CORA Cork Open Research Archive
Cartlann Taighde Oscailte Chorcaí

Title	The structural modification and rehydration behaviours of milk protein isolate powders: The effect of granule growth in the high shear granulation process
Authors	Ji, Junfu;Cronin, Kevin;Fitzpatrick, John;Maguire, Pierce;Zhang, Hongzhou;Miao, Song
Publication date	2016-05-30
Original Citation	Ji, J., Cronin, K., Fitzpatrick, J., Maguire, P., Zhang, H. and Miao, S. (2016) 'The structural modification and rehydration behaviours of milk protein isolate powders: The effect of granule growth in the high shear granulation process', Journal of Food Engineering, 189, pp.1-8. doi: 10.1016/j.jfoodeng.2016.05.018
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1016/j.jfoodeng.2016.05.018
Rights	© 2016, Elsevier Ltd. All rights reserved. This manuscript version is made available under the CC BY-NC-ND 4.0 license. - https://creativecommons.org/licenses/by-nc-nd/4.0/
Download date	2026-11-01 08:38:47
Item downloaded from	https://hdl.handle.net/10468/14943

UCC
University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

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

Junfu Ji [a, b], Kevin Cronin [b], John Fitzpatrick [b],Pierce Maguire[c], Hongzhou Zhang [c], Song Miao [a, *]

[a] *Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland*

[b] *School of Engineering, University College Cork, Cork, Ireland*

[c] *School of Physics & CRANN, Trinity College Dublin, Dublin 2, Ireland*

***Corresponding author.**

E-mail address: song.miao@teagasc.ie (S. Miao)

© 2016. This manuscript version is made available under the Elsevier user licensehttp://www.elsevier.com/open-access/userlicense/1.0/

Abstract

The effects of granule growth in high shear granulation on the structuresand 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 are used to compare the densities, granule shapesand 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 denselypackedstructures allowed the granules to be more easily wetted by water. The large granules showed quicker release of materials into water untilreaching a critical size, where more mechanical energyis potentially required for furthergranule break down.All the agglomerated MPI granules solubilised much more slowly than the standard MPI powder.

*Keywords:*Milk protein isolate, High shear granulation, Granule structure, Wettability, Dispersibility, Solubility

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 rolein industry, due to its convenience forprocess, preservation and transportation(Ann Augustin and Clarke, 2011).Milk protein isolate powdersare 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 dryingarenormallyfine particles withdense structures, thus itmay 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 issuespotentially restrictthe applications of milk protein powders, as powders are required to have good handling properties, as well as quick and complete rehydration behaviour 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 tostrongly 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 processesresult 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 atomizebinding 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 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 alsonecessary to find out if the high shear granulation process displays differentbeneficial roles on the milk protein powder due to its unique and special effects on the structural modification.

High shear granulationis a complex process and commonly consists of different groups of rate processes: 1) wetting and nucleation; 2) coalescence andconsolidation; 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 distributethe 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 secondaryagglomerates, 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

92 entrapped air and increase the internal pore saturation so as toreduce the granule
93 size and porosity,whichsignificantly influence the final structures of formed
94 granules(Barrera-Medrano et al., 2007).Consequently, it is necessary to investigate
95 how the differentgranule growth processes affect the structural formation of milk
96 protein powders during the high shear granulation. However, as the growth
97 processes always happen simultaneously and there is no clear definition to
98 distinguish them, it is difficult to characterise the granules by the individual growth
99 process(Hapgood et al., 2007). In that case, the granules with different particle sizes,
100 which werecaused bythese growth rate processes, will be used to compare the
101 structural and physical properties in this study.

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

Consequently, it isessentialto 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 usedin the high shear granulation, was purchased from Arla Food Ingredients (Viby J, Aarhus,Demark).

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 solutionwas added into the bowl by droplets at the dosing speed of 4 $mL \cdot min^{-1}$. 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 minutes, which made sure the total granule size distribution was

properly mono-dispersed. After that, a fluidised bed (VFC-Lab Micro flo-coater, Vector Corporation, Lowa, USA), which provided the air with a temperature of 50 ℃ and the flow velocity of 200 l·min^{-1}, was used to dry the granulesuntil 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/+75μm).The particles of sizelarger than 1000μm orthe 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℃temperature for 24 hours 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 Masterszier 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

166 Gas Pycnometer (AccuPyc II 1340, Micromeritics Instrument Corporation, Georgia,
167 USA). Sample was placed in the cell and purged with a flow of helium to degas the
168 cell by ten pressurisation cycles. All the density measurements were repeated at
169 least three times. Finally, the porosity was calculated using the tapped density and
170 the apparent density.

171 *2.4.2 Granule shape*

172 The shape of a granule is usually quantified by three parameters, which are
173 circularity, convexity and elongation. In this study, they were measured by Malvern
174 MorphologyG3 (Malvern Instruments Ltd, Worcestershire, UK). The detailed method
175 was described by Ji et al. (2015). Briefly, a volume of sample was dispersed
176 uniformly into a single layer on the glass plate. Then, the microscope was used to
177 observe these particles and give out the average values of circularity, convexity and
178 elongation. All the measurements were repeated at least five times.

