, milk protein is obtained from skimmed milk by ultrafiltration to remove lactose and minerals; subsequently micellar casein can be achieved by microfiltration to further separate whey protein; therefore, whey protein is also produced from the permeate (Chandan, 2011; Kilara, 2011; O'Mahony & Fox, 2013). In addition, some non-micellar caseinate, e.g. sodium caseinate and calcium caseinate, can be produced from acid casein by adding alkali solution (sodium hydroxide or calcium hydroxide respectively) (Farrell, Brown, & Malin, 2013; Pitkowski, Nicolai, & Durand, 2009). These milk protein materials are widely used in dairy products and infant formula, or used as emulsifiers and stabilisers in food and beverages (Chandan, 2011; Moughal, Munro, & Singh, 2000). However, whatever the type of milk protein, liquid materials are usually spray-dried into the powdered forms for the ease of handling, storage and transportation (Ann Augustin & Clarke, 2011; Selomulya, et al., 2013). In that case, the various milk protein powders are necessarily required to be rapidly and completely rehydrated again before use, as complete rehydration is a prerequisite for expressing the functionality of the dried ingredients. The literature has already reported that micellar casein powders were difficult to disperse in water and whey protein powders also have very poor wettability (Gaiani, et al., 2006; Gaiani, Schuck, Scher, Desobry, & Banon, 2007; Schuck, et al., 2007). Comprehensive assessment is still needed for the rehydration characteristics of these common milk protein powders. Consequently,

it is of interest to investigate their rehydration ability and understand their rehydration mechanism.

It is commonly believed that the rehydration process mainly consists of three sequential stages, which are wetting, dispersing and solubilisation. Wetting is the first step where the particles contact liquid while dispersing and solubilisation are the critical phases where primary particles start to release materials from the particle surface into the liquid (Forny, Marabi, & Palzer, 2011; Ji, Fitzpatrick, Cronin, Crean, & Miao, 2016; Richard, et al., 2013). Once any of these three processes is limited, the time for the whole rehydration is prolonged. Casein-dominated powders are believed to be poorly-dispersible due to the strong interactions among the micellar structures. Hence, they usually take a longer time to totally dissolve in water (Baldwin & Truong, 2007; Havea, 2006; Schokker, et al., 2011). However, whey protein powders demonstrate poor wetting behaviour where the material floats on the surface of the solution, which is considered to be the rate-limiting factor for whey protein rehydration (Gaiani, Scher, Schuck, Desobry, & Banon, 2009). Therefore, it is necessary to characterise the individual behaviours of milk protein powders during wetting, dispersion and solubilisation processes as different milk protein powders exhibit completely different wettability, dispersibility and solubility (Schuck, Jeantet, & Dolivet, 2012).

Agglomeration is a particle size enlargement process that creates granulates by adding a binder and forming bridges to link primary particles together. The process is used to change the structural and physical properties by increasing the size of the particles and the voids between particles, and also by decreasing the bulk density of powders (Rajniak, et al., 2007). Hence, the modified structure is believed to influence

the rehydration characteristics of powders. For example, the wetting phase is affected by large particles with large pores, which allow water to penetrate into particles more easily (Hogekamp & Schubert, 2003). Dispersibility is also related to the particle size and the density of powders (Goalard, Samimi, Galet, Dodds, & Ghadiri, 2006). Some studies reported that the agglomeration process played a beneficial role in the wetting behaviour of milk protein isolate powders but no significant improvement for dispersion (Gaiani, et al., 2007; Ji, Cronin, Fitzpatrick, Fenelon, & Miao, 2015). Therefore, it is of interest to find out if the agglomerated powders can positively affect the rehydration behaviours for the cases of other protein powders. The rehydration process of milk protein can be described generally in the following mechanism: wetting of the powders; detachment of powders into primary particles; release of materials from particles into the aqueous phase and simultaneous continuous erosion of the surface layer until the collapse of particles and their complete dissolution (Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2009). The agglomerated powders may also have an additional step which is the dissolution of the solid bridges linking the particles with the resulting granules dispersing into primary particles (Forny, et al., 2011). To the best of our knowledge, few reports have investigated this mechanism for the rehydration kinetics of milk protein and compared with its agglomerated form.

The objective of this study is to investigate the effect of agglomeration on the rehydration properties of high protein dairy powders (protein content >80%). Milk protein isolates (MPI), whey protein isolates (WPI), micellar casein (MC), sodium caseinate (SC), calcium caseinate (CC) are used as the model systems. The results will be used to exhibit the rehydration characteristics and also to better explain the rehydration mechanism of milk protein powders and their agglomerates.

118

119 **2. Materials and methods**

120 *2.1 Materials*

121 The composition of the milk protein powders used in this study is showed in
122 Table 1. MPI and SC were supplied by Kerry Ingredients (County Kerry, Ireland).
123 WPI was supplied by Davisco Food International (Le Sueur, MN, USA). CC was
124 produced by Teagasc (County Cork, Ireland). Skim milk (Kerry Ingredients, County
125 Kerry, Ireland) was used to produce MC by a pressure driven process with 100 kDa
126 molecular weight membranes and then the obtained retentate was vacuum
127 evaporated to increase the solid content to approximately 38%. The concentration
128 process was performed at 65 °C. Finally, the MC powders were obtained by a spray
129 drying process, where the inlet and outlet temperatures were 180 °C and 85 °C, and
130 the drying air-flow rate was 750 m³·h⁻¹. Before the measurements, all the powders
131 were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 45 °C overnight to obtain the
132 final moisture content of about 1.5% and then kept in the desiccators.

133 *2.2 Agglomeration process*

134 The agglomeration process of all these milk protein powders was carried out by
135 a top-spray fluid bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Iowa,
136 USA). 50 g of each model powder was fed into the product vessel. As different milk
137 powders have different fluidisation behaviours in the fluidised bed, the appropriate
138 upward flowing air stream from 30 L·min⁻¹ to 250 L·min⁻¹ was adjusted for the
139 fluidisation of each powder (MPI: 200 L·min⁻¹; WPI: 70 L·min⁻¹; MC: 250 L·min⁻¹; SC:

30 L·min⁻¹; CC: 40 L·min⁻¹). Meanwhile, the adjustable amount of 15% lactose solution binders, based on the different granulation behaviours of these milk protein powders, were injected by a peristaltic pump (1 mL·min⁻¹). (25 g liquid was used for MPI, MC and CC granulation process, while WPI and SC needed 20 g and 10 g binders respectively.) The air pressure on the nozzle was 1 Bar. When the lactose binders had been used up, the agglomerates were dried by air for another 15 minutes at 50 °C. After that, all agglomerated powders continued to be dried in the vacuum oven together with the standard powders to ensure similar moisture content.

2.3 Wettability measurements

Wetting process can be described as: firstly, the interface of solid and gas is replaced by the interface of solid and water; secondly, inward diffusion of the liquid through the capillary structures of the porous powder particle (Yuan & Lee, 2013). Three methods were used to quantify the wettability of powders. Wetting time by immersionsal wetting procedures can be used as an initial screening and distinguish between powders with general good or poor wettability. Modified Washburn method by capillary rise wetting was used to describe the water diffusion capacity of these powders, while contact angle in spreading wetting procedure is a widely used index to evaluate the wettability by water droplet overcoming interfacial tensions between the solid and gaseous phase.

