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and

University College Cork, Ireland

THE POST-DEHYDRATION PROCESSING AND THE EFFECTS ON THE STRUCTURAL MODIFICATIONS AND FUNCTIONALITIES OF MILK PROTEIN POWDERS

Thesis present by

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For the degree of

Doctor of Philosophy

(PhD in Process and Chemical Engineering)

Under the supervision of

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Dr. Kevin Cronin, Dr. John Fitzpatrick (University College Cork)

March 2017

DEDICATION

To my family with love, respect,

and gratitude

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All these began from one midsummer day in 2013. When I stepped in Ireland, it is an unforgettable moment, as I realised I would spend the most valuable four years on this beautiful green island. Since then, my subsequent life has been completely changed. PhD study is like a roller coaster ride of success and failure; you never know what you're going to face next. There are full of joy and happiness, also accompanied by trouble and upset. However, all these experience composed of the colourful and meaningful PhD life.

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I am very happy to have this chance to make a little contribution to science.

Junfu Ji

Spring, 2017

ABSTRACT

The variability of the raw materials, the diversity of the chemical compositions and the heterogeneity of structures are believed to contribute to the complexity in the physicochemical behaviours of dairy powders and their different reactivity under hydrothermal conditions. Post-dehydration technology, including agglomeration and coating processes, is widely used as an effective method to homogenise the dairy powders and modify the structural and physical properties of the particles, so as to solve the issues during powder processing, transport and storage by controlling the key parameters of the process.

In the present study, the various rehydration behaviours (wetting, dispersing and dissolving) of different high protein milk powders (milk protein isolate MPI, whey protein isolate WPI, micellar casein MC and sodium caseinate SC) are firstly assessed to find the suitable methods to quantify these dynamic processes. Then these powders were agglomerated by the use of fluidised bed to investigate the possible effects on their rehydration processes. Based on the previous assessment, milk protein isolate powder (MPI) was selected as the model system, which was agglomerated by both fluidised bed (FB) and high shear mix (HS) granulators, using different liquid binders (water, lactose, sucrose) and comparing the different granule sizes (granule growths). The impact of both agglomeration methods on the particle size, shape, density and porosity, as well as the consequent effects on the wettability, dispersibility, flowability and water adsorption are investigated. Finally, different lecithin additions by Wurster coating and fluidised bed agglomeration were also compared to focus on the structural modification and dynamic wetting process of whey protein isolate powders.

The results showed that the MPI powders agglomerated by FB generally provide 2 to 4 times (100 mm - 200 mm) increase in size of the primary powders. The formed agglomerates had the least spherical shapes and roughest surfaces and thus resulted in the porous structures with lowest bulk density (both loose and tapped) and highest porosity values. However, MPI granules produced by HS could reach sizes of more than 1000 mm, which are ~20 times that of the primary powders. The densely packed structures for those HS granules caused the highest bulk density and lowest porosity values. Their shapes were more like spheres with comparatively smooth surfaces. For their effects on the rehydration of different milk protein powders, FB had the beneficial roles on improving the dynamic wetting process of MPI and MC powders, by requiring shorter wetting time, being more quickly penetrated by water droplets and absorbing more water by capillary force. The MPI granules based on HS were more easily wetted by water. The effects are more significant if the larger MPI granules are produced and bigger interstitial spaces are formed. But the influences on the wettability of WPI and SC were limited, as their materials tend to form an impermeable layer at the powder/water interface when contacted with water. Only if using lecithin solution as a liquid binder, WPI could be completely wetted in several seconds. Agglomeration processes showed no clearly advantageous influences on the solubilisation process of different milk protein powders. The densely packed structures created by HS largely delayed the release of materials during the rehydration of MPI powders. However, the densely packed structures made MPI adsorbed least moisture and showed the slowest adsorption kinetics during storage at different relative humidity. Meanwhile, these MPI granules have significantly better powder flow behaviours. Agglomeration processes can

effectively reduce the minimum outlet diameters of hoppers for reliable flow from both mass-flow or core-flow hoppers.

The present study provided information about the post-dehydration process as a useful technique to modify the structural and physical characteristics of milk protein powders, which could be helpful to enhance the wetting process during rehydration, control the water adsorption behaviours and significantly improve the powder flowability.

TABLE OF CONTENTS

DEDICATION I
ACKNOWLEDGEMENT II
ABSTRACT IV
TABLE OF CONTENTS VII
DECLARATION XV
ABBREVIATIONS XVI
LIST OF PUBLICATIONS XVIII

Introduction 1

CHAPTER ONE

Literature Review 6
Abstract 7
1 Introduction 8
2 Fundamental of post-dehydration process 9
2.1 Wet granule growth agglomeration 10
2.1.1 Fluidised bed agglomeration 12
2.1.2 Mixer agglomeration 13
2.1.3 Tumbling agglomeration 15
2.1.4 Coating process 17
2.2 The effect of granule growth process 19
2.2.1 Wetting, binder distribution and nucleation 20
2.2.2 Coalescence and Consolidation 21
2.2.3 Attrition and Breakage 22
3 Powder characteristics 23
3.1 Particle size 23
3.2 Shape properties 24
3.3 Density and porosity 25
3.4 The effects of post-dehydration processes on the physical and structural properties of powders 26

4 The functionalities of powders 30
4.1 Rehydration behaviours 30
4.1.1 Particle wetting 31
4.1.2 Sinking below water surface 32
4.1.3 Dispersing into individual particles 32
4.1.4 Dissolution in water 33
4.2 Powder flowability 33
4.3 Water adsorption 35
4.4 The potential effects of post-dehydration process on the functionalities of a powder 37
5 The application of post-dehydration process on dairy powders 37
6 Conclusion 40
Reference 42

CHAPTER TWO

Assessment of measurement characteristics for rehydration of milk protein based powders 48
Abstract 49
1 Introduction 50
2 Materials and Methods 54
2.1 Materials 54
2.2 Wettability measurements 55
2.2.1 Wetting time by immersional wetting procedure 55
2.2.2 Modified Washburn method by capillary rise wetting 56
2.2.3 Water adsorption by condensational wetting 56
2.2.4 Contact angles by spreading wetting 57
2.3 Dispersibility measurements 57
2.3.1 Dispersibility Index 57
2.3.2 Particle size measurements by laser light scattering method 58
2.3.3 NIR transmission measurements by Lumisizer 59
2.3.4 Conductivity measurements during particles dispersing 60
3 Results and Discussion 60
3.1 Wetting behaviours of milk protein powders based on different wetting procedures 60

3.1.1 Wetting time by immersional wetting 60
3.1.2 Modified Washburn capillary rise wetting method 61
3.1.3 Water adsorption by condensational wetting 62
3.1.4 Contact angles by spread wetting 64
3.2 Dispersing behaviours of typical dairy powders based on different measurements 67
3.2.1 Dispersibility index 67
3.2.2 Particle size measurements by Light scattering 68
3.2.3 NIR transmission measurements by Lumisizer 70
3.2.4 Conductivity measurements 75
4 Conclusion 77
References 80

CHAPTER THREE

Rehydration behaviours of high protein dairy powders: the influence of agglomeration on wettability, dispersibility and solubility 83
Abstract 84
1 Introduction 85
2 Materials and methods 87
2.1 Materials 87
2.2 Agglomeration process 88
2.3 Wettability measurements 89
2.3.1 Wetting time 89
2.3.2 Modified Washburn method 90
2.3.3 Contact angle 91
2.4 Dispersibility and solubility measurements 91
2.4.1 Particle size measurements 91
2.4.2 Sediment height 92
2.5 Scanning electron microscopy 93
3 Results and discussion 93
3.1 The wettability of high milk protein powders 93
3.2 The dispersibility and solubility of high milk protein powders 98
3.3 The effect of agglomeration on the wettability and dispersibility of high milk protein powders 101

3.3.1 The effect of agglomeration on wetting behaviours 101
3.3.2 The effect of agglomeration on dispersion and solubilisation behaviours 102
3.4 The mechanism for the rehydration process of MPI powders 104
4 Conclusion 108
References 110

CHAPTER FOUR

Effects of fluid bed agglomeration on the structure modification and rehydration behaviour of milk protein isolate powders 113
Abstract 114
1 Introduction 115
2 Materials and Methods 117
2.1 Materials 117
2.2 Fluid bed agglomeration 117
2.3 Powder characterisation 118
2.4 Density and Porosity 118
2.5 Particle Shape 119
2.6 Rehydration properties 120
2.6.1 Wettability 120
2.6.2 Solubilisation 120
2.6.2.1 Particle size measurement of dispersed particles 121
2.6.2.2 Dissolved solids measurement 122
2.7 Statistical analysis 122
3 Results and Discussion 123
3.1 Influence of binders on physical properties of agglomerates 123
3.1.1 Density and porosity 123
3.1.2 Morphology 127
3.2 Influence of binders and agglomerate size on rehydration behaviour 129
3.2.1 Wettability 129
3.2.2 Solubilisation 131
3.2.2.1 Particle size measurement of dispersed particles 131
3.2.2.2 Dissolved solids measurement 133

4 Conclusion 135
References 137

CHAPTER FIVE

The structural modification and rehydration behaviours of milk protein isolate powders: the effect of granule growth in the high shear granulation process 140
Abstract 141
1 Introduction 142
2 Materials and methods 145
2.1 Materials 145
2.2 High shear granulation 145
2.3 Powder characterisation 146
2.4 Physical properties 146
2.4.1 Granule size, density and porosity 146
2.4.2 Granule shape 147
2.5 Wettability 147
2.5.1 Wetting time 147
2.5.2 Capillary rise wetting 147
2.5.3 Contact angle 148
2.6 Granule dispersibility 148
2.7 Dissolution 149
2.8 Granule microstructure by SEM 149
2.9 Statistical analysis 149
3 Results and discussion 150
3.1 Effect of different granule sizes on the physical and structural properties of MPI 150
3.1.1 Density and porosity 150
3.1.2 Granule morphology 153
3.2 Effect of different granule sizes on the wettability of MPI 154
3.2.1 Wetting time by immersional wetting procedure 154
3.2.2 Capillary rise wetting 155
3.2.3 Contact angles by spreading wetting procedure 156

3.3 Effect of different granule sizes on the dispersibility and solubility of MPI 158
3.3.1 Particle size changes during MPI granules solubilisation 158
3.3.2 Dissolution of MPI granules 161
4 Conclusion 162
Reference 164

CHAPTER SIX

The effects of fluidized bed and High Shear mixer granulation processes on water adsorption and flow properties of milk protein isolate powder 166
Abstract 167
1 Introduction 168
2 Materials and method 171
2.1 Materials 171
2.2 Methods 171
2.2.1 Fluidised bed granulation 171
2.2.2 High shear granulation 172
2.3 Powder characterisation 172
2.4 Water adsorption analysis 173
2.5 Powder flow analysis 174
2.5.1 Flow function test 174
2.5.2 Wall friction test 175
2.5.3 Two forms of flow obstructions for conical hopper design 175
2.6 Statistical analysis 178
3 Results and discussion 178
3.1 Structural characteristics 178
3.2 Water adsorption 180
3.3 Flow properties 184
3.3.1 Flow function 184
3.3.2 Bulk density 186
3.3.3 Wall friction angle 187
3.3.4 Conical hopper design 188
4 Conclusion 190

Reference **192**

CHAPTER SEVEN

Enhanced wetting behaviours of whey protein isolate powder: the different effects of lecithin addition by fluidised bed agglomeration and coating processes **194**

Abstract **195**

1 Introduction **196**

2 Materials and methods **198**

2.1 Materials **198**

2.2 Fluidised bed agglomeration and coating **199**

2.3 Powder characterisation **200**

2.4 Physical and structural properties **200**

2.4.1 Particle size, density and porosity **200**

2.4.2 Particle shape **201**

2.5 Wetting behaviour **201**

2.5.1 Wetting time by immersional wetting procedure **201**

2.5.2 The dynamic contact angles by spreading wetting procedure . **202**

2.6 Capillary flow **202**

2.7 Film strength at powder / water interface **203**

2.8 Microstructures of agglomerated and coated powders **204**

3 Results and discussion **205**

3.1 Effects on the physical and structural properties of WPI powders . **205**

3.1.1 Particle size, density and porosity **205**

3.1.2 Particle morphology **207**

3.2 Effects on the wetting process of WPI powders **210**

3.2.1 Wetting time by immersional wetting procedure **210**

3.2.2 Contact angles by spreading wetting procedure **211**

3.3 Effects on the capillary flow and the film formation **215**

3.3.1 Capillary flow **215**

3.3.2 The effects of agglomeration and coating on the film strength **217**

4 Conclusion **219**

CHAPTER EIGHT

General Discussion 223
1 The effects on the structural and physical properties 225
1.1 The effect of different process types 225
1.2 The effect of granule growth 226
1.3 The effect of different binders 227
2 The effects on rehydration behaviours 227
2.1 The effect of different processes 228
2.2 The effect of granule growth 229
2.3 The effect of different binders 230
3 The effects on flowability and water adsorption 231
4 Overall conclusion 232
5 Future work 234
Reference 236

APPENDIX 237
Published Literatures 237

DECLARATION

I hereby declare that the work submitted is entirely my own and has not been submitted to any other university or higher education institute, or for any other academic award in this university.

_____ Date: _____

ABBREVIATIONS

A	Agglomerated
ANOVA	One-way analysis of variance
CC	Calcium caseinate
CI	Compressibility index
DI	Dispersibility index
D(10)	Particle size below which 10% of material volume exists
D(50)	Particle size below which 50% of material volume exists
D(90)	Particle size below which 90% of material volume exists
$D_{arching}$	Critical arching diameter
D_{rh}	Critical rat-hole diameter
FB	Fluidised bed agglomeration
HS	High shear mixer agglomeration
MC	Micellar casein
MPI	Milk protein isolate
NA	Non-agglomerated
RH	Relative humidity
SC	Sodium caseinate
SMP	Skimmed milk powder
SEM	Scanning electron microscope
SSA	Specific surface area
WPI	Whey protein isolate
ε	Porosity
ρ_T	Tapped bulk density
ρ_P	Particle density

ρ_b	Loose bulk density without compressing
ρ_c	Compressed bulk density
ρ_a	Critical arching bulk density
ρ_r	Critical rat-hole bulk density
ff_c	Flow index
g	Gravity acceleration
σ_a	Critical arching stress
σ_r	Critical rat-holing stress
θ_a	Critical hopper half angle for arching
θ_r	Critical hopper half angle for rat-holing
$\emptyset_{\mathrm{e}}$	Effective angle of internal friction
$\emptyset_{\mathrm{w}}$	Angle of wall friction
$\emptyset_{\mathrm{a}}$	Critical angle of internal friction for arching
$\emptyset_{\mathrm{wa}}$	Critical angle of wall frictions for arching
$\emptyset_r$	Critical angle of internal friction for rat-holing
$\emptyset_{\mathrm{wr}}$	Critical angle of wall frictions for rat-holing

LIST OF PUBLICATIONS

Peer-reviewed publication

1. Ji, J., Fitzpatrick, J., Cronin, K., Maguire, P., Zhang, H., Miao, S., (2016). Rehydration behaviours of high protein dairy powders: The influence of agglomeration on wettability, dispersibility and solubility. *Food Hydrocolloids* 58, 194-203.

2. 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.

3. Ji, J., Cronin, K., Fitzpatrick, J., Maguire, P., Zhang, H., 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, 1-8.

4. Ji, J., Fitzpatrick, J., Cronin, K., Fenelon, M., Miao, S., (2016). The effects of fluidised bed and high shear mixer granulation processes on water adsorption and flow properties of milk protein isolate powder. *Journal of Food Engineering* 192, 19-27.

5. 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.

6. Ji, J., Cronin, K., Fitzpatrick, J., Crean, A., Miao, S., (2017). Enhanced wetting behaviours of whey protein isolate powder: the different effects of lecithin addition by fluidised bed agglomeration and coating processes. *Food Hydrocolloids* in press.

Conference Presentation

1. Ji, J., Cronin, K., Fitzpatrick, J., Miao, S., Rehydration behaviours of high protein dairy powders: The influence of agglomeration on wettability, dispersibility and solubility. IDF Dairy Science & Technology Symposia 2016, Dublin, 11-13th April. **(Poster and oral presentation)**.

2. Ji, J., Cronin, K., Fitzpatrick, J., Miao, S., The structural modifications of milk protein isolate powders: The effect of granule growth in the high shear granulation process. IUFoST World Congress of Food Science and Technology, 2016, Dublin, 21-25 August, 2016. **(Poster presentation)**.

3. Ji, J., Fitzpatrick, J., Cronin, K., Miao, S., Assessment of rehydration measurements of dairy powders and the agglomerates, ICEF12 - 12th International Congress on Engineering and Food 14-18 June 2015, Québec, Canada. **(Poster presentation)**.

4. Ji, J., Fitzpatrick, J., Cronin, K., Miao, S., The agglomeration process of milk protein powders: the influence on structure modification and rehydration behaviours. 2nd Food Structure and Functionality Forum Symposium - From Molecules to Functionality 28 February – 2 March 2016, Singex, Singapore. **(Oral presentation)**.

5. Ji, J., Fitzpatrick, J., Cronin, K., Crean, A., Miao, S., Assessment of wetting and dispersing measurements of dairy powders and the agglomerates, 7th International Granulation Workshop and Conference: 1st – 3rd July 2015, University of Sheffield, UK. **(Poster presentation)**.

6. Ji, J., Fitzpatrick, J., Cronin, K., Fenelon, M., Miao, S., Effects of different binders on the structure modification and reconstitution behaviour of dairy powders in fluid bed agglomeration, The 1st Congress On Food Structure Design, Porto, 15 - 17 October 2014. **(Poster presentation)**.

7. Ji, J., Fitzpatrick, J., Cronin, K., Fenelon, M., Miao, S., Physical properties and reconstitution behaviour of milk protein isolate powders: effect of fluid bed agglomeration with different binders. 43rd Annual Food Research Conference 10th - 11th December 2014 UCD O'Brien Science Centre, Belfield, Dublin 4. **(Oral presentation)**.

8. Ji, J., Fitzpatrick, J., Cronin, K., Crean, A., Miao, S., Assessment of rehydration measurements for milk protein based powders, 44th Annual Food Research Conference, December 14th, 2015. Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork. **(Poster presentation)**.

Introduction

Food powders are used in daily life for many purposes (infant formulae, flour, coffee, sugar, salts, spices, etc.) and provide technological solutions to the issues of food products, as powders are easy to process, transport, store and preserve (Bhandari et al., 2013; Ortega-Rivas et al., 2006). Contrary to model powders, which are homogeneous, spherical, monodisperse particles, the real food powders exhibit great heterogeneity in particle size, morphology and structures. It is due to food powders are the powders, which consist of tens of thousands of individual particles. Hence, a great dispersion is always found in their physical and structural properties (Cuq et al., 2013). Meanwhile, powders are complex materials and they are a complicated mixture of solids, liquids and gases, rather than perceived as just a collection of solids. Therefore, the variability of the raw materials, the diversity of the chemical compositions and the heterogeneity of structures are believed to contribute to the complexity in the physicochemical behaviours of food powders, as well as result in their various reactivity under hydrothermal conditions.

In the dairy industry, most dairy powders present similar problems, regarding to the characteristics in particle size, shape, density and porosity. As dairy powders are produced by the dehydration process of liquid milk products, they usually consist of fine particles with large size distributions and dense structures (Schuck et al., 2012; Schuck, 2013). Fat content (if present) tends to appear on the surface of particle. It may cause the undesired physical and surface properties, which negatively influence the quality of powders and the subsequent functionalities (Jayasundera et al., 2009; Kim et al., 2002; Kim et al., 2005). In addition, if taking into consideration the different milk compositions (protein, lactose, fat, minerals), there have been found

many issues affecting the functionalities of dairy powders, e.g. prolonged rehydration process (for high protein and fat powders) (Crowley et al., 2016; Gaiani et al., 2007), poor flowability (for all powders) (Crowley et al., 2014; Fitzpatrick et al., 2005; Fitzpatrick et al., 2004), easy to adsorb moisture and tend to form caked lumps during storage (lactose-based powders) (Carpin et al., 2016; Fitzpatrick et al., 2007; Fitzpatrick et al., 2010). Consequently, these are the barriers that limit the end-uses and processing capability of dairy powders. It is necessary to find the methods to optimise the undesired physical and structural characteristics and also aim to improve the functionalities by the potential ways.

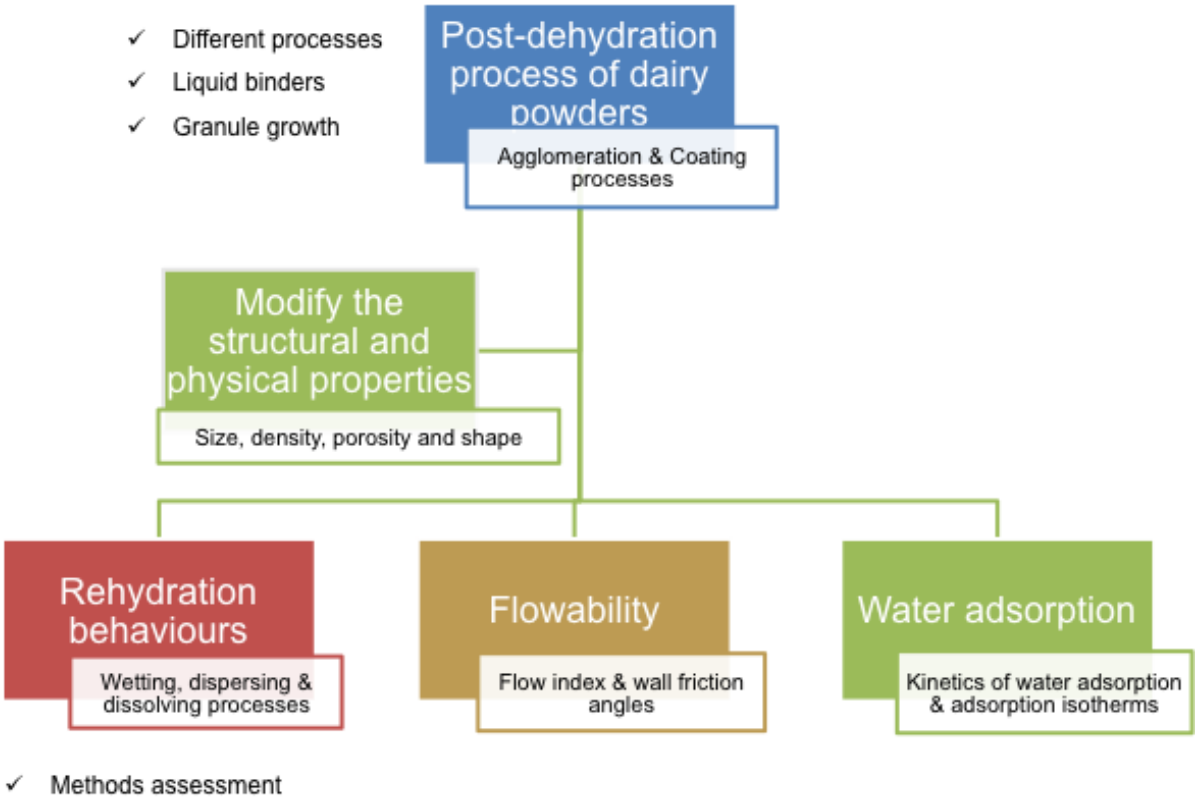
Agglomeration and coating processes can alter the physical and chemical properties of powders which may be used to overcome powder problems and improve functionality, such as rehydration ability (Knight, 2001). During the processes, the binders or coating materials are added onto primary particles, acting as the bridges or layers to create new particles or agglomerates with different structures and physical properties. Both of these two processes are defined as the typical post-dehydration technology, which have been widely applied in powder productions (Litster and Ennis, 2013; Salman et al., 2007). Basically, they are often used, by manufacturers to improve powder performance, but still in an empirical fashion. Besides that, most of the published research is related to pharmaceutical materials (Pietsch, 2005; Pietsch, 2008), only a few are focus on the food powders, especially for dairy powders. In that case, the effects of post-dehydration processes on the physical and structural modification of dairy powders need to be clearly identified. Due to some limited functionalities, e.g. rehydration, flowability and water adoption, are found to be closely corresponding to the structures of dairy powders, it will also be interesting to investigate the relationships between post-dehydration

process and the functionalities of dairy powders, and thus improve these physicochemical behaviours by controlling the key parameters of the process.

In present study, the high milk protein powders (casein-based, whey-based, and milk protein isolate) are used as the model powders. They are agglomerated by the use of fluidised bed and high shear mixer agglomeration to firstly compare their effects in particle size, shape, density and porosity; and then investigate their various rehydration behaviours (wetting, dispersing and dissolving), flowability and water adsorption. In addition, Wurster coating process is also used to compare to the fluidised bed agglomeration by the differences appearing in the structures and wettability of formed whey protein powder. The overall objectives can be divided into three, which are illustrated in the Figure below.

1. Firstly assess the different measurements for the rehydration of different dairy powders, in order to find the most suitable methods to quantify the rehydration processes. (Chapter 2)
2. Then aim to investigate the effect of fluidised bed agglomeration on the wettability, dispersibility and solubility of different dairy powders. (Chapter 3)
3. Focus on the effect of different liquid binders and agglomerate size on the structural modifications of milk protein powder. (Chapter 4)
4. Study the granule growth rate process of high shear agglomeration and its influences on the structures and rehydration behaviours of milk protein powder. (Chapter 5)
5. Compare the different effects of fluidised bed and high shear agglomeration on water adsorption and flowability of milk protein powder. (Chapter 6)

6. Use the different lecithin additions by fluidised bed agglomeration and Wurster coating process and then compare their different impacts on the structures and dynamic wetting process of whey protein powder. (Chapter 7)



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CHAPTER ONE

Literature Review

Abstract

This study investigated the effects of different post-dehydration techniques, e.g. wet agglomeration and coating processes, on the physical and structural modification, as well as the subsequent functionalities of powders. It is found that the processes contribute differently on the particle size, shape, particle density and porosity of the formed granules, due to the various granule growth mechanisms. Fluidised bed agglomeration produces large granules with porous structures; while the granules formed by mixer agglomeration have the extruded structures with high particle density. The centrifugal forces provided by drum agglomeration cause the intermediate granules with more spherical shape. More resistant agglomerates associated with smaller size and less porous structures may be produced by layering the coating materials. Meanwhile, the physical and structural modifications may also influence the powder rehydration, flow and water adsorption properties. During the dynamic rehydration process, the first wetting behaviour is determined by the porosity and the surface properties, while sinking and dispersing processes are contributed by the particle size and density. Flowability of a powder is also influenced by the particle size, surface contact area between particles (internal frictions) and between particle and walls (wall friction). In addition, big particle surface area, large interstitial space between particles and internal pores inside of single particle result in the quick water transfer and more moisture uptake. Consequently, regarding to the functional issues found in dairy powders, the post-dehydration technology has the potential for improving the functionalities of dairy powders, by controlling the key parameters affecting the formation of dairy powder structures.

Keywords: post-dehydration, physical properties, structural modification, powder functionalities, dairy powder

1 Introduction

Dehydration is widely used in food industry to convert liquid product into powdered forms for the enhanced shelf-life and the convenient end-uses. In order to express the functionalities of the dried food powders, they have stringent requirements regarding rehydration behaviours, flowability, caking, structural and physical properties, which are believed to influence the subsequent handling and processing (Cuq et al., 2011; Ortega-Rivas et al., 2006; Sharma et al., 2012). However, some problematic food powders after dehydration usually exhibit fine particle sizes, undesired bulk densities and porosity values, which negatively limit the functionalities of food powders or even cause problems during processing (Bhandari et al., 2013). For example, in dairy industry, milk powders produced by spray drying generally consist of small cohesive particles (especially for those dairy powders containing high content of milk protein) (Schuck et al., 2012). These particles may cause the dense structures, prolonged rehydration process, poor flowing properties and caking behaviours (Carpin et al., 2016; Crowley et al., 2014; Crowley et al., 2016; Schuck et al., 2007). Therefore, additional processes acting on the dried powders, which are called post-dehydration technology, are often used as a method to improve the functionalities of powders by modifying the physical and structural properties, or surface compositions of the initial particles.

There are mainly two types of post-dehydration technologies in the food industry, which are agglomeration and coating (Cuq et al., 2013a; Dhanalakshmi et al., 2011). They are both commonly used to assist the development of food powder materials with improved properties, e.g. wettability, dispersibility, flowability, reduced dustiness and bulk density (Saleh and Guigon, 2007; Turchiuli et al., 2005). The characteristic of agglomeration is the formation of larger entities from particulate materials. Those

particles stick together by the formed bridges, which provide short-range physical forces to connect the primary particles. The bonds between particles are usually caused by either solids themselves or via the added binders (Cuq et al., 2013b). Agglomeration usually uses a liquid binder to form the interparticle bonds and powders are motivated by air or mechanical agitation to promote liquid dispersion and granule growth. Agglomeration processes include fluidised bed agglomeration, mixer agglomeration and tumbling agglomeration (Jacob, 2007; Salman et al., 2007a). Otherwise, the interparticle bonds can also be created by compression process, which applies pressure to create the physical forces to adhere single particles. The class of processes includes roll pressing, extrusion and tableting agglomeration (Litster and Ennis, 2013). All these common agglomeration processes are particle size enlargement processes, which modify the structures and surface properties of powders based on the different granule growth mechanisms. In addition, coating processes introduce coating materials by different addition methods on powders to achieve special objectives, such as protection of core materials and improvement of surface properties. The addition of the liquid coating materials can be used through Wurster coating apparatus or spouted bed coaters. More resistant agglomerates associated with smaller size and less porous structures may be produced by layering the coating materials (Saleh and Guigon, 2007). Consequently, both agglomeration and coating play a critical role on the physical and surface characteristics of food powders, which may potentially contribute to providing and improving subsequent functionalities.

2 Fundamentals of post-dehydration processes

Mechanisms associated with post-dehydration process for food powders are varied and complex, as there are many processes based on the different equipment

(Jacob, 2007). The types of common post-dehydration processes are shown in Table 1-1, which lists the relevant equipment and applications. For agglomeration processes, pressure agglomeration has been developed to produce the pharmaceutical pellets and tablets (Guigon et al., 2007; Pietsch, 2008; Wilson and Rough, 2007). However, wet granule growth agglomeration is most widely used in food industry. As the common used equipment, fluidised bed is often designed for the production of agglomerated dairy powders and infant formulae (Szulc and Lenart, 2013; Turchiuli et al., 2013), while high shear mixer can be used to generate large agglomerated cereal and starch granules (Cunningham, 2007; Pathare, 2010). Therefore, on the basis of literature review in the field of food powders, details of wet agglomeration processes are discussed and shown below.

2.1 Wet granule growth agglomeration

Wet agglomeration refers to the growth of granules induced by the addition of a liquid binder over the agitated powder bed. The binding liquid is used to develop adhesion forces between particles. Different types of particle motions (e.g. shearing, rotation, translation, etc.) are mainly responsible for dispersing the liquid over the particles and controlling the time of particle collision, which promote the granule growth mechanisms (Cuq et al., 2013a). Thus, wet agglomeration can also be subdivided into fluidised bed, mixer and tumble agglomeration, which are operated by different equipment and based on the different agglomeration rate processes. Generally, the wetted particles can bind with other primary particles to form the nuclei agglomerates. Two or more nuclei can coalesce together by contacting with each other and then they may be deformed and consolidated by different degrees of compactions (Hapgood et al., 2007). This may result in agglomerates with the completely different physical and structural properties (Barrera-Medrano et al., 2007).

Table 1-1 Application of post-dehydration processes in food industries

	Technology	Equipment	Application	References
Wet agglomeration	Fluidised bed agglomeration	Fluidised bed driers	Dairy powders; Infant formulae	(Cuq et al., 2013a; Szulc and Lenart, 2013; Turchiuli et al., 2013)
	Mixer agglomeration	Horizontal pan, pin mixer	Cereal powder; Starch	(Cunningham, 2007; Pathare, 2010)
	Tumbling agglomeration	Rotary drums, pans, bowl and plate granulators	Fruit and vegetable powders	(Cremer et al., 2014; Pietsch, 2005)
Pressure agglomeration	Roller pressing	Compacting rolls	Pharmaceutical excipient; Drugs	(Bindhumadhavan et al., 2005; Gereg and Cappola, 2002; Kleinebudde, 2004)
	Tableting	Compacting/tableting presses	Pharmaceutical Tablets; Nutrition bars	(Bodmeier, 1997; Kamel et al., 2008; Pietsch, 2005; Wells, 1993)
	Extrusion	Piston/screw extrusion systems	Effervescent and paracetamol granules	(Lindberg et al., 1988; Vervaet and Remon, 2005)
Wet Coating	Wurster Coating	Fluidised bed Wurster apparatus	Lecithination; Probiotics	(Millqvist-Fureby and Smith, 2007; Saleh and Guigon, 2007)

2.1.1 Fluidised bed agglomeration

In fluidised bed granulator, the particles are set in motion by air, instead of mechanical agitation. Pneumatic mixing is used to agitate the particles when an atomizable liquid binder (suspensions, solutions or emulsions) is transported onto their surfaces. Agglomerates are then produced by the aggregation of the primary particles, which are combined together through the liquid bridges supported by Van der Waals forces (Litster and Ennis, 2013; Mörl et al., 2007). After drying by the hot air, the liquid bridges gradually become solid bridges, which enable the formed agglomerates to have stronger strength and to support the granule growth process (Chua et al., 2011; Osborne et al., 2011). In addition, the process also integrates a number of other processes including wetting, size enlargement, shaping and homogenization into a single step by using heat and mass transfer. Areas of application have a wide range of industries, like foodstuffs, pharmaceutics, detergents and fertilizers (Boerefijn et al., 2007; Mörl et al., 2007; Palzer, 2007a; Pietsch, 2005). Fig.1-1 shows a typical fluidised bed granulator. The heated inlet air from bottom enters into the fluid bed via a distributor, which makes particles agitate uniformly. Liquid binder is then sprayed by an atomising nozzle located above, in or below the bed. Filters are set on the top of vessels and used to remove dust from the exit air. Generally, the particles produced from fluidised bed agglomeration present the comparatively large particle sizes associated with porous structures and low bulk density, which is similar to the shape of “raspberry”. However, the tailor-made powders are always designed according to the actual requirements on the functionalities of powders. Fluidised bed agglomeration is a complex process, influenced by several process variables, e.g. process related variables (fluidizing airflow rate, inlet air temperature, binder droplet size, binder feed rate and nozzle

pressure), equipment related variables (equipment size and shape, position of nozzle, number of spray guns), formulation related variables (raw materials, moisture content and flowability of materials, binder types) (Hemati et al., 2003; Hirata et al., 2013; Masic et al., 2012; Palzer, 2007b; Parveen et al., 2012; Rajniak et al., 2007; Schaafsma et al., 2000; Seo et al., 2002; Tan et al., 2006). These factors are all believed to affect the final powder products, which may exhibit different particle sizes, bulk densities, porosity values and shape properties.

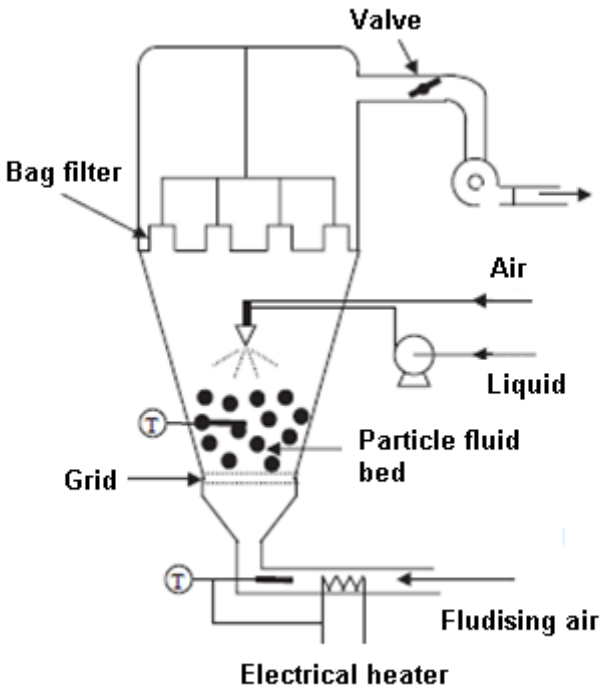

Fig.1-1 Top-sprayed fluidised bed agglomeration (Turchiuli et al., 2005)

2.1.2 Mixer agglomeration

Different from fluidised bed, mixer agglomeration process uses a mechanical impeller to provide particle motion. As it is shown in Fig.1-2, the blenders can be either placed horizontal- or vertical-axis to mix the powder bed. The rotational speed can reach between 100 rpm to 1500 rpm to meet the requirements of the desired

agglomeration behaviours. In addition, a smaller chopper is typically used to assist the growth of small agglomerates and fracture large ones, which homogenises the powder properties (size, shape, etc.) and also helps to prevent the formation of “huge lumps” during the process. Liquid binder is also sprayed or poured onto the moving powder bed and then the agitation forces leads to the uniform dispersion of the binder (Reynolds et al., 2006). It is somewhat similar to fluidised bed agglomeration; however, the differences in those powders’ structures still exit, as high-density granules with smooth surfaces are often produced, especially at the condition of high speed rotation. It has been found that, the granules after consolidation present much denser structures rather than the open “raspberry” structures formed by fluidised bed (Cuq et al., 2013a; Litster and Ennis, 2013). At the same time, if comparing to other wet agglomeration processes, mixer granulators are suitable for a wider range of powder materials, including fine cohesive and sticky materials and viscous liquid binders. However, there are also some parameters and operating conditions that influence the growth and properties of granules. These factors include material variables (liquid to solid ratio, binder viscosity, wettability, etc.) and operating variables (impeller speed, process time, methods for binder addition, etc.), which are considered to be significantly affect the particle size, density and shape circularity of the formed granules (Ax et al., 2008; Badawy et al., 2000; Knight et al., 2001; Kokubo and SUNADA, 1996; Mills et al., 2000; Osborne et al., 2011; Rahmanian et al., 2009). Consequently, though this technology is commonly applied in the pharmaceutical, agrochemical and detergent industries, it is still interesting to use this kind of agglomeration method for the production of food powders, as it also shows the potential uses and benefits for some of functionalities

of food powders, due to its special and unique effect on the structural formation of food granules.