179 *2.5Wettability*

180 *2.5.1 Wetting time*

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

186 *2.5.2 Capillary rise wetting*

187 Powder wettability can also be quantified by the Washburn method(Washburn,
188 1921), which is based on the powder capillary rise wetting behaviour. It measured
189 the liquid that penetrated into powders by recording its penetration length or
190 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 ℃temperature.After that, the additional mass of wetted powder was recorded in 10 minutes. 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 toquantify 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.

2.6Granule 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 Masterszier 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 minutes for a total of 140 minutes and at 25 ℃ ± 2 ℃temperature ranges. The results of D (50) and D (10) were presentedas a function of mixing time.

2.7Dissolution

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 ℃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 minutes), each suspension was centrifuged at 3000 g and 25 ℃for 10 minutes(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.

2.8Granule 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 x and 150 x) were performedrespectively, 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 SEMimages 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 granulesS5 had the highest apparent density and the larger granules had progressively lowerapparent densities. For bulk densities, it is interesting to find that largest granules S1 with 1075μm 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 to 425 μm, had the lowest loose and tapped densities of all the granules. The porosity values of all the samples are also presented inTable 1. Similarly, the MPI granules generally had significantly lower porosity 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 porosity 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 aggregatesfused by the standard particles. At the same time, they were solidified by the force of agitation, which

resulted in the less air entrapped and the small interstitial spacesin 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 volume among these particles(Iveson et al., 2001). It may be the reason why S3 and S4 have the comparatively lower bulk densities and higher porosity than other granules.When the secondary agglomeratesreached the critical size, the bonds werenot strong enough to connect other particles. In that case, the granules stopped growing andthey were highly deformed again by the mechanical solidification (Reynolds et al., 2005). Hence, as it showed in Fig.1 A&B, the more compacted largegranules S1 and S2 formed andthe particles were closely arranged on the surface. However, it is difficult to conclude the effect of granule growth precisely due to the formed granulesmay break into fragments by breakages. That will also influence the structures of obtained granules,which needs 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 hadboth highest circularity and convexity values of 0.891 and 0.965 respectively, which were the most spheroidal shape and smoothest surface ofall 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 smoothby the uniformly force from ploughshares and chopper(Litster and Ennis, 2013). As the granule size increased, it is found that

290 granules formedwith significantly lower circularity and convexity values.Especially for
291 S3, it had only 0.767 for circularity and 0.866 forconvexity,which is even lower than
292 that of unagglomerated MPI.In Fig.1C&D, it is also clear to see that S3 and S4 had
293 less rounded shapes. It is commonly considered that the agglomeratedsecondary
294 granules may cause irregular shaped particles and also rougher surfaces, due to the
295 bridges formed between particleswhich modified the shapes(Barrera-Medrano et al.,
296 2007; Hapgood et al., 2007; Reynolds et al., 2006). Furthermore, when granule size
297 reached S1 or S2, the coalescence stage is no longer the dominant growth process.
298 Their shapes again became more rounded and smoother than S3 or S4, by the
299 influence of further densification (Fig.1A&B). But for elongation, which is used to
300 quantify the ratio of particle length and width, there is no significant difference among
301 these granules with different particle size, because single granule was homogenised
302 based on the force from high shear agitation. Thus, their elongation values were all
303 about 0.26, while the standard MPI had a comparatively longer shape.

304 *3.2Effect of different granule sizes on the wettability of MPI*

305 *3.2.1 Wetting time by immersional wetting procedure*

306 According to the results in Table 3, the agglomerated granules, regardless of
307 the particle size, took significantly less time to be wetted by water than that of
308 standard powders. The wettability seemed to correspond to the particle size of
309 sampleswith larger granules showing better wettability.S1 and S2 displayedthe best
310 wettability taking less than 10 seconds to be fully wetted. The other granules all had
311 shorter wetting times than 60 seconds, which can be considered as the easy wetting
312 powders. However, the standard powders took more than 20 minutes to completely
313 immerse below the water surface, due toan impermeable hydrophobic layerformed to
314 separatethe water surface and dry powder(Ji et al., 2016).Thiswasnot a problem for

315 the agglomeratedgranules after high shear granulation process. The surface tensile
316 strength of the assembly of granules is reduced by the size enlargement when
317 contacting with water. Hence, the granules separated during wetting process rather
318 than adhering together as fine particles(Knight, 2001). However, particle size is not
319 the only factor that influences the wetting behaviours.Ji et al. (2016)demonstrated
320 that the agglomerated MPI produced by fluidised bed granulation, which had a
321 medianparticle size of about 180 μm, still floated on the water surface for more than
322 8 minutes. Therefore, the densely packed granules with higher density also
323 significantly improve the wettability of MPI due to there beingfewer pores in the
324 matrix(Hogekamp and Schubert, 2003).