2.3.1 Wetting time

This traditional method evaluates the wettability by measuring the time required to achieve complete wetting. A set quantity of powder is gently discharged onto the surface of water and allowed to immerse spontaneously without agitation. Powder

wetted in less than 60 seconds is usually considered easy to wet while powder which takes longer than 120 seconds is considered non-wettable. Thus, in this study, 6 g of each sample was dropped into a 400 ml beaker containing 100 ml of distilled water at 20 °C (GEA Niro, 2005). The beakers were chosen as the same size with a diameter of 70 mm and a surface area of approx. 38.48 cm². Wetting time is recorded by a timer and all the measurements were repeated three times. Images of WPI particles were also captured by an optical microscope (Olympus BX51M) just after the particles contacted with water on glass slides. Images taken at different magnifications were used to show the formation of external layers outside the particles surface, which restrained the water from further wetting of the particles.

2.3.2 Modified Washburn method

The wettability of powders can also be measured by the Washburn method (Washburn, 1921). The detailed principles of a modified Washburn method including the instrument was described in the study of Ji, et al. (2015). It is based on a capillary rise wetting procedure which quantifies the wettability by the weighing of the additional mass of wetted powder as a function of time. A 2 g sample was used each time in this study and was loaded into a cylindrical glass tube with an open base bottom, which was covered by both a piece of filter paper and gauze. After that, the tube was fixed just above the surface of water which allowed the water to penetrate into the particles by capillary force. Finally, the additional mass of wetted powder was recorded at 10 minutes. All the measurements for each sample were repeated three times.

2.3.3 Contact angle

Contact angle (θ) is a widely used primary parameter to quantify the wettability of a solid surface by a liquid (Yuan, et al., 2013). A small contact angle ($\theta < 90^\circ$) represents good wettability for the solid, and a large contact angle ($\theta > 90^\circ$) represents poor wetting behaviour. As the wetting behaviour is a dynamic process that liquid penetrate into powder bed, in this study, it was followed by observing the changes of contact angles. An optical tensiometer (Attension Theta, Biolin Scientific Ltd., Espoo, Finland) was used to measure the contact angle based on sessile drop spread wetting. A 12 μL deionised water droplet was gently dripped on the surface of the powder substrate to carry out the dynamic live measurements at a temperature of 20 $^\circ\text{C}$. The powder substrate was prepared by a leveller to ensure a smooth surface formed when measuring the tangent angle at the contact point of the three phases. The change of contact angle was recorded as a function of time and each sample was measured five times.

2.4 Dispersibility and solubility measurements

2.4.1 Particle size measurements

In general, the dispersion process corresponds to the decrease of particle size, due to the release of materials from the surface of primary particles (Fang, Selomulya, Ainsworth, Palmer, & Chen, 2011). Thus, the change of particle size distribution (PSD) of the suspension during agitation is an applicable method to monitor the dispersion process of milk protein powders, especially for the case of casein-dominant powders with poor dispersibility (Mimouni, et al., 2009). A Malvern Mastersizer 3000 (Malvern Instruments Ltd, Worcestershire, UK) equipped with a 4 mW He-Ne laser operating at a wavelength of 632.8 nm was used to measure the PSD in this study. The samples were diluted in a 120 ml dispersion unit, which was

filled with $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ distilled water and agitated at a speed of 2000 rpm. The appropriate amount of each milk protein powder was weighed out in order to reach the ideal level obscuration of 8% for the machine. 5 mg of MPI, agglomerated MPI and MC were precisely weighed to make sure the results of specific surface area (SSA) are comparable, while WPI, SC, CC and their agglomerates were weighed 100 mg for the measurements. Both PSD and SSA were continuously measured by 2 minutes intervals as the particles were mixed, until D (50) reached approx. $1\mu\text{m}$ (D (50) is defined as the diameter of 50% particles). Triplicate measurements were carried out for each powder.

2.4.2 Sediment height

Light transmission technology together with an analytical centrifuge (L.U.M. GmbH, Berlin, Germany) was used to measure the sedimentation behaviour of samples. Initial sediment and compressed sediment can be exhibited by the varied intensities of the transmission of NIR light based on different optical density in suspension along the sample cell during the centrifugation (Crowley, et al., 2015). The sediment height was determined by the area of greatest optical density, which is the area of lowest transmission value having subtracted the steady-state value caused by the cell bottom. In this study, 1.5 g of each of the samples was rehydrated into 100 mL $25\text{ }^{\circ}\text{C}$ deionised water to create 1.5% (w/v) concentration suspension. A magnetic stirring bar (length 2.5 cm) was used to agitate the suspension at 400 rpm for 30 minutes, and then followed by sampling 400 μL at a constant distance (1 cm) from bottom of the beaker to fill into polycarbonate cells. Two centrifugations were set up for the measurements, which included firstly 36 g for 10 minutes and then followed by 168 g for a further 10 minutes. The measurements were performed every

234 10 seconds for the first 10 minutes 36 g centrifugation and then every 60 seconds for
235 next 10 minutes 168 g centrifugation.

236 *2.5 Scanning electron microscopy*

237 2 g of standard MPI powder were added to 100 mL distilled water to create the
238 2% (w/v) suspension. Stirring was performed by an overhead mixer (Eurostar 40
239 digital, IKA, Staufen, Germany) and a 4-bladed stirrer of 50 mm diameter (R 1342,
240 IKA) for different rehydration time at 25 °C (60 minutes, 90 minutes and 150 minutes).
241 One or two drops of each MPI suspension was deposited for 5 minutes on the silicon
242 substrates, which were rinsed by 100 mM phosphate buffer (pH=7) in advance. 3%
243 glutaraldehyde solution was used to fix the chemical structures of rehydrated milk
244 protein for 15 minutes (Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2010a). After
245 that, distilled water was used to wash the samples to remove the fixing chemicals.
246 The samples were dehydrated by graded ethanol, which were 50%, 70%, 90% and
247 100% (Dalglish, Spagnuolo, & Goff, 2004), and then they were further dried in a
248 desiccator with P₂O₅ until they were suitable to be observed by scanning electron
249 microscopy in a vacuum environment ($\sim 5 \times 10^{-6}$ mbar). A field emission scanning
250 electron microscope (Zeiss Supra, Carl Zeiss Microscopy GmbH, Jena, Germany)
251 was used for imaging at 1.5 kV.