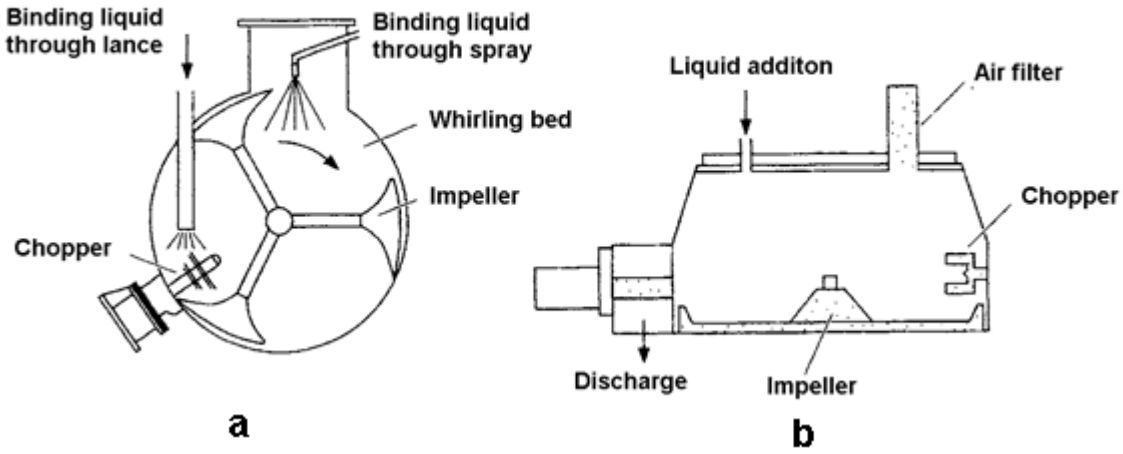

Fig. 1-2 (a) Horizontal and (b) vertical high-shear mixer granulators (Reynolds et al., 2006)

2.1.3 Tumbling agglomeration

Tumbling agglomeration is also one of the most widely used agglomeration method in powder industries. Particles are set in motion by the tumbling movement, which is achieved by the balance between gravity and centrifugal forces (Walker, 2007). After spraying a liquid binder via nozzles or distributor pipe systems onto the powder bed, the rolling motion then leads to the size enlargement process by collisions of moist particles. Meanwhile, the morphology and structures of agglomerates are modified and usually formed more spherical “balls” (Litster and Ennis, 2013). A schematic design of a typical drum granulator is shown in Fig.1-3. The device is usually equipped with a rotating cylinder or drum, which is slightly inclined to the horizontal to facilitate the transportation of material through the drum. In order to minimise back-spill of the inlet material and increase depth of the bed inside the drum, two dam rings are both assembled at the inlet and exit sides of the

drum. Powder materials are transported by chutes, pipes or conveyors and wetted by the liquid near the inlet side of the drum. Scrapers are often, but not always, used to limit building up on the drum wall. As tumbling granulators normally produces granules with the big granule size (in the range of 2 to 20 mm), small agglomerates are difficult to be produced based on the particle growth mechanism. In addition, centrifugal forces created by tumbling drums always consolidate the formed granules, which present the comparatively low porosity values. Thus, the tumbling granulators are mostly used in pharmaceutical industries to produce high density pellets or pills. However, during the granule growth process, the operation conditions play a marked role on controlling the physical and structural properties of final granules. For example, drum rotational speed and residence time are both have the pronounced effects on the shape (circularity, convexity) of particles. Feed characterises including initial size distribution of materials, binder feed rate and moisture content (ratio of liquid to solids) are also believed to influence the rate of size enlargement (Adetayo et al., 1993; Gluba, 2003; Litster and Ennis, 2013; Ramachandran et al., 2008). Consequently, tumbling agglomeration process still exhibits a large range of applications for powders and thus may also have the potential use in the area of food powders, in particular for novel food product design.

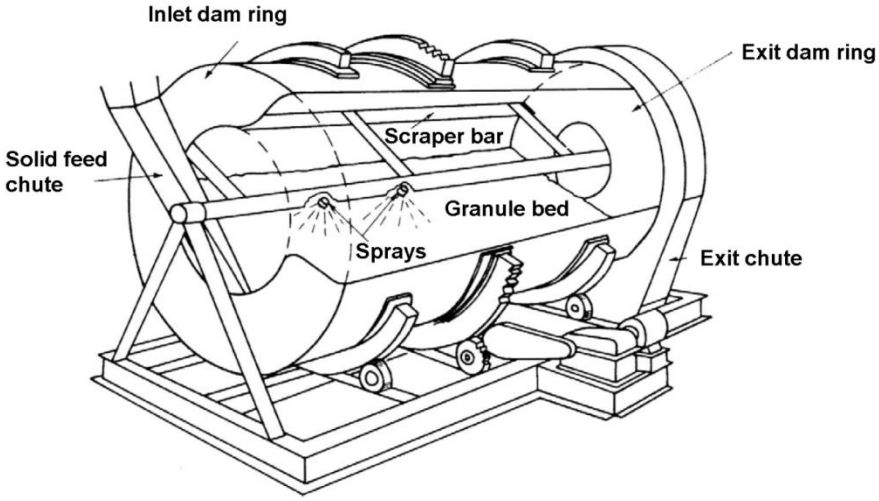

Fig.1-3 The rolling drum granulator (Litster and Ennis, 2013)

2.1.4 Coating process

The coating process aims to cover powders, agglomerates, granules or other particulate materials by a coating agent, which usually forms a layer surrounding the surface of the solids. The thickness of layers can be nanoscale dimensions (chemical deposition), or a few micrometres (film coating), or even reach several millimetres, e.g. sugar coating (Saleh and Guigon, 2007). The coating process is performed to: 1). Protect core materials from oxygen, humidity, light or other undesired environment; 2). Improve the sensory properties (appearance, aroma, taste) of products; 3). Conserve nutrients or active substance in food products; 4). Control or delay the release rate of the involved core materials; 5). Prevent caking behaviour during storage and transport; 6). Confer the specific interfacial properties to the solids (e.g. lecithination of hydrophobic food powders for rehydration). According to the particular application, different methods have been developed to introduce the coating agent into the powder bed: sprayed the solution or suspension, or applied in the form of fine dry powders (Dewettinck and Huyghebaert, 1999). In

the most of cases, the coating layer is more likely to be deposited as a shell of core materials, than forming the liquid bridges between wetted particles, which is different from the granule growth mechanism of agglomeration process. However, it still depends on the drying rate of particles, as the particle may grow by layering if fast drying before a collision between wetted particles. Otherwise, the agglomeration may dominate the granule growth behaviours. Basically, more resistant agglomerates associated with smaller size and less porous structures may be produced by coating process. Agglomeration is expected to enlarge the particle size while coating aims to cover particles to attain one of the several functionalities mentioned above (Saleh and Guigon, 2007). There have been developed many apparatus for coating based on the different applications so far, e.g. fluidised bed coater, spouted bed coater, Wurster apparatus and rotary drum, pan and disc coaters. Wurster apparatus may be the most used configuration of all for film coating (Teunou and Poncelet, 2002). This system combines the conception of fluidised bed and spouted bed techniques together, which is shown by Fig.1-4. A draft tube called Wurster column is placed coaxially in the bed. It is used to order the circulation of particles by the upward gas stream inside of the draft tube and then fall downward besides the draft tube. The coating solution or suspension is spayed by nozzle, which is fixed in the centre of the distributor plate at the bottom of bed.

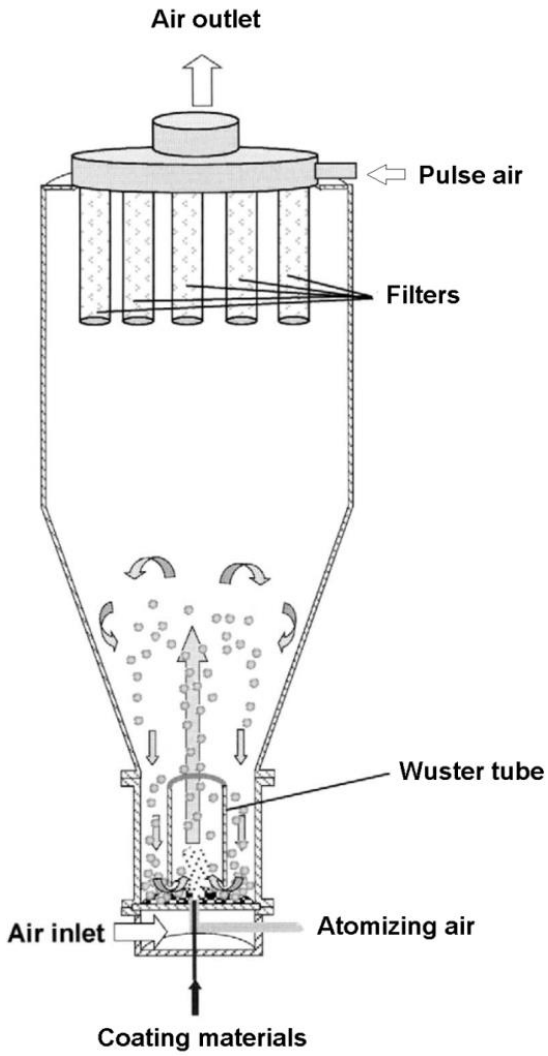

Fig.1-4 Wurster coating apparatus (Saleh and Guigon, 2007)

2.2 The effect of granule growth process

Wet agglomeration is a complex process with different competing physical phenomena occurring simultaneously in the granulator. This process is commonly believed to be the dynamic granule growth process, in which granules are continuously forming and breaking down. The physical phenomena can be divided as three groups, which determine the characteristics of final granule (Iveson et al., 2001) (Fig. 1-5).

1) Wetting, binder distribution and nucleation;

2) Consolidation and growth;

3) Attrition and breakage.

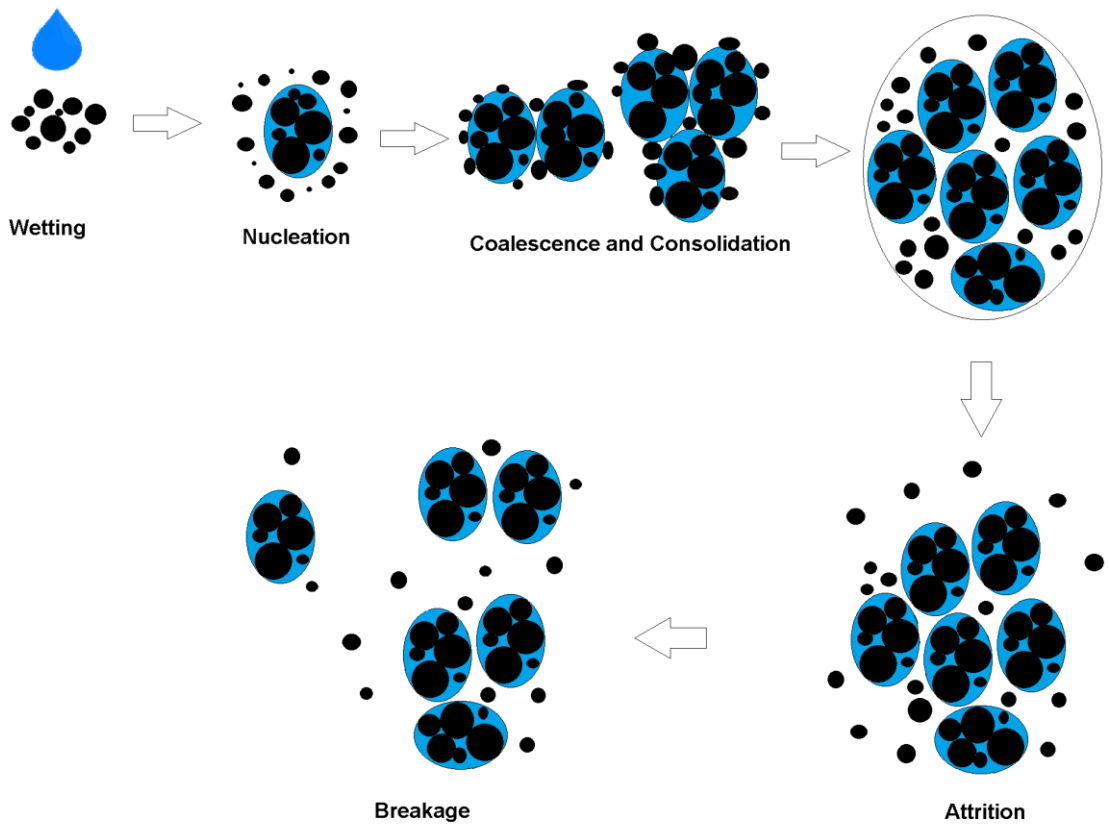

Fig.1-5 Different rate processes in agglomeration (a) wetting and nucleation; (b) Coalescence and consolidation; (c) breakage and attrition

2.2.1 Wetting, binder distribution and nucleation

The addition and distribution of liquid binders onto the powder bed is the first stage of agglomeration process. Particle wetting behaviour occurs by the penetration and spreading of the binder droplets, which means the voids between powders particles are replaced by the liquid (Fig.1-5). Ideally, if powders have good wettability, each drop will penetrate into the particles quickly and completely, and then engulf

particles to form a single granule nucleus (Litster, 2003). Otherwise, poor wettability of powder may cause the slow imbibition rate of liquid, which thus accumulate on the surface of particles. This behaviour is easy to create the large wet agglomerates, while other non-agglomerated particles may need longer time for process recycling. Therefore, nucleation is a critical stage in determining the final quality of the granules as good wetting behaviour may ultimately result in the narrow particle size distribution. In addition, nucleation also gives the granules nuclei with loosely structures due to the formation of liquid bridges connecting primary particles. The nucleation process is largely affected by the characteristics of the liquid spray, the flux of powder through the spray zone and the wetting properties of the formulation (Litster and Ennis, 2013).

2.2.2 Coalescence and Consolidation

Coalescence process is considered to be mainly responsible for the granule growth by forming large granules. The process occurs based on the collisions between neighbouring granule nuclei, between nuclei and primary particles, or between granules and the equipment. For successful coalescence, two conditions may be required: 1) the energy of impact must be absorbed during collision; and (2) a strong bond must form at the contact between the colliding granules. Otherwise, the granules may rebound or even if formed the bridges between them may easily rupture by the continuous collisions (Hapgood et al., 2007). The use of liquid at the surface of the granule plays a key role for the growth by coalescence, as coalescence rate is very sensitive to liquid content with different viscosity (Keningley et al., 1997). At the same time, consolidation behaviour always happens together with the coalescence of granules. It reduces the size and porosity of granules as well as squeezes out entrapped air from the pores inside, which is closely correlated with

the density and strength of final granules. The extent of the consolidation is dependent on the agitation in the granulator and the resistance of the granule to deformation (Saleh et al., 2005). Stronger agitation forces and weaker yield stress may result in larger deformation of granules, especially for those coarse powders, which can form much denser structures (Cuq et al., 2013a). Therefore, these modifications in granule size and density are believed to be controlled by coalescence and consolidation.

2.2.3 Attrition and Breakage

Attrition and breakage refer to agglomerate fracture into two or more smaller sized segments due to impact or compaction in the granulator, drier or in subsequent handling (Salman et al., 2007b). It is more likely in the high intensity mixer or for those large granules formed by the weak bridges. There are usually different phenomena for the appearance of attrition and breakage, e.g. surface attrition (erosion & abrasion), particle breakage (fracture & shattering) (Fig.1-5). Some of the breakage is inevitable as part of agglomeration processes, and is able to limit granule excessive growth, which helps to control the final granule size and shape, as well as improving the compositional homogeneity of the product. However, in some circumstances, breakage occurs as an undesired process, which produces fine and dusty particles detaching from dry granules, or creates cracks in the granules (Reynolds et al., 2005). The type and extent of breakage are largely dependent on the particle material properties including hardness, fracture toughness and elastic modulus; and also the granulation conditions, e.g. binder viscosity, agitation forces and process time, etc. It may be possible for a tough granule to survive from a high level of impacts before it finally shatters, while a granule with a lower toughness and/or more irregular shape may progressively break into smaller fragments with

increasing impact stress and /or increasing number of impact events (Hapgood et al., 2007). Consequently, it is a challenge to avoid the undesired breakage, due to there is always a balance toward specifying more porous granules vs. the design and production of granules with stronger resistance to attrition.

3 Powder characteristics

3.1 Particle size

Powder properties are believed to be largely dependent on several single particles characteristics, which include particle size, shape, surface, density, and adsorption properties. Of these features, particle size is most important and essential, as size is always used as a benchmark to classify, categorize, or characterize a powder (Ortega-Rivas et al., 2006). Due to real particles being produced with irregular shapes, an equivalent diameter must be ascribed to the particle of interest, which corresponds to the diameter of a sphere with the same surface or volume. The dispersion of particle diameters is usually expressed as particle size distributions, which are characterized by a mean diameter and span measurement. Particle size distribution influences a great number of bulk behaviour of powders, e.g. flowability, rehydration abilities, fluidisability and compressibility (Fitzpatrick et al., 2004a; Ortega-Rivas et al., 2006; Selomulya et al., 2013). In addition, surface area of particles is also determined by the particle sizes. Small particle size is often corresponding to large surface area, which thus causes stronger interaction between particles themselves or between particles and a surrounding fluid. In that case, those powders with small size are easily to be adhered by undesired bridges, based on the consolidation environment with relative humidity and temperature. It causes poor flow behaviour during conveying or the formation of caked lumps, which brings many problems for subsequent handling processes (Schulze, 2007).

3.2 Shape properties

Particle shape properties are considered to mainly influence the performance in powder handling process. For example, different shapes of particles present the various packing behaviours of powders, which mean they have different bulk densities and storage capacity. Rounded particles will pack more tightly than angular particles, in particular for those particles with exaggerated shapes e.g. fibres, flakes and platelets (Bhandari, 2013). Besides the variation in bulk density, angular particles have also been shown to have smaller contact area of particle surfaces, and thus potentially influence the flowability of powders (Schulze, 2006). Even though shape property is very important, there is little work that has been published based on the research of food powders. Actually, the morphology of a real powder particle has very complex characteristics that are difficult to be assessed, as particles are 3-dimensional objects with random shapes (Endoh, 2006; Fayed and Otten, 1997). Therefore, at a very basic level, particle shape can be described qualitatively using indicators like circularity, convexity and elongation (Fig.1-6). Firstly, the circularity value between 0 and 1 was defined as the ratio of the perimeter of the surface equivalent disc (Pe) to the real perimeter of the particle silhouette (Pr). The bigger value means the more alike to the equivalent circle. Secondly, the convexity describes the compactness of a particle. The maximum theoretical convexity is 1 that means the particle surface is very smooth. Finally, elongation stands for aspect ratio of particles and a needle shape has a high value which is close to 1 (Ji et al., 2015).

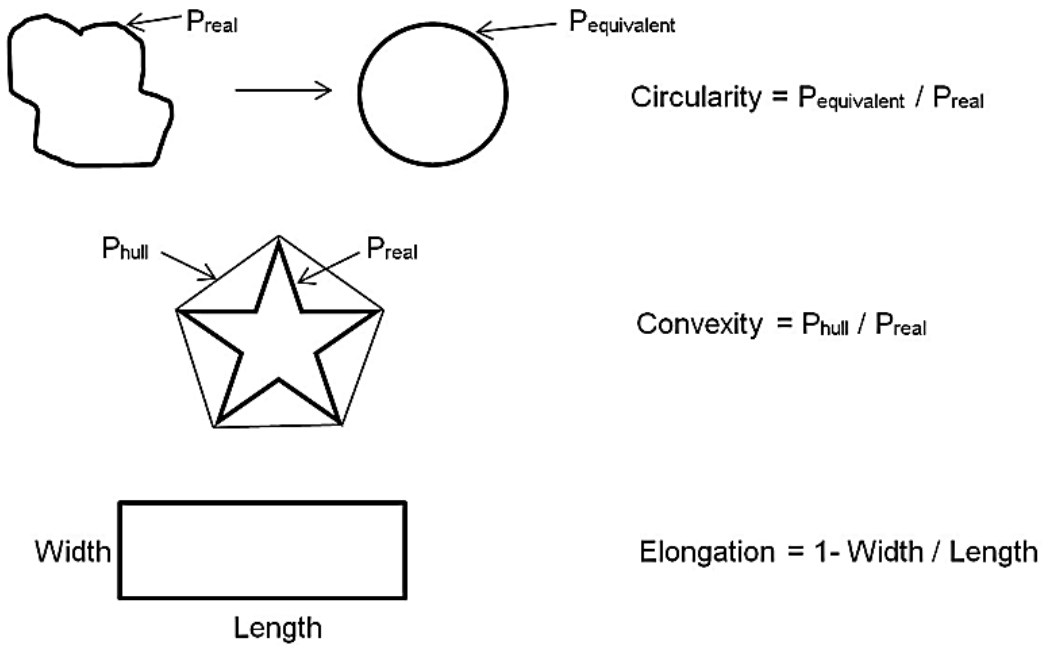

Fig.1-6 Representation of the shapes factors: Circularity, Convexity and Elongation (Ji et al., 2015)

3.3 Density and porosity

Density is normally defined as mass divided by volume. However, a powder is really a solid gas mixture, where there are interstitial spaces between the individual particles as well as internal pores and voids inside of the particle itself. Hence, the existence of gas in the powder results in three density definitions, which are bulk density, particle density and solid density. 1.) Bulk density refers to the weight per unit volume and is currently calculated by measuring the volume of 100 g of powder sample in a 250 mL graduated glass cylinder; 2.) Particle density is regarding as the weight of particle solids per unit volume; 3.) Solid density corresponds to the mass of powder solid (exclude the occluded air and interstitial air) per unit volume (Fitzpatrick, 2013; Litster and Ennis, 2013). They are all important attributes in products for shipment in bulk, saving packaging material and transport costs. For bulk density, there are two factors playing critical roles, which are the particle density and the

amount of the interstitial air, which depends on the particle size and shape properties of powders. Large sized particles with irregular shapes allow more spaces existing between particles and thus cause comparatively lower bulk density. Particle density is influenced by many factors, e.g. the composition of the solids (solid density), and the internal pores inside of individual particle. The pores and voids formed in the particle matrix are believed to be controlled by both processing conditions and the type of materials, which may have the natural foaming ability. For example, protein content trends to produce foams during spray drying process. Thus, reduced particle density is often achieved by forming the occluded air in dried particles (Sadek et al., 2015). In addition, excessive agitation of rotary atomizers is also found to increase the volume of occluded air in spray dried powders (Schuck et al., 2012). Porosity is a measure of the void spaces in a material, and is a fraction of the volume of voids over the total volume. It is usually used to describe the internal microstructure of the particles or agglomerates. Porosity value can be calculated by bulk density and solid density and is showed as a percentage between 0 to 100%. Thus, porosity is mainly contributed by the occluded air in particles and the interstitial air between particles (Bhandari et al., 2013).

3.4 The effects of post-dehydration processes on the physical and structural properties of powders

It is undoubtedly that agglomeration process increases the particle size of powder, as the process itself is designed as the size enlargement. However, owing to the different agglomeration equipment and processing conditions (Fig.1-7), the final granules present the increased sizes by different degrees (Cuq et al., 2013a). When using the higher viscosity liquid binders, stronger bridges are able to adhere more primary particles, which mean the final granule is able to reach the larger size.

Meanwhile, if applying stronger agitation forces for agglomeration (e.g. high shear mixing), molecular forces are dramatically increased by the decrease of distances between particles. Hence, more small particles are involved in the architecture of a granule, which may form the structures with higher strength (Barrera-Medrano et al., 2007). In addition, as shown in the previous section 2.2, the granule growth has different growth rate processes, which also contribute to the final granule size. For example, coalescence behavior is mainly responsible for the increase of particle size, while consolidation and breakage will decrease the size on the contrary. Therefore, the final particle size distributions of formed granules are considered to be closely related to the endpoints, where agglomeration process stops (Iveson et al., 2001). Coating process sometimes can also be used to increase the particle size by layering the coating materials, but contribute with different extents compared to agglomeration (Saleh and Guigon, 2007).

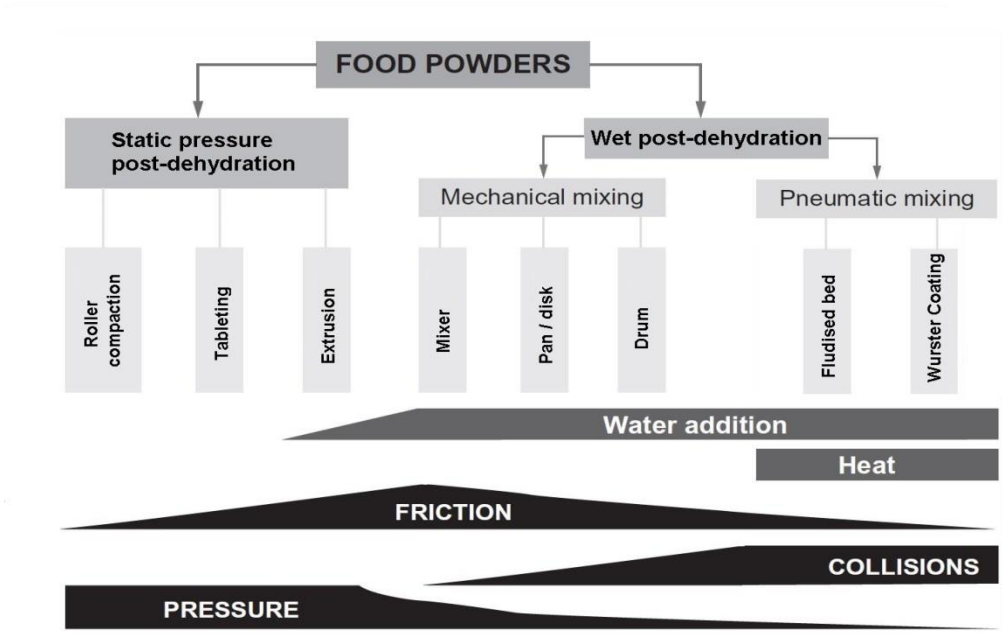

Fig.1-7 Diversity of post-dehydration technologies (Cuq et al., 2013a)

Post-dehydration processes play the different roles on modifying the shape properties and densities of granules, due to their own particularities in granule growth mechanisms (Litster and Ennis, 2013). As it is seen from Fig.1-7, powders in fluidised bed are pneumatically mixed by an air steam under the low shear conditions. This may cause the progressive formation of granules, which have less spherical shapes with rougher surfaces, because of the coalescence of the primary particles. Besides that, particles motivated by hot fluidising air-flow are quickly dehydrated and are less consolidated after they are connected by liquid bridges, which mean this kind of agglomeration tends to produce granules containing more internal voids. Thus, low particle density (more spaces inside) and low bulk density (low particle density and large interstitial gaps due to irregular shapes) are usually obtained for those fluidised bed agglomerates (Turchiuli and Castillo-Castaneda, 2009). Instead of low shear rates, mechanical mixer agglomeration process generates moderate or higher shear mixing by the rotating blades. High deformation thus occurs for the granules when they are consolidated by the violent collisions. The deformation not only causes the extrusion of particle structures, squeezing the air away from the powder matrix, but also physically modifies the shape properties of granules, forming the comparatively more rounded shape and smoother surfaces (Knight, 2001). In addition, fluidised bed coating and drum agglomeration also contribute differently to the density and shape properties of powders. They generally produced spherical particles due to their granule growth taking place by layering materials (coating materials or other primary particles) onto their nuclei. However, their effects on the modification of density are largely depended on the operation conditions and types of equipment.

Besides the effects on particle size, shape and density, post-dehydration process is also believed to influence the surface properties of powders, which is an important feature that corresponds to the surface physicochemical reactivity of powders (Murrieta-Pazos et al., 2012a). The most significant factor that determines the surface reactivity is the surface composition (Kim et al., 2009; Nijdam and Langrish, 2006). For example, spray dried whole milk powders have more fat content (less lactose) on the surface; therefore this may lead to undesirable poor wettability and poor flowability, which restrain the functional applications of the powder (Kim et al., 2002; Kim et al., 2005). However, if using agglomeration processes to add the suitable liquid binders (e.g. carbohydrate) onto the surface of particles, the surface compositions are thereby modified, where most of the fat content may be replaced by the binding materials. (Murrieta-Pazos et al., 2012b). It thus potentially improves the solubility and/or flowability of whole milk powders. In addition, the coating process produces dense particles with one or more layers, which are generated by spraying a solution onto the particles. This also provides a new surface composition with modified characteristics and specific purposes, such as protecting core materials, controlling the release rate in solution, etc. But the extent of change in surface composition and the coverage of the added substances still depend on many other factors, e.g. the shape and size of primary particles, the efficiency of process, the types and additions of liquid binders or coating materials (Lakkis, 2008). Overall, it will be interesting to compare the different effects of various post-dehydration techniques on the modification of powder surfaces, as well as to identify the possible relationships between these processes, surface properties and the subsequent functionalities.

4 The functionalities of powders

For food powders, there are a great number of functionalities regarding to the handling process and the end-use of products in the food industry. First of all, rehydration processes, including wetting, sinking, dispersing and dissolving behaviours, are believed to be the benchmark to determine the overall quality of powder products (Hogekamp and Schubert, 2003). Food powders are normally required to be rapidly and completely rehydrated into liquid phrase before use, as complete rehydration is a prerequisite for expressing the functionality of the dried ingredients (Richard et al., 2013). Furthermore, the recent need for food powders rehydration has been developed to dissolve into cold water with only simply stirring in a short time. Therefore, it is a big challenge for those food powders, which present inherent poor rehydration abilities (Anema et al., 2006; Gaiani et al., 2007a; Havea, 2006; Schuck et al., 2007). In addition, flowability and water adsorption are also important functionalities for the processing of food powders, namely manufacturing, handling, transport and storage. Poor flowability may restrict discharge from silos effecting throughput and product quality (Schulze, 2008); and the undesired water adoption behaviour may cause powder caking, instability of some materials (e.g. carbohydrate) and quality loss of the product (Carpin et al., 2016; Fitzpatrick et al., 2010; Hartmann and Palzer, 2011). Consequently, it is necessary to investigate these functionalities comprehensively and find the current problems, as well as the potential improvement methods.

4.1 Rehydration behaviours

Rehydration of powders is a dynamic process that generally consists of four stages based on the relevant reconstitution behaviours. 1.) Particles wetting and swelling in the aqueous phase. 2.) Sinking below the liquid surface. 3.) The

agglomerated particles break up and disperse into individual primary particles. 4.) Completely dissolve to form homogeneous solution. These stages often overlap and can be considered to occur concurrently during rehydration, which is dependent on the type of food powders (Fang et al., 2007; Forny et al., 2011). Due to the complexity of the rehydration process, it is necessary to be discussed individually for the purpose of this review.

4.1.1 Particle wetting

Wetting process is the first step where solids initially meet the liquid and then the liquid phase replaces the gaseous phase at the surface of a solid. For powders, good wettability usually means water is easily absorbed by those solids and subsequently immerses the particle matrix quickly, which need to overcome surface tension at the interface of water and solids. According to the Washburn capillary rise model (Washburn, 1921), it is commonly believed that the penetration depth of water is largely dependent on the structural and physical properties of powders. Those conditions favoured by the ideal fast wetting behaviours include the particles with large sizes, the porous structures with high porosity as well as small contact angles (Rouquerol et al., 2013). Some studies have also reported that water droplets easily penetrated the agglomerated dairy powder bed, which had high occluded air volume (more pores) inside of single granules (Crowley et al., 2016; Forny et al., 2011; Yuan and Lee, 2013). In addition, surface compositions also determine the wettability of dairy powders. For example, the presence of free fat on the surface of whole milk powders adversely delays water penetration due to its hydrophobicity. Lactose crystallisation may also cause the lipid migration by forming bridges and expelling free fat onto the surface.

4.1.2 Sinking below water surface

Sinking is referred to the process that particles fall below the liquid surface after they are sufficiently wetted. At this stage, powders are able to begin their solubilisation behaviours. Sinkability of powder is believed to be controlled by the particle density, which accounts for the true solid density and also the bulk density including the inter-particle void volume, and internal pore volume. Hence, the higher particle density combined with the less occluded air lead to a comparatively faster sinking rate (Fang et al., 2007; Schubert, 1993; Thomas et al., 2004). True density depends on the material composition of powders while the bulk density is influenced by the process conditions, e.g. spray drying or post-dehydration processes.

4.1.3 Dispersing into individual particles

Powder particles start to disperse into aqueous phase as individual particles before they are completely dissolved. When food powders are produced from liquid into powdered forms by drying process, most of them are partly agglomerated by solids bridges. Thus, it is necessary to dissolve these bridges first and break up into small primary particles. Otherwise, poor dispersibility may result in large lumps which restrain water penetration into single primary particles or prolong the fragmentation and erosion of powders (Schuck et al., 2007). It will negatively influence the subsequent dissolving step. The studies demonstrated that high porosity and large particles size appeared to be the essential criteria for good dispersing behaviours (Goalard et al., 2006). At the same time, the process is also dependent on the compositions of food powder as the structures of some ingredients (e.g. milk protein and lactose) affect the release rate of materials during dispersion and thus is closely associated with the dispersing extent of the powders (Crowley et al., 2015).

4.1.4 Dissolution in water

Dissolution is the final stage of powder rehydration and most physical functionalities are based on the complete disappearance and release of molecules to form the homogeneous solution. In general, the solubility of powder is mainly controlled by the nature hydrophobicity or hydrophilicity of food materials. For example, the solubility of milk protein is based on the hydrophilic part (polar residues) to interact with water molecules by hydrogen bonds, while hydrophobic residues avoid water molecules (Baldwin, 2010). In that case, the small hydrophilic molecules appear on the surface cause the fast dissolution rate. On the other hand, the dissolving stage is more like an end-point of rehydration process rather than a separated behaviour itself. Therefore, any delayed previous process (wetting, sinking and dispersing) may also influence the final soluble status of food powders.

4.2 Powder flowability

Powder flowability is the ability of powders to overcome the resistance to flow, which refers to the ease of powder movement, without forming lumps, clusters or aggregates (Schulze, 2006). The resistance involves the surface interactions between particles in contact and it can be categorised as internal friction and cohesion. Internal friction usually occurs as the frictional resistance of a particle moving over another particle under normal pressure; while cohesion resistance is caused by the attraction forces between particles, which are classified as van der Waals, electrostatic and magnetic forces. Of these cohesion forces, Van der Waals forces are believed to play the most important role for dry powders. The force is due to the positive and negative attractions between atoms on the surfaces of particles and thus is highly dependent on the contact area. The smaller sizes of powders with

the greater contact area usually correspond to the stronger Van der Waals attractions. In addition, the attraction is also found to be closely related to the distance between the particles. The force increases dramatically with the decrease of distance. Therefore, the bulk powders compacted by the normal stress, e.g. tablet, present the comparatively poor flowability due to the strong cohesion (Fitzpatrick, 2013; Stoklosa et al., 2012). Besides the physical and structural properties of powder particles, the differences in surface compositions are also considered to influence the cohesion degree of powders. For example, some studies in dairy powders reported that, the presence of water or oils on the surface of whole milk powders contributes to the different behaviours in their bulk flow properties (Fitzpatrick et al., 2007; Kim et al., 2005; Teunou and Fitzpatrick, 1999). Liquid will increase the contact area and may also form the liquid bridges between particles, which produce capillary forces as a result of surface tension. Consequently, stronger cohesion forces may occur based on the capillary forces. That is also the main reason for the appearance of caking phenomenon, negatively affecting the flowability of dairy powders.