325 *3.2.2 Capillary rise wetting*

326 From Fig.2, it can be seen that the agglomerated MPI granules absorbed
327 significantly more water by capillary force than the standard powders in 10 minutes.
328 The results are consistent with the wetting time measurements, the granules with
329 large size also have the better wettability based onthe capillary rise wetting
330 procedure. The standard MPI only adsorbed0.244 g water while S1 and S2 adsorbed
331 most, exceeding8.5 g water. This is due to the larger void spaces between each
332 granule, which causes a higher pore radius that results in a positive correlation with
333 the depth of liquid intrusion(Lazghab et al., 2005; Palzer et al., 2003; Yuan and Lee,
334 2013). This is shown by the Washburn modelas Eq. (1)(Washburn, 1921):

335 $$l^2 = \frac{\cos\theta \cdot r \cdot \gamma \cdot t}{2 \cdot \eta} \quad (1)$$

336 where l is the penetration depth of the liquid, η is liquid viscosity,γ is the liquid surface
337 tension, r is radius of pores, θ is the contact angle and t is time for penetration.Hence,
338 it indicatesthat the large pores between the particles result in greaterpenetration

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 μm, 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 witha median size of 180 μm. 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 seconds, which was much longer than that of the agglomerated MPI granules with different sizes. These granules took less than 10 seconds 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 seconds for the contact angle to decreaseto 40°. Thisis not simply due to the granule's high porosity, as the standard powders have an evenhigher value, as shown in Table 1. Thus, it is believed that the granules having larger voids betweenthe particles result in the easy-wetting behaviour(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 powder.

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.4A&B, 50%of the standard MPI particles werecompletely rehydrated into water in about 32 minutes, while the most of the agglomerated granules werefound to be more difficult to disperse based on the slower decrease of particle size. Particularly, there were almost no size changesfor S4 and S5 for the whole 140 minutes, which indicatedthat 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 phaseby the different releasing rates.In Fig.4A, the largest granulesS1 took the longest time of 130 minutesto reach 200 μm particle size, although its dissolutionrate was quickest of all. S2 and S3 also requiredmore than 100 minutes achieving a relatively stable particle size. It is surprisingto see that these three granules all finally decreased to a constant size, which is about 200 μm. Howeverfor S4 and S5, which had smaller sizes initially (111 μm and 75μm 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 minutes and the materials were solubilised in about 120 minutes. S3 also showed similar dispersionprocess but it began with smaller size and still was not totally dissolvedat 120 minutes.

Generally, the micellar casein that exists in milk protein powder has slow dispersion behaviour, due to its complex structures of inter-linked networkof casein

micelles(Mimouni et al., 2010; Schuck et al., 2007).However, the poor dispersibility of the agglomerated granules isdetermined by other more important factors. It can be explainedas the strong interactions for the granule structures, caused bysolidificationin 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 werethe most compacted, which led to the slowest release rate of materials(Hapgood et al., 2007). It is conceivable that the size of remaining particlescorresponds closely to the granule strength that can resist the agitation force, as higher mechanical energyis required to separate the primary aggregatesand 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 disperseand 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 minutes, while the largegranules took longer time to reach a peak in particle size. For example, the size of S1 can increase to about 1500 μm in 8 minutes. It is indicated that water

neededmore time to completely penetrate into the large granuleswith the longer diameter (Palzer, 2007).

3.3.2 Dissolution of MPI granules

Fig.5shows the dissolved MPI solids percentage in solution as a function of mixing time. The standard MPI displays the best dissolution behaviour compared with others, asnearly 60% of its solidsdissolved after 5 hours mixing time. The agglomerated granules displayed much lower dissolution ability withonly30% solids being solubilisedin the supernatant after 5 hours mixing; S4 and S5 with the smallest granule size showed the least dissolved solids of only about 25%.It is very similar to the results of dispersibility of the different granuleswhere 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 thusalso limited.

In addition, the solid percentage of all the samples increased comparatively quickly over the first 30 minutes and was then followed by slower dissolution behaviour for the next 300minutes. 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 processwere found to have modifiedphysical 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.

Thesemodifications made powders that were more easily wetted by water, especially for the large granules. At the same time, theyalso resulted in poorer dissolution due toprolonged water penetration into the denser structures. Comparatively, the large granules exhibited quicker release of materials into water untilreaching 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.

Acknowledgements

The study was supported financially by the Food Institutional Research Measure (FIRM) of the Department of Agriculture and Food and Marine Ireland under the project 11-F-001 entitled 'Formulation and Design for Food Structure and stability'.

Reference

Ann Augustin, M., Clarke, P.T., (2011). Dry Milk Ingredients. *Dairy Ingredients for Food Processing*, 141-159.

Barkouti, A., Turchiuli, C., Carcel, J., Dumoulin, E., (2013). Milk powder agglomerate growth and properties in fluidized bed agglomeration. *Dairy Science & Technology* 93(4-5), 523-535.

Barrera-Medrano, D., Salman, A.D., Reynolds, G.K., Hounslow, M.J., (2007). Granule structure. *Handbook of powder Technology* 11, 1189-1212.Elsevier Publishing, Amsterdam.

Chandan, R.C., (2011). Dairy ingredients for food processing: An overview. *Dairy Ingredients for Food Processing*, 3-33.

Cuq, B., Gaiani, C., Turchiuli, C., Galet, L., Scher, J., Jeantet, R., Mandato, S., Petit, J., Murrieta-Pazos, I., Barkouti, A., Schuck, P., Rondet, E., Delalonde, M., Dumoulin, E., Delaplace, G., Ruiz, T., (2013). Advances in food powder agglomeration engineering.*Advances in food and nutrition research* 69, 41-103.

Ennis, B.J., (2010). Theory of granulation: an engineering perspective. *Handbook of Pharmaceutical Granulation Technology* 3, 6-58.