252

253 **3. Results and discussion**

254 *3.1 The wettability of high milk protein powders*

According to the results of the immersion wetting procedure (Table 2), all of the milk protein powders are difficult to wet with water, due to their particles floating on the surface of the water and not sinking completely below the surface even after 20 minutes. It is not surprising because dairy powders with high protein content (>80%) are usually hydrophobic (Havea, 2006; Hussain, Gaiani, & Scher, 2012). Fig. 1 shows the WPI particles coated by layers just after contacting water. An impermeable layer was formed at the powder/water interface. This may result in the non-hydrated regions, where water had no access to penetrate into the particles. The traditional wettability method based on immersion wetting process provides an initial screening of the milk protein powders. The Washburn method was used to further differentiate these powders with poor wetting behaviours, as illustrated in Fig. 2. This shows that MC and CC uptake the most weight of water among all the milk protein powders, which were 0.469 g and 0.555 g, respectively. WPI and SC only adsorbed less than 0.1 g water in 10 minutes because water cannot penetrate into these powders spontaneously under the high contact angle ($\theta > 90^\circ$) and negative capillary pressure (Lazghab, Saleh, Pezron, Guigon, & Komunjer, 2005; Palzer, Sommer, & Hiebl, 2003). Therefore, milk protein powders, especially WPI and SC, are believed to very quickly reach the point at which the weight of water balances the capillary pressure.

Contact angle (θ) based on the droplet spreading wetting is also a commonly used index to evaluate the wettability of powders (Gao & McCarthy, 2006). It considers the changes in θ values as a function of time to quantify the dynamic process other than a static state (Mittal, 2006). As shown in Fig. 3A, it can be seen that the contact angle of MC reduced significantly with a final angle of 20° in just about 10 seconds, which showed the best wetting behaviours of all powders.

However, for MPI powder, the water droplet took a much longer time (280 seconds) to reach an equilibrium angle. Moreover, in Fig. 3B, CC, SC and WPI were believed to have extremely poor wettability, due to the high initial contact angles only changing by about 10° (CC & SC) and 40° (WPI) respectively, even after 300 seconds of measurement. The contact angle results were consistent with the results based on Washburn measurements, except for CC, which took up the most water weight by capillary force. This may be because when CC particles contacted water, they seemed to quickly adsorb water and form a thick gel-like film. That may cause a certain amount of water to combine with CC particles and the formed film was likely to prevent further water penetration. However, the precise explanation is still unknown and needs further study in the future.

3.2 The dispersibility and solubility of high milk protein powders

The dispersibility of milk protein powders can be quantified by the light scattering method, as it is used to measure the changes of particle size during powder dispersion (Ji, et al., 2015). In Fig. 4A&B, MC and MPI powders exhibited slow dispersion, based on the long mixing time required for the migration of particle size from the original size (about 50 µm) to the size when particles were mostly solubilised (below 1 µm). MC took approximately 20 minutes to reach an equilibrium size while MPI needed 40 minutes to reach complete dissolution. The particle size (D50) of CC powder remained at about 80 µm, which suggests that the CC particles were mostly not dissolving into water during the 90 minutes. In Fig. 4B, SC exhibited very good dispersion behaviour as its particle size decreased dramatically below a size of 1 µm within just 6 minutes. WPI disappeared very quickly within 2 minutes, as the machine did not detect any signals of particles after 2 minutes mixing. (The

dissolved WPI are nanoscale, which is out of detecting range.) At the same time, it is interesting to see that the particle size of MC, MPI and CC increased over the initial couple of minutes. This is due to particles absorbing water just following the wetting stage and this swelling process leads to the increase in particle size at the first stage of dispersion. The same phenomenon was presented by others (Bhandari, Bansal, Zhang, & Schuck, 2013; Gaiani, et al., 2006).

Besides the measurement of particle size, sedimentation is also used to describe the solubilisation behaviour of powders. As explained in the Methods section, sediment formation is determined according to the intensity of light transmission, due to the compressed sediment created the area of greatest optical density (Crowley, et al., 2015). Thus, the lowest transmission value is observed and used to calculate the sediment height in Table 3. It can be seen that WPI and SC have no sediment at all after 30 minutes rehydration and no matter 36 g or 168 g centrifugation. These findings were consistent with the previous results based on the rate of change of particle size, which means that WPI and SC are both powders with good dispersibility from the initial particle size to the lower measurement limit of the machine. MC, MPI and CC all had sediment with a height higher than 3 mm under 36 g centrifugation and about 2.5 mm height under the 168 g centrifugation, after 30 minutes rehydration. This shows that micellar casein-dominant powders, including MPI and MC, require long times to be completely rehydrated because of the strong interactions between the micellar structures, and this has also been concluded by others (Crowley, et al., 2015; Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2010b; Schuck, et al., 2007). The structures mainly consist of casein micelles, linked together by calcium phosphate bridges and surrounded by a layer of casein molecules which helps to stabilize the micelle in solution (Farrell, et al., 2013;

McMahon & Oommen, 2013; Schokker, et al., 2011). Thus, the release of micelles from powder particles is time-consuming. However, the artificial non-micellar form of caseinate powders, e.g. SC, are more easily dissolved into water (Pitkowski, et al., 2009). It is surprising to find that CC showed extremely poor solubility in water at a temperature of 25 °C, which is totally different from the behaviour of SC. Some papers report similar results, including calcium induced aggregation and precipitation of caseinate solution due to the specific binding of calcium which results in aggregation and precipitation that is considered to be hydrophobic (Guo, Campbell, Chen, Lenhoff, & Velez, 2003; Thomar, Benyahia, Durand, & Nicolai, 2014). Consequently, CC powders may be difficult to reconstitute into water again, but this still depends on pH and temperature (Moughal, et al., 2000).

3.3 The effect of agglomeration on the wettability and dispersibility of high milk protein powders

3.3.1 The effect of agglomeration on wetting behaviours

Firstly, Fig. 2, which is based on the capillary rise wetting procedure, shows that all the agglomerated powders adsorbed more water than the standard powders. Even if the agglomerated WPI, SC and CC formed similar impermeable films as they formed on the surface of the standard powders when contacting the water, the agglomerates still presented comparatively better wetting behaviours. The agglomerated MC was shown to improve in wettability by the most, with a water uptake of 4.9 g in 10 minutes. The agglomerated MPI also showed an increase of about 0.8 g. The agglomeration process not only largely increased the size of milk protein particles, but also created the granules with high porosity due to the formation of void structures (Turchiuli & Castillo-Castaneda, 2009). Hence,

agglomerated powders usually have better wettability than standard powders, as liquid is more easily able to permeate between the powder particles and wet them more quickly (Lazghab, et al., 2005). Similar results were observed from Fig. 3ABC, which compared the droplet contact angles of agglomerated powders and standard powders. The agglomerated MPI took about 50 seconds to obtain the equilibrium angle of 40°, which was a significant decrease in time when compared to the non-agglomerated powder. A similar trend was found for agglomerated WPI, which displayed lower contact angles over the 300 seconds measurement time. In comparison to WPI and MPI, the agglomeration process appeared to only slightly enhance the wettability of MC, but this is because the contact angle changed so much more rapidly for MC. For agglomerated CC powder, only a small difference of 20° was found after water contacting particles for 300 seconds, and there was no obvious difference between SC and its agglomerate for the whole process, as the external layer prevented the droplet penetrating into the particles.

Although large particles with loose and porous structures potentially explain the beneficial influence of agglomeration on the wettability of these milk protein powders (Ji, et al., 2015; Yuan, et al., 2013), Table 2 shows that most of the agglomerated powders still needed longer than 20 minutes for completely wetting (only agglomerated MPI and MC had significantly shorter wetting times of about 480 seconds and 320 seconds, respectively). This is because wetting behaviour depends mainly on the hydrophobicity of milk protein powders, more than their physical and structural properties. In other words, it is not surprising to see that agglomerated WPI, SC and CC maintained long wetting times, as agglomeration can't change the native properties of milk protein powders or completely change the difficult-to-wet powders into easy-to-wet ones (Forny, et al., 2011).