Two basic flow patterns can be observed if bulk solids are discharged from a silo: core-flow (also often referenced as funnel-flow) and mass flow (Fitzpatrick et al., 2004b). In the case of core-flow, the most significant behaviour is that cohesive powders will move out through a central funnel, which is formed by the no-flow particles remaining at the internal walls of hopper during the discharge. The lack of flow at the walls is primarily on the basis of the friction that develops between the particles and the internal wall material/surface finish used in the construction of the silo. When the internal friction of powder particles becomes weaker than the friction acting at the wall, powder bed will fail internally and then a flow channel will develop.

All the solids are in motion to give a first-in and last-out discharge regime, which have a critical impact on the handling performance and product quality. On the other hand, mass-flow is known as an alternative flow pattern, which only occurs if the hopper walls are steep and smooth. In that case, the inventory of the vessel is drawn down evenly across the cross-sectional area, giving a first-in and first-out discharge regime. That will also provide the materials with high repeatability and consistency in discharge rate before reaching the outlet (Schulze, 2007).

4.3 Water adsorption

Moisture content is very important for all aspects of food powder handling processes (Ortega-Rivas et al., 2006). On the basis of different unhindered or hindered mobility, it can be classified as free and bound water. The amount of free and bound water held by the product is believed to be controlled by the water-holding or water-binding capacity of the material, respectively (Watano, 2006). Basically, ‘bound water’ is considered as that portion of water held in the material which shows physical properties significantly different from those of free, or bulk water. In that case, hydrogen bond between water and acceptors is found to be stronger than that between liquid water and water-solvating nonpolar groups. The interactions of water and low-moisture product may be categorised as monolayer, multilayer and water bound in capillaries. 1) Vicinal water may form a monolayer but is unable to act as a solvent; 2) Multilayer water associated with water-water bonds result in the rapid increase of moisture content in the isotherm; 3) entrapped water caused by the capillary condensation, which may act as a solvent for various solutes (Al-Muhtaseb et al., 2002). However, due to the complexities and interactions of the binding forces involved, there is no universal definition of bound water. In the food industry, the most used conception is water activity, defined as:

$$aw = {}^{p}/_{p0}$$

where p is the partial pressure of water in the food , and p_0 the vapour pressure of pure water at the same temperature (Hedegaard and Skibsted, 2013).

The relationship between water activity and total moisture content of a product can be expressed as a sigmoid curve, which is called a sorption isotherm. An adsorption isotherm is usually obtained by placing a dry material into different environment of increasing relative humidity and measuring the weight gain due to water uptake; while a desorption isotherm refers to the opposite (put a wet material into same environment and measure the weight loss) (Schuck et al., 2012). The isotherms present the water adsorption capability as well as water retention, contributing to moisture content during storage and the stability in physical and chemical properties. In addition, water sorption always occurs as the dynamic process, which needs time to transfer water within the matrix from the surrounding atmosphere before equilibrium. Thus, it is also important to measure the kinetics of water sorption, which is necessary to monitor the product quality, especially in the food industry. The behaviour depends to a large extent on the surface and structural properties of the product, i.e., sorption area, porosity, composition and the state of individual components (Guillard et al., 2013). These factors are all considered to affect the rate and extent of entry and exit of water molecules into the solid matrix. For example, many studies have claimed that lactose crystallisation significantly decreases the water uptake of skimmed milk powders when relative humidity increases to 40%. This is due to crystallisation beings accompanied by a release of four or five water molecules and thus causes the drop in water adsorption (Bronlund and Paterson, 2004; Hedegaard and Skibsted, 2013; Murrieta-Pazos et al., 2011; Schuck, 2013; Shrestha et al., 2007). Besides that, different dairy powders, e.g. whey protein, micellar casein, caseinates, skimmed milk powders, all exhibit various

sorption behaviours by adsorbing different amount of water at the same temperature (Schuck et al., 2012).

4.4 The potential effects of post-dehydration process on the functionalities of a powder

Many functionalities of a powder have been demonstrated to be closely related to its structural and physical properties (Cuq et al., 2011; Sharma et al., 2012). As it is discussed previously, wetting behaviour during the rehydration of a powder is dependent on the porous structures and the surface compositions of the particles (Lazghab et al., 2005); sinking and dispersing process is influenced by particle density, porosity as well as particle size (Gaiani et al., 2007b). Thus, it is very possible to use the post-dehydration techniques, including various agglomeration processes and coating processes, to improve the rehydration process of a powder by optimising these physical characteristics and changing the surface properties. Similarly, flowability and water adsorption are also determined by surface area of a powder, particle size and probably the morphology of particles. Consequently, it will be interesting to identify and validate the relationships based on different powders first, e.g. different formulated dairy powders; and then investigate the feasibility of the application of post-dehydration technology for the better control of flowability and water adsorption behaviours.

5 The application of post-dehydration process on dairy powders

The composition of milk consists of proteins, carbohydrates, fats, minerals and water. As the development of filtration technology, different milk materials can be separated from raw milk (Oftedal, 2013). For example, fat content can be removed by centrifugation from whole milk to produce skimmed milk; 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 and 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 et al., 2013; Pitkowski et al., 2009). After that, the majority of these liquid milk materials are dehydrated and converted into the powdered form for extended applications in new value added dairy products and beverages (Ann Augustin and Clarke, 2011).

However, the dairy powders exhibit a lot of problems and issues for their functionalities, which largely limit the subsequent processing capacity. As it is shown in Table 1-2, it gives the rehydration abilities of some typical dairy powders. Most of them exhibit either poor wettability or difficult-to-dissolve. For example, the micellar casein dominant powders (e.g. milk protein isolate, micellar casein) showed the prolonged solubilisation process due to the strong interaction between casein micelles structures. These structures made of calcium phosphate nanoclusters are considered to be difficult to break up and thus need long time to dissolve into water (Crowley et al., 2015; Dalgleish, 2011; Schuck et al., 2007). Meanwhile, although whey protein is considered to be fast-dissolving in water, whey protein isolate is still found to have extremely poor wettability, which also adversely delays the subsequent dispersing and dissolving processes (Gaiani et al., 2007b). Some studies reported that most dairy powders produced by spray drying process, especially for those milk protein powders, had comparatively small particle size with low interstitial air, which may result in the problematic rehydration (Bouvier et al.,

2013; Chen and Patel, 2008; Mimouni et al., 2010). In addition, these fine particles including dense structures are also believed to be the main reasons to cause poor flowability behaviour during conveying and susceptibility to moisture adsorption during storage and transport (Fitzpatrick et al., 2005; Fu et al., 2012; Rennie et al., 1999). It is more likely to occur on the lactose-based dairy powders, which tend to combine with moisture molecules and thus forming the crystallised structures and caked lumps, negatively affecting the product quality (Carpin et al., 2016). Consequently, post-dehydration processes can be used as a potential method to improve these functionalities of dairy powders, which are influenced by the physical and structural properties.

Table1-2 Rehydration abilities of the typical dairy powders

	Wettability	Sinkability	Dispersibility & Solubility
Whole milk (fat >26%)	Poor	Poor	Difficult
Skimmed milk	Instant	Quickly	Easy
Milk protein isolate (protein >85%)	Poor	Poor	Difficult
Micellar casein (protein > 80%)	Poor	Poor	Difficult
Sodium caseinate	Extremely poor	Extremely poor	Quickly
Calcium caseinate	Poor	Poor	Difficult
Whey protein isolate (protein > 90%)	Extremely poor	Extremely poor	Quickly
Whey protein concentrate 35	Poor	Poor	Quickly
Whey permeate	Instant	Quickly	Quickly

Reference from Schuck et al. (2012)

6 Conclusion

It has been found that the post-dehydration techniques can be used to modify the physical and structural properties of powders by forming new granules with normally bigger particle size, different shape properties, and changed bulk and particle densities. These kinds of modifications are largely dependent on the selection of post-dehydration processes, which are based on various granule growth mechanisms. The fluidised bed agglomeration tends to produce large granules with porous structures, while mixer agglomeration usually produces granules with compressed structures, which means high particle density and high strength structures. Drum agglomeration creating the median consolidation will produce the intermediate granules but have more spherical shape due to the centrifugal forces. For coating process, more resistant agglomerates associated with smaller size and less porous structures may be produced by layering with coating materials.

On the other hand, different granule growth rate processes are also responsible for the extent of the physical and structural modifications. Nucleation is a critical stage in determining the final quality of the granules as good wetting behaviour may ultimately result in the narrow particle size distribution. Coalescence is the main process where nuclei start to grow dramatically, while consolidation behaviour reduces the size and porosity of granules by different degrees. Attrition and breakage may also further influence the granule size and shape at the end of the process.

Some functionalities of a powder are closely related to its physical and structural characteristics. During the dynamic rehydration process of a powder, the wetting behaviour is determined by the porosity and the surface properties, while sinking and dispersing processes are highly determined by the particle size and density.

Flowability of a powder is also influenced by the particle size, surface contact area between particles or particle and walls. In addition, big particle surface area, large interstitial space between particles and internal pores inside of single particle result in the quicker water transfer and more moisture uptake. Consequently, regarding to these factors on the subsequent functionalities, the post-dehydration technology exhibits the potential effects on improving the processing capacity and end-uses of the powder. As most of post-dehydration processes are used in pharmaceutical materials, few studies have been done in the area of food powders, especially for dairy powders. Meanwhile, the spray dried dairy powders present many limitations in rehydration, bulk flow and water adsorption. Therefore, it is of industrial interest to investigate the application of post-dehydration technologies for overcoming problematic powder functionalities and improving the functionality of high protein dairy powders in particular.

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CHAPTER TWO

Assessment of measurement characteristics for rehydration of milk protein based powders

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Abstract

Rehydration is an important powder property and is regarded as a critical issue by the dairy industry. Traditional powder rehydration measurements are relatively empirical with poor reproducibility. Thus, more reliable techniques tailored for dairy powders should be developed based on varied rehydration behaviours and applications. In this paper, a critical assessment to identify the measurement characteristics of milk protein powder rehydration is presented. Milk protein based powders were used as model systems. Four different wettability measurements (Immersion, Capillary rise, Condensation and Spreading) and four different dispersibility measurements (Dispersibility Index, Light scattering of particles in suspension, Light transmission and Conductivity of suspension) are compared and analysed. The results show that the method based on immersional wetting procedure is only appropriate for skimmed milk powder while the method for capillary rise wetting is more useful for the agglomerated milk protein powders with porous structures. Contact angle changes in the spreading wetting approach is found to be a straightforward technique to show the hydrophobicity or hydrophilicity of milk protein powders. If compared with traditional dispersibility measurements, light transmission of suspension is suitable to reflect optical properties of slow dispersion process. Light scattering methods can also be used to measure the dynamic size change of particles during the dispersion process. Furthermore, the conductivity of suspensions is a useful indicator to quantify the dispersibility indirectly by the release of minerals during rehydration. It is necessary to understand the specialities and applications of dairy powders before choosing the appropriate rehydration measurement methods.

Keywords: Milk protein powders, wettability, dispersibility, rehydration measurements

1 Introduction

Rehydration properties are considered as an important benchmark to determine the overall quality of powder products. In the dairy industry, powder rehydration is regarded as a critical issue as some powders exhibit poor wettability with the materials floating on the surface of solution and others dispersing very slowly accompanied by lump formation, which is especially the case for high-protein-containing powders (Anema, Pinder, Hunter, & Hemar, 2006; Havea, 2006). Traditional dairy powder rehydration measurements, which were often designed for the analysis of instant skimmed milk powder or whole milk powder, are thus relatively crude with poor reproducibility for other specialty milk protein products (i.e., micellar casein, whey protein or milk protein isolate powders). Therefore, more analytical approaches have been developed to observe each dynamic step and to find the methods to quantify the kinetics of powder rehydration process (Crowley, et al., 2015; Fang, Selomulya, & Chen, 2010; Forny, Marabi, & Palzer, 2011; Freudig, Hogekamp, & Schubert, 1999; Gaiani, Scher, Schuck, Desobry, & Banon, 2009; Marabi, et al., 2008; Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2009). However, it is a challenge to find a universal method to measure the rehydration abilities of varied dairy powders, as they present significantly different behaviours during the rehydration process. Recent studies have shown that whey protein isolate powder has poor wettability and that the wetting stage is the main limiting factor for whey protein rehydration. In comparison, the slow dispersion of micellar casein is responsible for its extended rehydration time. Whereas for milk protein isolate, both wetting and dispersing processes are rate-limiting steps (Gaiani, Schuck, Scher, Desobry, & Banon, 2007; Schuck, et al., 2007). Consequently, it is necessary to examine the feasibility of the existing techniques for determination of the rehydration

of milk protein powders and to validate the every typical powder and technique case by case in order to find the most appropriate one.

It is commonly believed that wetting is the critical step in powder rehydration process, as powder materials with poor wettability have limited access to contact with water which then causes the formation of non-hydration regions. In general, wetting behaviour can be assessed through different procedures including immersional wetting, capillary wetting, condensational wetting and spreading wetting in Fig.2-1, which was modified and developed from the other researches (Israelachvili, 2011; Lazghab, Saleh, Pezron, Guigon, & Komunjer, 2005). The immersional wetting process uses the time required for a given mass of powder to submerge fully below the liquid surface as a measure of wettability. But it is mainly of practical use for dairy powders that are easy to wet whereas milk protein based powders tend to float on the surface of the liquid and so wetting time is no longer a useful measure. Thus, it is interesting to assess which kind of dairy powders will be suitable for characterisation by this traditional immersional wetting process. Secondly, capillary rise wetting is a process whereby the liquid penetrates into the solid porous structure by capillary force. For this case, the Washburn method is mostly used, which can be quantified by the mass of adsorbed liquid as a function of time (Ji, Cronin, Fitzpatrick, Fenelon, & Miao, 2015; Thakker, Karde, Shah, Shukla, & Ghoroi, 2013; Washburn, 1921). However, the feasibility of this approach for dairy powders is still not validated, as some researches have shown that spontaneous liquid penetration only occurs if the contact angle between the liquid and solid is lower than 90° (Yuan & Lee, 2013). Also the wetting behaviour by capillary rise is not only influenced by the actual wettability but also by the porous architectures of solids (Buckton & Newton, 1986). Thirdly, the condensational wetting process concerns the

adsorption of moisture vapour on a solid surface and faster wetting usually corresponds to higher rates of vapour sorption (Israelachvili, 2011). The method uses different salts solution in desiccators to provide varied relative humidity environment for powder adsorption (Schuck, Jeantet, & Dolivet, 2012). Hence uptake of water vapour may represent totally different wetting behaviours for milk protein powders compared to wetting by liquid water where surface tension effects need to be considered. Finally, the spreading wetting process focuses on the contact angle when a given amount of a liquid spreads over a solid substrate (Israelachvili, 2011; Rouquerol, Rouquerol, Llewellyn, Maurin, & Sing, 2013). The method examines a single liquid drop penetrating into solids and thus evaluates the wettability by monitoring the changes in contact angles over time.

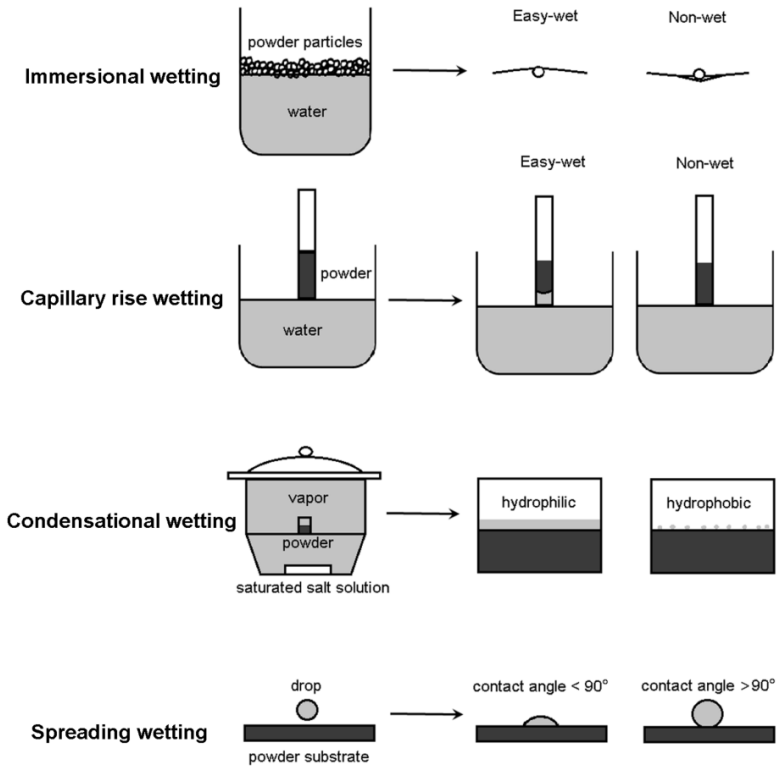

Fig.2-1 Different wetting procedures

In summary, all four methods corresponding to different wetting procedures have been widely used in pharmaceutical research, however few applied in dairy powder research. Therefore, it is important to identify whether the analytical methods based on these four wetting procedures are suitable for the typical milk protein powders.

Dispersibility is also believed to be an important step in the rehydration process, as it is necessary for particles to be dispersed into the liquid before dissolving (Galet, Vu, Oulahna, & Fages, 2004; Goalard, Samimi, Galet, Dodds, & Ghadiri, 2006). The dispersion process is accompanied by the transfer of particle mass, particle size and particle energy, which can be used as the indicators to quantify the process (Forny, et al., 2011). The use of the dispersibility index is the traditional standard method to measure the amount of dry matter combining simple mixing in a liquid followed by sieving. Limitations of this method are that it cannot monitor the dynamic dispersing process and it is often influenced by the wetting behaviour of powders as they need to be wetted first. Therefore, more effective methods have been found for improved monitoring of the particles dispersibility. The most common method is the use of an optical fibre sensor to collect the intensity of light scattering of particles in suspension. Based on the principles of forward light scattering, it has been used to measure the particle size distribution over the mixing time and to monitor the dispersibility of powders in terms of the variation in particle size (Chen & Lloyd, 1994; Galet, et al., 2004). Moreover, transmission of near-infrared light has also been used to exhibit the dynamic process of solids dispersing in the suspension during centrifugation (Crowley, et al., 2015). Although some studies have shown light scattering and transmission to be reliable methods to monitor dispersion behaviour for food powders and milk protein powder (Crowley, Kelly, & O'Mahony, 2014; Fang, Selomulya, & Chen, 2007), it is still required to examine and investigate the

selectivity of these methods with other dairy powders as they present completely different dispersion behaviours. Additionally, conductivity is another possible approach to express the kinetics of dispersing process via the release of minerals in suspension (Zhuang, Zhou, Nguyen, & Hourigan, 1997). Numerous studies reported that some minerals had approximately the same dissolution rate as micellar casein (Holt, 1997; Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2010). However, it is still not fully understood whether the conductivity method is capable of quantifying the dispersion of MPI or MC and other non-casein dairy powders.

In this paper, four wettability methods and four dispersion methods are applied to measure the rehydration behaviour of six milk protein powders, which are whey protein isolate (WPI), micellar casein (MC), sodium caseinate (SC), milk protein isolate (MPI), MPI agglomerate and skimmed milk powder (SMP). The objective is to evaluate the advantages, drawbacks and limitations of each of the methods and to identify which methods are more suitable for assessing the rehydration behaviour of milk protein powders.

2 Materials and Methods

2.1 Materials

MPI, SC and SMP were supplied by Kerry Ingredients (County Kerry, Ireland). WPI was supplied by Davisco Food International (Le Sueur, MN, USA). MC was produced from skimmed milk powder by firstly microfiltration with 100 kDa molecular weight membranes. The retentate is concentrated by vacuum evaporation and the concentration process was performed at a temperature of 65 ℃. The solid concentration of about 38% was then obtained by the water removal. Finally, the concentrated solution was spray dried to obtain the MC powders. The inlet and outlet

temperatures were 180 ℃ and 85 ℃, respectively, and the drying air-flow rate is 750 $m^3 \cdot h^{-1}$. The manufacture of agglomerated MPI powder was described in details in the study of Ji, et al. (2015). Briefly, 100 g 15% lactose solution was used as the binding liquid which was progressively added to 200 g MPI powder (1 $mL \cdot min^{-1}$) in a top-spray fluidised bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Lowa, USA). The temperature of injected air was 50 ℃ and the air flow rate was 200 $L \cdot min^{-1}$. After the addition of lactose solution, the obtained powder was dried with hot air at 100 $L \cdot min^{-1}$ flow rate and 50 ℃ temperature for a further 15 minutes. The compositions of the milk protein powders are shown in Table 2-1. All the powders were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 45 ℃ overnight to obtain the final moisture content of about 1.5%. They were kept in the desiccators before the wettability and dispersibility measurements.

Table 2-1 Composition of dairy powders investigated in this study

Dairy powder	Protein (%,w/w)	Moisture (%,w/w)	Lactose (%,w/w)	Fat (%,w/w)	Ash (%,w/w)
MPI	86.0	4.0	<1.0	1.5	6.0
Agglomerated MPI	82.0	5.0	6.2	1.4	5.6
WPI	90.0	5.0	<1.0	1.0	3.0
MC	84.0	5.0	2.0	1.0	7.5
SC	88.0	5.7	<1.0	0.7	4.7
SMP	36.0	4.0	51.0	0.8	8.2

2.2 Wettability measurements

2.2.1 Wetting time by immersional wetting procedure

This method is used to quantify the wettability of dairy powders by the time needed to achieve complete wetting of a given quantity of powder, when powder is gently dropped on the surface of water and immersed without any agitation (Schuck, et al., 2012). In this study, 6 g powder samples were filled into a standard 400 mL beaker, which contained 100 mL of distilled water with 20 ℃ temperature. Powder was considered as wettable if wetting time was less than 60 seconds and non-wettable if wetting time was greater than 120 seconds (GEA Niro, 2005). All the measurements were repeated three times.

2.2.2 Modified Washburn method by capillary rise wetting

Washburn method is a common technique to measure the wettability of powders based on capillary rise wetting behaviour. It usually monitors the rate that a liquid penetrates into powders or granules by recording the penetration depth of the liquid inside the capillary as a function of time (Washburn, 1921). However, the method can be derived and developed into other forms, e.g. the depth of penetrated liquid is instead of mass. The principle of the instrument was described in the study of Ji, et al. (2015). A 2 g powder sample was loaded into a cylindrical glass tube with an open base bottom covered by filter paper and gauze. The tube was set just above the surface of distilled water at 25 ℃. The wettability of powder was quantified by the additional mass of the wetted powder in 10 minutes, which was the weight of adsorbed water by the powder. Each sample was measured five times.

2.2.3 Water adsorption by condensational wetting

Condensational wetting procedure can be considered as water vapour adsorption and was determined by static-gravimetric method. Triplicate 1 g powder samples of each dairy powder were stored in empty glass vials of known weight. The

powders were kept in desiccators with a stable relative humidity, which ranged from 11% to 75%, until equilibrated. The hygroscopic environment (R.H.) was provided by different saturated salt solutions which were LiCl (11%), CH_3COOK (22%), $MgCl_2$ (33%), K_2CO_3 (43%), $Mg(NO_3)_2$ (53%), $NaNO_2$ (65%) and NaCl (75%). The desiccators were evacuated before they were stored in a 25 ℃ incubator. The weight of powder was measured for at least 96 hours until it reached a constant value. The results were expressed as equilibrated moisture content as a function of water activity to show the water vapour adsorption isotherms.

2.2.4 Contact angles by spreading wetting

The measurement of contact angle is a direct method to measure the tangent angle at the contact point of three phases. Due to the dynamic process for the wetting behaviour, it is usually to monitor the rate of change of contact angle to quantify the wettability of powders (Crowley, et al., 2015). Thus, an optical tensiometer (Attension Theta, Biolin Scientific Ltd., Espoo, Finland) was used to measure contact angle (θ) of 12 μL deionised water droplet by the sessile drop technique with dynamic live measurements at a temperature of 20 ℃. Before measurement powders were loaded into an aluminium pan (ø=100 mm, h=7 mm) and a smooth surface was formed by passing a leveller across the surface. The volume of the remaining water droplet above the solids during the wetting process was also evaluated (Yuan, et al., 2013). The measurements for each sample were repeated at least 5 times.

2.3 Dispersibility measurements

2.3.1 Dispersibility Index

The Dispersibility Index (DI) is defined as the percentage (%) of dry matter that passes through a sieve after mixing for a short time with a spatula. The sieve with mesh size of 250 μm is used to separate the dispersed particles from the suspension based on the extent of dispersion (Schuck, et al., 2012). In this study, 10 g powder was added into a 250 mL beaker with 100mL deionised water at 25 ℃ and then mixed vigorously with a spatula for 15 seconds in order to make 25 complete circle stirring movements along the diameter of the beaker. After that, the reconstituted samples were then poured onto the 250 μm sieve to separate the dispersed particles in the suspension based on the extent of dispersion, and the samples that passed through the sieve were collected in a bottle for further drying at 105 ℃ temperature overnight in an oven. The extracted dry matter was weighed and used to calculate the DI as following Equation (1):

$$DI = \frac{W_d \cdot (100 + w)}{w \cdot \frac{100 - W_m}{100}} \quad (1)$$

Where w is the weight of sample, W_d (%, w/w) is the dry matter after sieving, W_m (%, w/w) is the free moisture content of the powder. The measurements for each sample were repeated 3 times.

2.3.2 Particle size measurements by laser light scattering method

Laser light scattering method based on Malvern Mastersizer 3000 (Malvern Instruments Ltd, Worcestershire, UK), was used to quantify the powder dispersion process in term of decreasing rate of particle size. The detailed measurement principle of the machine was described in the study of Ji, et al. (2015). In order to reach the ideal obscuration range of the machine, approximately 5 mg MPI, MC, SMP and 100 mg WPI and SC were added into dispersion unit with 120 mL distilled

water at a temperature of 25 ℃ ± 2 ℃ and then agitated at 2000 rpm. Triplicate measurements were carried out for each powder. Particle size distributions were recorded every 2 minutes until D (50) reached ~1 μm (the diameter of 50% particles was just lower than 1 μm) (Ji, et al., 2015; Mimouni, et al., 2009).

2.3.3 NIR transmission measurements by Lumisizer

Lumisizer (L.U.M. GmbH, Berlin, Germany) is an analytical centrifuge, which was used to quantify the dispersibility of milk protein powders by measuring the intensity of transmitted near-infrared light in suspension. 1.5 g samples were rehydrated into 100 mL deionised water at a temperature of 25 ℃. 1.5% (w/v) concentration suspension was then obtained through agitating by a magnetic stirring bar (length 2.5 cm) with a rate of 400 rpm for 30 minutes. After that, 400 μL suspensions were sampled by 16 gauge needles to fill into polycarbonate cells. The sampling positions always had a constant distance (approximate 1 cm) from bottom of the beaker. The measurements were carried out by two different centrifugations; firstly 36 g for 10 minutes and then followed by 168 g for further 10 minutes. The intensity of the transmission of NIR light was measured in the distinct regions of the sample cell and was related to the different phases of dispersion, including stable solution, initial sediment and compressed sediment, which created the varied optical densities. The transmission profiles were presented every 10 seconds for the first 10 minutes 36 g centrifugation and then every 60 seconds for next 10 minutes 168 g centrifugation. Integral transmission of each profile was calculated by software SepView 4.1 (L.U.M. GmbH, Berlin, Germany) and is shown as a function of time. Meanwhile, compressed sediment height under 36 g and 168 g of centrifugation was determined by the area of greatest optical density, which means the area of lowest

transmission but subtracting the steady-state value caused by the cell bottom (Crowley, et al., 2015).

2.3.4 Conductivity measurements during particles dispersing

Conductivity meter (FE30-Kit-FiveEasy™ conductivity, Mettler Toledo Ltd., Greifensee, Switzerland) was used to measure the release of minerals accompanied by the rehydration of powders and showed the ionic strength of reconstituted powders. Each sample weighting 8 g was poured into 400 mL deionised water and wetted by the vortex as rapidly as possible. A 2% w/v solid suspension was created and mixed at 500 rpm in a 25 ℃ water bath. Deionised water was used and had a conductivity value of 67 $\mu s \cdot cm^{-1}$. The probe was calibrated at 25 ℃ with a standard solution of known conductivity value of 1314 $\mu s \cdot cm^{-1}$ before placed in the suspension. The values were recorded every 10 seconds for the first 2 min, followed by every 60 seconds for next 10 minutes and every 10 minutes for final 90 minutes. The measurements for each sample were repeated at least 3 times.

3 Results and Discussion

3.1 Wetting behaviours of milk protein powders based on different wetting procedures

3.1.1 Wetting time by immersional wetting

As can be seen from Table 2-2, only the skimmed milk powder can be considered to be wettable with a wetting time of 22 seconds. The other powders required very long times in excess of 20 minutes (although the agglomerated MPI did have a time of 8 minutes). The result is not surprising because skimmed milk powder contains high content hydrophilic lactose, which allows water easily penetrating into the particles and thus sinking and dispersing quickly in the water. But for other high protein

powders, there was an impermeable hydrophobic layer formed between the water surface and powders. This layer separated the water and the powder so that water had no access to penetrate into powder particles and caused the formation of non-hydration regions (Gaiani, et al., 2007; Schubert, 1993). In that case, the interface of solid and gas was difficult to be replaced by the interface of solid and water due to the high content of hydrophobic milk protein powder with low porosity. Therefore, the traditional method based on immersional wetting procedure was not suited for the milk protein powders with poor wettability. Moreover, as powder wetting behaviour is a dynamic process, it is better to measure the kinetics of wettability, which usually can be quantified by the associated free energy change when the type of interface is transformed (Yuan, et al., 2013).

Table 2-2 Wetting time of dairy powders by immersional wetting procedure

	SC	WPI	MPI	Agglomerated MPI	MC	SMP
Wetting time	>20min	>20min	>20min	8min ± 2min	>20min	22s ± 3s

3.1.2 Modified Washburn capillary rise wetting method

It is obvious to see that capillary rise wetting method is largely dependent on the inter-particle pores of powder samples and the choice of liquid, which determines the surface tension and viscosity (Forny, et al., 2011). Hence, it is the reason why agglomerated MPI with porous structure showed the greatest wettability in Fig.2-2, which absorbed more than 1 g water in 10 minutes (Ji, et al., 2015). At the same time, MC powder also showed comparatively good wetting behaviour as it absorbed nearly 0.5 g water. But for SC and WPI powders, they were only slightly wetted by water because water cannot penetrate into a powder spontaneously if high contact

angle (θ>90℃) and negative capillary pressure (Lazghab, et al., 2005; Palzer, Sommer, & Hiebl, 2003; Yuan, et al., 2013). Moreover, it is interesting to find that SMP powder only gained about 0.1 g weight after 10 minutes of the capillary wetting procedure, which should be wetted by water much more easily. However, SMP might dissolve quickly in the measuring water during measurement so that pure water was replaced by the drops of solution saturated with SMP. It caused the viscosity of liquid to increase, which decreased the rate of water uptake at the point at which the weight of water balances the capillary pressure (Stamm, Gissinger, & Boymond, 1984). Consequently, the modified Washburn method based on capillary effect was concluded to be sensitive to agglomerates with high porosity but not applicable for dairy powders that are easy-dissolved.

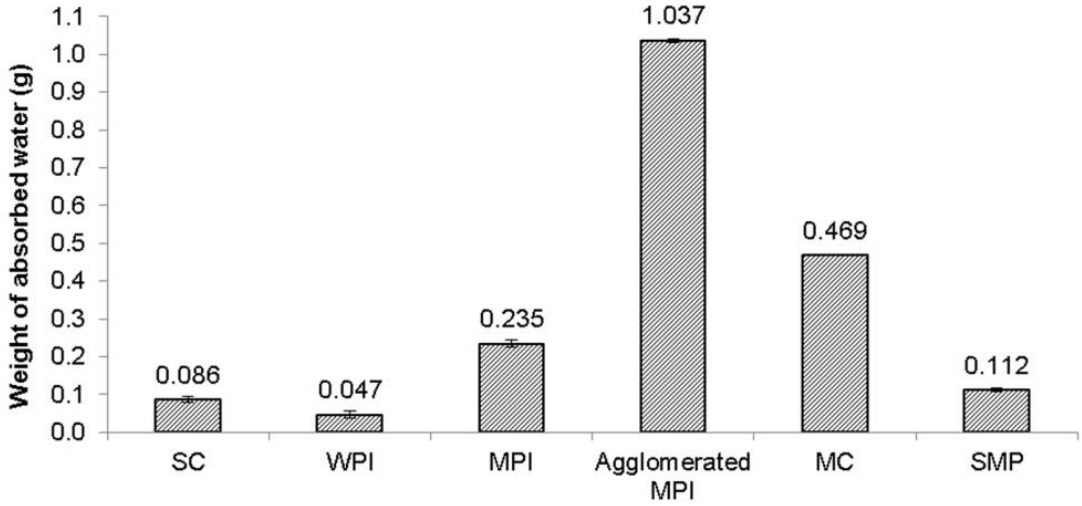

Fig.2-2 Mean weight of absorbed water for samples (SC, WPI, MPI, Agglomerated MPI, MC and SMP) after 10 minutes

3.1.3 Water adsorption by condensational wetting

In Fig.2-3, WPI and SC powders were found to adsorb the greatest mass of moisture at relative humidity value from 11% to 75%. It is inconsistent with the results measured by other wettability methods, which showed WPI and SC powders

had extremely poor wettability. It is explained previously as the formation of an impermeable layer at the powder-water interface. However, for condensational wetting behaviour, the water vapour seemed to more easily penetrate into powdered solids and wetted them without creating any films or layers, although the vapour may condense into liquid droplets during the process (Depalo & Santomaso, 2013; Lazghab, et al., 2005). Hence, WPI and SC may have the higher rates of vapour adsorption and better wettability by the condensational wetting mechanism. Fig.2-3 also illustrates that unagglomerated MPI and agglomerated MPI powders have no obvious difference in the isotherm data, which means that agglomeration process played no special role on MPI's water sorption behaviour. SMP exhibited different water adsorption isothermal behaviour from other powders, with no increase in moisture adsorption between the water activity values of 44% and 53%. This behaviour is consistent with previous reports that demonstrated lactose content in SMP reduced water adsorption due to crystallisation (Bronlund & Paterson, 2004; Jouppila & Roos, 1994; Shrestha, Howes, Adhikari, & Bhandari, 2007).

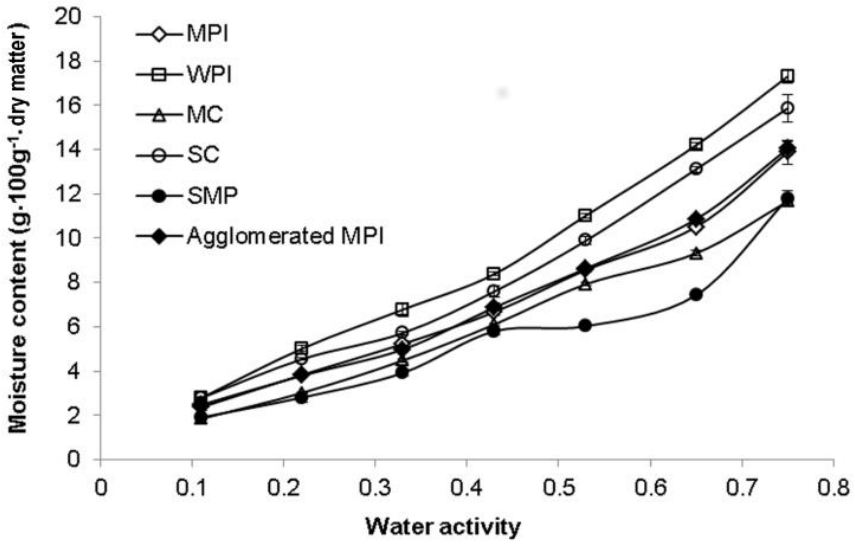

Fig.2-3 Water vapour adsorption isotherms of dairy powders (MPI, WPI, MC, SC, SMP and Agglomerated MPI) at 25 ℃ environment

Water adsorption phenomenon of different milk protein powders has been discussed many times elsewhere (Berlin, Anderson, & Pallansch, 1968; Foster, Bronlund, & Paterson, 2005; Kinsella & Fox, 1986; Murrieta-Pazos, et al., 2011). Few of them mentioned the adsorption properties as an indicator of powder wettability. Generally, wetting behaviour is evaluated as the critical first step of rehydration process of powders (Depalo, et al., 2013; Hogekamp & Schubert, 2003). But in this study, condensational wetting was discussed as an exceptional issue due to solids being wetted by water vapour instead of contacting water or water droplets directly. This method is different from other three wetting methods (immersion, capillary rise and spreading) based on the contact angle of liquid phase and solid phase (Kwok & Neumann, 1999), while condensational wetting procedure focused on the adsorption of saturated vapour, where the interfacial effects are less pronounced. Therefore, though this static-gravimetric method for water sorption measurement could quantify the vapour wetting with high accuracy and good reproducibility, it is not able to assess the wettability regarding powder rehydration process. But vapour wetting may still provide some insights into general wettability of dairy powders.