Forny, L., Marabi, A., Palzer, S., (2011). Wetting, disintegration and dissolution of agglomerated water soluble powders. *Powder Technology* 206(1), 72-78.

Gaiani, C., Scher, J., Schuck, P., Desobry, S., Banon, S., (2009). Use of a turbidity sensor to determine dairy powder rehydration properties. *Powder Technology* 190(1), 2-5.

Gaiani, C., Schuck, P., Scher, J., Desobry, S., Banon, S., (2007). Dairy powder rehydration: influence of protein state, incorporation mode, and agglomeration. *Journal of dairy science* 90(2), 570-581.

Gao, L., McCarthy, T.J., (2006). Contact angle hysteresis explained. *Langmuir* 22(14), 6234-6237.

GEA Niro, (2005). *GEA Niro Method, No. A 5A: Wettability.*Retrievedfrom http://www.niro.dk/niro/cmsdoc.nsf/WebDoc/ndkw6dknxs on 19 August 2015.

Goalard, C., Samimi, A., Galet, L., Dodds, J.A., Ghadiri, M., (2006). Characterization of the dispersion behavior of powders in liquids. *Particle & Particle Systems Characterization* 23(2), 154-158.

Hapgood, K., Iveson, S., Litster, J., Liu, L., (2007). Granulation Rates Processes.*Handbook of powder Technology* 11, 897-977.Elsevier Publishing, Amsterdam.

Hogekamp, S., Schubert, H., (2003). Rehydration of food powders. *Food Science and Technology International* 9(3), 223-235.

Iveson, S.M., Litster, J.D., Hapgood, K., Ennis, B.J., (2001). Nucleation, growth and breakage phenomena in agitated wet granulation processes: a review. *Powder Technology* 117(1), 3-39.

Jacob, M., (2007). Granulation equipment. *Handbook of powder Technology* 11, 417-476.Elsevier Publishing, Amsterdam.

Ji, J., Cronin, K., Fitzpatrick, J., Fenelon, M., Miao, S., (2015). Effects of fluid bed agglomeration on the structure modification and reconstitution behaviour of milk protein isolate powders. *Journal of Food Engineering* 167, 175-182.

Ji, J., Fitzpatrick, J., Cronin, K., Crean, A., Miao, S., (2016). Assessment of measurement characteristics for rehydration of milk protein based powders. *Food hydrocolloids* 54, Part A, 151-161.

Knight, P., (2001). Structuring agglomerated products for improved performance. *Powder Technology* 119(1), 14-25.

Lazghab, M., Saleh, K., Pezron, I., Guigon, P., Komunjer, L., (2005). Wettability assessment of finely divided solids. *Powder Technology* 157(1–3), 79-91.

Lillford, P.J., Fryer, P.J., (1998). Food Particles and the Problems of Hydration. *Chemical Engineering Research and Design* 76(7), 797-802.

Litster, J., Ennis, B., (2013). *The science and engineering of granulation processes*. Springer Science & Business Media.

Mimouni, A., Deeth, H.C., Whittaker, A.K., Gidley, M.J., Bhandari, B.R., (2009). Rehydration process of milk protein concentrate powder monitored by static light scattering. *Food hydrocolloids* 23(7), 1958-1965.

Mimouni, A., Deeth, H.C., Whittaker, A.K., Gidley, M.J., Bhandari, B.R., (2010). Rehydration of high-protein-containing dairy powder: Slow- and fast-dissolving components and storage effects. *Dairy Science & Technology* 90(2-3), 335-344.

Mort, P., (2007). Scale-up of high-shear binder-agglomeration processes. *Handbook of powder Technology* 11, 853-896.Elsevier Publishing, Amsterdam.

Palzer, S., (2007). Agglomeration of dehydrated consumer foods. *Handbook of Powder Technology*11, 591-671.Elsevier Publishing, Amsterdam.

Palzer, S., (2011). Agglomeration of pharmaceutical, detergent, chemical and food powders—similarities and differences of materials and processes. *Powder Technology* 206(1), 2-17.

Palzer, S., Sommer, K., Hiebl, C., (2003). Penetration of Porous Systems by Nonwetting Liquids. *Chemical Engineering & Technology* 26(9), 962-966.

Rajniak, P., Mancinelli, C., Chern, R., Stepanek, F., Farber, L., Hill, B., (2007). Experimental study of wet granulation in fluidized bed: impact of the binder properties on the granule morphology. *International journal of pharmaceutics* 334(1), 92-102.

Reynolds, G., Fu, J., Cheong, Y., Hounslow, M., Salman, A., (2005). Breakage in granulation: a review. *Chemical Engineering Science* 60(14), 3969-3992.

Reynolds, G.K., Le, P.K., Nilpawar, A.M., (2006). High shear granulation. *Handbook of Powder Technology*11, 3–19.Elsevier Publishing, Amsterdam.

Richard, B., Le Page, J.F., Schuck, P., Andre, C., Jeantet, R., Delaplace, G., (2013). Towards a better control of dairy powder rehydration processes. *International Dairy Journal* 31(1), 18-28.

Salman, A.D., Hounslow, M., Seville, J., (2007). *Handbook of Powder Technology, Vol. 11: Granulation*. Elsevier Publishing, Amsterdam.

Schubert, H., (1993). Instantization of powdered food products. *International Chemical Engineering* 33(1), 28-45.