3.3.2 *The effect of agglomeration on dispersion and solubilisation behaviours*

As described previously, SC and WPI powders dispersed rapidly into water. The effect of agglomeration on these two powders was not significant, as it is difficult to see differences in the dispersion process for the agglomerates and the standard powders based on the measurements of particle size changes (Fig. 4B). Same conclusions are determined from Table 3, where there were no sediments detected after 30 minutes rehydration with 36 g or 168 g centrifugation. Therefore, it can be concluded that the influence of agglomeration process on the WPI and SC is limited as they already had good dispersibility and solubility. For the slow-dispersing powders (Fig. 4A), there was no measured size increase or swelling at the beginning of the dispersion process, which means that agglomerates have shorter swelling time based on their quicker penetration by water (Ji, et al., 2015). Besides that, the rate of change of MPI and CC agglomerate size were shown as being almost the same as their non-agglomerated powders. The agglomerated MC took significantly longer to disperse than the non-agglomerated MC, which means agglomeration prolonged the MC dispersion process (Gaiani, et al., 2007; Schuck, et al., 2007). It is commonly believed that the slow dispersion process of MPI or MC is caused by the slow water transfer into the “skin” of inter-linked casein micelles (Mimouni, et al., 2010a). The agglomeration process just modifies the physical structures by binding particles together but does not accelerate the release of materials from the primary particles, which is responsible for the extended dispersion time of micellar casein powders. Generally, the possible ways to increase the dispersion rate are based on the destruction of the micellar structure by adding mineral salts, e.g. phosphate or citrates solutions (Schuck, et al., 2002), or by the physical approach of ultrasonication (McCarthy, Kelly, Maher, & Fenelon, 2014). The casein micelles are

dissociated and then quickly dissolved into water. Therefore, fluidised bed agglomeration process played no significant beneficial role on the dispersion of micellar casein powders. Similarly, the solubility of CC precipitate is also influenced by the chemical environment rather than the physical structural modification produced by agglomeration (Thomar, et al., 2014).

Consequently, it may be concluded that the effect of agglomeration on the wettability and dispersibility of dairy powders are different. According to the results of five dairy powders that were investigated in this study, their wetting behaviours were found to be dependent on the modification of physical properties while their dispersing behaviours were mainly controlled by the native dispersibility of primary particles. Thus, the agglomeration process may accelerate the rehydration of powders whose wetting process is their rate-limiting step, such as WPI. If for the powders with dispersing as their rate-limiting step, such as MC, agglomeration plays no positive role and may even negatively influence rehydration. However for MPI, both wetting and dispersing processes are rate-limiting steps. Hence, it is necessary to evaluate the effect of agglomeration on a complete rehydration process to find out whether it shortens or prolongs the rehydration time (Ji, et al., 2015). Some other powders like SC and CC may have problems in wetting or dispersing due to the individual native hydration behaviours (Post, Arnold, Weiss, & Hinrichs, 2012). Therefore, agglomeration is believed not to significantly change their rehydration properties.

3.4 The mechanism for the rehydration process of MPI powders

The MPI powder exhibited how the specific surface area (SSA) and D (50) of particles changed as they dispersed and dissolved into water, which can be

observed in Fig. 5A. Different from the gradually decrease of D (50), it is interesting to find that the SSA increased very slowly for the first 20 minutes but it is followed by dramatic growth for the next 40 minutes. It can be attributed to the disruption of the aggregates and the release of the primary particles with smaller size at the beginning of the dispersion process, but it only caused a slight increase in SSA. However, after 20 minutes of stirring time, the materials from micellar structures started to be released into the surrounding water. In that case, the SSA increased significantly as more and more materials dissolved. It also can be explained by Fig. 5B, which exhibited the volume density of unagglomerated MPI particles with different size for the different stirring time. Similarly, the volume of large particles decreased slowly at first 20 minutes but decreased sharply due to the collapse of the structures. Therefore, the dissolved small particles appeared from 20 minutes and the volume of these particles increased rapidly during the solubilisation process.

The dissolution mechanism of standard milk protein isolate can be described in the following steps: i) powder particles come into contact with water; ii) particles start to de-agglomerate from aggregates into the individual primary particles; iii) the continuous release of materials from the surface of these primary particles into aqueous phase; iv) erosion of the external layer of particles and finally full dissolution. It considers that milk protein powder produced by atomization in a spray-dryer usually consists of primary particles and these particles contain internal vacuoles based on the spray dry process (Bhandari, et al., 2013; Fang, et al., 2011). Thus, the dispersion process of milk protein isolate is mainly contributed by the disappearance of the aggregates of primary particles and also the release of micellar casein materials (McKenna, 2000).

The SEM images in Fig. 6 clearly demonstrate the erosion of the particle surface under the effect of water transfer during the rehydration process. Before wetting by water, MPI particles have smooth surfaces, which can be seen from Fig. 6A. After wetting and dispersing for a period of time, the most significant difference is the increase in the roughness of the surface of the rehydrating particles. This is due to water beginning to penetrate the external layer of micellar casein (Fig. 6B). For the longer rehydration periods, a much rougher surface was observed and large breaches appeared to indicate the further erosion of the outer skin by water (Fig. 6C), but the particle still did not completely break down due to the strong interactions between the micellar structures. Finally, sufficient materials were solubilised and the insides of micelles were exposed leading to the eventual collapse of the structures (Fig. 6D). Therefore, it is believed that the compactness skin outside of micellar casein particles is responsible for restraining the individual micelles into the surrounding liquid phase.

The agglomerated MPI were found to undergo a very similar solubilisation process as the non-agglomerated MPI with the only difference being at the beginning of the dispersion (Fig. 5A). The size of the agglomerates decreased sharply to about 75 μm , which is almost the same as the unagglomerated particles after swelling. It is due to the lactose solid bridges linking the particles being easily dissolved and the agglomerates being quickly dispersed into the non-agglomerated particles. This is exhibited by the schematic of agglomerated MPI rehydration in Fig. 5A. (Forny, et al., 2011; Schubert, 1987). After that, there was no significant difference between agglomerates and non-agglomerates during the solubilisation process. Consequently, agglomerated MPI is believed to have one additional step at first, which is the dissolution of the solid bridges.

476

477 **4. Conclusion**

478 The rehydration properties of five common high protein milk powders and their
479 agglomerates were investigated in this study. The application of a variety of
480 measurement techniques provided a more complete insight into the rehydration
481 behaviour of the powders which exhibited different wetting and dispersion
482 behaviours. Poor wettability was the rate-limiting factor for WPI and SC rehydration,
483 while poor dispersibility was the main problem for MC rehydration. Both MPI and CC
484 displayed both poor wettability and poor dispersion. Agglomeration had a beneficial
485 role on the droplet penetration process, and this was more significant for WPI and
486 MPI powders. In capillary rise wetting procedure, agglomerated MPI and MC present
487 the significantly better wettability. Agglomeration had no beneficial effect on
488 dispersibility as it does not influence the structure of the primary particles. In fact, it
489 may even have slowed dispersion by adding the additional step of dissolving the
490 solid bridges between the particles.