3.1.4 Contact angles by spread wetting

Contact angle is usually used as a primary parameter to indicate the degree of wetting process with a small contact angle ($\theta<90°$) representing good wettability and large angle ($\theta>90°$) corresponding to poor wettability (Gao & McCarthy, 2006; Mittal, 2006). As the surface of liquid is exposed to wet the fresh surface of solid after liquid drop and solid interact, it is important to monitor the rate of change of contact angle until reaching an equilibrium angle. It means wetting behaviour is dynamic procedure other than a static state (Link & Schlünder, 1996). Thus, in this study, it showed how

the contact angle of samples changed and also the volume of droplets above the substrate decreased as a function of time.

According to Fig. 2-4A-B, the contact angle of SMP reduced dramatically in just 5 seconds with a final angle of 60° and 3.5 µL water volumes remained. MC powder was second fastest, which took about 15 seconds to reach the equilibrium. Meanwhile, agglomerated MPI was found to be more easily and quickly penetrated by water droplet than that of unagglomerated MPI, because of the significant effect of agglomeration process on improving the wettability of MPI (Ji, et al., 2015). WPI and SC powders exhibited extremely poor wetting behaviours with contact angles changing only by about 40 degrees and 10 degrees in 5 minutes, respectively. This method showed advantages due to its simple operation, straightforward observation and high selectivity for dairy powders (Crowley, et al., 2015). It only needs a small amount of liquid and a small powder contact surface area (Letellier, Mayaffre, & Turmine, 2007). However, there are still some limitations for the optical tensiometer method. Firstly, the dynamic contact angles were difficult to measure with high reproducibility and accuracy at high speed rate (Hunter, 2001), this was noted for the results of SMP, MC and agglomerated MPI. Also granule beds with rough surfaces can also pose problems in the assignment of the tangent line, as non-smooth surface is likely to cause variations of contact point along the contact line (Rotenberg, Boruvka, & Neumann, 1983). Although the limitations regarding of how flat the surface should be for measurements are unknown, there are a series of techniques for powder presentation to prepare the surface as smooth as possible, including solid compacts by a hydraulic press (Crowley, et al., 2015), dip coating (Spelt & Vargha-Butler, 1996) and surface polishing (Vargha-Butler, Kashi, Hamza, & Neumann,

1986). Care should be taken to minimize alteration in the physical architecture of the powder particles during generation of a powder bed with a smooth surface.

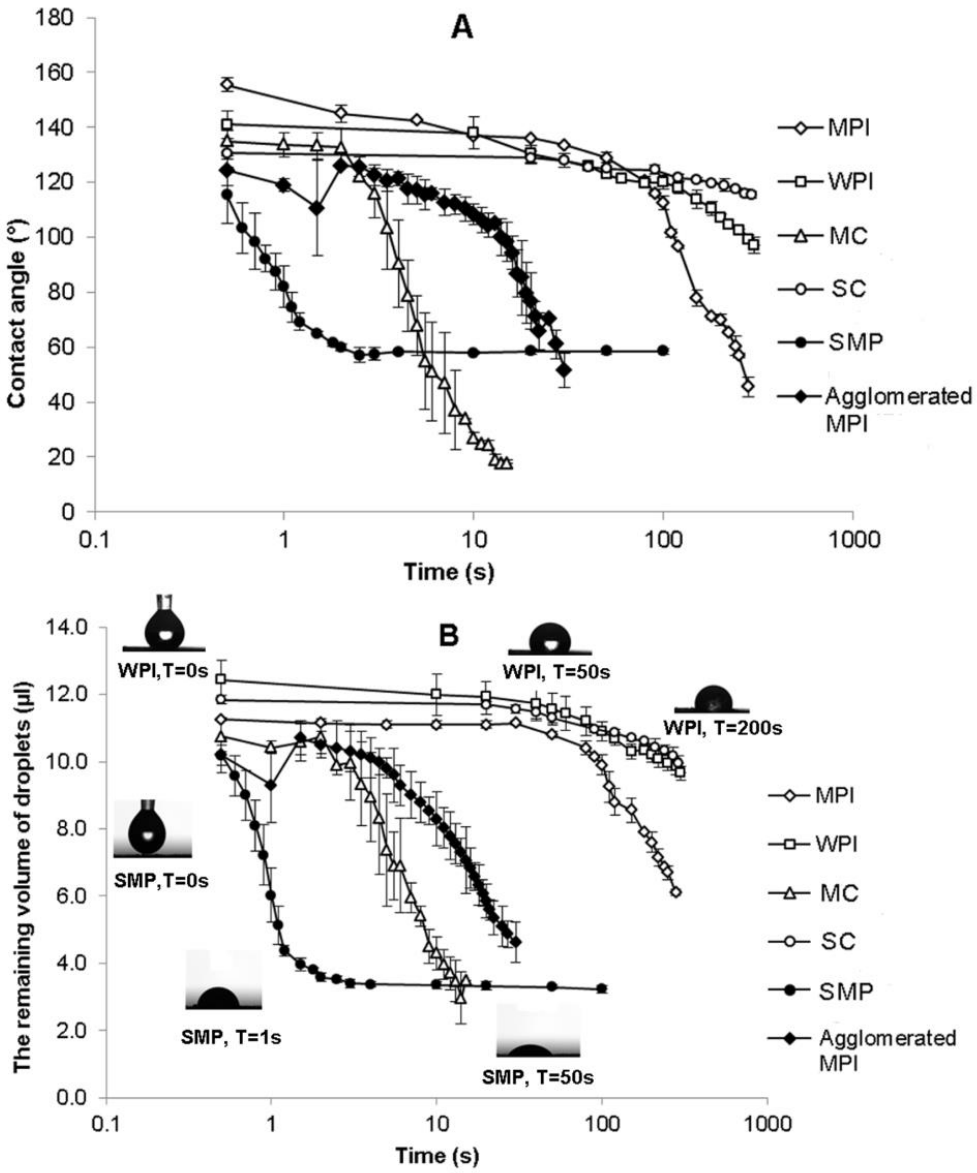

Fig.2-4AB A: The change of contact angle (°) as a function of time using the sessile drop technique in approx.20 ℃ temperature. **B:** The change in the volume of droplet (µL) above the solids as a function of time during the wetting process in approx.20 ℃ temperature. The initial volume of water droplet was approx.12 µL.

3.2 Dispersing behaviours of typical dairy powders based on different measurements

3.2.1 Dispersibility index

DI is most widely used parameter to describe the dispersibility of powder particles by measuring the mass percentage of dry matter that pass through the sieve after simple stirring. This method is easy to operate and can quantify the dispersion behaviour of dairy powders directly with low-cost. Fig.2-5 shows the dispersibility of SMP and MC was the highest with 95% and 49% DI values, respectively. The result of SMP was similar to that reported by Schuck, et al. (2012), but not for MC, which is only 24% DI value according to their research. It is due to some drawbacks in the selectivity of this traditional method as it is not suitable for other milk protein powders with poor wetting behaviour. The results in Fig.2-5 show the DI values of WPI and SC were only 39.58% and 6.63% respectively, which were lower than expected. This was caused by samples not being properly wetted before they began to disperse in the suspension. The periphery of most WPI and SC particles were surrounded by impermeable layers during the simple stirring process which restrained materials from contacting with water. Therefore, the feasibility of the DI method is believed to be largely dependent on the wettability of dairy powders. Besides that, the reproducibility and accuracy of the measurements also rely on the consistency of multiple operators in treatment of stirring and transferring suspension into sieves, even if there are clear guidelines to follow. Furthermore, the DI parameter is not adequate to quantify the whole dispersion process as it only shows the final state of dispersed particles. Whereas, dispersion is a dynamic process accompanied by the release of materials and the transfer of particle size, particle mass and energy (Forny, et al., 2011).

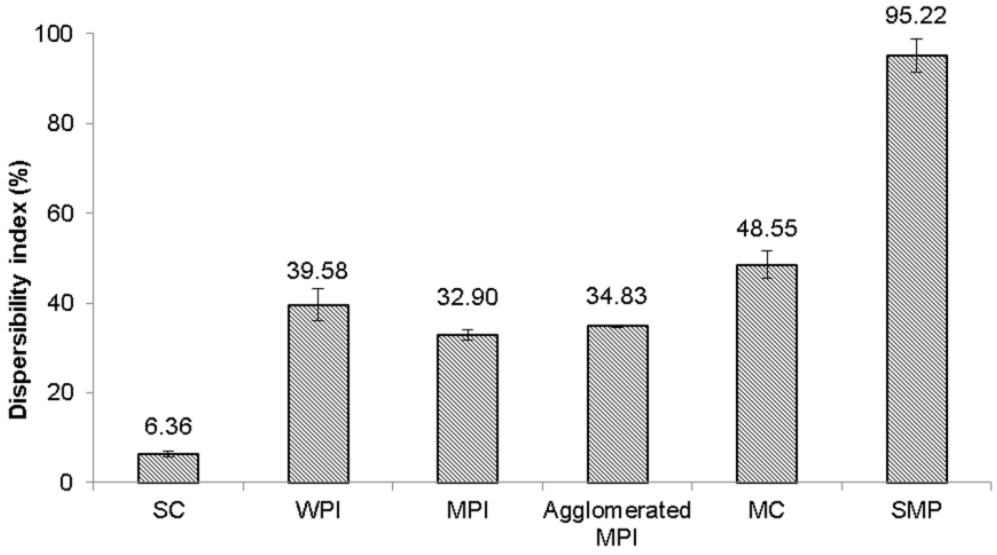

Fig.2-5 Dispersibility index for samples (SC, WPI, MPI, Agglomerated MPI, MC and SMP)

3.2.2 Particle size measurements by Light scattering

Light scattering method has been shown to be an applicable tool to measure the dispersibility of powders based on the change of particle size and the undissolved particle volume concentration (Chen, et al., 1994; Ji, et al., 2015; Mimouni, et al., 2009; Richard, et al., 2012). It is commonly believed, during the rehydration process, the size of dispersing particles is decreasing and thus the dispersibility can be quantified by the decrease rate of particle size. Meanwhile, it is necessary to evaluate the volume concentration due to powders consist of thousands of single particles. Thus, Fig.2-6A showed how the volume concentration of undissolved particles decreased during the dispersion as a function of time. Using standard MPI powder as an example, the initial particle size of MPI was about 70 μm with high volume concentration (Single peak A) at the first stage of rehydration. As dispersion proceeds, the migration of peak and a bimodal distribution of particle size is observed, which results from the continuous release of particle materials into the

surrounding aqueous phase (Fang, Selomulya, Ainsworth, Palmer, & Chen, 2011). With further rehydration, the volume concentration of small particles increased until another primary peak (Peak B) appeared and thus remained at a constant size of 0.3 μm at 60 minutes mixing time. The relationship of the particle size distribution of different dairy powders and the mixing time are present in Fig.2-6B. Based on these results carried out by the light scattering, the migration of particles size of casein-dominant powders (MC, unagglomerated MPI and agglomerated MPI) with a slow-dispersion process can be clearly observed. MC powder took approximately 20 minutes to be mostly solubilised while MPI needed 40 minutes. There was no significant difference between agglomerated and unagglomerated MPI, which was previously explained in the study of Ji, et al. (2015). At the same time, it was difficult to quantify the dispersibility of SMP by this method as it dispersed into water rapidly within less than 2 minutes. The same situation was found for SC, which formed lumps with big particle size initially but then collapsed quickly. Moreover, it is interesting to find that Mastersizer cannot detect any signals of scattered light from WPI suspension. It is because WPI particles had already dissolved in a very short time just after wetted by water entirely. Consequently, it was concluded that the static light scattering method was useful to monitor the slow-dispersing process of MC and MPI powders but it could not accurately quantify the quickness of the easy-dispersing dairy powders.

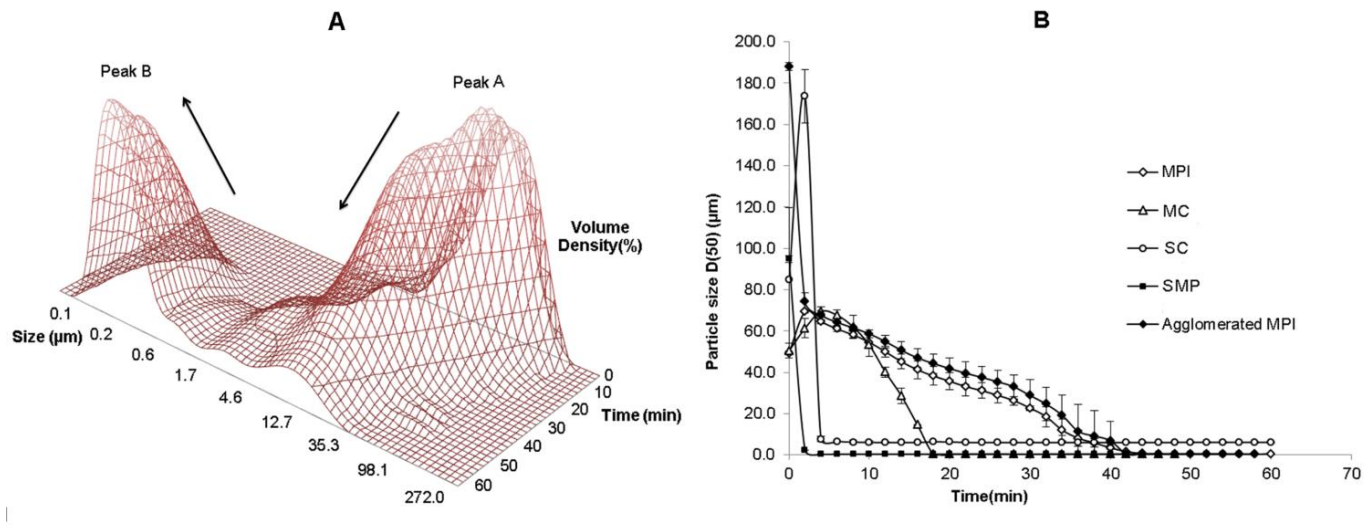

Fig.2-6AB A: Volume density (%) based particle size distributions of dispersing MPI particles measured as a function of time (every 2 minutes for 60 minutes mixing time) during the rehydration process at 25 ℃ ± 2 ℃ and 2000 rpm. The size of initial large primary particles with large volume (Peak A) decreased with an increase in small dissolved particles (Peak B). **B:** Particle size D (50) measurements of dispersed particles of SC, MPI, Agglomerated MPI, MC and SMP. (WPI sample cannot be measured by Mastersizer as WPI dissolved rapidly and the dissolved solids is nanoscale)

3.2.3 NIR transmission measurements by Lumisizer

In Fig.2-7A, different regions of sample cell were identified based on the different light transmission properties of the suspension during a centrifugation process. For example, stable transmission value meant the stable supernatant, which was caused by dissolved small particles, while sediment formation of primary particles was explained by the low transmission value. Thus, it is possible to evaluate the dispersion behaviour of dairy powders by using the Lumisizer, according to the intensity of light transmission of different dispersion phases along

the sample cell (Crowley, et al., 2014). Meanwhile, the height of sediment under two different centrifuge speeds (36g and 168g) can also be calculated to show the final solubility of powders at the 30 minutes mixing time (Fig.2-7B). It is not surprising to see that there was no sediment for WPI, SC and SMP powders, as they have good dispersibility and solubility. This was also shown by the previous results in Fig.2-6B. Almost the same sediment height was observed for MPI and MC powders under the effect of 36 g centrifugation, while MC had slightly more compressed sediment when using 168 g centrifugation. In addition, when MPI powders were agglomerated by fluidised bed granulation process, there appeared to be a greater number of particles dissolved into water and less sediment was formed. But these results were only based on one specific time point, which was at 30 minutes mixing time. Dispersion and dissolution are kinetic processed and thus it is suggested to be advantageous to measure the sedimentation behaviour as a function of time until powders were completely solubilised (Fang, et al., 2007; Hogekamp, et al., 2003; Ji, et al., 2015). On the other hand, integral transmissions (%) were calculated and provided by the software of Lumisizer in Fig.2-7C to evaluate the dispersion behaviour of powders. Each integral transmission value was used to stand for one transmission profile based on different centrifugation time. Fewer primary particles were found for the agglomerated MPI dispersion compared to the non-agglomerated MPI dispersion, due to higher transmission value showed in Fig.2-7C. It meant agglomerated MPI particles were comparatively more easily to disperse into water at 30 minutes mixing time. Even though this method is regarded as a simple way to measure the dispersibility and solubility together, however, there is an important drawback that needs to be mentioned. The actual intensity of light transmission is largely dependent on the type of dairy powders. In other words, it is pointless to compare

the disperse behaviours of dairy powders with different compositions, as they have different spectroscopy behaviour and NIR transmission in solutions. It is only of feasible to compare the non-agglomerated MPI and agglomerated MPI, which had very similar constituents. For this reason, the transmission values of WPI, SC and SMP were completely different, although they all dissolved within 30 minutes.

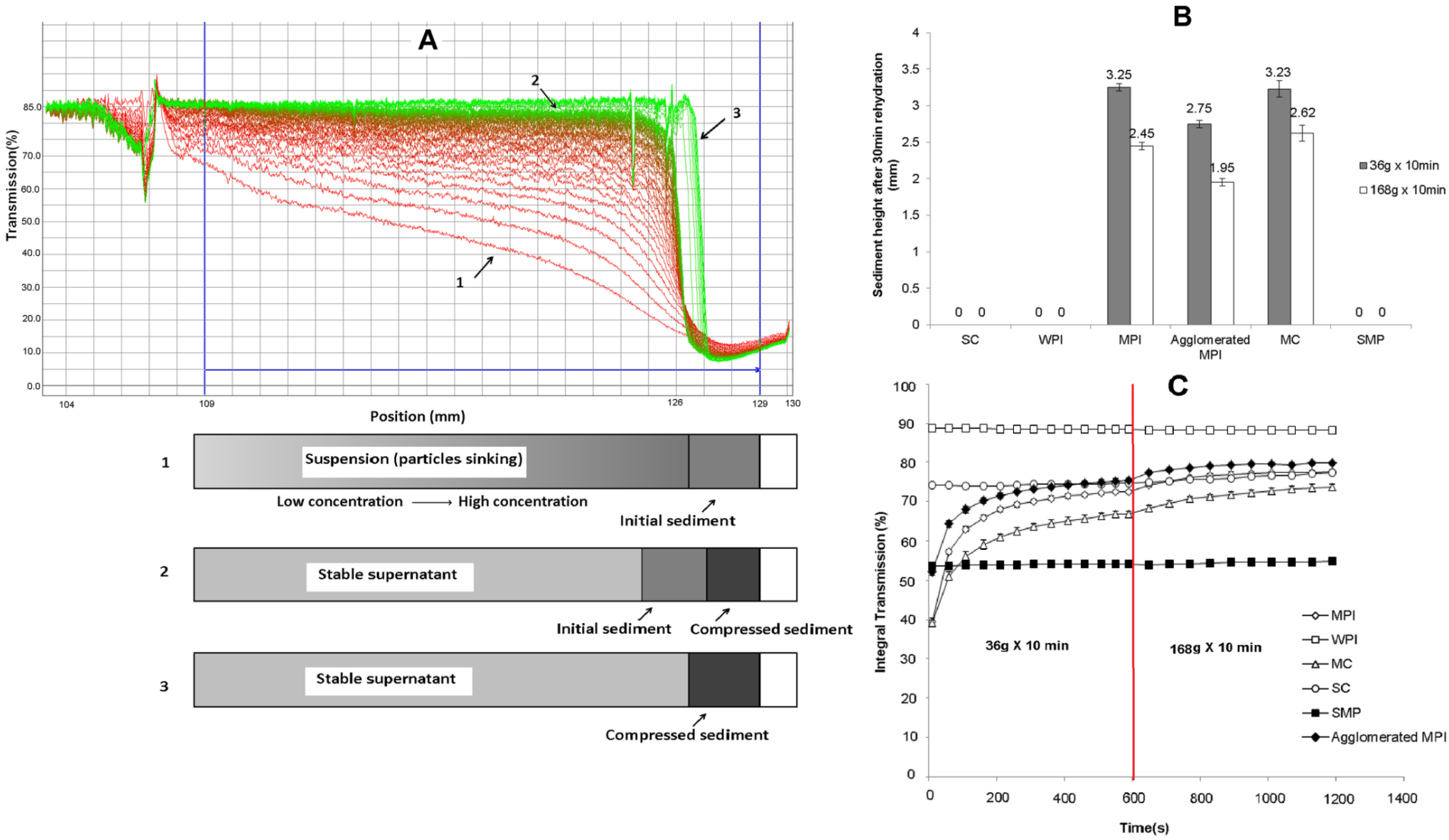
A
Transmission(%)
Position (mm)
1
2
3
Suspension (particles sinking)
Low concentration → High concentration
Initial sediment
Stable supernatant
Initial sediment
Compressed sediment
Stable supernatant
Compressed sediment
B
Sediment height after 30min rehydration (mm)
3.25
2.45
2.75
1.95
3.23
2.62
36g x 10min
168g x 10min
SC
WPI
MPI
Agglomerated MPI
MC
SMP
C
Integral Transmission (%)
36g X 10 min
168g X 10 min
MPI
WPI
MC
SC
SMP
Agglomerated MPI
Time(s)

Fig.2-7ABC. A: A schematic illustration explaining the sedimentation behaviour of MPI suspension was showed by the transmission (%) of NIR light through the sample cells by centrifugation time. Profiles were measured every 10 seconds for first 10min with 36 g centrifugation and every 60 seconds for next 10 minutes with 168 g centrifugation. Each measurement profile showed the distinct regions corresponding the different positions along the sample cell. The different transmissions represented the regions of dispersed particles and undissolved primary particles, which respectively formed stable supernatant, initial sediment and compressed sediment after centrifugation. Representative profiles based on different time (1: 10 seconds, 2: 10 minutes, 3: 20 minutes) were showed as examples. **B:** The sediment formed by 1.5% (*w/v*) sample suspension, which were rehydrated by 400 rpm stirring condition for 30 minutes at 25 ℃ distilled water, after 36 g and 168 g centrifugation for both 10 minutes. The height of sediment was determined by the regions of low transmission subtracted the steady- state value that caused by cell bottom (from 129 mm). **C:** Integral transmission was calculated by the software of SepView 4.1 (L.U.M. GmbH, Berlin, Germany). Each integral transmission value (%) represented the overall transmission through the sample cell (from 109 mm to 129 mm) by a function of centrifugation time.

3.2.4 Conductivity measurements

The conductivity method is considered as a possible way to quantify the solubilisation process of casein-dominant powders. The primary species that contributed to conductivity were believed to be soluble minerals, while the contribution of proteins and lactose can be ignored due to big molecular size or uncharged material respectively (Mucchetti, Gatti, & Neviani, 1994; Zhuang, et al., 1997). At the same time, some studies believe that calcium, phosphorus, magnesium together with caseins all belong to the slow-dissolving fraction (Mimouni, et al., 2010) because most of them come from the casein micelle structures and exist as colloids in typical milk (Holt, 1997). These slow-dissolving salt constituents also exhibited similar kinetics of solubilisation with caseins (Mimouni, et al., 2010). Therefore, this is the reason why the conductivity of MPI and MC suspension increased slowly but continuously over time just as the solubilisation progress (Fig.2-8). The conductivity meter was used to monitor the dispersion process of particles by measuring the release of slow-dissolving salts in suspension. It is thus, possible to compare the kinetics of solubilisation of these two dairy powders based on the changes in conductivity. At the same time, the conductivity of agglomerated MPI was found to increase faster than unagglomerated MPI at first 80 seconds while for the next 90 minutes, they present the almost same kinetics. It is because agglomerated MPI is more easily wetted and thus fast-dissolving salts are more quickly dissolved into water than that of unagglomerated MPI. SMP and WPI powders, which also belong to fast-dissolving samples, reached the individual steady conductivity values in very short time (less than 10 minutes) as shown in Fig.2-8. It is not possible to evaluate their dispersion process corresponding to the conductivity values because there is no proof yet to show the relationships of salts and these fast-dissolving dairy

constituents, even though Marabi, et al. (2008) reported that the final steady-state conductivity meant the complete rehydration of these powders. Besides that, it is obvious to see that the initial conductivity of all samples increased quickly at first, which was considered to be caused by the release of fast-dissolving salts in suspension, e.g. sodium and potassium, when samples were wetted by water progressively (Mimouni, et al., 2010). Furthermore, it is remarkable that the specific conductivity values of these dairy powders depend on how much salts remain in the powders during the manufacturing process. Consequently, conductivity methods for casein-dominant powder dispersion should only focus on the kinetics of conductivity instead of the value itself, which are always determined by varied membrane processes and different batches (de la Fuente, 1998).

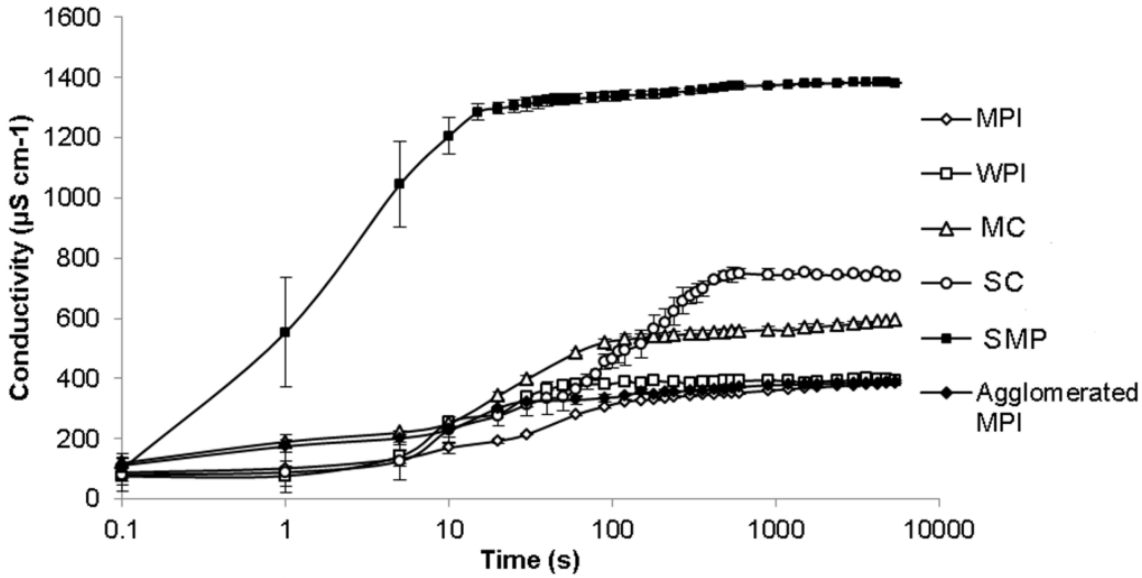

Fig.2-8. The change of conductivity by a function of mixing time for the 2% (*w/v*) concentration sample suspension, with 500 rpm stirring condition at 25 ℃. (Distilled water was used in suspension, which had conductivity value of 67 $\mu s \cdot cm^{-1}$.)

4 Conclusion

The measurement characteristics of wettability and dispersibility of milk protein based powders were discussed in this paper. Due to the different potential use for the dairy powders, such as, MPI and WPI can be used in nutritional beverages or infant formulas while MC and SC are the important materials in cheese making, an overall assessment of the methods based on these dairy powders was summarized in Table.2-3 with their advantages, drawbacks and limitations.

For the wettability measurements, the traditional method with immersion wetting process may be used as an initial screening and can differentiate between powders that wet reasonably well from those that are poor wetting. Contact angle methods are believed to be very useful for quantifying and comparing the wettability of milk protein powders. But it still needs to ensure the surface of powdered sample is as smooth as possible so that more accurate contact angles can be observed. Washburn method based on capillary rise wetting is also capable of assessing the wettability of some dairy powders. The major problem with this approach is with powders that readily solubilise when contacted with water, as they may form a solubilised viscous layer at the water-powder interface that inhibits capillary rise. This can lead to misleading results, for example, SMP is a good wetting powder but has a low capillary rise in the Washburn test.

For the dispersibility measurements, particle size measurements by light scattering method is suitable for all the powders tested, especially for slow-dispersing milk protein powders, e.g. MC and MPI powders. One problem with this approach is it cannot accurately measure how quickly the fast dispersing powders are dissolving, such as SMP, because of the time required to do the measurement. The poor dispersibility of some powders at a specific stirring time is also possibly

described by the light transmission of the suspension using an analytical centrifuge. However, once again the fast-dispersing dairy powders, like SMP, WPI or SC, are difficult to quantify their dispersing process in water as they dissolve quickly once wetted completely. The DI method is only useful for assessing powders that wetted well and dispersed fairly quickly, such as SMP. It is not suited for powders that wetted poorly because they form lumps and disperse slowly because of poor wetting. For example, WPI has poor DI, due to its poor wettability, even though it is a good dispersing powder. Conductivity method is believed to have potential for casein-dominant dairy powders due to the similar release rate of colloidal salts and micellar casein.

Acknowledgements

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Table 2-3 Summaries of the methods characteristics of dairy powders wettability and dispersibility *

Method	Accuracy ?	Speed ?	Reproducible ?	Dynamic method?	Suitable dairy powders?	Application limits	Industrial setting?	Equipment	Potential benefits
Immersional wetting method	1	3	2	No	SMP or other easy-wet milk protein powders	Not be able to distinguish the wetting behaviour of poor wetting powders	Yes	Beaker and slide	Cheap; fast measuring
Washburn method	3	3	3	No**	MC, MPI and agglomerates	Used for Newtonian liquids only and not suitable for easy-solubilising powders	Yes	Cylinder glass tube	Quantitative method; fast measuring
Water adsorption static method	3	1	2	Yes	No dairy powders***	Moisture vapour wetting by different mechanism	Yes	Desiccators and incubators	Automotive; no operator-dependent
Contact angle	3	3	2	Yes	All milk protein powders	Need the surface of powdered samples as smooth as possible	Yes	Optical tensiometer	Direct method; fast measuring; small sample amount
Dispersibility Index	2	1	1	No	Easy-wet dairy powders without lump formation	Bad reproducibility with multiple operators and not capable for poor-wetting powders	Yes	Spatula and sieve	Cheap; easy to operate
Light scattering	3	3	2	Yes	slow-disperse milk protein powders	Difficult to measure fast-disperse milk protein powders	Yes	Online measuring equipment	Direct method; automotive; small sample amount
Light transmission of suspension	2	3	2	No	slow-disperse milk protein powders	Not suitable for fast-disperse milk protein powders	Difficult	NIR light equipment	Automotive; quantitative method
Conductivity of suspension	3	3	2	Yes	Only casein-dominant powders	Only useful with the premise of same release rate of salts and protein particles	Yes	Online measuring equipment	Automotive; quantitative method

* 1: low level; 2: medium level; 3: high level

** It could be developed into a dynamic method

*** Not suitable for the wettability of powder rehydration

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CHAPTER THREE

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 (Oftedal, 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.

2 Materials and methods

2.1 Materials

The composition of the milk protein powders used in this study is showed in Table 3-1. MPI and SC were supplied by Kerry Ingredients (County Kerry, Ireland). WPI was supplied by Davisco Food International (Le Sueur, MN, USA). CC was produced by Teagasc (County Cork, Ireland). Skim milk (Kerry Ingredients, County Kerry, Ireland) was used to produce MC by a pressure driven process with 100 kDa molecular weight membranes and then the obtained retentate was vacuum evaporated to increase the solid content to approximately 38%. The concentration process was performed at 65 ℃. Finally, the MC powders were obtained by a spray drying process, where the inlet and outlet temperatures were 180 ℃ and 85 ℃, and the drying air-flow rate was 750 $m^3 \cdot h^{-1}$. Before the measurements, all the powders were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 45 ℃ overnight to obtain the final moisture content of about 1.5% and then kept in the desiccators.

Table 3-1 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.

2.2 Agglomeration process

The agglomeration process of all these milk protein powders was carried out by a top-spray fluid bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Lowa,

USA). 50 g of each model powder was fed into the product vessel. As different milk powders have different fluidisation behaviours in the fluidised bed, the appropriate upward flowing air stream from 30 $L \cdot min^{-1}$ to 250 $L \cdot min^{-1}$ was adjusted for the fluidisation of each powder (MPI: 200 $L \cdot min^{-1}$; WPI: 70 $L \cdot min^{-1}$; MC: 250 $L \cdot min^{-1}$; SC: 30 $L \cdot min^{-1}$; CC: 40 $L \cdot min^{-1}$). 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 $mL \cdot min^{-1}$). (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 ℃. 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 immersional 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 ℃ (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 cm^2. 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 (θ<90°) represents good wettability for the solid, and a large contact angle (θ>90°) 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 ℃. 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 ℃ ± 2 ℃ 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.1μm (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 ℃ 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

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

2.5 Scanning electron microscopy

2 g of standard MPI powder were added to 100 mL distilled water to create the 2% (*w/v*) suspension. Stirring was performed by an overhead mixer (Eurostar 40 digital, IKA, Staufen, Germany) and a 4-bladed stirrer of 50 mm diameter (R 1342, IKA) for different rehydration time at 25 ℃ (60 minutes, 90 minutes and 150 minutes). One or two drops of each MPI suspension was deposited for 5 minutes on the silicon substrates, which were rinsed by 100 mM phosphate buffer (pH=7) in advance. 3% glutaraldehyde solution was used to fix the chemical structures of rehydrated milk protein for 15 minutes (Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2010a). After that, distilled water was used to wash the samples to remove the fixing chemicals. The samples were dehydrated by graded ethanol, which were 50%, 70%, 90% and 100% (Dalgleish, Spagnuolo, & Goff, 2004), and then they were further dried in a desiccator with P_2O_5 until they were suitable to be observed by scanning electron microscopy in a vacuum environment (~5×10^{-6} mbar). A field emission scanning electron microscope (Zeiss Supra, Carl Zeiss Microscopy GmbH, Jena, Germany) was used for imaging at 1.5 kV.

3 Results and discussion

3.1 The wettability of high milk protein powders

According to the results of the immersion wetting procedure (Table 3-2), 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. 3-1 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. 3-2. 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 (θ>90°) 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.

Table 3-2 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.

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. 3-3A, 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. 3-3B, 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.

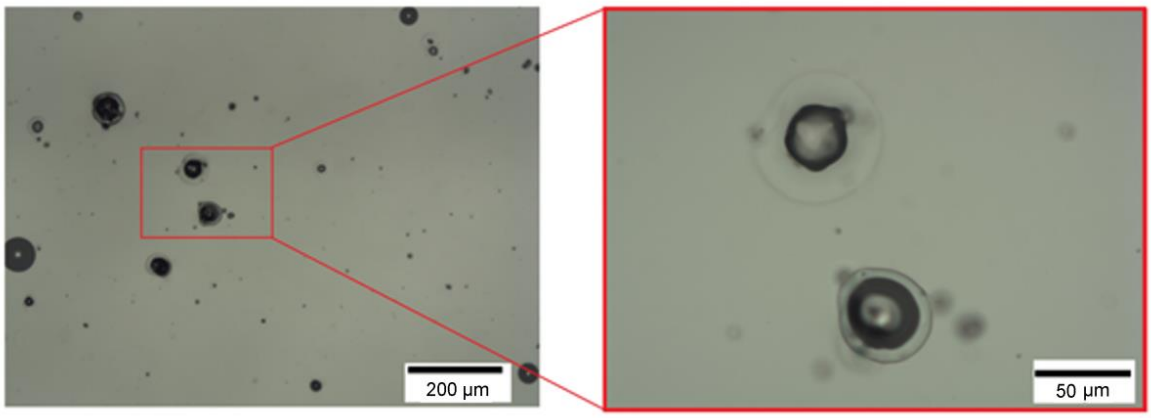

Fig.3-1 Optical microscopy images of WPI particles, upon which formed the impermeable hydrophobic layers when wetted by water. The particles were dispersed in water on glass slides. (Left: scale =200 μm; Right: scale = 50 μm)

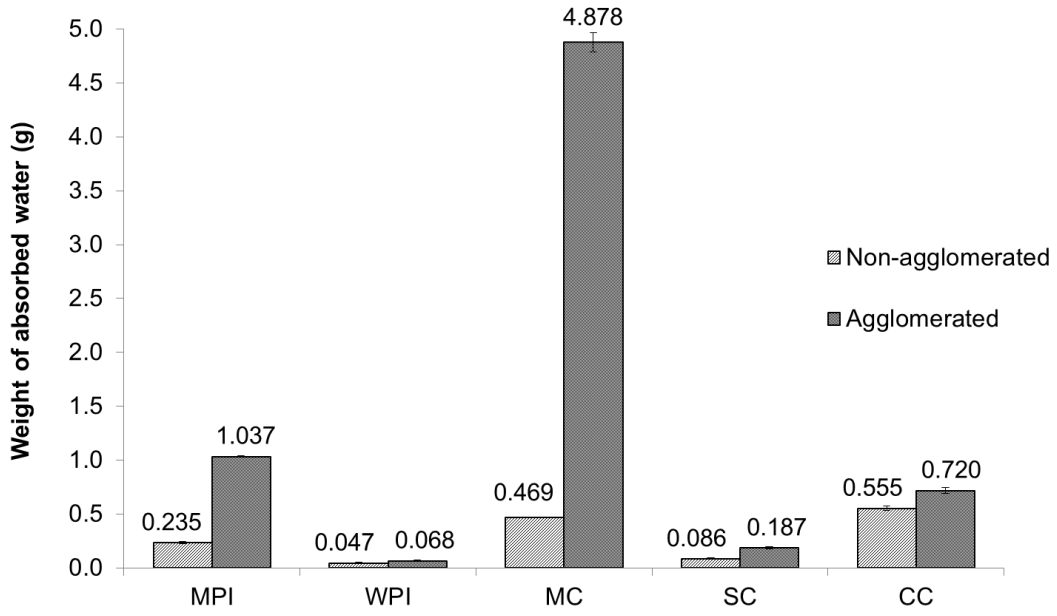

Fig.3-2 Weight of adsorbed water for samples (MPI, WPI, MC, SC, CC and their agglomerates) by capillary rise wetting after 10 minutes.