Schuck, Mejean, S., Dolivet, A., Gaiani, C., Banon, S., Scher, J., Jeantet, R., (2007). Water transfer during rehydration of micellar casein powders. *Lait* 87(4-5), 425-432.

Selomulya, C., Fang, Y., Bhandari, B., Bansal, N., Zhang, M., Schuck, P., (2013). Food powder rehydration. *Handbook of Food Powders: Processes and Properties*, 379.

Turchiuli, C., Smail, R., Dumoulin, E., (2013). Fluidized bed agglomeration of skim milk powder: Analysis of sampling for the follow-up of agglomerate growth. *Powder Technology* 238, 161-168.

Washburn, E.W., (1921). The Dynamics of Capillary Flow. Physical Review 17(3), 273-283.

Yuan, Y., Lee, T.R., (2013). Contact angle and wetting properties, *Surface science techniques*. Springer, pp. 3-34.

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)

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

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

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 minutes) **A:** D (50); **B:** D (10).

Fig.5. Solubilisation as measured by dissolved MPIpercentage (%) versus different mixing time.

Table 1 Bulk Density, Apparent density and Porosity of powders *

Table 2 Morphological descriptors of powders *

Table 3 Wetting time of dairy powders by immersional wetting procedure

Figure 1

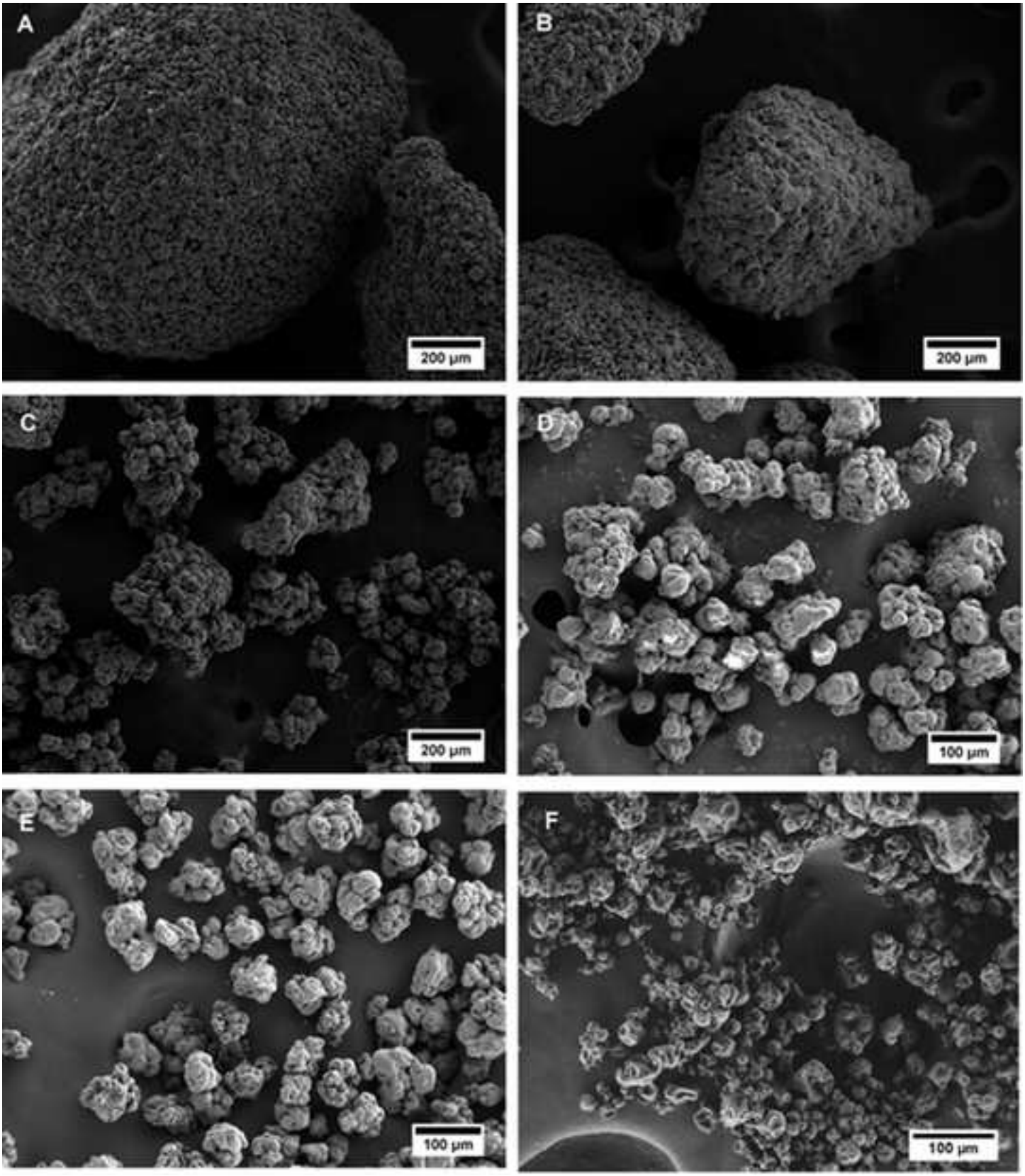


Figure 2

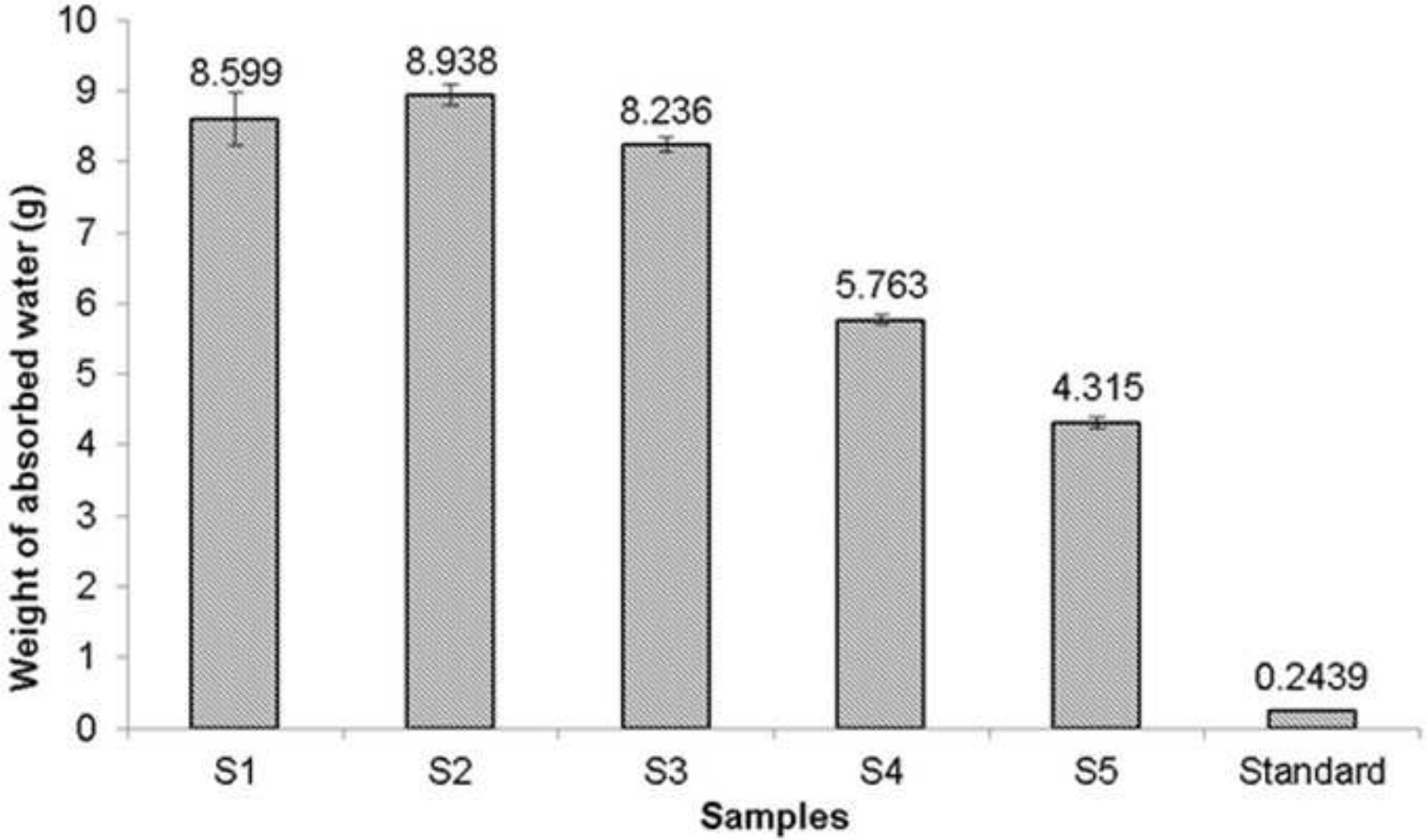

Weight of absorbed water (g)
10
9
8
7
6
5
4
3
2
1
0
8.599
8.938
8.236
5.763
4.315
0.2439
S1
S2
S3
S4
S5
Standard
Samples