491

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617

Table 1 Composition and particle size of milk protein powders

Table 2 Wetting time of milk protein powders

Table 3 Sediment height after 36 g and 168 g centrifugation for both 10 minutes

Fig.1. Optical microscopy images of WPI particles, upon which formed the impermeable hydrophobic layers when wetted by water. The particles were dispersed in water on glass slides. (Left: scale =200 μm ; Right: scale = 50 μm)

Fig.2. Weight of adsorbed water for samples (MPI, WPI, MC, SC, CC and their agglomerates) by capillary rise wetting after 10 minutes.

Fig.3ABC. **A:** The change of contact angle ($^{\circ}$) as a function of time for MPI, MC and their agglomerates using the sessile drop technique in approx. 20 $^{\circ}\text{C}$ temperature. **B:** The change of contact angle ($^{\circ}$) as a function of time for WPI, SC, CC and their agglomerates. **C:** Images of MPI, WPI and MC as examples to show how the water droplets penetrated into powders by the different time intervals.

Fig.4AB. **A:** Particle size D (50) measurements of dispersed particles of MPI, CC and their agglomerates for every 2 minutes in $25 \pm 2^{\circ}\text{C}$ water. **B:** Particle size D (50) measurements of SC, MC and their agglomerates. (WPI quickly dispersed into water and Mastersizer cannot detect its particle size. Even agglomerated WPI can only be measured for the first 4 minutes)

Fig.5AB **A:** Schematic of MPI and agglomerated MPI particles rehydration in water, based on the change of particle size D (50) and specific surface area as a function of time. **B:** Volume density (%) based size distributions of dispersing MPI particles measured as a function of time. It showed the volume concentration of both undissolved and dissolved powder particles.

Fig.6ABCD SEM images of MPI particles after different rehydration time. **A:** spray-dried particles before rehydration (1.4 kV); **B:** particles after 60 minutes rehydration (1.5 kV); **C:** particles after 90 minutes rehydration (1.5 kV); **D:** particles after 150 minutes rehydration (1.5 kV). The white arrow in panels C indicates the presence of large breaches caused by water erosion.

Table 1 Composition and particle size of milk protein powders

| | MPI | | WPI | | MC | | SC | | CC | |
|-----------------------------|---------------|----------------|---------------|----------------|---------------|----------------|---------------|----------------|---------------|----------------|
| | NA | A | NA | A | NA | A | NA | A | NA | A |
| Protein (%, w/w) | 86.0 | 82.0 | 90.0 | 84.0 | 84.0 | 80.1 | 88.0 | 86.0 | 87.0 | 81.4 |
| Lactose (%, w/w) | 1.0 | 6.2 | 1.0 | 6.5 | 2.0 | 7.3 | 0.1 | 2.4 | 0.2 | 6.6 |
| Moisture (%, w/w) | 4.0 | 5.0 | 5.0 | 5.2 | 5.0 | 6.8 | 5.7 | 5.9 | 5.5 | 6.3 |
| Particle size D(50) (µm) | 49.3 ± 1.5 | 188.0 ± 2.0 | 54.5 ± 1.8 | 179.0 ± 4.0 | 50.0 ± 1.4 | 220.0 ± 6.0 | 85.0 ± 1.0 | 208.0 ± 3.0 | 65.7 ± 2.1 | 194.0 ± 3.0 |

*NA = non-agglomerated; A = agglomerated.

Table 2 Wetting time of milk protein powders

| | | MPI | WPI | MC | SC | CC |
|------------------------------|----|-----------|-------|----------|-------|-------|
| Wetting time (seconds) | NA | >1200 | >1200 | >1200 | >1200 | >1200 |
| | A | 480 ± 120 | >1200 | 320 ± 14 | >1200 | >1200 |

*NA = non-agglomerated; A = agglomerated.

Table 3 Sediment height after 36 g and 168 g centrifugation for both 10 minutes

| | | MPI | | WPI | | MC | | SC | | CC | |
|----------------------|----------------|-------------|-------------|-----|---|-------------|-------------|----|---|-------------|-------------|
| | | NA | A | NA | A | NA | A | NA | A | NA | A |
| Sediment height (mm) | 36 g x 10 min | 3.25 ± 0.05 | 2.75 ± 0.11 | 0 | 0 | 3.23 ± 0.12 | 3.65 ± 0.23 | 0 | 0 | 3.63 ± 0.17 | 3.87 ± 0.17 |
| | 168 g x 10 min | 2.45 ± 0.05 | 1.95 ± 0.10 | 0 | 0 | 2.62 ± 0.10 | 2.78 ± 0.15 | 0 | 0 | 2.57 ± 0.12 | 2.70 ± 0.06 |

*NA = non-agglomerated; A = agglomerated.