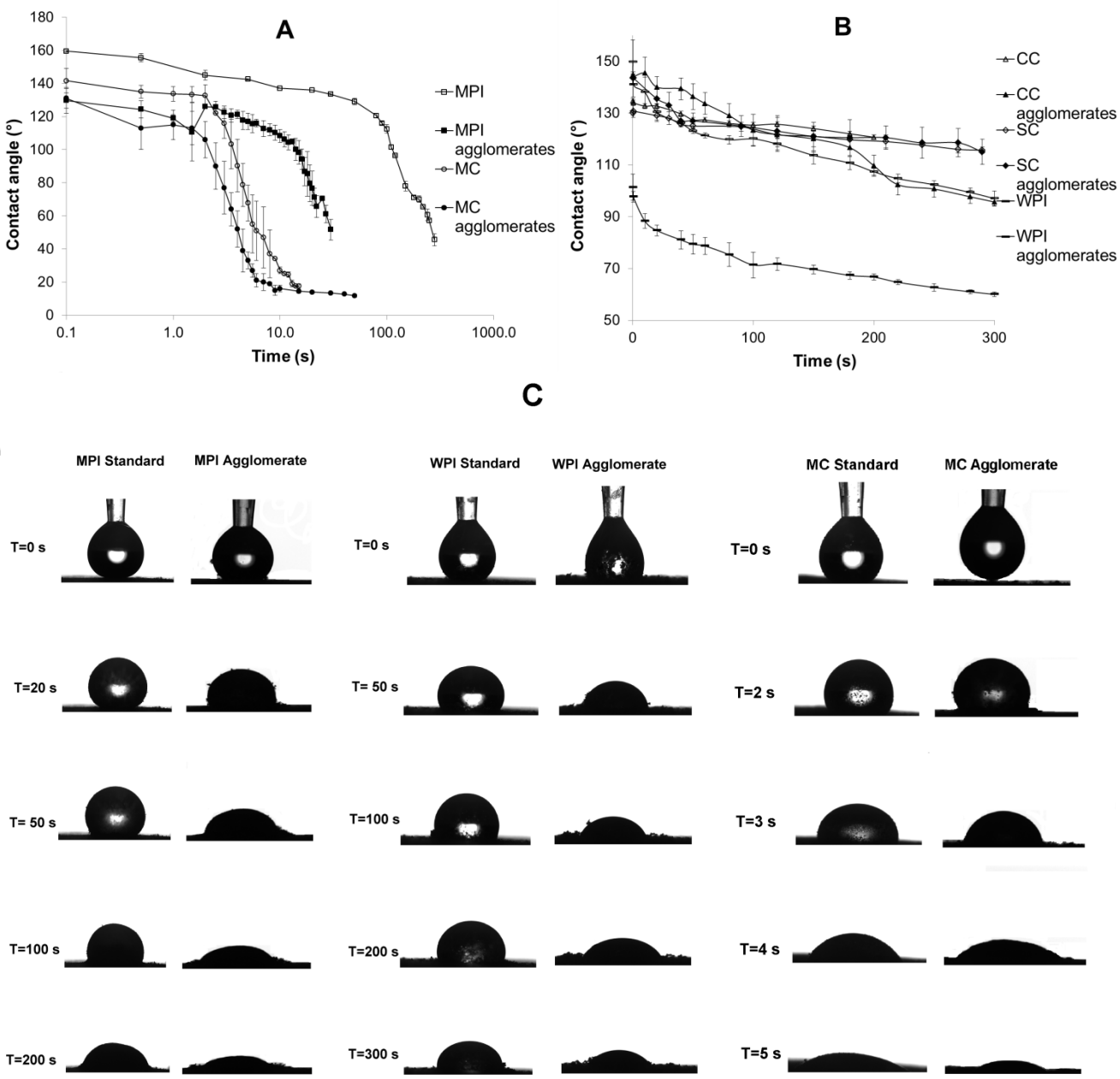

Fig.3-3ABC A: The change of contact angle (°) as a function of time for MPI, MC and their agglomerates using the sessile drop technique in approx. 20 ℃ temperature. **B:** The change of contact angle (°) as a function of time for WPI, SC, CC and their agglomerates. **C:** Images of MPI, WPI and MC as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

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. 3-4A&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. 3-4B, 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).

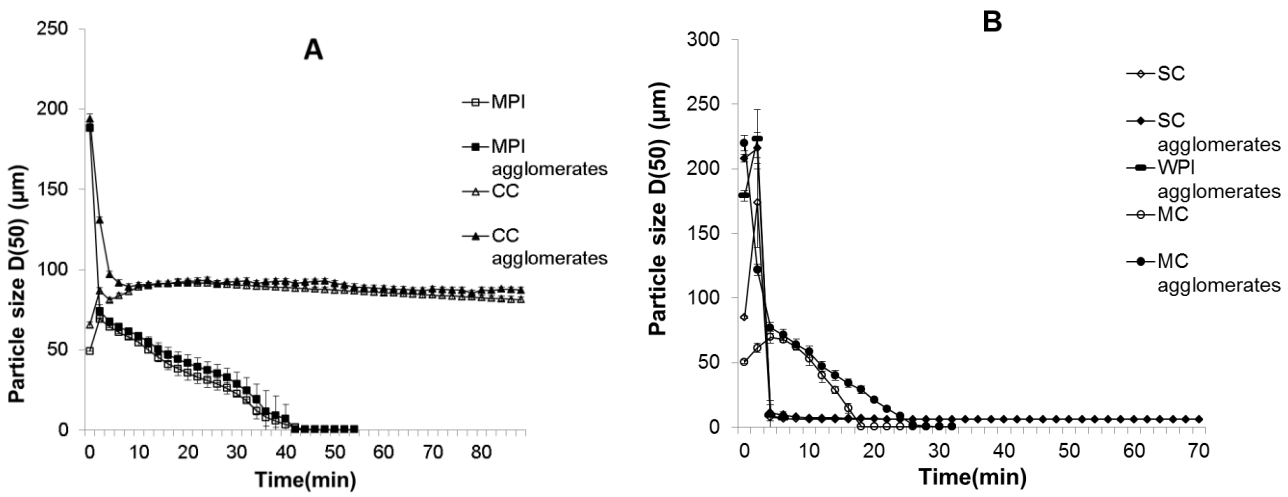

Fig.3-4AB A: Particle size D (50) measurements of dispersed particles of MPI, CC and their agglomerates for every 2 minutes in 25 ± 2℃ water. **B:** Particle size D (50) measurements of SC, MC and their agglomerates. (WPI quickly dispersed into water and Mastersizer cannot detect its particle size. Even agglomerated WPI can only be measured for the first 4 minutes)

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 3-3. 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 ℃, 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, & Velev, 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).

Table 3-3 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.

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. 3-2, 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. 3-3ABC, 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 3-2 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. 3-4B). Same conclusions are determined from Table 3-3, 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. 3-4A), 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. 3-5A. 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. 3-5B, 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.

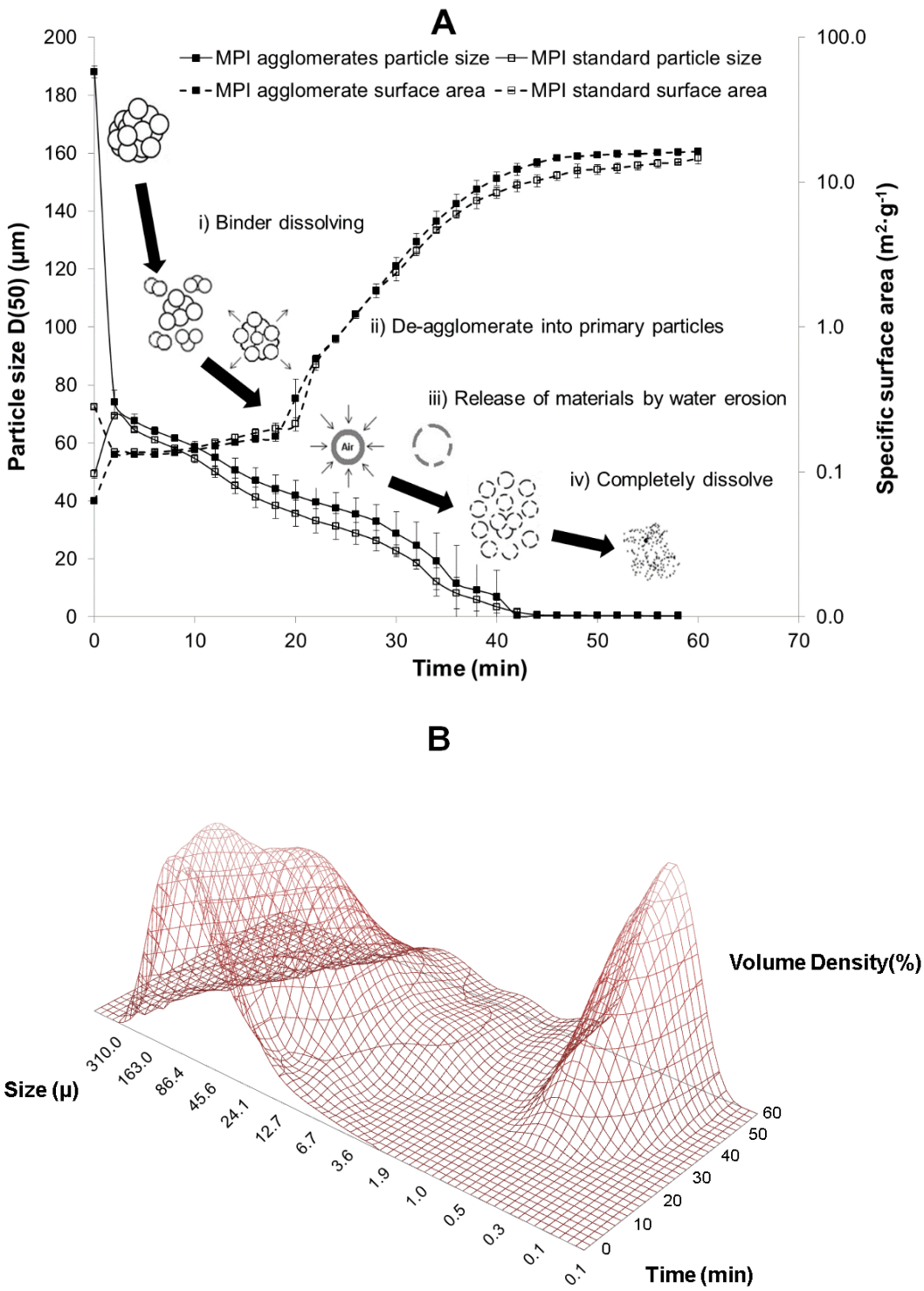

Fig.3-5AB A: Schematic of MPI and agglomerated MPI particles rehydration in water, based on the change of particle size D (50) and specific surface area as a function of time. **B:** Volume density (%) based size distributions of dispersing MPI particles measured as a function of time. It showed the volume concentration of both undissolved and dissolved powder particles.

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. 3-6 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. 3-6A. 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. 3-6B). 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. 3-6C), 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. 3-6D). 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.

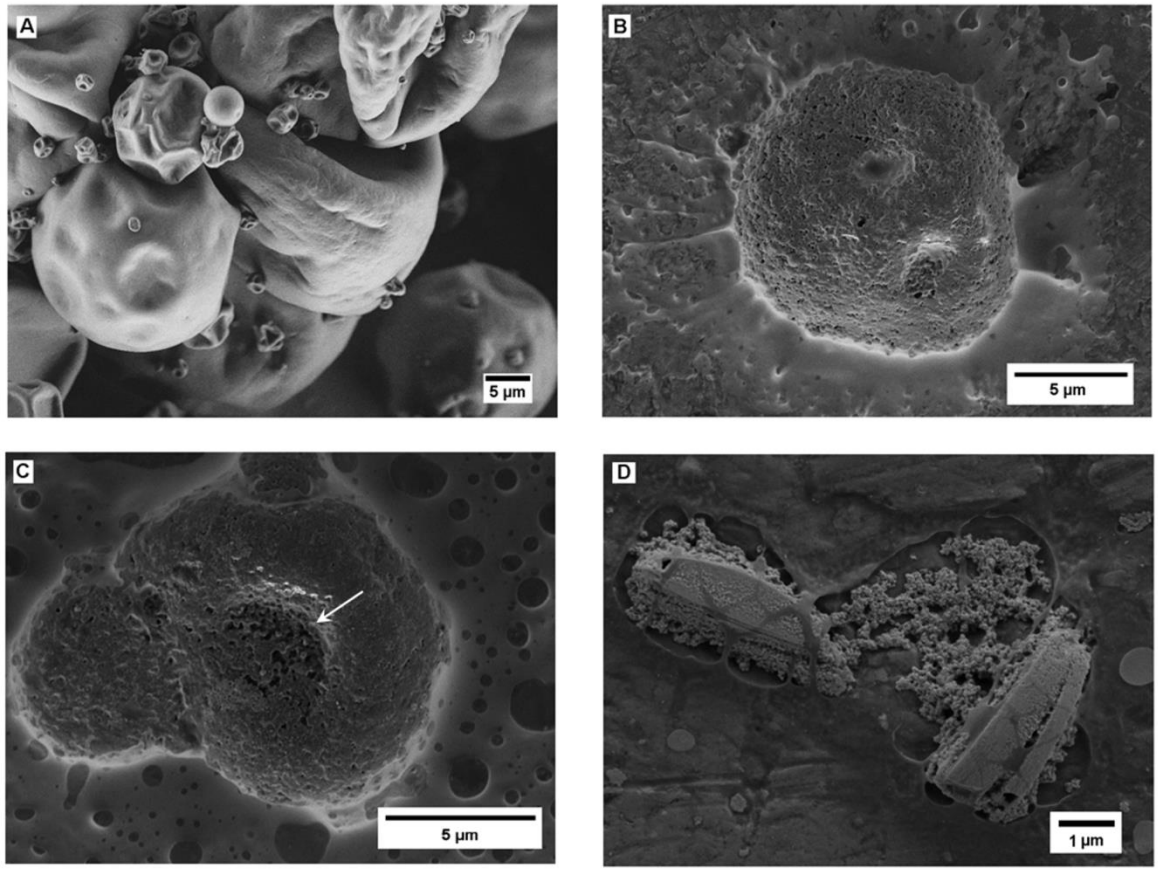

Fig.3-6ABCD SEM images of MPI particles after different rehydration time. **A:** spray-dried particles before rehydration (1.4 kV); **B:** particles after 60 minutes rehydration (1.5 kV); **C:** particles after 90 minutes rehydration (1.5 kV); **D:** particles after 150 minutes rehydration (1.5 kV). The white arrow in panels C indicates the presence of large breaches caused by water erosion.

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. 3-5A). 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. 3-5A. (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.

4 Conclusion

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

Acknowledgements

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CHAPTER FOUR

Effects of fluid bed agglomeration on the structure modification and rehydration behaviour of milk protein isolate powders

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Abstract

The effect of agglomeration on the density, morphology and subsequent rehydration behaviours of milk powders was investigated. In this study, milk protein isolate, as a model system, was agglomerated in a fluid bed granulator with three different binders: water, lactose and sucrose solution (*15% w/v*). Morphology was quantified by circularity, convexity and elongation. Wettability was measured by the modified Washburn method. Powders solubilisation was quantified by dynamic particle size measurement and the kinetics of dissolved solids concentration in solution. The results showed that granules with water as the binder produced significantly lowest circularity and convexity and highest elongation. An increase in the size of the agglomerated MPI corresponded with an increase in the wettability but a decrease in the ability of solubilisation in water. Granules agglomerated with hydrophilic sugars were found to contribute differently which improved the wettability significantly but no improvement for the kinetics of dissolution.

Key Words: Fluid bed agglomeration, binders, wettability, solubilisation, morphology, density

1 Introduction

Fluidized bed agglomeration, as one of the most used granulation methods, is a process by which granulated particles are obtained by spraying a binder as solution, suspension, or melt onto a fluidized powder bed (Rajniak et al., 2007a; Turchiuli et al., 2013; Weber et al., 2007). In the food industries, powders are usually required to have good handling properties (dust-free, good flowability and easy to rehydrate). Milk protein isolate powder (MPI), as a widely used dairy ingredient, not only have fine particles and dense structures but is also difficult to rehydrate (Gaiani et al., 2007). The process of fluid bed agglomeration is applied to optimise the physical and structural properties of dairy powers, such as, particle size, densities, porosity, shape (Szulc and Lenart, 2013) and subsequently the rehydration behaviour (Knight, 2001). Because there is strong interaction between the fluid bed process and the properties of obtained powders (Knight, 2001), controlling the process conditions is a potential way to improve the quality of MPI powders.

The use of binders in fluid bed agglomeration is one of the most frequent methods to modify the structure of agglomerates. They form solid bridges adhering primary particles and create new structures with pores and voids. Therefore, they affect the rate of particles size enlargement, densities and morphology of the granules (Keningley et al., 1997; Mills et al., 2000). However, different binders have different bonding efficiency due to varied chemical compositions, mechanical properties, concentration, viscosity and inter-particular interactions between the particles and the binder. For example, sucrose or glucose usually produces hard and brittle bridges while gelatin and acacia gum provide slow disintegration and high hardness to the agglomerates (Barbosa-Cánovas and Juliano, 2005). In food systems, aqueous solutions of lactose and sucrose are the most used binders in fluid bed agglomeration. Thus, the relationship between types of binders and

agglomerates structure properties needs to be clearly identified. Although some pharmaceutical research related to agglomerate behaviour in fluidized beds have been published (Abberger et al., 2002; Chua et al., 2011; Parveen et al., 2013; Rajniak et al., 2007b; Seo et al., 2002), less attention has been given to milk powder systems, especially high protein-based powders which also present great potential for improvement to the quality of dairy powder structures.

The rehydration ability of milk protein powders is an essential attribute as most of them are dissolved before use. It is commonly believed that the whole rehydration process mainly consists of three sequential stages which are wetting, dispersing and dissolving phases (Forny et al., 2011; Gaiani et al., 2007; Hogekamp and Schubert, 2003; Richard et al., 2012). Each stage is affected by the different physical properties. Generally, wettability depends on large particles with large pores in between and also small contact angles (Hogekamp and Schubert, 2003); dispersibility is influenced by particle size, porosity and density (Goalard et al., 2006); dissolution is favoured by the presence of small hydrophilic molecules on the surface (Lillford and Fryer, 1998). Using sugar solutions as binders in agglomeration modifies the powders' structure and surface composition and influences the interaction with water. Consequently, the performances of different binders on the rehydration ability should be investigated. Furthermore, as the reconstitution process is dynamic and powders with high protein content have relatively poor wettability and dispersibility (Gaiani et al., 2007; Richard et al., 2012), it is impossible to quantify the total process according to traditional standard methods. Moreover, different rehydration stages often overlap (Fang et al., 2007) and it is a challenge to observe each stage independently, particularly dispersing and dissolving stages. Hence new methods were developed to better quantify the functionality of powders in this study. For example, the modified Washburn method, as a dynamic wettability measurement,

was found to describe the ability of the powder particles to overcome the surface tension between themselves and the liquid (Depalo and Santomaso, 2013). Meanwhile, particle size measurement by static light scattering was used to monitor the solubilisation (both dispersing and dissolving) of powders during rehydration process (Richard et al., 2012). Final solubility was expressed as the kinetics of dissolved solids concentration (w/w %) in water.

The overall aim of this study was to acquire a better understanding of the influence of fluid bed agglomeration of milk protein isolate (MPI) powder, using three different binders and two agglomerate size fractions, on improving the rehydration ability of MPI. Within this study, the influence of the three binders on the physical properties of the agglomerates, including powder densities, porosity and morphology, was also investigated.

2 Materials and Methods

2.1 Materials

Milk protein isolate (MPI) was supplied by Kerry Ingredients (County Kerry, Ireland). The composition of MPI is 86% protein, 1.5% fat, 6% ash and <1% carbohydrate. The binding liquids used in the fluid bed agglomeration were: distilled water; aqueous solutions of lactose, 15% w/v (Arla Food Ingredients, Viby J, Aarhus, Demark) and aqueous solutions of sucrose, 15% w/v (Sigma Aldrich, USA).

2.2 Fluid bed agglomeration

A top-spray fluidised bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Lowa, USA) was used to carry out the agglomeration of MPI. 200g MPI powder was fed into the bottom of product vessel and fluidised by upward flowing air stream. The temperature of injected air was 50 ℃ and the air flow rate was 200 L

min^{-1}. 100g binding liquid was injected from the top of vessel by a peristaltic pump (1mL min^{-1}) and sprayed into small droplets by a two-fluid spray nozzle. The air pressure on the nozzle was 1 bar. When the binding solution had been used up, the product was dried for 15min at 50 ℃ and the air flow was reduced to 100L min^{-1}.

2.3 Powder characterisation

Three different samples were obtained based on three different binders in the fluid bed granulation (A_1: Water binding, A_2: Lactose solution binding, and A_3: Sucrose solution binding). The 106μm, 180μm and 300μm level sieves (Endecotts, London, UK) were used to obtain two different agglomerate size fractions (P_1: 106μm~180μm and P_2:180μm ~ 300μm). Including unagglomerated MPI standard powder (ST), a total of 7 powders (ST, A_1P_1, A_1P_2, A_2P_1, A_2P_2, A_3P_1, and A_3P_2) were investigated in this study. The obtained samples were dried overnight in the vacuum oven (Jeiotech, Seoul, Korea) at 60 ℃ temperature and then kept in the desiccator to cool down into room temperature.

2.4 Density and Porosity

Loose and tapped bulk densities were measured using a graduated cylinder and a tapped machine (Funke Gerber, Berlin, Germany). The volume occupied by a given mass of powder (50g) after 100 taps was measured three times to calculate the tapped bulk density. Gas Pycnometer (AccuPyc II 1340, Micromeritics Instrument Corporation, Georgia, USA) was used to measure the particle density of samples, which were placed in the sample cell and purging with a flow of helium to degas the cell by ten pressurisation cycles. Furthermore, porosity (ε) was calculated using tapped bulk density ρ_T and particle density ρ_A. The relation shows as Eq. (1):

$$\varepsilon = (\boldsymbol{\rho}_A - \boldsymbol{\rho}_T)/\boldsymbol{\rho}_A \times \mathbf{100} \qquad (1)$$

2.5 Particle Shape

The shape properties were described by Malvern Morphology G3 (Malvern Instruments Ltd, Worcestershire, UK). 15mm^3 volume samples were placed in the dispersion unit to be dispersed into single layer on the glass plate so that they can be observed by the microscope. Generally, three parameters were used to quantify and indicate the shape properties of powders (Fig.4-1). Firstly, the circularity value between 0 and 1 was defined as the ratio of the perimeter of the surface equivalent disc (P_e) to the real perimeter of the particle silhouette (P_r). The bigger value means the more alike to the equivalent circle. Secondly, the convexity describes the compactness of a particle. The maximum theoretical convexity is 1 that means the surface of particle is very smooth. Finally, elongation stands for aspect ratio of particles and a needle shape has a high value which is close to 1. These indicators were usually expressed as average value for bulk population distribution. Each sample was measured five times to obtain the average value.

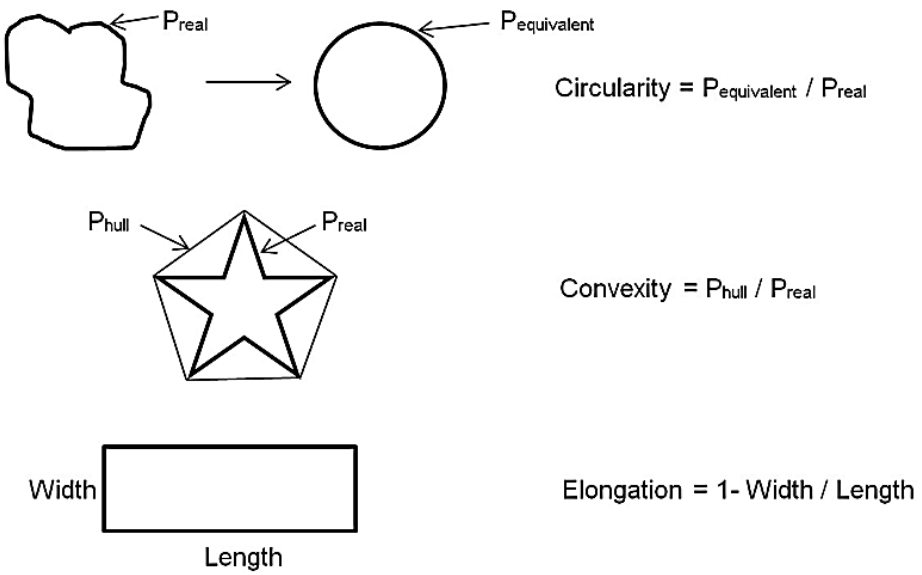


Fig.4-1 Definition of the shapes factors: Circularity, Convexity and Elongation measured by Malvern Morphology G3.

2.6 Rehydration properties

2.6.1 Wettability

Dynamic wettability measurement was based on the Washburn method (Washburn, 1921) which applied the capillary force to wet the powder (Fig.4-2). In this study, 2g samples were added into a glass tube without bottom (powder holder), and covered by filter paper and a piece of gauze at the bottom of the tube to prevent the powders falling down. Then the tube was fixed just above the distilled water (24℃) surface. After 10 minutes, an analytical balance was used to measure the additional mass of wetted powder. Each sample was measured five times.

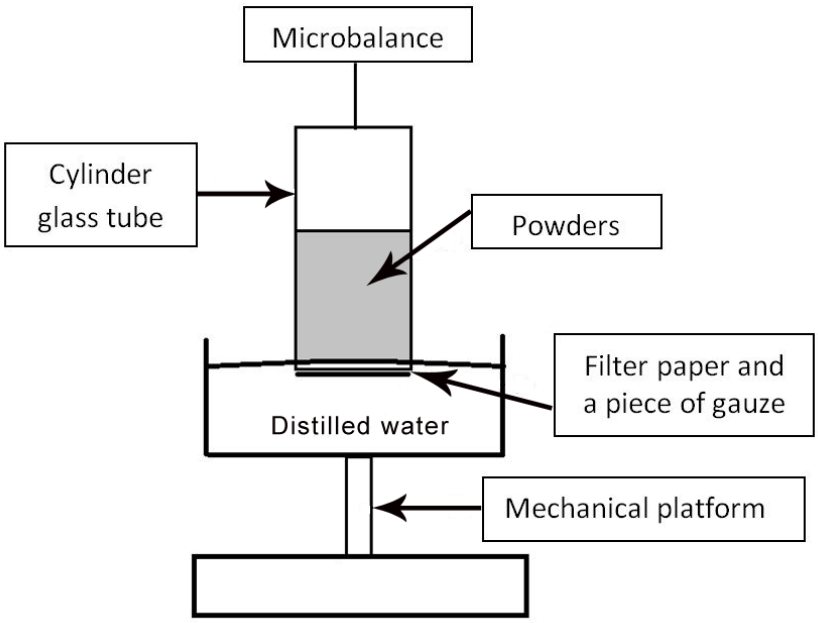


Fig.4-2 Scheme of modified Washburn method to quantify the wettability of MPI powders by measuring the weight of adsorbed water (24℃) in 2g powders after 10 minutes.

2.6.2 Solubilisation

Due to it is difficult to observe the dispersing and dissolving phases independently, solubilisation ability of the powders, including dispersibility and dissolution, were expressed as the reduction rate of particle size in dispersant based

on granule erosion and break-up (Chen and Lloyd, 1994; Goalard et al., 2006; Richard et al., 2012). An optical fibre sensor (Fig.4-3) (Galet et al., 2004; Larsen et al., 2003), which collected the light backscattering of the particles, was used to determine the kinetics of solubilisation and reflect the quality of powder's rehydration behaviour. Another used method to quantify the solubility of powder was the measurement of the concentration of dissolved powder (w/w %) in distilled water by time under the stirring.

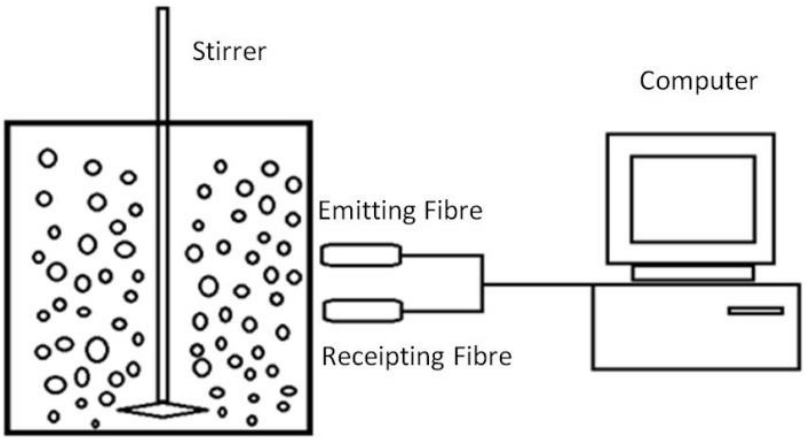


Fig.4-3 Scheme of Light scattering method to quantify the solubilise ability of MPI powders to monitor the particle size of dispersed particles every 2 minutes in 25 ± 2℃ water at mixing condition of 2000rpm.

2.6.2.1 Particle size measurement of dispersed particles

Particle size measurement of dispersed particles was measured by laser light scattering using Malvern Masterszier 3000 (Malvern Instruments Ltd, Worcestershire, UK) equipped with a 4mW He-Ne laser operating at a wavelength of 632.8nm. Samples were diluted into 120ml dispersion unit with distilled water to reach obscuration of 8%. Refractive indexes for solvent, particle and adsorption were set as 1.33, 1.45 and 0.01, respectively. In this study, in order to be within the ideal obscuration range of machine, a constant mass of samples (approximate 5mg) were

introduced into dispersion unit with 2000rpm agitation and 25℃ ± 2℃ temperature range. The solid in liquid concentration was set at 0.004%. During the triplicate measurements, samples were detected every 2 minutes until D (50) reached ~1μm (the diameter of 50% particles was just lower than 1μm). The average results were used to monitor the particle size reduction as powders dispersed and dissolved.

2.6.2.2 Dissolved solids measurement

For dissolved powder concentration measurement, samples weighing 1g were added into 50ml water in the beakers and slightly mixed by spoon to make the powders wet completely and sink below the surface of water. Then samples were placed in 24 ℃ water bath and stirred by 3-pitched-blade impeller (impeller diameter: 4cm) at a rate of 300rpm for different mixing time (30min, 60min, 90min, 120min, 150min, 180min, 210min, 240min). After that, the suspensions were put into 50ml centrifuge tubes and centrifuged at 3000 g and 24 ℃ for 10 minutes (Eppendorf Centrifuge 5810R, Hamburg, Germany). 2ml supernatant was taken and analysed by solid analyser machine (Smart System 5, CEM, North Carolina, USA), to evaluate the concentration of solids (*w/w %*) in the solution. All the results were repeated three times

2.7 Statistical analysis

Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was carried out by SPSS software (PASW, Statistics 1.8). It was used to perform statistical differences 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 Influence of binders on physical properties of agglomerates

3.1.1 Density and porosity

Bulk density is defined as the mass of powders divided by the total volume occupied by them. The total volume includes particle volume, inter-particle void volume, and internal pore volume. Tapped density corresponds to the occupied volume after packing by tapping the container, which means voids between particles are reduced (Turchiuli and Castillo-Castaneda, 2009). It is commonly believed that agglomeration creates granules with lower bulk density due to the formation of voids structures (Kowalska and Lenart, 2005; Szulc and Lenart, 2010). Same trends were observed in Table 4-1, where loose and tapped bulk density of unagglomerated MPI powders were 0.298 g/cm^3 and 0.356 g/cm^3 respectively, which were significantly ($p < 0.05$) higher than those of agglomerated MPI powders. Furthermore, if compared with the bulk densities of six agglomerated samples, an increase in the size of the agglomerate was found to correspond to a decrease of bulk density. But the different binders appeared to have no particular effect on bulk loose and tapped densities for both particle size fractions. The loose bulk densities of samples were all about 0.21 g/cm^3 and 0.18 g/cm^3 for small and large size fractions respectively. And the tapped bulk densities were about 0.26 g/cm^3 and 0.20 g/cm^3 respectively. For particle density, the agglomerates formed by distilled water were similar to that of ST while those formed by lactose and sucrose had lower particle densities, which were lower than 1.3 g/cm^3. Similar results were shown by Szulc and Lenart (2013), where values of particle density were influenced by the type of binder liquid and the composition of samples. Besides that, Jinapong et al (2008) also reported that

agglomerated soymilk powders resulted in the lower particle density than the standard unagglomerated ones.

Porosity is defined as the ratio of void volume to total volume of the powder and void volume is the difference between the total volume and particles volume (Turchiuli and Castillo-Castaneda, 2009). Thus, porosity is largely dependent on the measurement of total and particles volumes. Generally, an increase in porosity of the agglomerated powders was observed in comparison with the primary ones (Werner et al., 2007). In this study, the porosity values of MPI samples showed in Table 4-1 can reach around 80% based on the low bulk density. Agglomerated skim milk powder (Hogekamp and Pohl, 2003) and agglomerated soymilk powders (Jinapong et al., 2008) also reported the similar porosity values. As the same trends to bulk density, agglomerated MPI samples also had significantly higher porosity than unagglomerated ones and larger particle size corresponded to higher porosity. Meanwhile, there was no big difference among the agglomerates with different binders in the same particle size fraction.