Figure 3

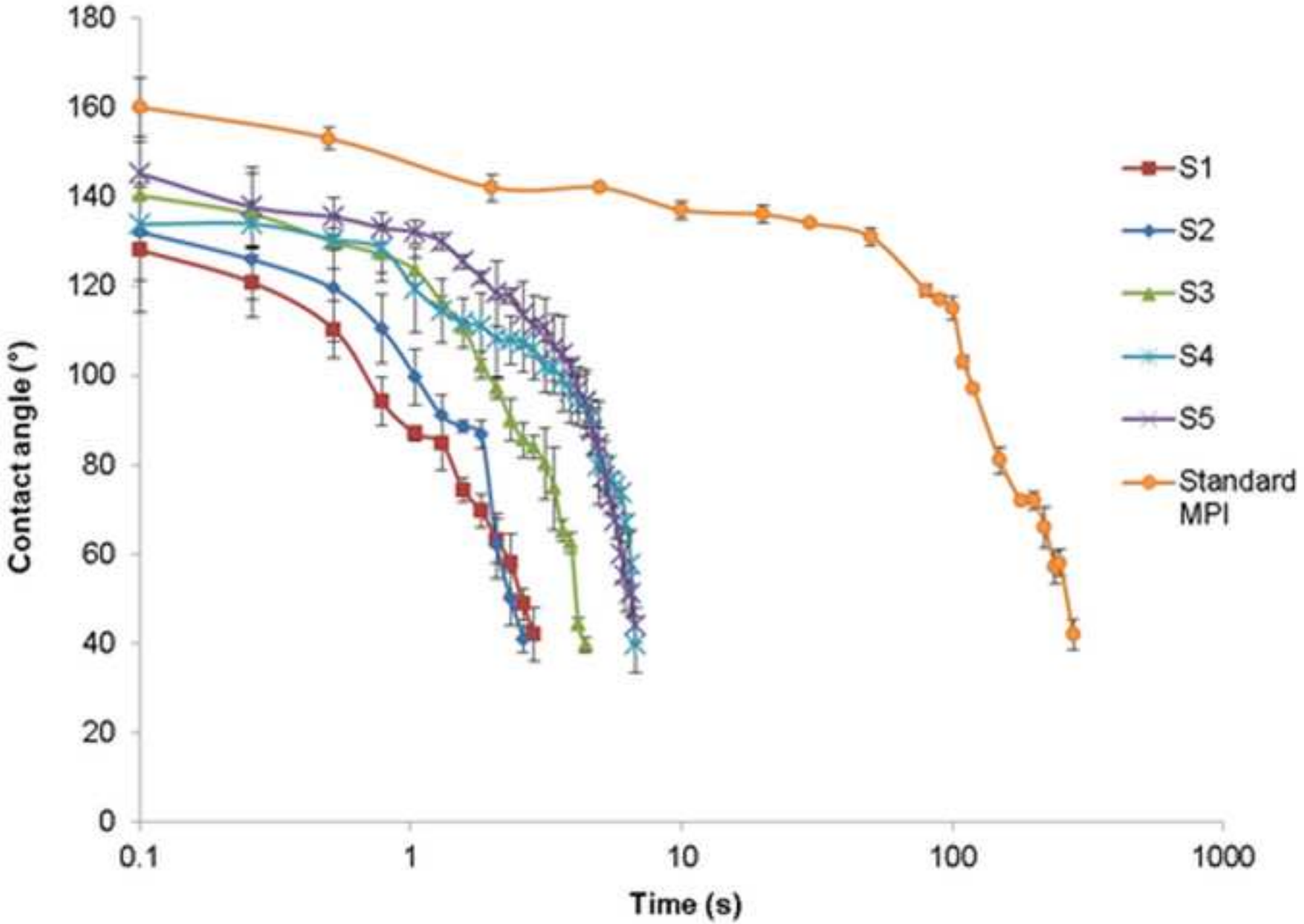

180
160
140
120
100
80
60
40
20
0
Contact angle (°)
0.1
1
10
100
1000
Time (s)
S1
S2
S3
S4
S5
Standard MPI