Figure 1

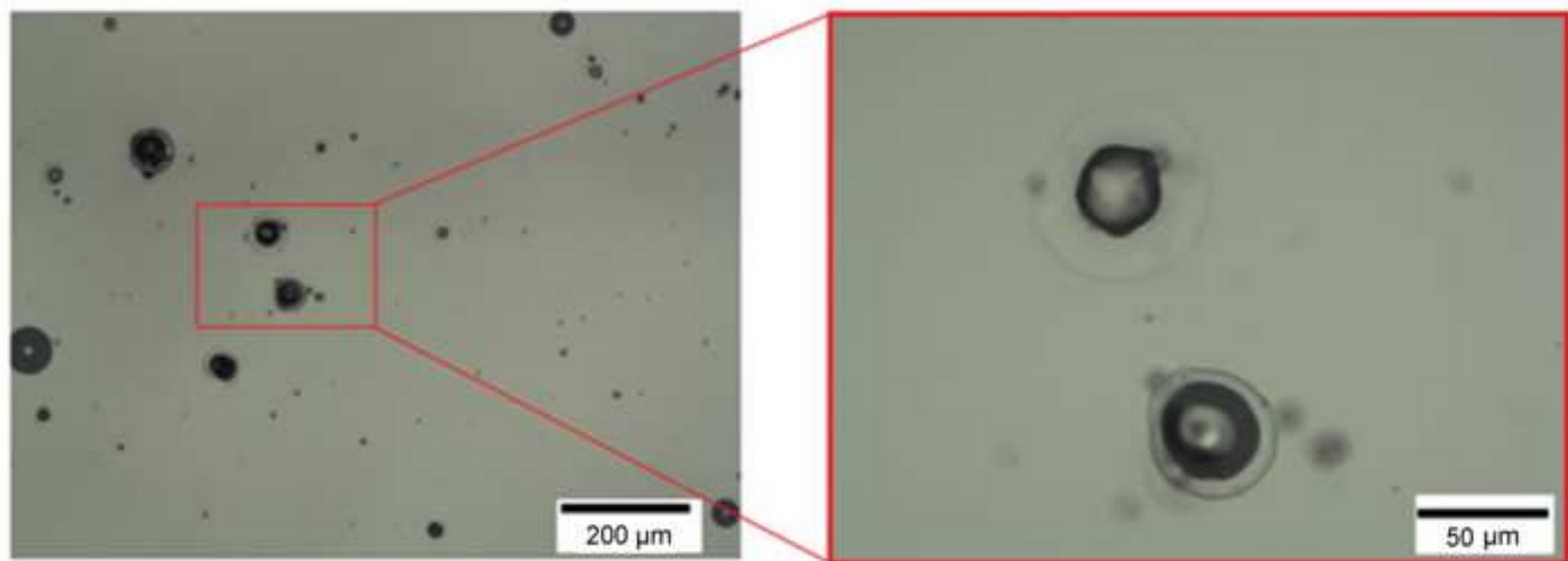


Figure 2

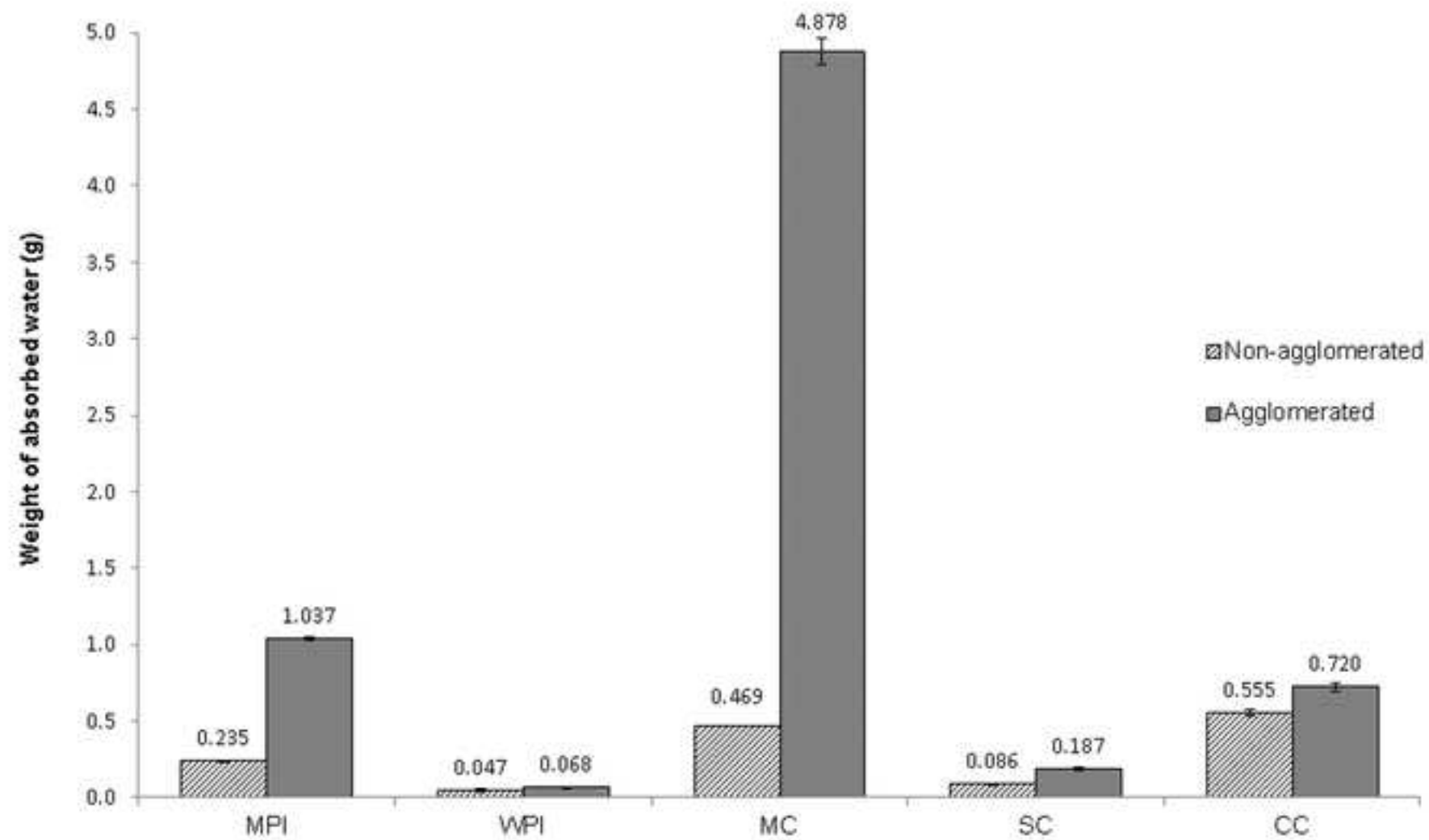


Figure 3