Table 4-1 Bulk Density, Particle density and Porosity of powders *

Samples	ST	A_1P_1	A_1P_2	A_2P_1	A_2P_2	A_3P_1	A_3P_2
Particle size D(50) (µm)	49.4 ± 0.2^{a}	106.2 ± 0.5^{b}	199.0 ± 1.2^{c}	102.5 ± 0.3^{d}	188.7 ± 1.0^{e}	103.4 ± 0.3^{f}	191.2 ± 1.4^{e}
Bulk Loose Density (g/cm^3)	0.298 ± 0.007^{a}	0.206 ± 0.009^{b}	0.184 ± 0.006^{c}	0.221 ± 0.006^{b}	0.179 ± 0.005^{c}	0.215 ± 0.007^{b}	0.181 ± 0.004^{c}
Bulk Tapped Density (g/cm^3)	0.356 ± 0.001^{a}	0.262 ± 0.000^{b}	0.198 ± 0.000^{c}	0.265 ± 0.001^{b}	0.199 ± 0.000^{c}	0.252 ± 0.001^{d}	0.207 ± 0.000^{e}
Particle Density (g/cm^3)	1.311 ± 0.004^{ab}	1.335 ± 0.020^{a}	1.302 ± 0.016^{bc}	1.282 ± 0.024^{bc}	1.278 ± 0.003^{cd}	1.254 ± 0.035^{de}	1.246 ± 0.027^{e}
Porosity (%)	72.85 ± 0.12^{a}	80.37 ± 0.30^{b}	84.79 ± 0.23^{c}	79.33 ± 0.32^{d}	84.43 ± 0.10^{c}	79.90 ± 0.41^{bd}	83.39 ± 0.34^{e}

* 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 4-2 Morphological descriptors of powders *

Powder Morphology	ST	A_1P_1	A_1P_2	A_2P_1	A_2P_2	A_3P_1	A_3P_2
Circularity	0.826 ±0.015[a]	0.642±0.006[b]	0.592±0.014[c]	0.669±0.008[de]	0.630±0.015[bc]	0.688±0.004[d]	0.668±0.002[e]
Convexity	0.937±0.008[a]	0.796±0.005[b]	0.728±0.010[c]	0.814±0.005[d]	0.761±0.017[e]	0.829±0.005[f]	0.789±0.007[b]
Elongation	0.262±0.010[a]	0.317±0.004[b]	0.293±0.003[c]	0.301±0.001[d]	0.266±0.001[a]	0.309±0.001[e]	0.281±0.005[f]

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

3.1.2 Morphology

The effect of the binders in fluid bed agglomeration on the morphological properties of powders was also investigated. Three morphological descriptors (Circularity, Convexity, and Elongation) followed by Malvern Morphology G3 identified the bulk shape properties. Examining Table 4-2, compared to the unagglomerated MPI powders, it is clear to find that agglomerated granules had significantly ($p<0.05$) lower circularity and convexity but higher elongation, which means the particles had less rounded shape, rougher surface and lower ratio of width / length. As it is seen in Fig.4-4, more irregular shapes were observed in agglomerates with larger particle size. It is due to initial primary particles (Fig.4-4A) rapidly aggregated into intermediate structures to create small agglomerates (Fig.4-4B) and then progressively grew to the big porous agglomerates (Fig.4-4C). Thus, the shape factors of particles were significantly changed. If focusing on the effect of different binders, water binding agglomerates had least similarity of a circle and most surface area among the three for both small and large particle size fractions. Even for the sugars binders, there still was significant difference between them in convexity and elongation. It is not surprised to the results because the higher binder liquid concentration resulted in the high compactness of agglomerates (Szulc and Lenart, 2013). Thicker bridges or layers were formed on the surface of agglomerates obtained by higher binder concentrations. Same tendency was found in soymilk powders (Dacanal and Menegalli, 2010; Jinapong et al., 2008) and also in other agglomerated spray-dried powders (Fuchs et al., 2006; Turchiuli et al., 2005). However, morphology of agglomerates is very difficult to predict because it also depends on the droplet deposition, droplet spreading, bridge breakage and the amount and the way that binders are introduced (Werner et al., 2007).

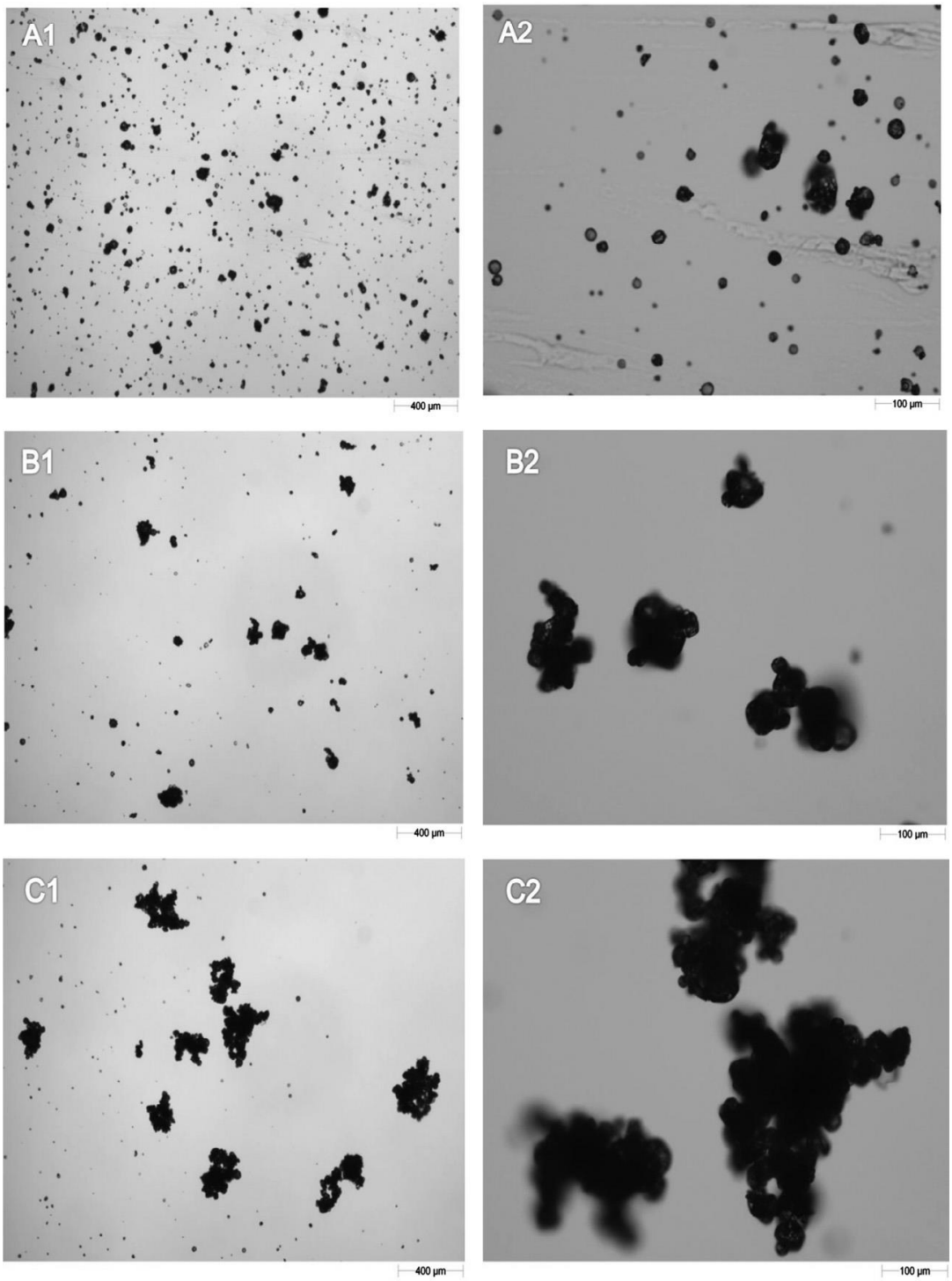


Fig.4-4 Comparison of images obtained by Malvern Morphology G3. (x25, scale =400µm; x100, scale = 100 µm) (A1 & A2: MPI standard powders; B1 & B2: small size fractions of agglomerates binding with water; C1 & C2: large size fraction of agglomerates binding with water.)

3.2 Influence of binders and agglomerate size on rehydration behaviour

3.2.1 Wettability

Wettability is the ability of the powder particles to imbibe a liquid and overcome the surface tension between them based on capillary force. Generally, the GEA Niro method is used to measure the wettability of “easy-wet” powders. However, for some powders with poor wetting ability, such as high protein powders in this study, it can be determined by the additional weight of powder after absorbing liquid in a specified time.

Wettability results are illustrated in Fig.4-5 for ST and the six agglomerated powders. Agglomeration had a major improvement on the wettability of MPI, as the agglomerated powders absorbed significantly more water than that of ST in 10 minutes. A major reason for this improvement was due to the increase in particle size, as presented in Table 4-1. Good wettability was generally favoured by the presence of large particles, resulting in larger voids between the particles which allow water to penetrate more easily into the powders (Freudig et al., 1999; Hogekamp and Pohl, 2003). And also for each binder, the larger particle size fraction produced the highest wettability.

Fig.4-5 also shows that binder type has an influence on wettability. The 15% lactose solution binder had the best wettability for both size fractions. For the smaller size fraction, the 15% sucrose solution binder was slightly better than the distilled water but worse for the larger size fraction. It is because the influence of binder composition on wettability is complex. The chemical nature of composition plays an important role, e.g. hydrophilic and hydrophobic nature (Fang et al., 2007; Freudig et al., 1999). Powders agglomerated with lactose and sucrose solution contain hydrophilic carbohydrates that results in the development of more hydrophilic bridge

surfaces that make powder wetting by water more easy. The binder composition will also influence the morphology of agglomerates produced, as seen in Table 4-2, and this in turn will influence how water penetrates into the powder.

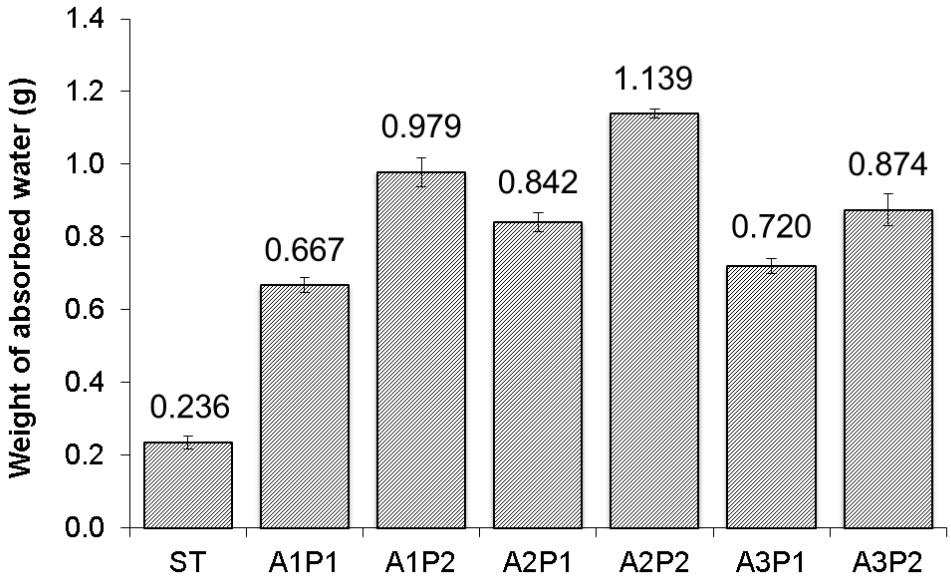


Fig.4-5 Mean weight of absorbed water for samples (ST, A_1P_1, A_1P_2, A_2P_1, A_2P_2, A_3P_1 and A_3P_2) after 10 minutes

It is commonly believed that particles with rounder and rougher surfaces lead to higher wettability whereas smoother and elongated powders have lower wettability (Gaiani et al., 2011; Perea et al., 2009; Yekeler et al., 2004). This is due to the lower roundness and higher elongation which result in a higher wetting angle than equivalent round particles; longer contact lines also cause stronger adhesion force of prismatic particles(Oliver et al., 1977). Comparing the hydrophilic lactose and sucrose binders, samples agglomerated with lactose showed rounder (lower elongation) and rougher (lower convexity) which may in part explain the better wettability. However, due to a complex influence on wetting behaviour, the precise

explanation of the effect of morphology is still unknown and needs further study in the future.

3.2.2 Solubilisation

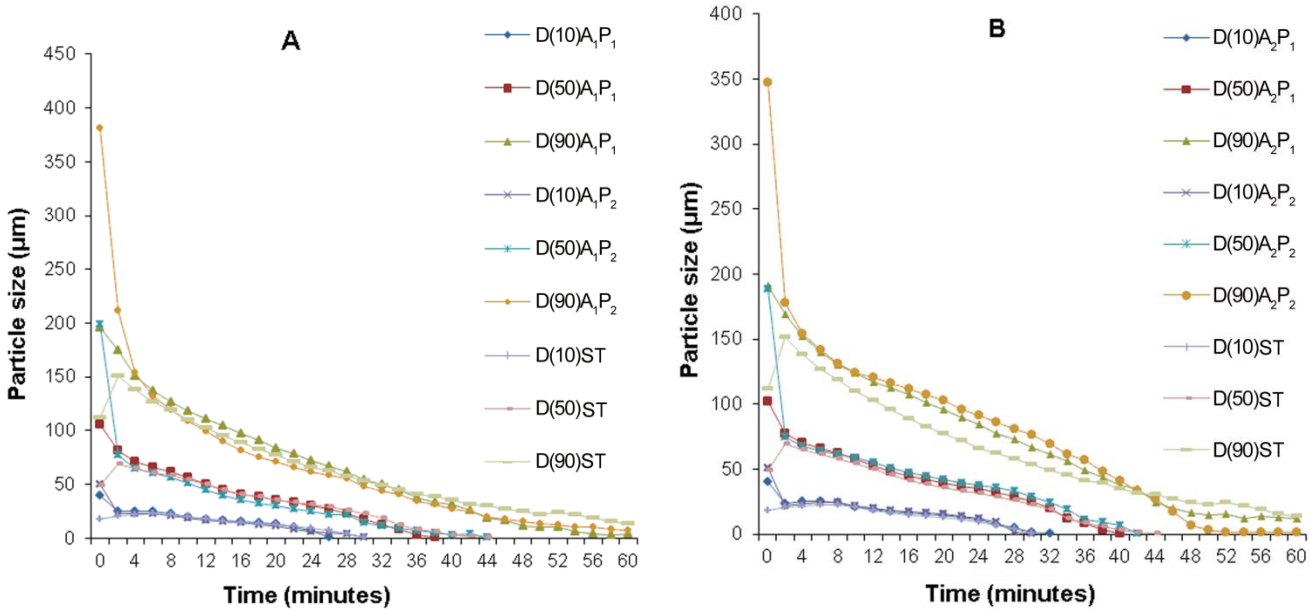
3.2.2.1 Particle size measurement of dispersed particles

This approach measured the evolution of particle size of wetted particles over time (as described in materials and methods). Fig. 4-6ABC illustrates the influence of initial particle size on the solubilisation of particles over time (as illustrated by the decrease in D(90), D(50) and D(10) size values). Fig. 4-6ABC shows an initial rapid decrease in particle size of the larger sized agglomerates. This is due to water easily penetrating into the agglomerate pore network, solubilising the solid bridges between the primary MPI particles and releasing them into solution. After this initial period of about 4 minutes, the particles attain a similar size, independent of initial agglomerated size fraction. This provides further evidence that the agglomerates have been broken down into their primary MPI particles.

This initial time period was followed by much slower solubilisation and it took around 60 minutes for the particles to mostly solubilise, as evidenced by the D90 values approaching zero. Fig. 4-6ABC shows that agglomeration with any of the binders had no significant beneficial impact on the solubilisation rate of MPI. This appears to be due to the solubilisation rate being controlled by the solubilisation of the primary MPI particles (Mimouni et al., 2009). This suggests that the primary MPI particles solubilise very slowly, possibly due to strong attractions between casein micelles within the powder. In fact, it may marginally increase the solubilisation time, because a few minutes may be required to break down the agglomerates into MPI primary particles. In addition, there also appears to be some differences based on the type of binder used, however it is not of major significance. Overall, the

solubilisation of the MPI powder was insensitive to agglomeration and the choice of binders.

In Figs. 4-6ABC, it is interesting to see that the particle sizes of ST increased over the first 4 minutes. This is because particles usually sorb water following the wetting stage and this behaviour is called swelling. Same phenomenon was founded in other's paper (Gaiani et al., 2009; Gaiani et al., 2007; Goalard et al., 2006). On the other hand, Fig. 4-6ABC did not show swelling with the agglomerates as they have much shorter swelling time due to their quicker penetration by water (Gaiani et al., 2009). Furthermore, swelling of agglomerates and primary particles occurred when the agglomerates were disintegrating, so any increase in size due to swelling was counteracted by the large reduction in agglomerate size.



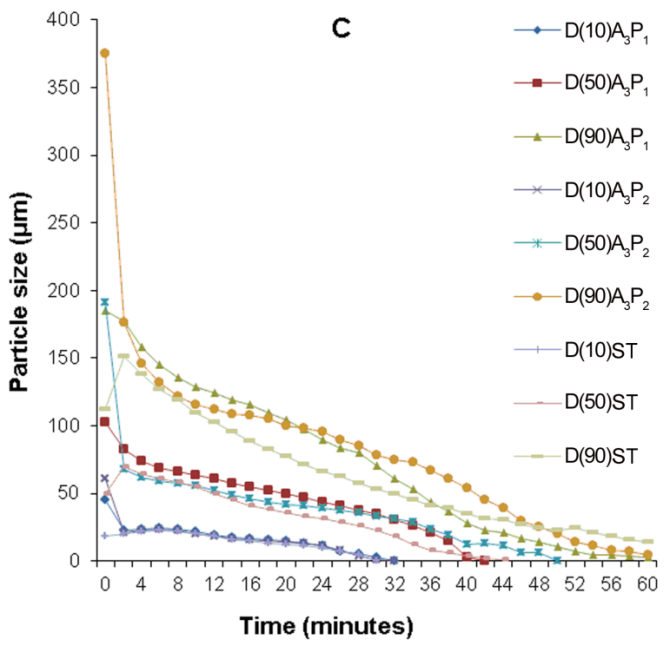


Fig.4-6 ABC Particle size measurement of dispersed particles versus time (every 2 minutes) in 25 ± 2 ℃ water at mixing condition of 2000rpm (A= water binding agglomerates and ST; B= lactose solution binding agglomerates and ST; C= sucrose solution binding agglomerates and ST.).

3.2.2.2 Dissolved solids measurement

Solubilisation was also expressed as the amount of solids that were dissolved into solution over time. As with Fig. 4-6ABC, Fig. 4-7 shows that agglomeration did not have a significant beneficial impact on the solubilisation rate of MPI. In fact, agglomerate solubilisation was slower than that of ST when using distilled water as a binder. This is in agreement with work by Schuck et al (2007) and Gaiani et al (2007). They found that granulation increased the solubilisation time of native phosphocasein powders. This is due to casein micelles interacting strongly within the primary particles and developing attractions that are difficult to break down (McKenna, 2000). Thus, water takes a long time to solubilise the powder particles and results in the slow solubilisation rate. In relation to agglomeration, water has to first penetrate into the agglomerates to release the primary MPI particles and this takes some additional time. Agglomerates formed by lactose and sucrose binders showed a somewhat

similar progression to ST, with similar dissolved solids concentrations above 200 minutes. The presence of lactose and sucrose on the surface of protein particles is believed to inhibit the interaction between casein micelles because they are more hydrophilic. Consequently, MPI powders agglomerated with lactose and sucrose solution are comparatively more easily dissolved into water than that agglomerated with water, as evidenced in Fig.4-7.

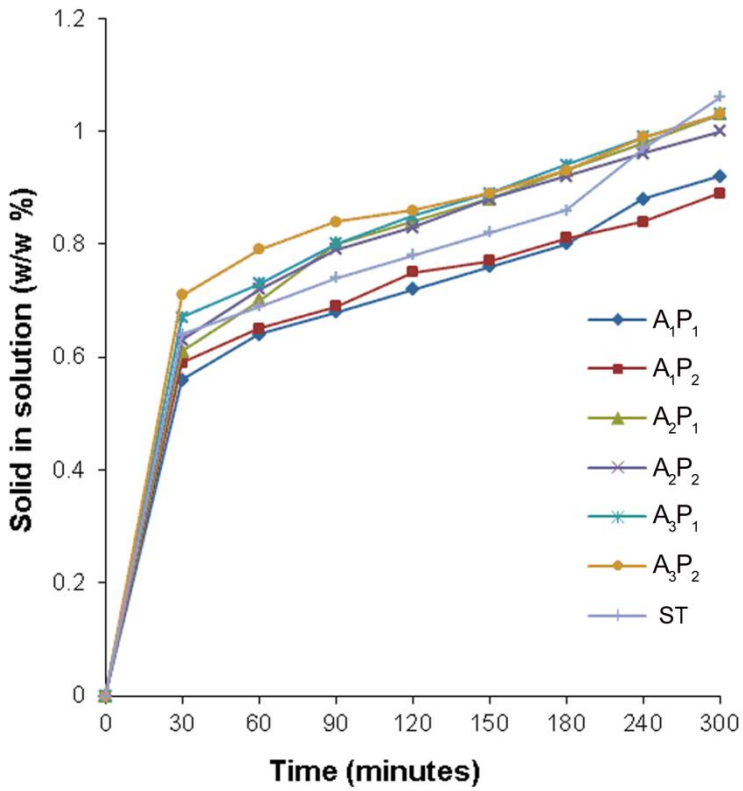


Fig.4-7 Solubilisation as measured by dissolved solids concentration (w/w %) versus time (every 30 minutes) after 10 minutes 3000g centrifugation

It is interesting to observe that there is a big increase in dissolved solids content of the ST and agglomerates over the initial 30 minutes where it increased form 0% to around 0.6%, whereas for the following 300 minutes, solids concentration continued to reach only 1%. This is most likely due to mass transfer considerations where at the beginning, the concentration gradient between particle surface and water is

greatest and the particle size, surface area and influence of turbulence are greatest. Meanwhile, the results in Fig. 4-7 showed that it took 300 minutes to reach 1% solids concentration, which represents about 50% of the initial mass of particles added. But in Fig. 4-6ABC the dissolution took about 60 minutes to totally dissolve the particles as the D90 value were nearly at zero. The huge difference is due to the different agitation speeds which it is commonly believed to significantly influence the rehydration time (Richard et al., 2012; Schober and Fitzpatrick, 2005). This may be a potential factor that can improve the rehydration properties of MPI powders.

4 Conclusion

In summary, fluid bed agglomeration with different binding liquids was found to modify the structures and physical properties of MPI powders. Agglomeration significantly decreased the bulk density; increased the porosity of powders; and formed particles with lower circularity and convexity but higher elongation. The type of binder also influenced the shape factors of agglomerates. Using water as binder created more irregular particles than using the other two sugar binders.

Both the agglomerate size and the binder type had significant influences on the improvement in wettability. Overall, the larger agglomerate size fraction produced with the lactose binder provided the best wettability. In relation to solubilisation of the wetted particles, agglomeration had no beneficial effect with any of the binders used. This low rate of solubilisation is because it is controlled by the solubilisation of the primary MPI particles, which appears to be very slow due to the strong interaction between casein micelles in the primary particles. Consequently, it would be interesting to explore how the size of these primary particles influences the rehydration behaviour and if this could be manipulated to greatly improve the solubilisation rate in particular.

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CHAPTER FIVE

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.

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 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 it 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 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 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 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 distribute 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 influence 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 were 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 larges 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, 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 solution was 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 $l \cdot min^{-1}$, 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/+75µm). 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 ℃ 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 particle 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 particle 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 100mL distilled water at 20 ℃ 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 ℃ 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 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 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 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 ℃ 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.

2.8 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 x and 150 x) 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 5-1, 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.5-1. 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 5-1, the smallest granules S5 had the highest particle density and the larger granules had progressively lower particle 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 to 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 5-1. Similarly, the MPI granules generally had significantly lower porosity than the standard MPI, as the porosity is mainly dependent on bulk density and particle 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%.

Table 5-1 Bulk Density, Particle density and Porosity of powders *

Sample	Characterisation	Particle size D(50) (μm)	Loose density (g/mL)	Tapped density (g/mL)	Particle 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 $P < 0.05$.

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 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 particle 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 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.5-1 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 needs further studies in the future.

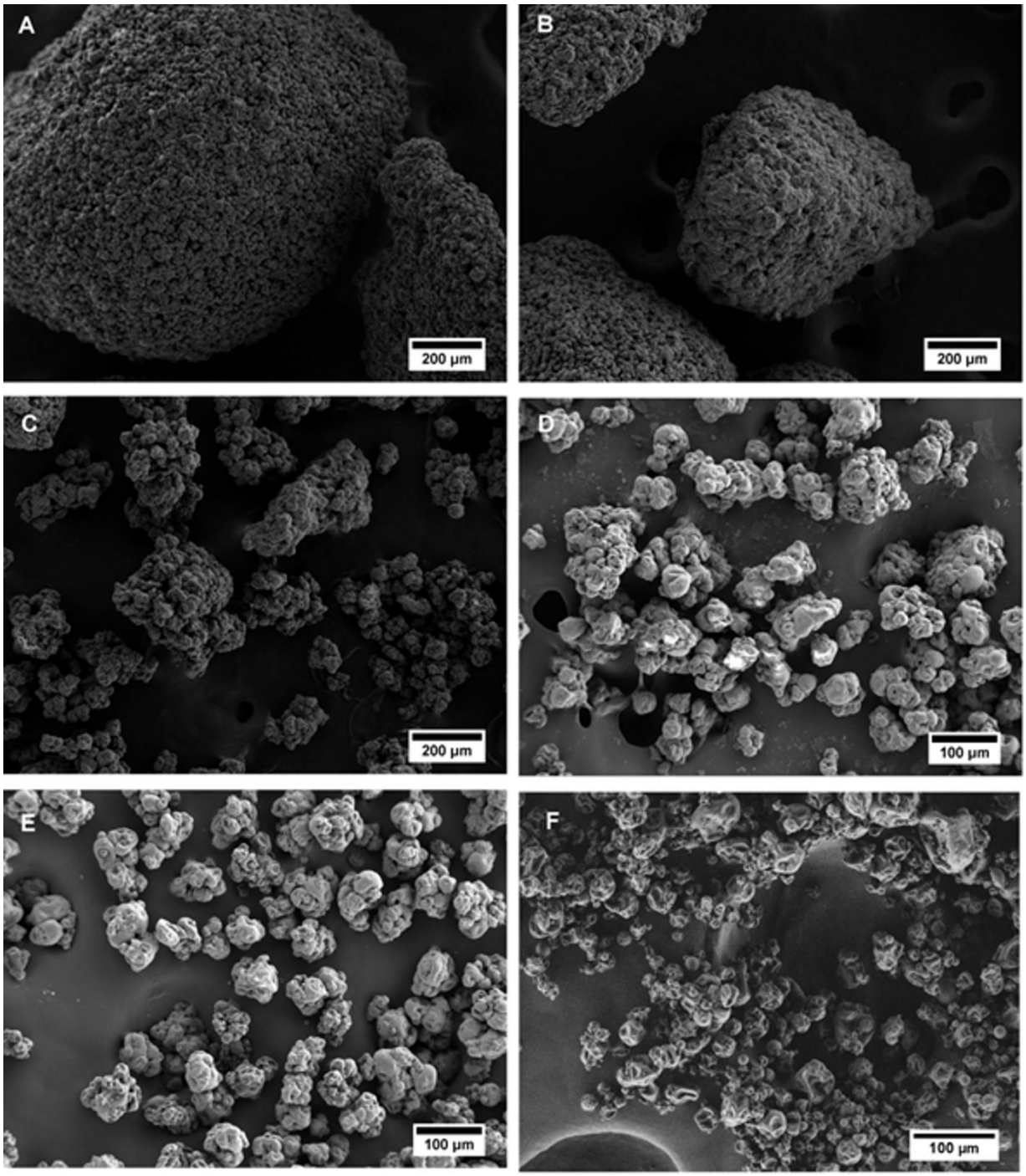

Fig.5-1. SEM images of MPI granules with different particle sizes by granule growth processes. (**A:** S1; **B:** S2; **C:** S3; **D:** S4; **E:** S5; **F:** standard MPI)

3.1.2 Granule morphology

Three parameters (Circularity, Convexity and Elongation) are used to describe the granules with different particle sizes. Examining Table 5-2, 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 is even lower than that of unagglomerated MPI. In Fig.5-1 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 is 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.5-1 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.

Table 5-2 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 $P < 0.05$.

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 5-3, 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 seconds to be fully wetted. The other granules all had shorter wetting times than 60 seconds, which can be considered as the easy wetting powders. However, the standard powders took more than 20 minutes 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 µm, still floated on the water surface for more than 8 minutes. 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).

Table 5-3 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

3.2.2 Capillary rise wetting

From Fig.5-2, it can be seen that the agglomerated MPI granules absorbed significantly more water by capillary force than the standard powders in 10 minutes. 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)：

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

where l is the penetration depth of the liquid, η is liquid viscosity, γ is the liquid surface tension, r is radius of pores, θ 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 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 with a 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),

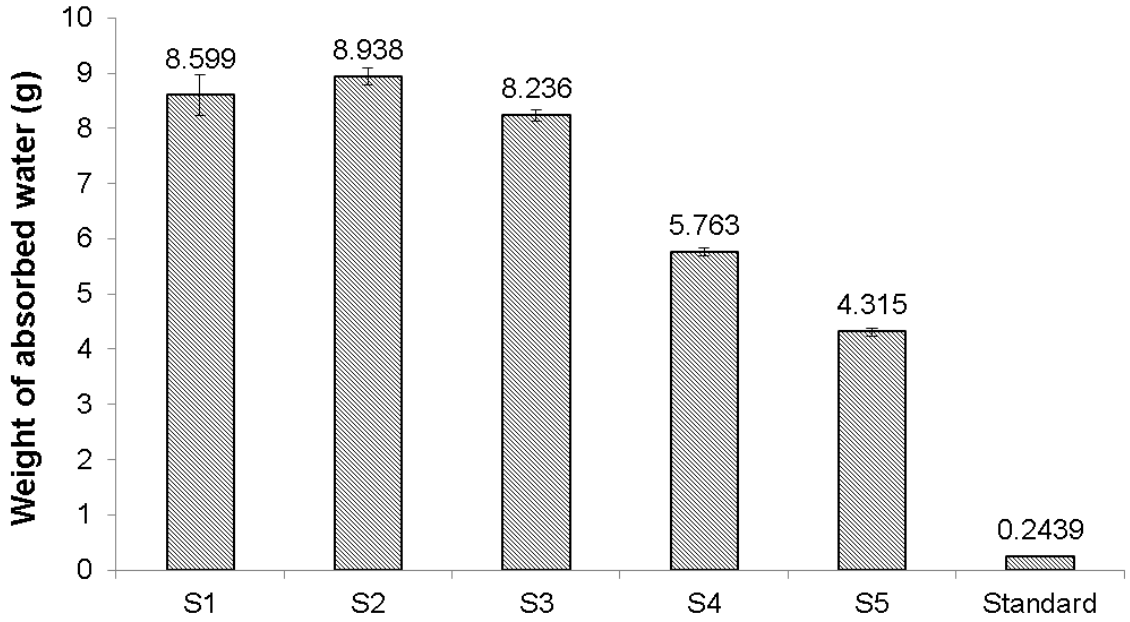

Fig.5-2 Mean weight of absorbed water for samples (the agglomerated MPI granules S1, S2, S3, S4, S5 and standard MPI) after 10 minutes

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.5-3, 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 decrease to 40°. This is not simply due to the granule's high porosity, as the standard powders have an even higher value, as shown in Table 5-1. Thus, it is believed that the granules having larger voids between the 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.

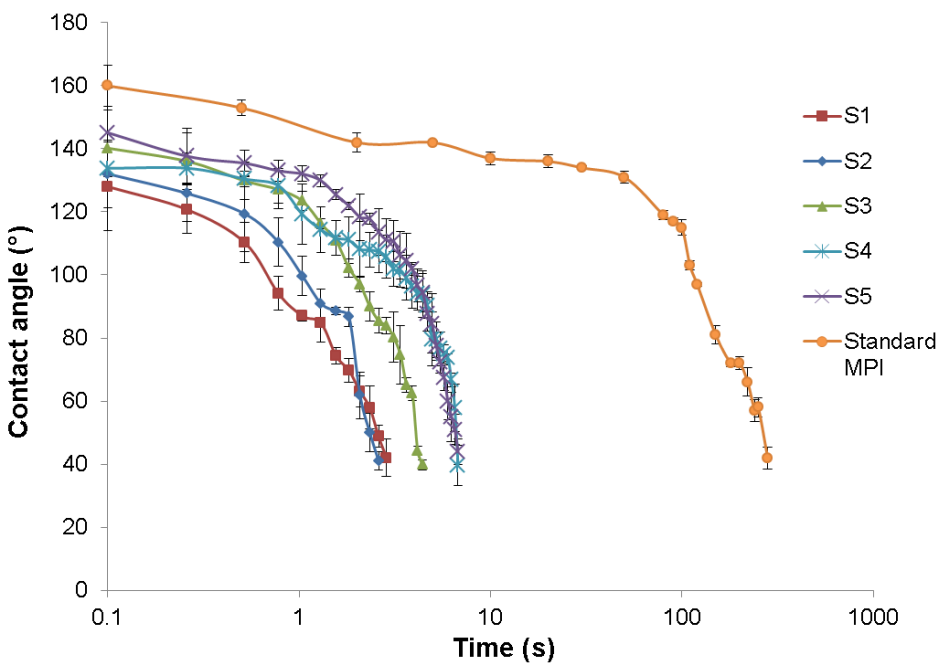

Fig.5-3. The change of contact angle (°) as a function of time using the sessile drop technique in approx.20 ℃ temperature.

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.5-4 A&B, 50% of the standard MPI particles were completely rehydrated into water in about 32 minutes, 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 minutes, 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.5-4A, the largest granules S1 took the longest time of 130 minutes to reach 200 µm particle size, although its dissolution rate was quickest of all. S2 and S3 also required more than 100 minutes achieving a relatively stable particle size. It is surprising to see that these three granules all finally decreased to a constant size, which is 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.5-4B, 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 dispersion process but it began with smaller size and still was not totally dissolved at 120 minutes.

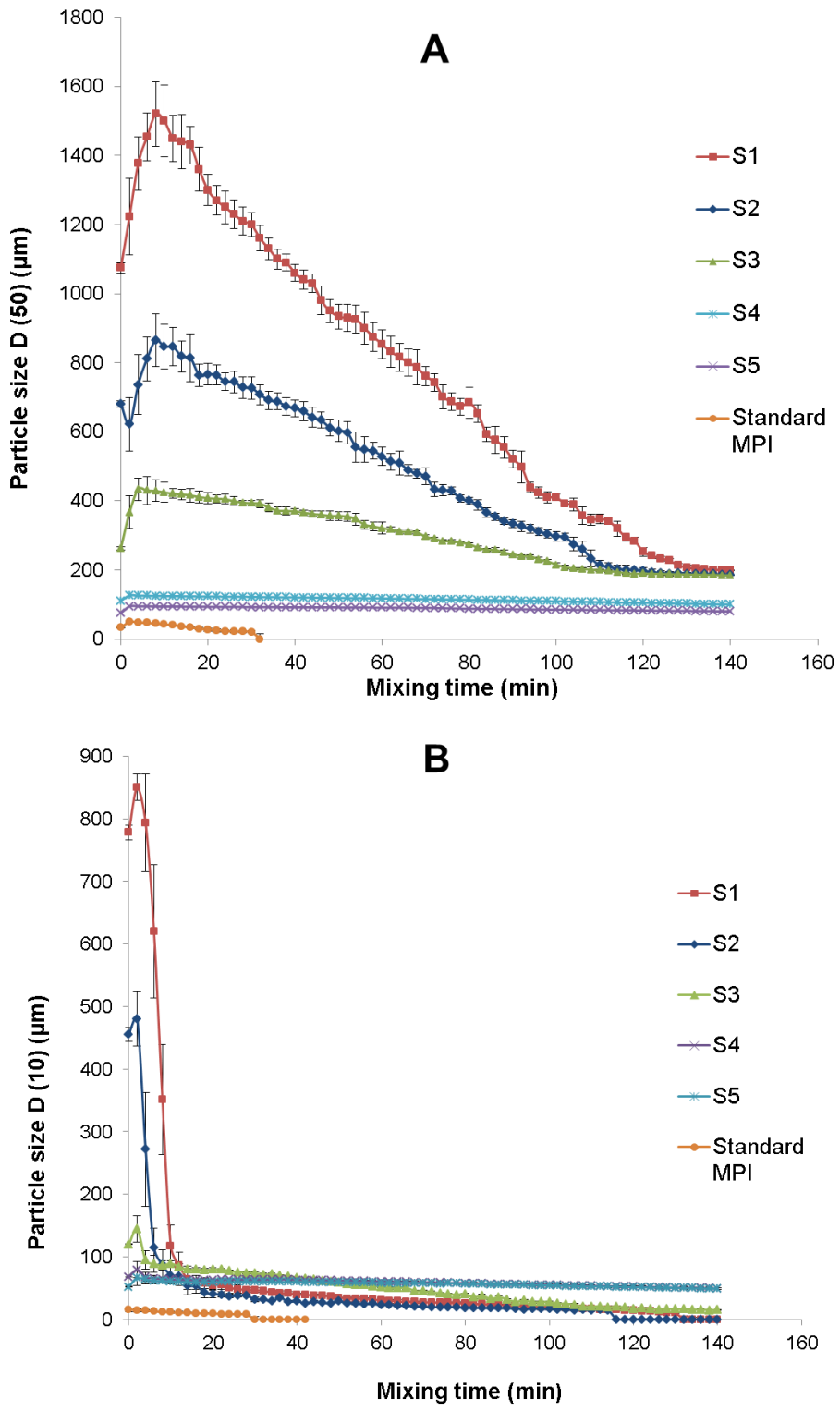

Fig.5-4 Particle size measurements of dispersed particles of the agglomerated granules S1, S2, S3, S4, S5 and standard MPI, as a function of mixing time (every 2 minutes) **A:** D (50); **B:** D (10).

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.5-4B.