Figure 4

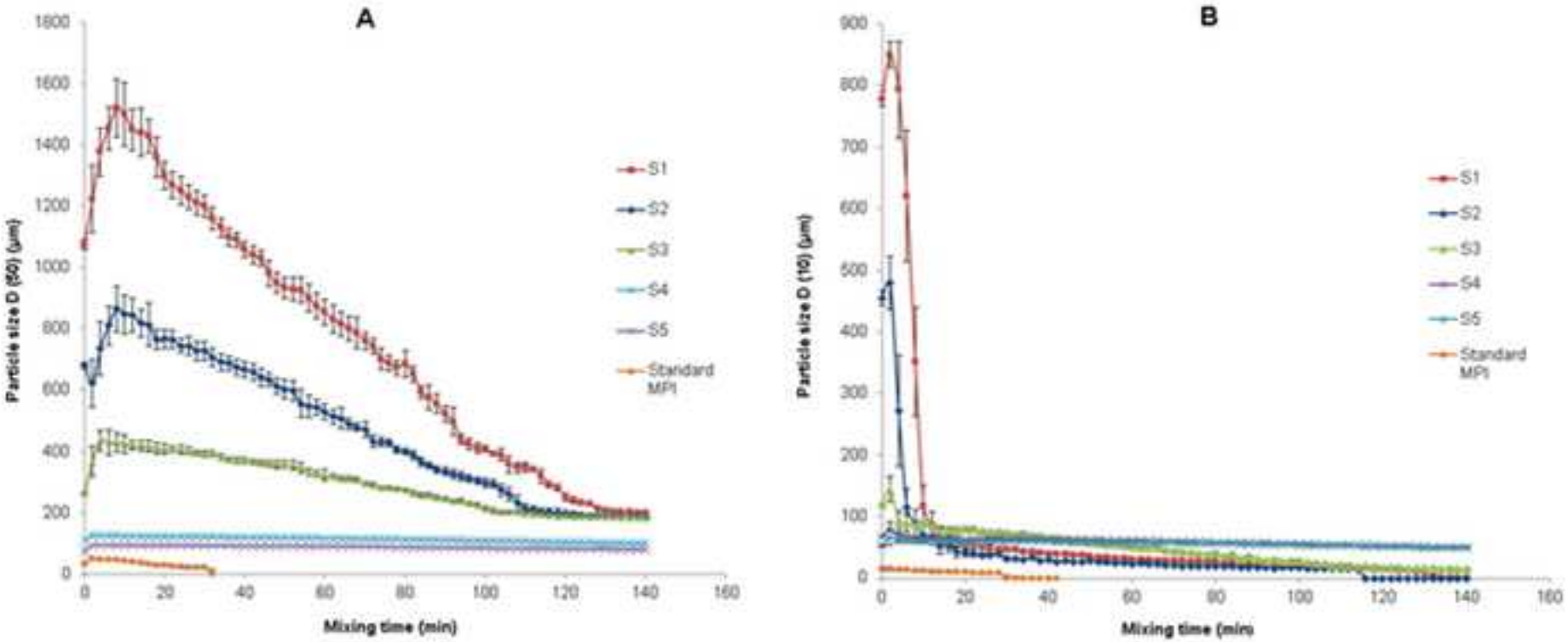

A
Particle size D (50) (µm)
Mixing time (min)
S1
S2
S3
S4
S5
Standard MPI
B
Particle size D (10) (µm)
Mixing time (min)
S1
S2
S3
S4
S5
Standard MPI

Figure 5

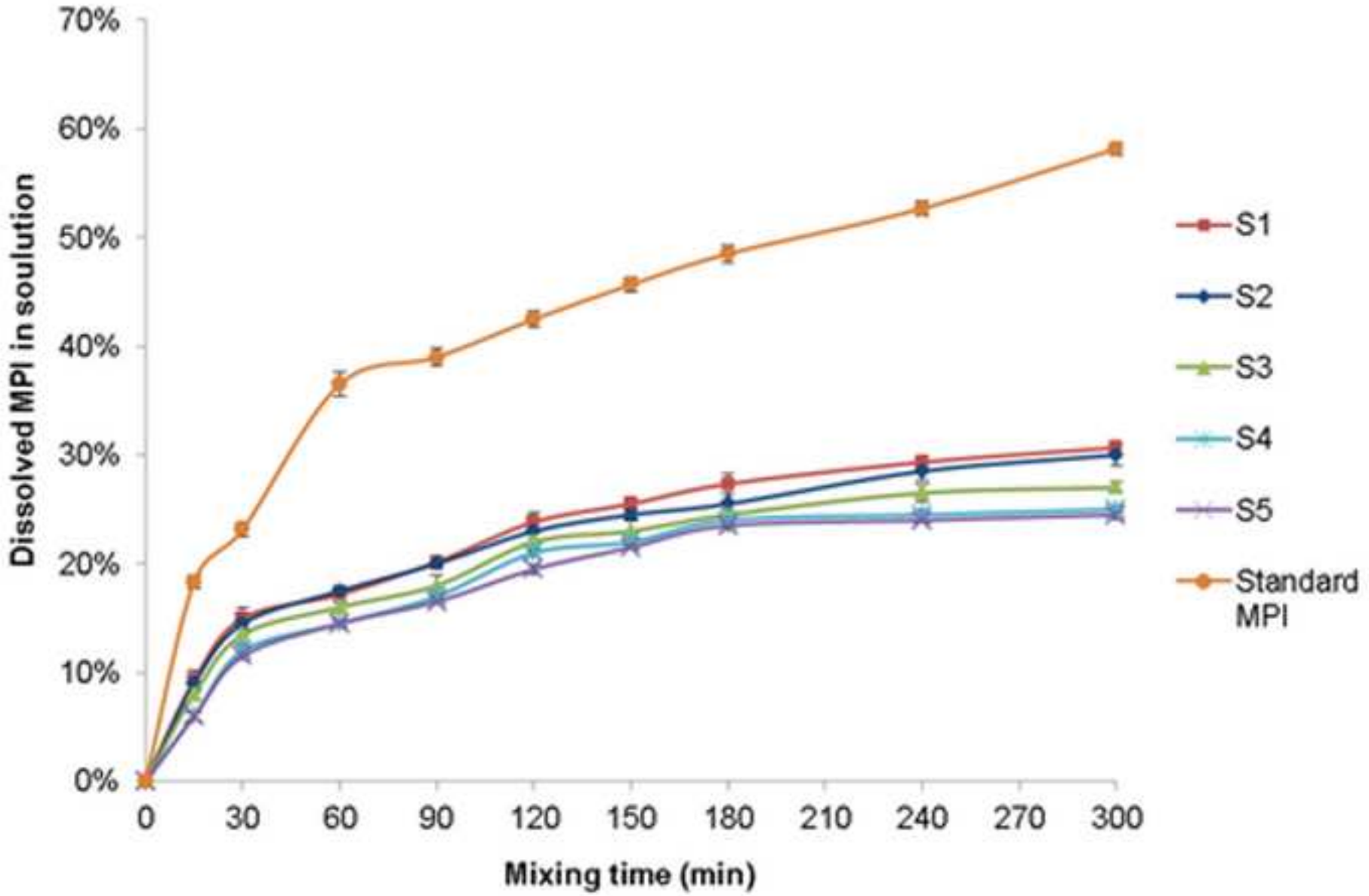

70%
60%
50%
40%
30%
20%
10%
0%
Dissolved MPI in soulution
0
30
60
90
120
150
180
210
240
270
300
Mixing time (min)
S1
S2
S3
S4
S5
Standard MPI

Table 1 Bulk Density, Apparent density and Porosity of powders *

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

* 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 2 Morphological descriptors of powders *

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

*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	>20min