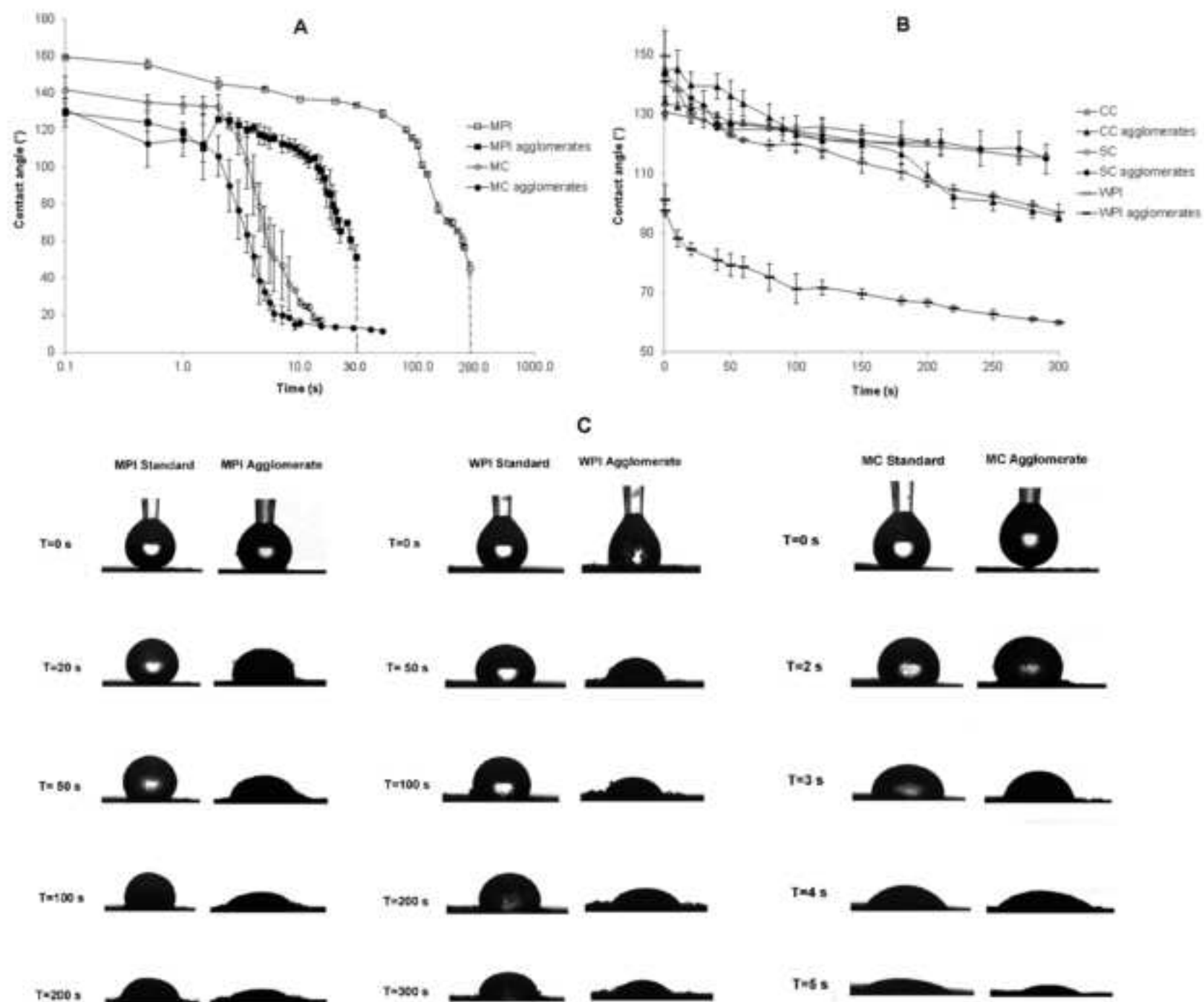


Figure 4

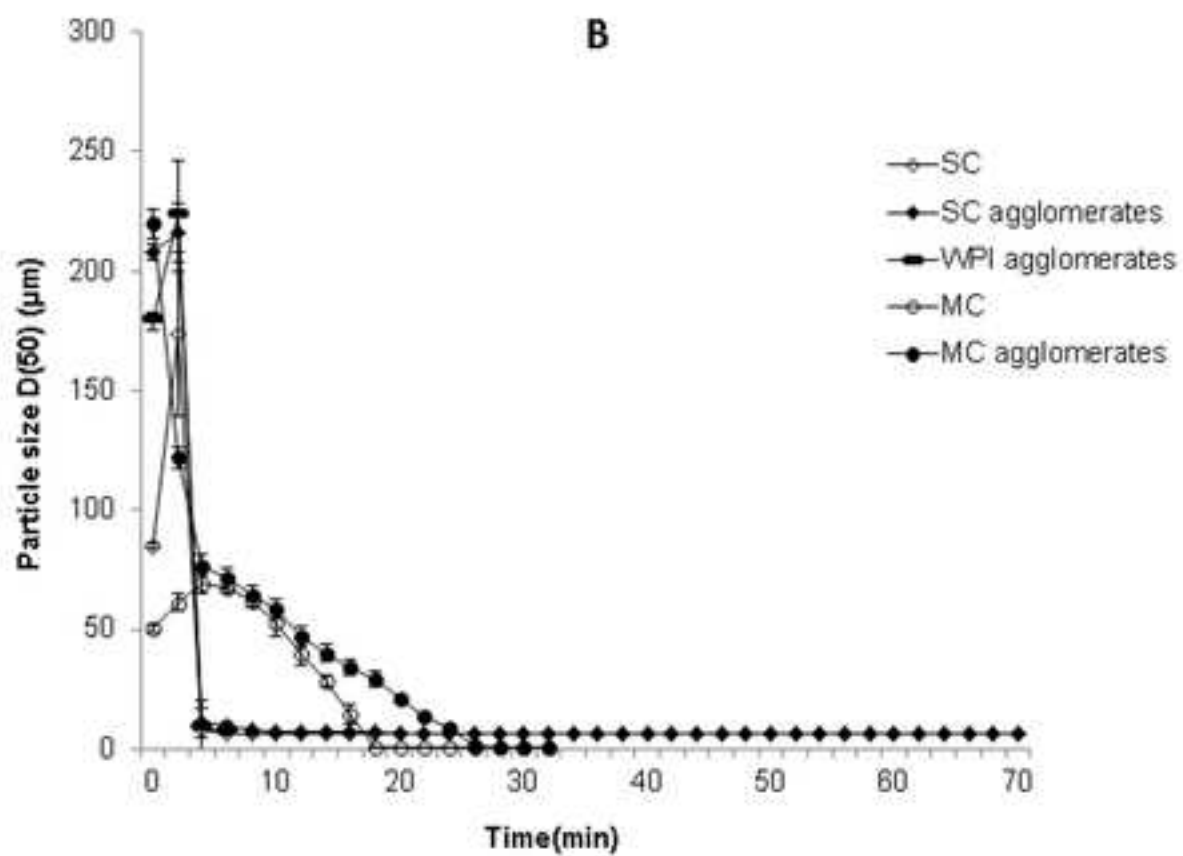
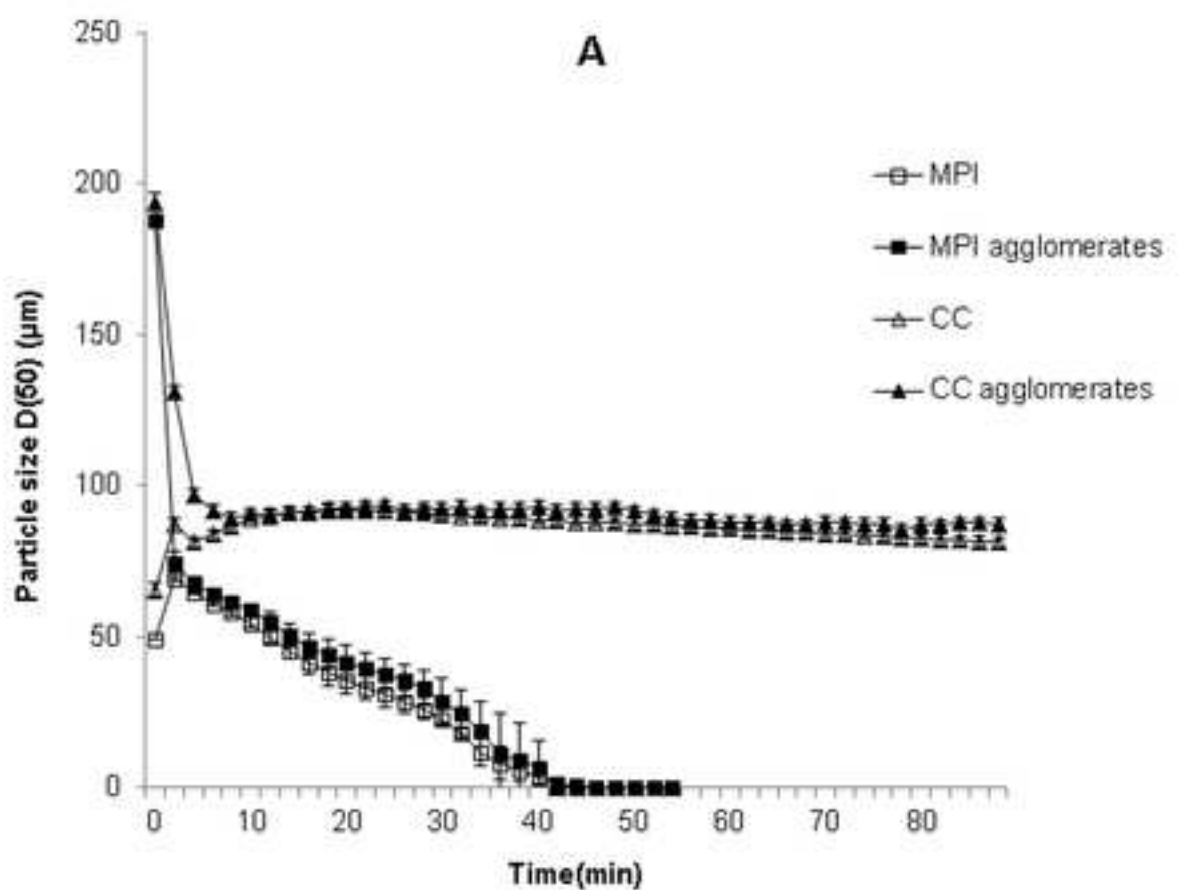