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 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 minutes. 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.5-5 shows the dissolved MPI solids percentage in solution as a function of mixing time. The standard MPI displays the best dissolution behaviour compared with others, as nearly 60% of its solids dissolved after 5 hours mixing time. The agglomerated granules displayed much lower dissolution ability with only 30% solids being solubilised in 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 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 minutes and was then followed by slower dissolution behaviour for the next 300 minutes. 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).

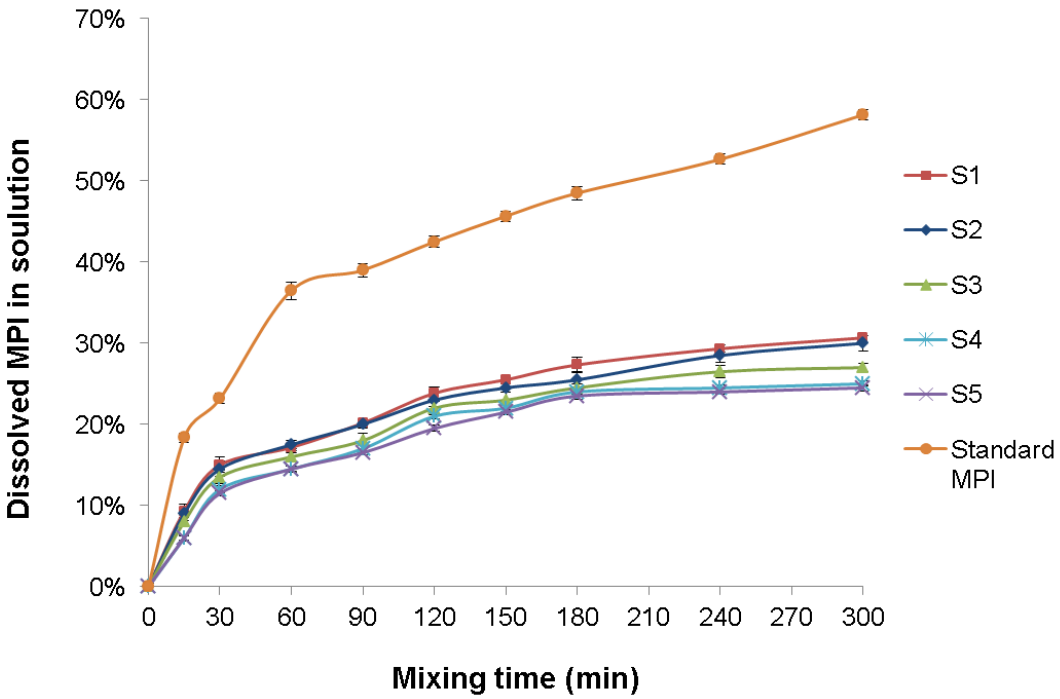

Fig.5-5. Solubilisation as measured by dissolved MPI percentage (%) versus different mixing time.

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.

Acknowledgements

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CHAPTER SIX

The effects of fluidized bed and High Shear mixer granulation processes on water adsorption and flow properties of milk protein isolate powder

Published in *Journal of Food Engineering*, 2017, 192, 19-27

Abstract

The effect of fluidised bed (FB) and high shear mixer (HS) granulation processes on water adsorption and flow properties of milk protein isolate powder (MPI) was investigated and compared. The agglomerated granules were characterised by different size fractions. It was found that granules produced from the HS process adsorbed less moisture, with slower adsorption kinetics, compared to those produced from using the FB. Granulation reduced the cohesiveness of the MPI powder, with HS having a significant greater impact due to the formation of the particles with higher bulk density and larger size. Particle size played a critical role that influenced water adsorption and flowability. Granulation processes contributed to different degrees to reducing the minimum outlet diameters of hoppers based on either mass-flow or core-flow discharges. HS granules had large wall friction angles, suggesting a need for steeper hopper walls for effective discharge.

Keywords: Milk protein isolate, Fluidised bed granulation, High shear mixer granulation, Flowability, Water adsorption, Hopper design

1 Introduction

Milk protein concentrates, manufactured from ultrafiltered skim milk, are widely used in nutritional beverages, sports nutrition bars and other dairy based products due to their high nutritional values. These powders provide a supply of milk solids in a stable and convenient form, especially for preservation and transportation (Ann Augustin and Clarke, 2011; Selomulya et al., 2013). However, milk protein based powders usually have fine particle size and dense structures, causing poor flow behaviour during conveying (Crowley et al., 2014; Ilari, 2002) and susceptibility to moisture adsorption during storage (Foster et al., 2005; Kinsella and Fox, 1986). Granulation is a size enlargement process that results in the formation of large granules with modified physical structure. Thus, it can be used as a potential process to improve the flow behaviour of bulk solids and influence the water adsorption behaviour (Szulc and Lenart, 2010, 2012).

Fluidised bed and high shear mixer agglomeration are the most widely used wet granulation processes (Jacob, 2007). Due to the different mechanisms of granule growth, the use of binders and intensity of solidification, the granules produced by these two processes have the completely different structures (Barrera-Medrano et al., 2007; Litster and Ennis, 2013). Generally, using a fluidised bed, binding liquids are atomized and converted into free-flowing solids, which then coalesce and agglomerate together by creating bonds between primary particles (Cuq et al., 2013). Granules, thus formed, without mechanical consolidation, usually have more irregular shape and high porosity, including large interstitial space and also internal pores inside single granules (Ji et al., 2015). In comparison, a high shear mixer granulation process provides strong agitation forces through an impeller with compacts particles so that the created granules are highly-packed, increasing bulk density and reducing porosity (Ji et al., 2016a; Reynolds et al., 2006). Furthermore, even granule growth

processes during the granulation process are also believed to influence physical characteristics (Hapgood et al., 2007). Generally, wetting and nucleation, as the first step of granulation, wets the powders by binders and forms nuclei aggregates with loose structures; the subsequent coalescence process produces secondary agglomerates from the nuclei, which have the comparatively less spherical shape and rougher surface; finally, consolidation compresses the agglomerates uniformly to squeeze out entrapped air and decreases the pore volume and porosity (Cuq et al., 2013; Litster and Ennis, 2013). However, fluidised bed granulation exhibits different granule growth mechanisms. As the binding liquid is sprayed as small droplets (which are much smaller than primary powders), coalescence mostly occurs by layering of materials on the surface of wet particles (Barkouti et al., 2013). The resulting particles are less consolidated due to their motion in air, and not by mechanical agitation (Jacob, 2007). Consequently, granules formed using a fluidised bed is often more porous than those from high shear mixer granulators. For these reasons, the different structures modified by these two processes are believed to contribute to the different functionalities of the bulk solids.

Moisture adsorption refers to a phenomena occurring at the physical interface between the bulk solids and their surrounding humid environment. It contributes to moisture content during storage and thus has an important role to play in physical and chemical stability of powders. The behaviour depends to a large extent on the powder particle surface area, i.e., sorption area, composition and porosity; these factors affect the rate and extent of entry and exit of water molecules into the solid matrix (Al-Muhtaseb et al., 2002). Commercial dairy powders, especially high protein powders, typically have small particle size and large surface area (Schuck et al., 2012). Hence, they are prone to adsorb moisture during storage, handling and processing, which can easily cause the undesired caking, crystallization and loss of

production (Fitzpatrick et al., 2008). Granulation can influence the water diffusion process by increasing particle size and modifying powder structures (Barrera-Medrano et al., 2007), altering storage and handling characteristics.

Flowability is another important parameter of milk protein powders and it has been suggested that small powder particles are generally regarded as less flowable compared to larger particles (Crowley et al., 2014). It is reported that materials with small particles and dense structures form cohesive arches by consolidation and interparticle adhesive forces, which can restrict discharge from silos (Schulze, 2007), effecting throughput and product quality. In general, there are two patterns for the flow of a powder out of a silo: 1) mass flow and 2) core flow (Fitzpatrick et al., 2004b). Mass flow is the desirable flow pattern where all the solids are in motion to give a first-in and first-out discharge regime. However, for a cohesive powder, 'arching' may still occurs at the hopper outlet, where a stable powder arch forms across the outlet, blocking the exit funnel. In addition, most flow problems happen in the core flow pattern, as cohesive powders will move out through a central funnel, which is formed by the no-flow particles remaining at the internal walls of hopper. This phenomenon may give rise to the formation of a stable rat-hole (Schulze, 2007). Thus, in order to make powders flow smoothly and discharge reliably, it is desirable to design for mass flow pattern. While studies (Fitzpatrick, 2007; Fitzpatrick et al., 2004a) report that particle size is a key determinant affecting flowability of powders, others claim particle shape and densities are also potential factors as they influence physical properties of surface contacts between particles (Cleary, 2008; Schulze, 2007). Thus, as an effective technique to modify these physical properties, the effect of granulation on the flowability of powders is important to investigate. So far, studies reporting granulation are mainly about pharmaceutical materials (Ennis, 2010; Gao et al., 2002; Iveson et al., 2001; Palzer, 2011); very few focus on dairy protein powders.

The objective of this study was to investigate the effect of two granulation processes, fluidised bed and high shear granulation, on water adsorption and flowability of milk protein powders. Powder granules formed by these two processes were analysed and their data was compared. The flow function and wall friction results were used to specify appropriate hopper outlet dimensions and hopper wall angles for both mass and core flow discharges.

2 Materials and method

2.1 Materials

In this study, Kerry Ingredients (Kerry, Ireland) supplied milk protein isolate powder (MPI) as a model powder, which consists of 86% milk protein, 5.2% moisture, 1.5% fat, 6% ash and less than 1% lactose. The lactose used as binders in fluidised bed and high shear mixer granulation, was purchased from Food Ingredients (Viby J, Aarhus, Demark).

2.2 Methods

2.2.1 Fluidised bed granulation

The agglomeration process of MPI was performed in a top-spray fluidised bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Iowa, USA). Each batch comprised of 200 g powder which was fluidised in the product vessel by upward flowing air stream from the bottom, at a flow rate of 200 L min^{-1}. The powders were preheated by a 50 ℃ air stream for 10 minutes, before 15% (w/v) lactose solution was introduced as a binding liquid. The liquid was injected via a peristaltic pump (1mL min^{-1}) and sprayed as small droplets by a two-fluid spray nozzle, located on the top of the vessel. The air pressure on the nozzle was 1 bar. After addition of 150 g of

lactose solution, drying was continued for 20 minutes at a reduced flow rate of 100L min^{-1}. Three batches of MPI granules were produced as replicates.

2.2.2 High shear granulation

A high shear granulator (4M8, Procept, Zelzate, Belgium) was also used in this study to agglomerate the MPI powders. As in 2.2.1, 200 g MPI powder for each batch was fed into a glass bowel, where an impeller and a chopper were both used to agitate the powders at a speed of 300 rpm and 500 rpm, respectively. The binding liquid in this granulation process was also 150 g 15% *w/v* lactose solution, which was injected into the bowel as droplets with a dosing speed of 4 mL min^{-1}. The impeller and chopper continued to mix the products at the same speed for 10 minutes. Finally, the fluidised bed in 2.2.1 was again used to dry the granules with air (50 ℃) at a flow rate of 100 L min^{-1} (Ji et al., 2016a). Three batches samples were prepared for the repeated measurements.

2.3 Powder characterisation

As different granule growth mechanisms occur in the fluidised bed and high shear mixer granulation processes, variations in particle size, shape and porosity of the formed granulated MPI is expected. Therefore, prior to comparison, the agglomerates were sieved into different size fractions. Two size fractions for agglomerates from fluidised bed granulation were prepared by 106µm, 180µm and 300µm level sieves (Endecotts, London, UK) (FB_1:180µm ~ 300µm and FB_2: 106µm~180µm). Five size fractions for agglomerates from high shear mixer granulation were prepared by 75 µm, 106 µm, 180 µm, 425 µm, 850 µm and 1000 µm level sieves (HS_1: 850 µm ~1000 µm; HS_2: 425 µm ~ 850 µm; HS_3: 180 µm ~ 425 µm; HS_4: 106 µm ~ 180 µm and HS_5: 75 µm ~ 106 µm). The particles that were not in

these fractions were removed. The non-agglomerated standard MPI (ST) used as the controlled samples. All the samples were further dried in a vacuum oven (Jeiotech, Seoul, Korea) at 60 ℃ for 24 hours and cooled down in desiccators to ambient temperature before measurements. The final moisture content of the powders can influence water adsorption and flow behaviour and therefore a value ranging between 2~3% was targeted. The measurement was carried out in the preliminary study (Ji et al., 2016a). Malvern Masterszier 3000 (Malvern Instruments Ltd, Worcestershire, UK), which applies laser light scattering technique, was used to measure the particle size of the samples. Three repetitions were carried out; D(10), D(50) and D(90) parameters were used as a measure of particle size.

2.4 Water adsorption analysis

Water adsorption isotherms were carried out by the static gravimetric method. Approximately 1 g powder was weighed into small glass vials of known weight. Triplicate samples for each powder were firstly dried in a vacuum oven at 50 ℃ for 24 hours to remove the residual moisture. The measurement was carried out in the preliminary study to make sure the residual moisture as low as possible (Ji et al., 2016a). Powders were kept in desiccators containing P_2O_5, equilibrated at room temperature, before placing in the desiccators with a stable relative humidity, which ranged from 11% to 65%. Different saturated salt solutions: LiCl (11%), CH_3COOK (22%), $MgCl_2$ (33%), K_2CO_3 (43%), $Mg(NO_3)_2$ (53%), and $NaNO_2$ (65%) were used to provide varied hygroscopic environments, respectively. During the equilibration, the desiccators were stored in two 25 ℃ incubators. The weight of powder was measured for at least 96 hours until it reached a constant value. The results were expressed as equilibrated moisture content as a function of water activity to show the adsorption isotherms. At the same time, the sorption kinetics was also conducted by

continuous measurement of mass increase (Schuck et al., 2012). The weight of powder was measured at 0, 3, 6, 9, 12 and 24 hours, and then at 24-hours intervals until equilibration. The results were exhibited as the moisture content for every 100 g dry matters as a function of time.

2.5 Powder flow analysis

The flowability of powders were quantified and analysed by a powder flow tester from Brookfield (Brookfield Engineering Laboratories, Middleboro, MA, USA). Flow functions and angles of wall friction were both measured to assess the flow behaviour of milk protein powder and its agglomerates. During the measurements, axial and torsional speeds for the tester were 1.0 mm s^{-1} and 1 rev h^{-1} (approx. 0.0167 rpm). The aluminium trough (230 cm^3, 15.2 cm internal diameter) of the annular shear cell was filled by the samples, which were levelled by different shaping blades (curved- and flat-) to create the smooth powder surface. The mass of solids based on the different bulk densities were recorded. Vane- or flat-profiled lids with 15.2 cm external diameter were attached to the compression plate of the tester for flow function and wall friction tests, respectively. All the measurements were repeated three times.

2.5.1 Flow function test

The flow function test is the primary measurement of powder flowability, which gives a measure of the strength of the bulk solids retained at a stress free surface following consolidation to a given stress level (Teunou et al., 1999). Hence, in this study, the unconfined failure test was carried out and five normal stresses between 0.2 and 4.8 kPa were applied to calculate the unconfined failure strength and major principle consolidation stress, based on Mohr circles from specific yield locus. The

flow function was then constructed by plotting the failure strength versus the consolidation stress, which can be quantified as the flow index (ff_c) (Schulze, 2007). Normally, the standard classification of this index is: 1) if ff_c <1, powder is non-flowing; 2) if 1< ff_c <2, powder is very cohesive; 3) if 2< ff_c <4, powder is general cohesive; 4) if 4< ff_c <10, powder is easy to flow; 5) and if ff_c >10, powder is very free flowing. Meanwhile, bulk density curve is also evaluated to describe bulk density changes as a function of stress acting on the powder. The compressibility index (CI) was calculated as follows:

$$CI\% = \frac{\rho_c - \rho_b}{\rho_c} \times 100$$

Where ρ_b is loose bulk density without compressing (kg m^{-3}); ρ_c is compressed bulk density at 4.838 kPa major principle consolidation stress (kg m^{-3}).

2.5.2 Wall friction test

Wall friction is the friction between materials surface (e.g. the wall of a bin or silo) and bulk solids (powders). The angle of wall friction represents the angle to which a wall surface must be inclined to cause powder to slip (Teunou et al., 1999). It is an important index for silo design for flow, which also can be considered as chute angle. In this study, a flat plate of stainless steel AISI 304 attached in the tester was used to measure the angles. In total 10 normal stresses (0.48, 0.97, 1.45, 1.93, 2.41, 2.89, 3.37, 3.86, 4.34, 4.82 kPa) were applied. Finally, the angles were obtained from the slope of a line drawn from the origin to a point on the maximum wall yield locus at a normal stress of 4.82 kPa.

2.5.3 Two forms of flow obstructions for conical hopper design

There are two forms of flow obstruction problems for bulk solids that may occur in a silo: arching in mass-flow pattern and rat-holing in core-flow pattern, which are illustrated in Fig.6-1. Hence, a hopper is usually designed for reliable flow aiming to avoid arching in mass-flow silos and rat-holing in core-flow silos. Critical arching diameter and hopper half angle are commonly used parameters to determine the outlet size of mass-flow silos. The critical arching diameter $D_{arching}$ (m) was calculated as follows (Chen et al., 2012; Crowley et al., 2014):

$$D_{arching} = \frac{2 \times \sigma_a \times 1000}{\rho_a \times g}$$

Where σ_a is critical arching stress (kPa); ρ_a is critical arching bulk density (kg m^{-3}); g is gravity acceleration (m s^{-2}).

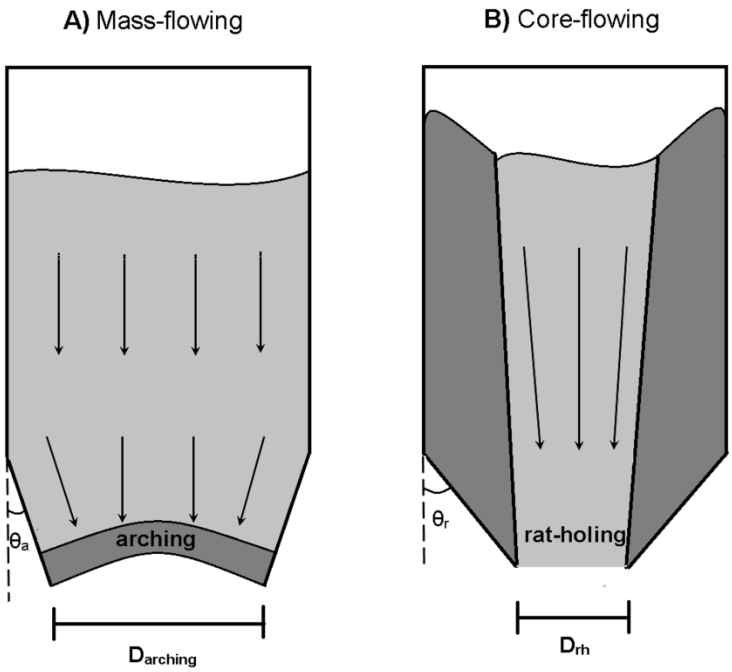

Fig.6-1 Schematically illustration of arching and rat-holing problems in hoppers during **A:** mass-flowing discharge pattern and **B:** core-flowing discharge pattern, respectively ($D_{arching}$: minimum outlet diameter to prevent arching; θ_r: critical hopper

half-angle to prevent arching; D_{rh}: minimum outlet diameter to prevent a stable rat-hole; θ_r: critical hopper half-angle to prevent a stable rat-hole).

The critical hopper half angle (θ_a) can be derived from the effective angle of internal friction ($\emptyset_e$) and the angle of wall friction ($\emptyset_w$) for a conical hopper (Schulze, 2007):

$$\theta_a = \frac{1}{2}\left[180° - \cos^{-1}\left(\frac{1 - \sin \emptyset_a}{2 \sin \emptyset_a}\right) - \emptyset w - \sin^{-1}\left(\frac{\sin \emptyset_{wa}}{\sin \emptyset_a}\right)\right]$$

Where $\emptyset_a$ is the critical angle of internal friction at the corresponding critical consolidation stress for arching (°); $\emptyset_{wa}$ is critical angle of wall frictions at the corresponding critical consolidation stress for arching (°).

For core-flow silos, the critical rat-hole diameter (D_{rh}) and the maximum inclination of the hopper walls to the vertical (θ_r) were used to design the conical hopper dimensions (Schulze, 2007). D_{rh} can be obtained for a conical silo, assuming a silo diameter of 2 m and a height of 8 m:

$$D_{rh} = \frac{G(\emptyset) \times \sigma_r \times 1000}{\rho_r \times g}$$

Where $G(\emptyset) = 0.7771 \times e^{0.0381\emptyset_r}$; $\emptyset_r$ is critical angle of internal friction (°); σ_r is critical rat-holing stress (kPa); ρ_r is critical rat-hole bulk density (kg m^{-3}).

Also, θ_r was assessed by $\emptyset_{wr}$:

$$\theta_r = 65° - \emptyset_{wr} \text{ (If bulk solids are poorly flowing)}$$

$$\theta_r = 90° - (\emptyset_{wr} + 10°) \text{ (If bulk solids are easy-flowing, i.e. granules)}$$

Where $\emptyset_{wr}$ is critical angle of wall frictions at the corresponding critical consolidation stress for rat-holing (°).

2.6 Statistical analysis

All the measurements were repeated three times and results were showed as mean ± standard deviations. One-way analysis of variance (ANOVA) was conducted by SPSS software (PASW, Statistics 1.8, 2009). The least significant difference (LSD) test, in relation to the applied variable using F-test, was used to compare the statistical differences of values relating to flow properties and hopper design. Significantly differences were considered when $P<0.05$.

3 Results and discussion

3.1 Structural characteristics

The physical and structural properties of the different granules, including particle size, density, porosity and morphology parameters are shown in Table 6-1. It can be seen that independent of granulation process used, injecting binders to promote adherence of primary particles, produces significantly ($p < 0.05$) larger particles. As milk protein powders are cohesive, high air velocity was required during FB agglomeration resulting in granules only 2 to 4 times (100 µm to 200 µm) in size of the primary powders. However, granules produced by HS can reach sizes of more than 1000 µm, which are ~ 20 times that of the primary powders. At the same time, the FB granules had lower bulk density and higher porosity than the HS granules. They also exhibited less rounded, rougher surface and higher ratio of length to width shapes based on the significantly lower values of circularity, convexity and higher values of elongation (Table 6-1). It can be more clearly observed from SEM images in Fig.6-2. The primary particles were highly-packed in the granule structures that

Table 6-1 Physical and structural properties of powders

Samples	Particle size D_{10} (µm)	Particle size D_{50} (µm)	Particle size D_{90} (µm)	Bulk density (g/mL)	Porosity (%)	Circularity (0.5)	Convexity (0.5)	Elongation (0.5)
ST	18.1 ± 0.2[a]	49.4 ± 0.2[a]	112 ± 2.1[a]	0.298 ± 0.0[a]	72.85 ± 0.1[a]	0.816 ± 0.023[a]	0.931 ± 0.009[a]	0.301 ± 0.012[a]
FB1	50.8 ± 0.3[b]	188.7 ± 1.0[b]	346.5 ± 3.5[b]	0.179 ± 0.0[b]	84.43 ± 0.1[b]	0.630 ± 0.015[b]	0.761 ± 0.017[b]	0.266 ± 0.001[b]
FB2	40.1 ± 0.2[c]	102.5 ± 0.3[c]	190.5 ± 1.5[c]	0.221 ± 0.0[c]	79.33 ± 0.3[c]	0.669 ± 0.008[c]	0.814 ± 0.005[c]	0.301 ± 0.001[a]
HS1	778 ± 11.2[d]	1075 ± 15.7[d]	1565 ± 35.1[d]	0.538 ± 0.0[d]	51.8 ± 0.2[d]	0.862 ± 0.018[d]	0.931 ± 0.015[a]	0.262 ± 0.000[c]
HS2	456 ± 10.1[e]	681 ± 9.6[e]	1029.5 ± 20.9[e]	0.500 ± 0.0[e]	53.0 ± 0.2[e]	0.870 ± 0.004[d]	0.933 ± 0.001[a]	0.258 ± 0.004[c]
HS3	119.6 ± 1.5[f]	263 ± 5.2[f]	482 ± 8.0[f]	0.431 ± 0.0[f]	61.0 ± 0.1[f]	0.767 ± 0.015[e]	0.866 ± 0.013[d]	0.262 ± 0.010[bc]
HS4	67.6 ± 0.2[g]	111 ± 2.1[g]	178.5 ± 0.5[g]	0.450 ± 0.0[g]	60.3 ± 0.1[g]	0.820 ± 0.006[a]	0.908 ± 0.005[e]	0.263 ± 0.002[bc]
HS5	52.2 ± 0.3[h]	75.0 ± 1.0[h]	107.5 ± 0.5[h]	0.526 ± 0.0[h]	53.8 ± 0.1[h]	0.891 ± 0.001[f]	0.965 ± 0.001[f]	0.263 ± 0.006[bc]

[a] Adapted from Ji et al. (2015 & 2016a)

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

formed by HS process while FB process created irregular agglomerates containing large interstitial pores resulting in larger specific volumes. It is commonly believed that the granules without consolidation will grow progressively by layering materials on the surface, while consolidation supplied by strong mechanical agitation will lead to plastic deformation of granules via a process of squeezing-out entrapped air, increased internal pore saturation and reduced porosity (Cuq et al., 2013). These significant differences in physical and structural properties can be attributed to different granule growth mechanisms as influenced by process type and equipment used (Jacob, 2007).

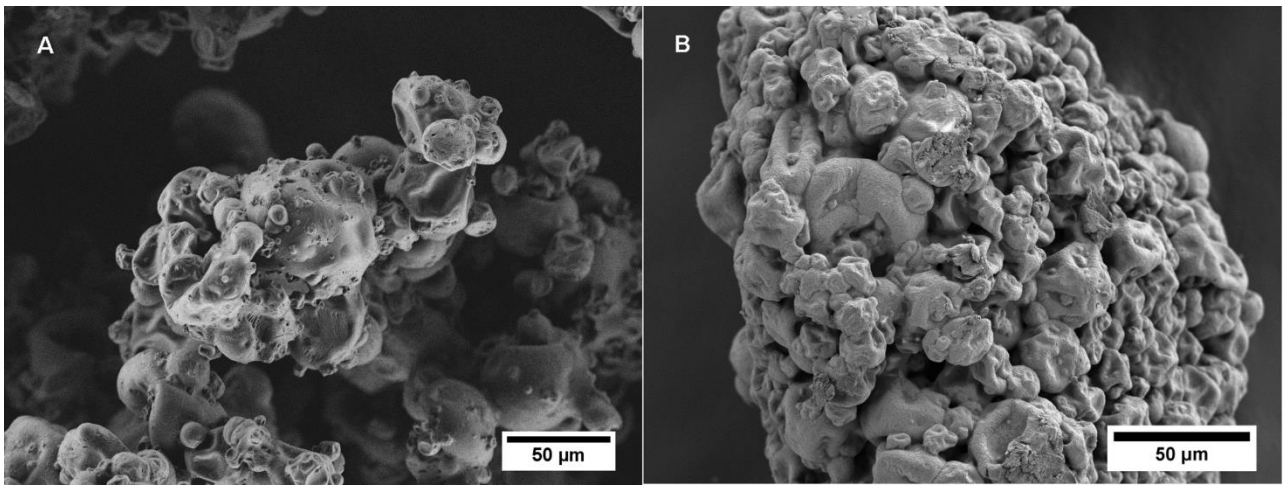

Fig.6-2 SEM Images of MPI granules produced from fluidised bed and high shear mixer granulation, **A:** Fluidised bed (FB); **B:** High shear mixer (HS).

3.2 Water adsorption

Fig.6-3 displays water adsorption isotherms of MPI powder and its granules made using the FB and HS processes, under different humidly controlled environments. For the water activity range of 0.11 to 0.65, the isotherms all had a linear slope, regardless of the type of granulation process used, including the non-agglomerated MPI. There was no significant difference between the standard MPI

(ST) and the granules from fluidised bed (FB1 & FB2), which adsorbed almost the same quantity of water. However, the granules from high shear mixer (HS1 to HS5) were found to adsorb less water from the surrounding environment, suggesting that moisture vapour is more difficult to penetrate into the structures and form layers on the surface of internal primary particles. In Fig.6-4, the water adsorption kinetics at varying humidity are given; FB1 and FB2 exhibited similar adsorption behaviour as standard MPI, which all equilibrated at about 12 hours. In comparison, the HS granules took longer time to reach constant weight and an effect that is more pronounced at the lower relative humidity environment (Aw: 0.22, 0.33 and 0.44). HS1 and HS2 powders, which had largest particle sizes (Table 6-1), adsorbed the least amount of water but continued to increase in weight until at least 24 hours, especially at the low relative humidity e.g. 0.22, 0.33 and 0.44 (Fig. 6-4). It is interesting to note that HS3 and HS4 adsorbed more water than HS1 and HS2, and required shorter time to reach equilibrium. This effect was again more evident at the lower relative humidity environment.

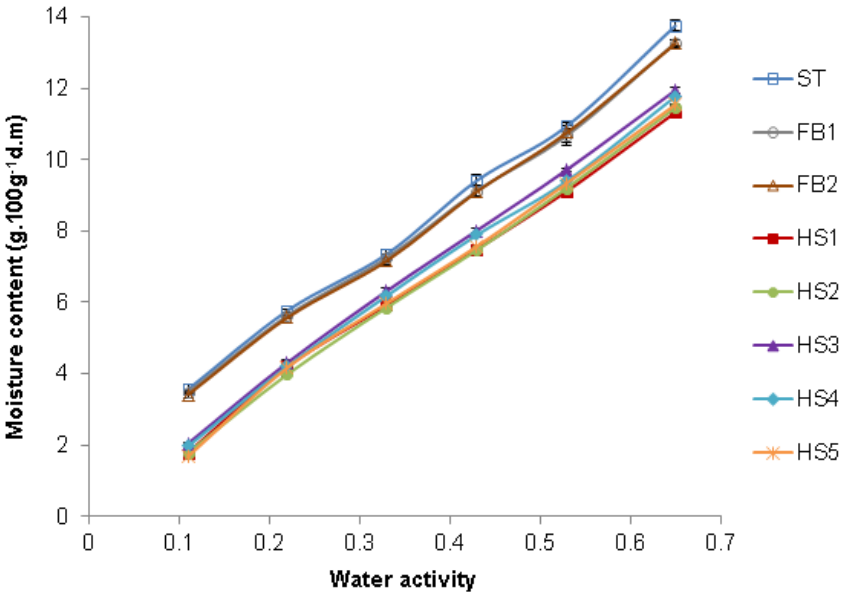

Fig.6-3. Water vapours adsorption isotherms of powders (ST, FB & HS) at 25 °C environment.

As shown previously, FB granules have high porosity, which is suggested to facilitate penetration of water into the granule matrix (Hapgood et al., 2007). The interior porous structures had no significant effect on the rate and extent of hydration, and water molecules seemed to enter and exit as easily as that occurring in non-agglomerated MPI. On the other hand, the agglomerated MPI produced from by the HS process had more compacted structure, restricting diffusion of water into the internal surface as a result of reduction of surface-binding sites for water to adsorb (Al-Muhtaseb et al., 2002), compared to those granules which are less compacted. In this case, the large particles with low specific surface area were believed to retard the moisture adsorption behaviour, which was the reason why HS1 and HS2 exhibited the prolonged process. However, granule size does not always correlate with total sorption area, e.g., FB2 was not different than FB1, even though it had a smaller particle size. Furthermore, HS3 and HS4 had different results, where more moisture content was adsorbed by them rather than HS5, but they had large sizes on the contrary. It can be explained by the granules produced by coalescence process, with comparatively rougher surface and porous structures than other granules from high shear mixer (Fig.6-2), which may cause the larger surface area to contact the water molecules (Murrieta-Pazos et al., 2011). The nuclei granules HS5 after solidification had high granule strength and more dense structures. Therefore, it may be more difficult for water molecules to access all internal primary particles, particularly those towards the centre of a granule. It is interesting to see that the kinetics of water adsorption was also influenced by the gradient of different hygroscopic environments. When equilibrium relative humidity was increased, additional water was progressively adsorbed by the protein powders. Condensational wetting may occur if relative humidity is higher than 0.5 and moisture may diffuse into these interior sites via capillary force (Ji et al., 2016b; Mathlouthi and Roge,

2003). Consequently, the difference of moisture content within HS granules was not significant and the difference between FB and HS was also reduced.

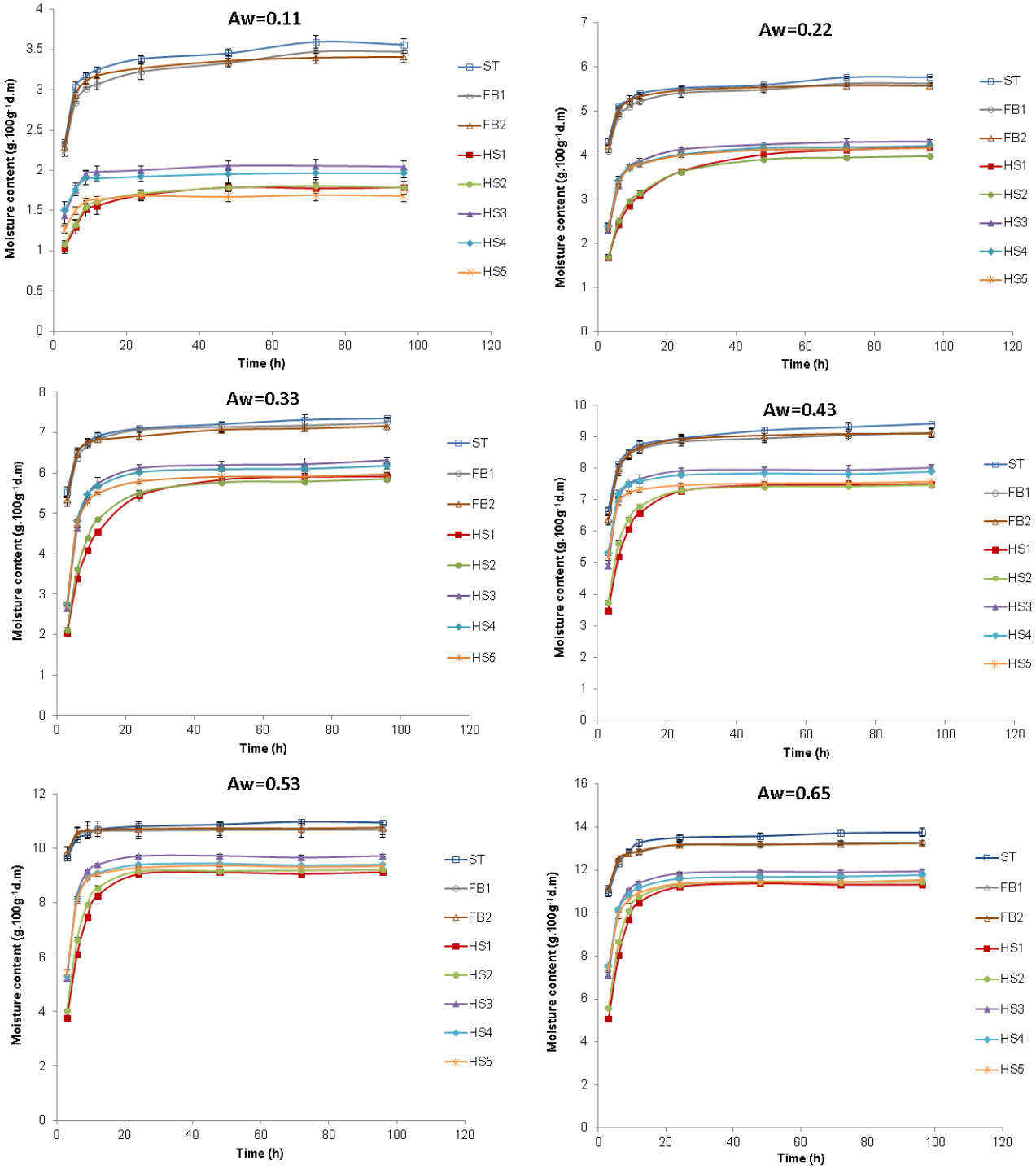

Fig.6-4. Kinetics of water vapour adsorption for the powders (ST, FB & HS) at six different hygroscopic environments (aw: 0.11; 0.22; 0.33; 0.43; 0.53; 0.65).