Figure 5

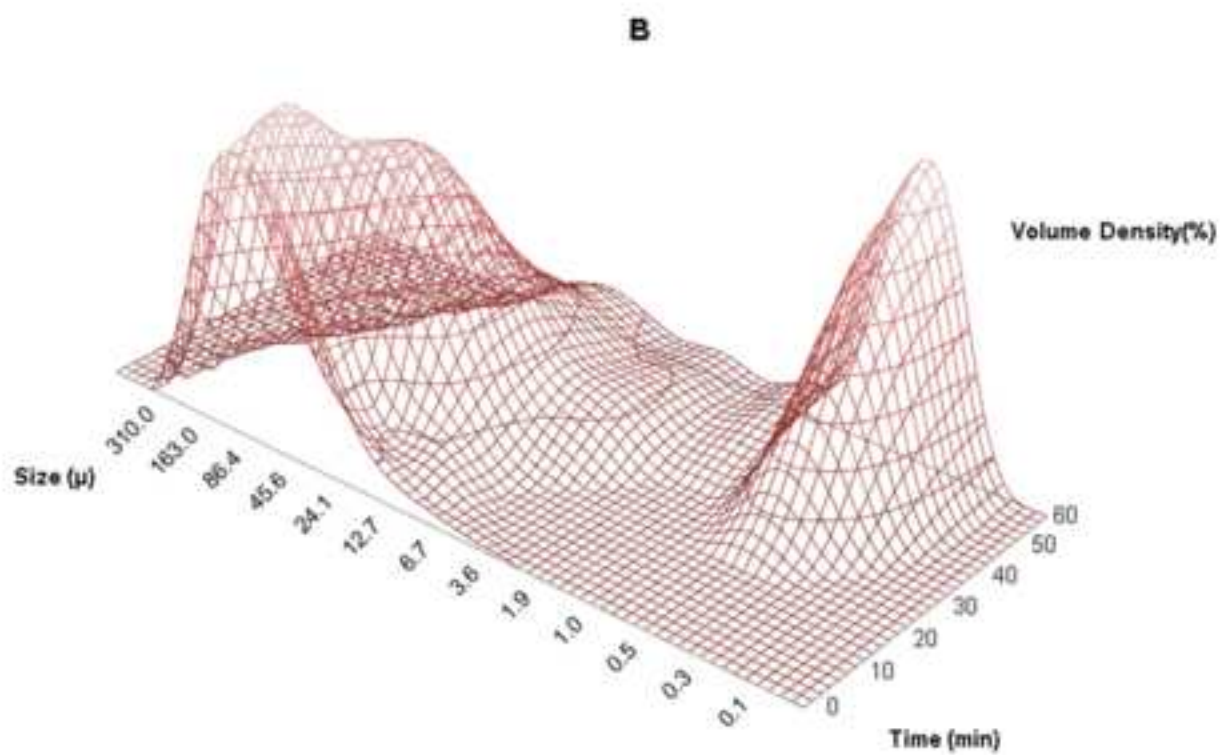
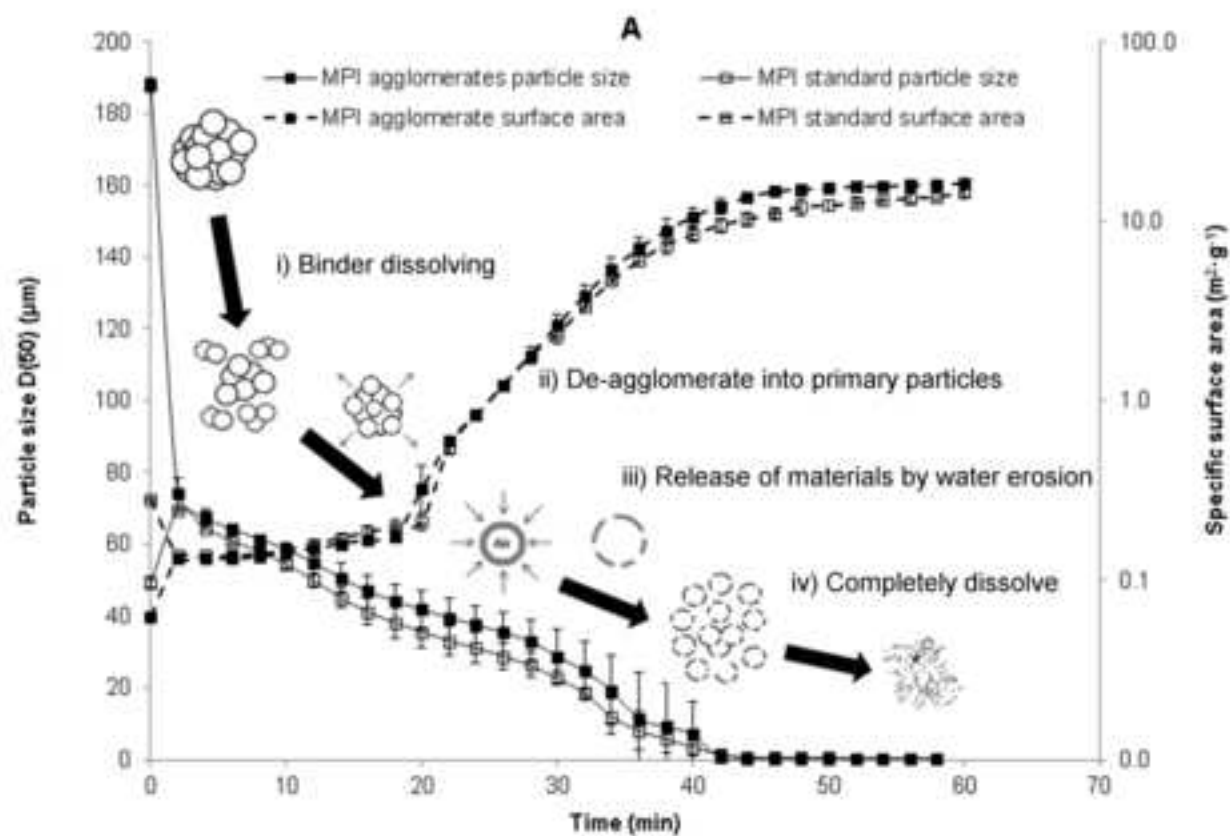


Figure 6