3.3 Flow properties

3.3.1 Flow function

The powders in a hopper are usually consolidated by stress, which is based on their own self-weights and varied from their positions in different regions of hopper or at different fill heights. Thus, the flowability of powders is often stress-dependent (Teunou et al., 1999). Fig.6-5 illustrates that the standard MPI powder was a poor-flowing powder and it was very cohesive when consolidating stress was lower than 1.2 kPa. Even if the stress increased to 13 kPa, the standard MPI was still considered as a cohesive powder. However, the applied granulation processes, i.e., FB and HS, were found to significantly improve the flow behaviour of milk protein powders. Firstly, FB1 and FB2, produced from fluidised bed, had a lower unconfined failure strength at the same consolidating stress, indicating they had comparatively better flowability and can be classified as easy-flowing powders. Particle size also displayed a beneficial role as is demonstrated when FB1 and FB2 are directly comparing at higher stresses than 3.2 kPa. The granules formed by the HS process were all free flowing in the annular shear cell, regardless of size fraction or the stresses that consolidated them. Only HS3 exhibited slightly higher unconfined failure strength than other HS granules.

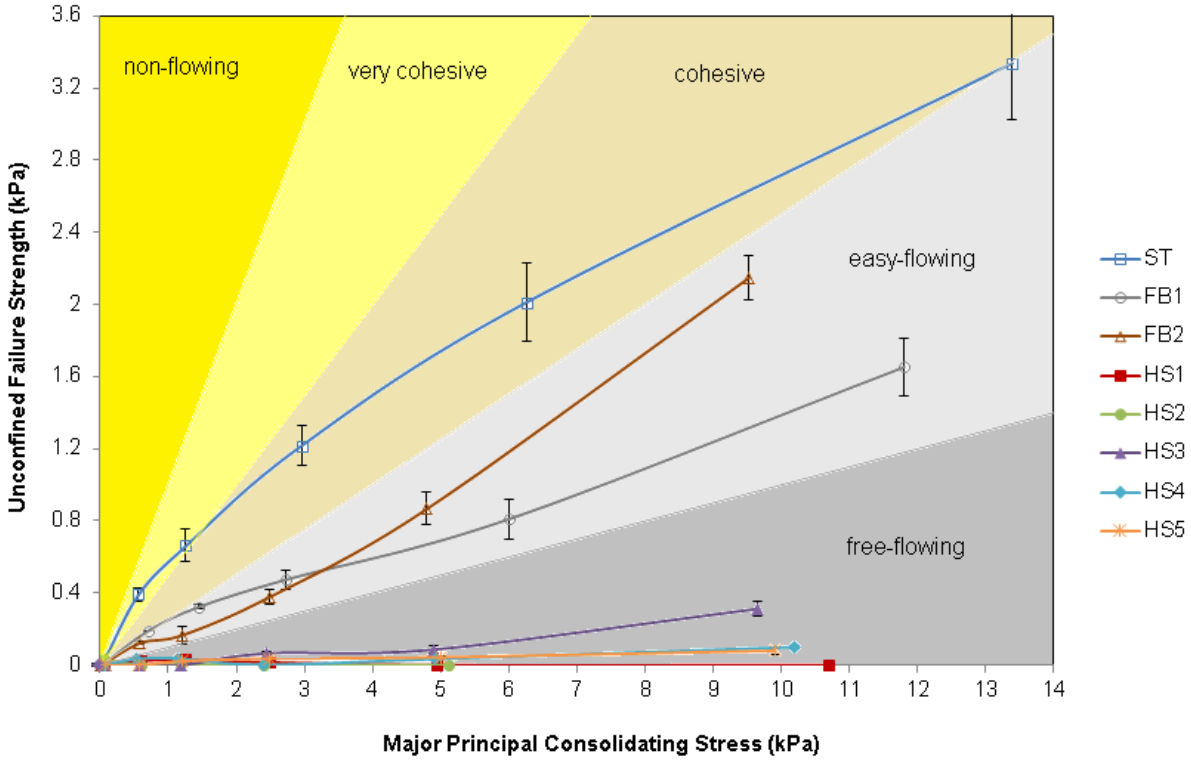

Fig.6-5 Flow function curves for unconfined failure strength as a function of major principle consolidation stress for the powders (ST, FB & HS).

It is commonly believed that adhesive forces are usually the source of such flow problems for fine-grained dry bulk solids. The major adhesive forces are based on van der Waals interactions and the intensity of the forces mainly depend on the particle size as well as the distance between individual particles (Fitzpatrick, 2007; Schulze, 2007). When the distances are small or the surfaces of particles are in contact, van der Waals forces have a large influence. Therefore, plastic deformation and rearrangement occurring at contact points may cause an increase in adhesive forces (Aarons and Sundaresan, 2006). This can be the reason why standard MPI powders with small size have poor flowability. For FB1 and FB2, their large sizes and rough surfaces resulted in an increase in distance and thus a reduction of adhesive forces. The granules of HS1 to HS5 also presented similar behaviour, as their

adhesive forces were no longer dominant compared to the gravity force. The dense packed structures allowed the granules to flow more freely (Schulze, 2007). In addition, smooth and spherical particles usually flow better than rough and non-spherical particles (Cleary, 2008) which may explain why HS3 showed the slightly poorer flowability than the other HS granules.

3.3.2 Bulk density

Different from solid density, bulk density is determined by the voids that exist between or within the individual particles, which also depends on the magnitude of the consolidation stress acting on them. The results of bulk density in Fig.6-6 showed that FB1 and FB2 had the lowest bulk density due to their significantly ($p < 0.05$) higher porosity compared to the other powder granules (Table 6-1). Their densities are lower than 200 $kg \cdot m^{-3}$ when no stress is applied. In contrast, the granules of HS1 to HS5 showed much higher values of at least 400 $kg \cdot m^{-3}$, as their structures were consolidated by agitation forces in the high shear mixer. For compressibility indexes, shown in Table 6-2, a significantly ($p<0.05$) higher value (39.5%) was observed for standard MPI powders compared to the granules. FB1 and FB2 were prone to be compressed by stresses, while HS1 to HS5 displayed the least plastic deformation. For example, for the HS1 and HS2 treatments, which had the largest granule size, their compressibility indexes were less than 10%, which indicates comparatively higher bulk strength. It is believed that the index is closely related to the volume of interstitial air as well as the internal occluded air (Bhandari et al., 2013). Therefore, the porous structures are considered as the major reason to influence the compressibility of powders. Meanwhile, high index values indicated that those powders were more likely to be compressed by self-weight in hoppers during

storage, which may cause the altered bulk density and also subsequently affect the handling properties (Crowley et al., 2014; Schulze, 2007).

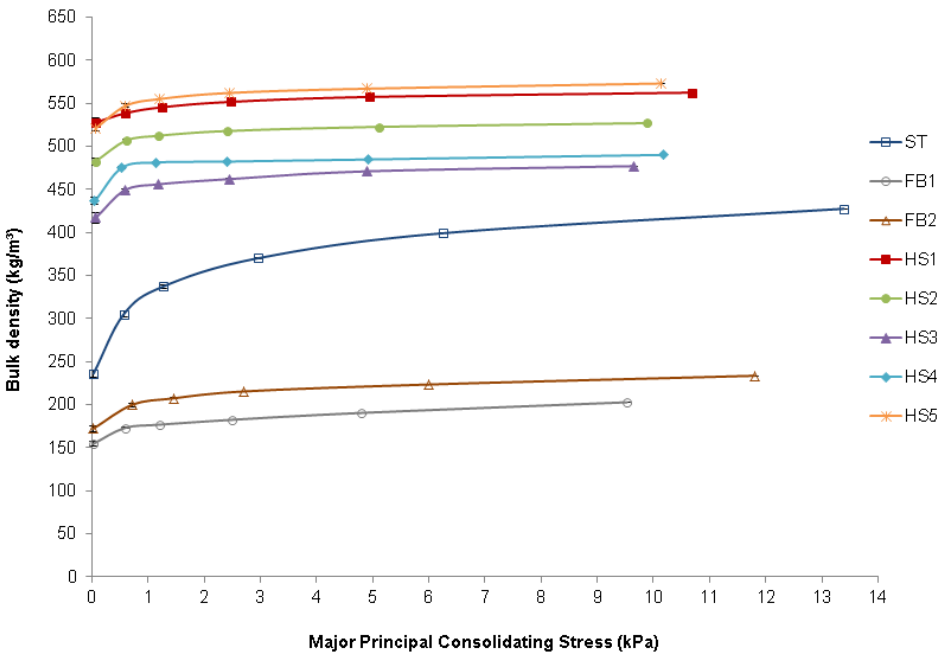

Fig.6-6 Bulk density as a function of major principal consolidating stress for the powders (ST, FB & HS)

3.3.3 Wall friction angle

If considering the friction between bulk solids and solid surfaces, e.g. the wall of a hopper, the angle of wall friction as a function of stress is important when quantifying the wall friction during hopper design. In Fig.6-7, FB1 and FB2 kept a constant angle of approximately 15° under the effect of different normal stresses. Standard MPI powder had a higher angle of 25° at the beginning of a 0.5 kPa stress and then followed by a slight decrease with increasing stress. Significant changes were observed for the granules of the HS process, which not only present large wall friction angles, but also varied as granule size changed. It is clear that decreasing particle size resulted in increased wall friction angles, regardless of the normal

stresses applied. HS4 and HS5 had the greatest angles of all, due to their high bulk density caused more force transferring through wall shear stress, which meant the large wall friction force and thus attained the big angles of wall friction (Aarons and Sundaresan, 2008; Artoni et al., 2009). Meanwhile, comparing with other granules from the HS granulation process, the smaller sizes of HS4 and HS5 have increased specific surface areas, which may produce stronger particle-wall interactions. There is a greater tendency for the granules with high wall friction angles to undergo deposition or segregation in a hopper, as the particles near the hopper walls move slower than that in the centre. Thus high wall friction may lead to the material near the walls discharging finally (Schulze, 2007).

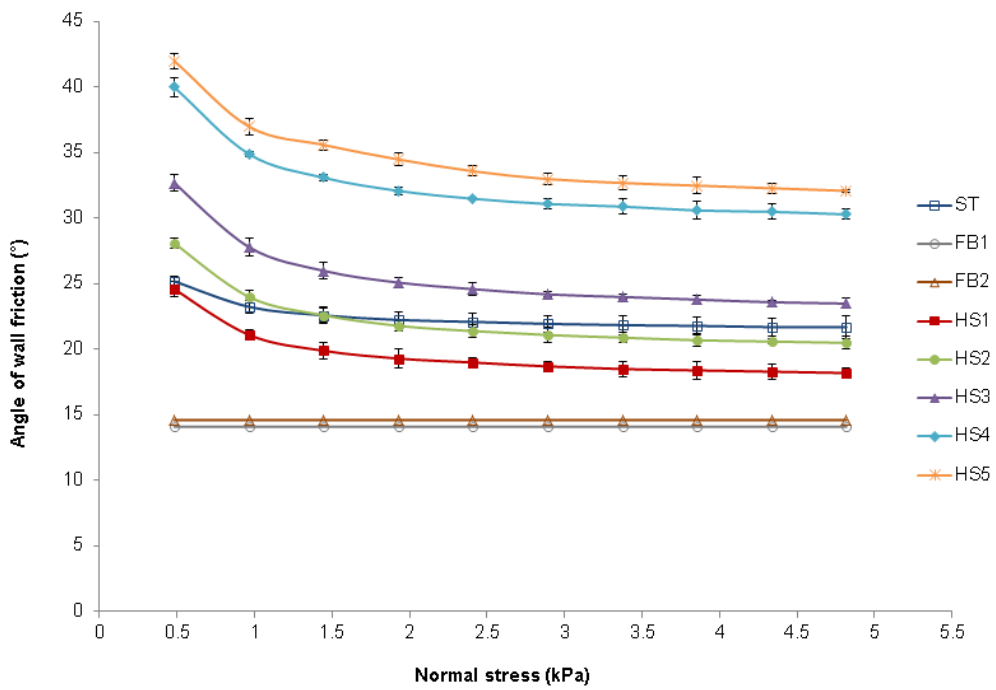

Fig.6-7 The angles of wall friction as a function of normal stress for the powders (ST, FB & HS)

3.3.4 Conical hopper design

The outlet diameter of conical hoppers and the inclination of the hopper wall to the vertical are very important parameters to determining bulk solids discharge from

hoppers (Fig.6-1) (Fitzpatrick et al., 2004b). As shown in Table 6-2, the minimum outlet diameters for preventing both arching in mass-flow discharge or rat-holing in core-flow discharge were compared for the different granules. The $D_{arching}$ values of granules were significantly lower than that of the standard powder, which had at least 0.26 m to avoid the occurrence of an arch at the outlet. The HS granules required the smallest hopper outlet diameters while the granules from fluidised bed needed slightly bigger diameters of about 0.1 m. In addition, the corresponding maximum hopper half angle of standard MPI that ensured mass-flow was 18.7°, which was lower than the values present by FB1 and FB2 with 34.4° or 32.7° respectively. However, there seemed no special requirements on half angles for HS granules, as they already displayed free flowing behaviours in the hopper. Similarly, for the core-flowing, HS granules need a hopper with smallest outlet diameter (0.2 m or even less) to ensure discharge smoothly. On the other hand, 0.75m and 0.8 m diameters were calculated for FB1 and FB2, respectively, which were still significantly lower than that of standard powder (1.5 m). The results were consistent with the previous flow function results, which indicated that the free flowing granules could discharge completely by gravity alone due to the strength of bulk solids being too weak to achieve a stable rat-hole. Therefore, comparatively smaller outlet dimension can be designed to support the ideal mass flow for those free- or easy-flow bulk solids (Fitzpatrick et al., 2004b). However, for maximum inclination of the hopper walls to vertical, the granules of fluidised bed showed the largest angles of 65°, while HS5 needed the steepest wall for the hopper, which had smallest angle. It is believed that the maximum inclination of hopper can be estimated based on Jenike's methodology as a function of wall friction angle (Schulze, 2007). Likewise, it is not surprising to see that the granules with high bulk density led to lower inclination because of their large angles of wall friction.

Table 6-2 Values for compressibility index and flow properties for conical hopper design, derived from shear cell testing

Sample	CI (%)	θ_a (°)	$D_{arching}$ (m)	θ_r (°)	D_{rh} (m)
ST	39.5 ± 4.8[a]	18.7 ± 4.1[a]	0.26 ± 0.03[a]	43.2 ± 0.7[a]	1.49 ± 0.20[a]
FB1	18.9 ± 2.4[b]	34.4 ± 5.7[b]	0.12 ± 0.02[b]	65.9 ± 0.1[b]	0.75 ± 0.07[b]
FB2	21.5 ± 2.1[b]	32.7 ± 5.3[b]	0.10 ± 0.00[c]	65.4 ± 0.1[c]	0.83 ± 0.11[b]
HS1	5.3 ± 0.2[c]	Free flow	0.01 ± 0.00[d]	55.4 ± 0.3[d]	0 ± 0.00[c]
HS2	7.7 ± 0.4[d]	Free flow	0.03 ± 0.01[e]	51.9 ± 0.3[e]	0 ± 0.00[c]
HS3	11.5 ± 0.9[e]	Free flow	0.03 ± 0.01[e]	47.3 ± 0.9[f]	0.20 ± 0.03[d]
HS4	10.0 ± 0.7[e]	Free flow	0.02 ± 0.00[de]	40.1 ± 1.0[g]	0.04 ± 0.00[e]
HS5	8.1 ± 0.4[d]	Free flow	0.02 ± 0.00[de]	37.8 ± 0.8[h]	0.02 ± 0.00[f]

* Values followed by a different superscript letter in the same line are significantly different at P < 0.05.

**CI: compressibility index; θ_a: critical hopper half-angle to prevent arching; $D_{arching}$: minimum outlet diameter to prevent arching; θ_r: critical hopper half-angle to prevent a stable rat-hole; D_{rh}: minimum outlet diameter to prevent a stable rat-hole.

*** Rathole diameter was derived for a conical silo, assuming a diameter of 2 m and a height of 8 m.

4 Conclusion

In summary, both methods produced MPI granules with significantly large particle sizes. High shear mixer granulator made granules with densely packed structures, which adsorbed least moisture and showed the slowest adsorption kinetics during storage at different relative humidity. The granules with loose and porous structures created by fluidised bed granulation, exhibited no significant

difference in water adsorption measurements when compared to the non-agglomerated powder. Large MPI granules were found to have significantly better powder flow behaviour. Besides the effect of particle size, bulk density and shape properties may both play important roles in flowability of powders, however further studies are needed to validate their individual influence on flowability. Overall, granulation processes can effectively reduce the minimum outlet diameters of hoppers for reliable flow from both mass-flow or core-flow hoppers. However, large wall friction angles caused by the HS granules (especially the smaller granules) may also require steeper hopper walls to discharge bulk solids and avoid them remaining at rest.

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CHAPTER SEVEN

Enhanced wetting behaviours of whey protein isolate powder: the different effects of lecithin addition by fluidised bed agglomeration and coating processes

Submitted to *Food Hydrocolloids*

Abstract

The effect of lecithin addition on the wettability of whey protein isolate (WPI) powders was investigated in this study. Different concentrations of lecithin solution (0.5%, 2% and 5% *w/v*) were added by fluidised bed agglomeration and Wurster coating processes. The formed WPI powders, with different particle sizes, were used to compare the densities, porosity and shapes properties, as well as the wetting behaviours, including wetting time, contact angles, water absorption by capillary flow and the strength of films formed at the powder / water interfaces. It was found that, if lecithin was used as bridges to adhere primary particle in agglomeration, the formed granules had large particle size, lower bulk density, higher porosity and more irregular shapes. The influences of the coating process on these properties were shown to be less significant, as lecithin was layered on the outside of the particle surfaces. Those physical and structural modifications in WPI powders caused the improvements in the wettability by different degrees. High coverage of lecithin by coating process gave the particles a more advantageous first step of wetting, showing smaller initial contact angles and weaker protein films; while the porous structures by agglomeration process resulted in quicker water penetration by capillary flow. They were both rate-controlling factors for wetting process, as the limited contribution was found if only controlled by any one of these factors. Consequently, high coverage of lecithin, high porosity of particles and large particle sizes were all necessary for enhancing the wetting behaviours of WPI powders.

Key words: lecithin addition, wetting behaviour, agglomeration, coating, whey protein isolates

1 Introduction

Whey protein isolate powder is widely used in the value-added food products, e.g. infant formula, reconstituted dairy products and beverages, due to its high percentage of pure protein and the ease of transportation and storage (Ann Augustin & Clarke, 2011). In general, full rehydration is of primary importance for powders due to its significant influence on the other functional properties. For dairy powders, they are all required to be “instant”, referring to dispersing quickly with a minimum of stirring and without the formation of lumps (Freudig, Hogekamp, & Schubert, 1999). Good wettability is a necessary property for dairy powders, as it is a prerequisite for the subsequent rehydration process (Hogekamp & Schubert, 2003; Richard, et al., 2013). However, WPI powders usually exhibit extremely poor wettability and they are prone to form lumps and float on the surface of solution (Gaiani, Schuck, Scher, Desobry, & Banon, 2007). A recent study has shown that there can be a gelatinous impermeable layer formed on the interface between the solids and solution when WPI powders contact water (Ji, Fitzpatrick, Cronin, Maguire, et al., 2016). Thereby, water was difficult to break through the barrier and penetrate into the materials matrix. The powder remains on the surface of the liquid and thus caused the prolonged rehydration process. For that reason, wetting is considered as a rate-controlling step for WPI powders. To shorten the whole rehydration process, improving wetting behaviour of WPI becomes important and necessary.

Wettability is the ability of particles to overcome the surface tension between liquid and themselves. The process is usually described as the dynamic penetration of a liquid into the pore network of particles due to capillary forces (Depalo & Santomaso, 2013; Yuan & Lee, 2013). It is mainly dependent on three factors: i) small contact angles; ii) high porosity with big interstitial voids volume; and iii) large

particle size (Fang, Selomulya, & Chen, 2007). Contact angle is a commonly used parameter to indicate the degree of hydrophobicity of powder surfaces. Small angle (<90°) means high hydrophilicity with good wettability for powders; while large angle (>90°) corresponds to high hydrophobicity, showing poor wetting behaviour (Forny, Marabi, & Palzer, 2011). It is believed that the repulsion of whey protein and water leads to large contact angles, owing to the nature of the non-polar protein molecules. Therefore, WPI powder surfaces contact poorly with water, which minimizes its contact area and causes the slow wetting process. In addition, the structures of powders are also known to significantly influence the capillary flow of water inside (Yuan, et al., 2013). As shown by the Washburn equation, big capillary radius may result in deeper depth of liquid intrusion (Washburn, 1921). This means liquid will more easily and more quickly move into the powders if they have porous architectures. However, WPI powders produced by spray drying usually have small particle sizes and dense structures, which result in the small capillary radius which limits capillary flow. Consequently, using surfactant to lower surface tension between water and WPI powders, as well as increasing particle size and porosity can be used to improve the wettability of WPI powders.

As a natural food grade surface-active agent, soy lecithin has the amphiphilic property which enables it to combine with both a water-soluble component and an oil-soluble component (Dashiell, 1989). It helps to decrease the surface tension between whey protein and water; thus WPI particles will be easier to adhere with water molecules. Fluidised bed granulation and Wurster coating are the two most used techniques, which can effectively transport lecithin solution onto powder particles (Cuq, et al., 2013; Sharma, Jana, & Chavan, 2012). The bottom-sprayed Wurster coating process atomizes the solution into small droplets and then evenly

forms a film on the surface of powders (Saleh & Guigon, 2007). It enables lecithin to cover the surfaces of whey protein powders, and contact water first during the wetting process. However, in agglomeration process, lecithin solution is used as bridges to adhere primary particles together. So the formed agglomerates not only have significantly big particle sizes, but also exhibit large internal pores within single particles and big interstitial voids between particles (Ji, Cronin, Fitzpatrick, Fenelon, & Miao, 2015). Hence, these two methods for adding lecithin and modifying the structures may make WPI powders easier to be wetted by water based on different approaches. To the best of our knowledge, few studies have used lecithin via fluidised bed Wurster coating and agglomeration processes to improve the wettability of whey protein powders. Therefore, it is of interest to explore if they play a significant beneficial role on the wetting behaviour of WPI powders and also if possible, on the formation of whey protein films, which restrain the wetting process (Crowley, et al., 2015; Gaiani, et al., 2006; Ji, Fitzpatrick, Cronin, Crean, & Miao, 2016).

The objective of this study is to improve the wettability of WPI powders, by adding lecithin with different solution concentrations, via fluidised bed agglomeration and Wurster coating processes. The effects of these two different processes on the wetting process of WPI particles and the formation of whey protein films was investigated. In addition, their modifications on the physical and structural properties (density, porosity and morphology) were also compared.

2 Materials and methods

2.1 Materials

WPI powders were supplied by Davisco Food International (Le Sueur, MN, USA). The composition is 90% protein, 3% ashes, 5% moisture, 1% fat and less than

1% lactose. Lecithin powders used in coating and agglomeration processes were purchased from Cargill (Trafford Park, Manchester, UK).

2.2 Fluidised bed agglomeration and coating

The agglomeration and coating processes were conducted by a fluid bed granulator/coater (VFC-Lab Micro flo-coater, Vector Corporation, Iowa, USA). The agglomerated WPI was produced by a top-sprayed fluidised bed. Three different concentrations lecithin solution (0.5%, 2% and 5%, *w/v*) were used as binding liquids. 100 g WPI of each batch was fed into the product vessel and fluidised by an upward flowing air stream, which had a flow rate of 70 L min^{-1} and a temperature of 50 ℃. After preheating the powders for 10 min, 50 g binding liquid was injected by a peristaltic pump at a speed of 1mL min^{-1}. The liquid was sprayed into small droplets via a two-fluid spray nozzle, which was placed on the top of vessel. The air pressure for the nozzle was set to 1 bar. When all the binding liquid had been added to powders, the product continued to be dried for 15 min at 50 ℃. Three batches of agglomerated WPI were produced for other triplicate measurements.

The Wurster process was applied to coat the lecithin solution on the surface of WPI particles. Different from agglomeration, the fluidised bed with bottom spray configuration was used as coating equipment in this study. Powders were coated by same concentration of lecithin solution (0.5%, 2% and 5%, *w/v*) in a cylindrical central tube (the draft tube). The rate of the upward flowing air stream was changed to 40 L min^{-1} for the appropriate circulation. The temperature of air was 50 ℃ and the spraying air pressure was 1 bar with injecting rate of 1mL min^{-1}. After that, the products were also dried for 15 min at 50 ℃ after removing the central tube. Three batches of coated WPI were prepared for measurements.

2.3 Powder characterisation

According to the particle size distributions of the obtained products, the agglomerated and coated WPI powders were sieved into two different size fractions. 106 μm and 180 μm level sieves (Endecotts, London, UK) were used to separate the agglomerated and coated particles (A_1 & C_1: 106 μm ~ 180 μm; A_2 & C_2: <106 μm), respectively. The remaining particles were removed if they were not in these fractions. Counting standard WPI powder, there are a total of 13 samples together based on three different concentration of lecithin solutions (ST, 0.5%A_1, 0.5%A_2, 2%A_1, 2%A_2, 5%A_1, 5%A_2, 0.5%C_1, 0.5%C_2, 2% C_1, 2%C_2, 5%C_1, 5%C_2). All the samples were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 40 ℃ overnight, before they were stored in desiccators and prepared for the further measurements.

2.4 Physical and structural properties

2.4.1 Particle size, density and porosity

The median particle size of the powders D(50) was measured by the Malvern Masterszier 3000 (Malvern Instruments Ltd, Worcestershire, UK) using light scattering technology. The machine was equipped with a 4mW He-Ne laser, which had a wavelength of 632.8 nm. Samples were feed by a standard powder disperser (Aero S) with a controlled rate, in order to reach the appropriate obscuration level of 6%. Triplicated measurements for each sample were carried out. .

A graduated cylinder and a tapping machine (Funke Gerber, Berlin, Germany) were used to measure loose bulk density and tapped bulk density of the powders. The volume occupied of 50 g of samples was measured to evaluate the loose bulk density; while the volume after 100 taps was used for the tapped bulk density. In addition, the particle density of powders in this study was measured by Gas Pycnometer (AccuPyc II 1340, Micromeritics Instrument Corporation, Georgia, USA),

which degased the sample cell via purging with a flow of helium for ten pressurisation cycles. Therefore, the porosity also can be calculated by particle and tapped bulk densities (Ji, et al., 2015). All the measurements were repeated for three times.

2.4.2 Particle shape

Circularity, convexity and elongation descriptors were used to quantify the morphology of a particle. Malvern Morphology G3 (Malvern Instruments Ltd, Worcestershire, UK) can use these parameters to determine the shape properties of powders by scanning and observing thousands of single particles. The study of Ji, et al. (2015) has described the details of the method. Briefly, 15 mm^3 volume samples were firstly dispersed into a single uniformly layer by a dispersion unit. After that, the microscope scanned all the particles gradually and then gave out the average values of circularity, convexity and elongation for bulk population distribution. Measurements were repeated five times.

2.5 Wetting behaviour

2.5.1 Wetting time by immersional wetting procedure

Wetting time is defined as the time needed for complete wetting of a specified mass of powder, which is gently discharged onto the surface of water and then immersed and wetted spontaneously without agitation (Schuck, Jeantet, & Dolivet, 2012). Thus, the recorded wetting time can be used to quantify the wettability of dairy powders. 6 g of powder was dropped into a 400 mL beaker containing 100 mL of distilled water at a temperature of 20 ℃. The beaker had a diameter of 70 mm and a surface area of about 38.5 cm^2. The test was repeated three times. The powders were considered to have good wettability if they needed wetting times less than 60 s.

In addition, an optical microscope (Olympus BX51M) was also used to capture the images to show the formation of external films on the surface of whey protein particles, when the materials just contacted water. Different bulk volumes of standard WPI powders (approx. 5 mm^3 and 100 mm^3) were dispersed by water on the glass slides, before they were observed by the microscope at a temperature of 20 ℃.

2.5.2 The dynamic contact angles by spreading wetting procedure

Static contact angle (θ) is an important index of the wettability of powders. It is the tangent angle at the contact point of liquid, solid and air phases. In general, small contact angle (θ<90°) means good wettability while poor wettability corresponds to large angles (θ>90°) (Yuan, et al., 2013). However, for dairy powders, the dynamic wetting behaviour is believed to be the process that a droplet penetrates into powder bed (Ji, Fitzpatrick, Cronin, Maguire, et al., 2016). Therefore, the change of contact angle is usually used to quantify the wetting process. In this study, the change of contact angle was monitored by an optical tensiometer (Attension Theta, Biolin Scientific Ltd., Espoo, Finland), based on sessile drop spread wetting procedure. Before the measurement, powders are firstly loaded on an aluminium pan with a diameter of 100 mm. A powder bed with a smooth surface was formed by passing a leveller across the surface. After that, a set volume of 12 mL deionised water droplet was gently dropped onto the surface of the powder bed and the change of angles was recorded by the machine as a function of penetrating time. Measurements were repeated five times.

2.6 Capillary flow

Water penetration process by capillary flow can be described by the Washburn method (Washburn, 1921), which records the penetration depth of the liquid inside

the capillary as a function of time. In this study, the penetration depth was replaced by the mass of adsorbed water (Ji, Fitzpatrick, Cronin, Crean, et al., 2016). A cylindrical glass tube used as the powder holder had an open base bottom, which was covered by filter paper and a piece of gauze. Then 2 g samples were loaded into the tube and set just above the surface of water. Time was recorded when the bottom touched the water (25 ℃). The additional mass of wetted samples was measured after 10 min. All measurements were repeated three times.

2.7 Film strength at powder / water interface

Films are formed at the interface of WPI solid and water phases that restrain the wetting process. The measurement for strength of films is thus necessary to be developed if investigating the effects of agglomeration and coating processes on the film formation. In this study, a force-displacement test was used to evaluate the strength of films formed by samples and water interface. A glass beaker with a diameter of 65 mm and a height of 37 mm was filled by 100 mL 25 ℃ deionised water. Powders were sieved onto water surface until filling the beaker. A smooth surface was created by a leveller via removing excess powders. Then a cylindrical stainless steel probes with a diameter of 35 mm was set centrally and moved axially downwards through the powders at a constant speed of 0.1 mm/s. The force/displacement was measured by the texture analyser (TA-HDi, Stable Micro Systems, Godalming, UK) equipped with a 5 kg load cell. During the measurement, a noticeable peak appeared as displayed in Fig. 7-1. It is caused by the peak force required to break through the films, which can be used as an index of the film strength. The films were formed by two different powder contact times (1min and 10 min). All the measurements were repeated 5 times.

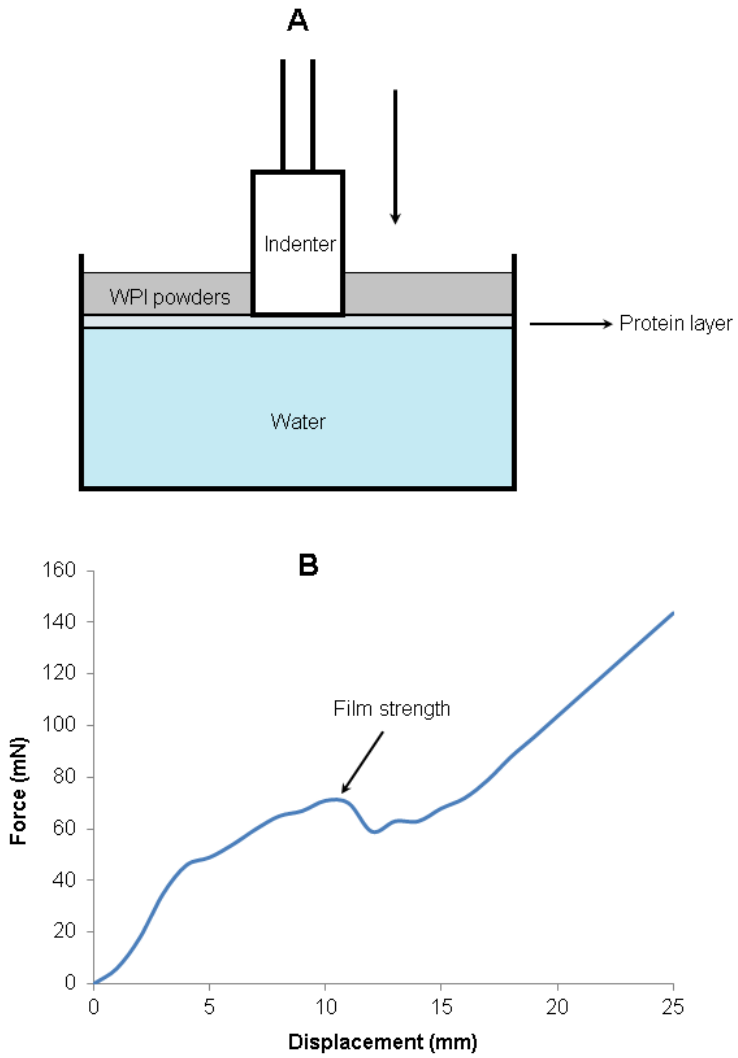

Fig.7-1 Scheme of force-displacement test for the film strength (**A:** plunger was moving axially through WPI powders; **B:** example result of the force-displacement test for standard WPI powder). The noticeable peak appeared in **B** is the force required to break through the films, which was used as the index of the film strength.

2.8 Microstructures of agglomerated and coated powders

Confocal scanning laser microscopy was performed to observe the lecithin distribution on these processed powders, using a Leica TCS SP5 microscope (Leica Microsystems GmbH, Wetzlar, Germany). A small amount of particles were carefully transferred to a glass slide and formed a single layer. A mixture of Nile red (100 μL of 0.125%, in distilled water) and fast green (100 μL of 0.01%, in distilled water) at a

ratio of 1:1 was used to stain the powders. Samples were then covered by a coverslip before they were observed by the microscopy at room temperature. Images of representative areas were taken and analysed using a 63× oil immersion objective (numerical aperture = 1.4) at an excitation wavelength of 633 nm, which was provided by a He–Ne laser. Similar microscope settings were maintained for agglomerated and coated samples for comparison.

3 Results and discussion

3.1 Effects on the physical and structural properties of WPI powders

3.1.1 Particle size, density and porosity

Table 7-1 shows how the agglomeration and coating processes affected the physical and structural properties of WPI powders. Firstly, the standard WPI particles (ST) had a median particle size of about 55 µm. The agglomerated WPI powders for both size fractions showed significant ($P<0.05$) larger particle sizes than ST. However, a large difference in particle sizes can be observed by the lecithin coated WPI powders with different size fractions. Even though the large coated particles (C_1) had the similar sizes as those of the large agglomerates (more than 100 µm), the coated particles within small sizes fraction (C_2) still only had about 40 or 50 µm in diameters, which was close to the size of ST. Their densities displayed the different results. The agglomerated WPI display significantly lower bulk and tapped densities than the other samples (both standard and the coated ones). It was also found that 0.5% C and 2% C had slightly lower bulk and tapped density values than that of standard WPI. But for particle density, all samples appeared to have almost same values, which were about 1.05 $g \cdot cm^{-3}$. Therefore, on the basis of tapped and particle densities, porosity properties of powders were calculated and presented in Table 7-1. The agglomerated WPI had the highest porosity values, which were even

Table 7-1 Physical and Morphological properties of WPI powders *

Sample	ST	0.5%A_1	0.5%A_2	0.5%C_1	0.5%C_2	2%A_1	2%A_2	2%C_1	2%C_2	5%A_1	5%A_2	5%C_1	5%C_2
Particle size D(50) (µm)	54.5 ± 1.8^{a}	109.0 ± 2.1^{b}	86.2 ± 0.4^{c}	103 ± 3.0^{d}	41.3 ± 0.6^{e}	110.8 ± 1.0^{b}	81.3 ± 1.1^{f}	118.0 ± 0.7^{g}	49.5 ± 0.5^{h}	115.0 ± 1.1^{i}	81.4 ± 0.7^{f}	114.4 ± 1.2^{i}	56.1 ± 1.0^{a}
Bulk density (g/cm^3)	0.340 ± 0.003^{a}	0.205 ± 0.003^{b}	0.261± 0.004^{c}	0.318 ± 0.004^{d}	0.329 ± 0.002^{e}	0.182 ± 0.005^{f}	0.257 ± 0.004^{c}	0.331 ± 0.007^{ae}	0.339 ± 0.006^{ae}	0.168 ± 0.006^{g}	0.241 ± 0.005^{h}	0.392 ± 0.005^{i}	0.409 ± 0.006^{j}
Tapped density (g/cm^3)	0.417 ± 0.001^{a}	0.236 ± 0.000^{b}	0.279 ± 0.000^{c}	0.346 ± 0.001^{d}	0.385 ± 0.001^{e}	0.204 ± 0.000^{f}	0.275 ± 0.000^{g}	0.357 ± 0.001^{h}	0.400 ± 0.001^{i}	0.192 ± 0.001^{j}	0.263 ± 0.000^{k}	0.408 ± 0.001^{l}	0.477 ± 0.001^{m}
Particle density (g/cm^3)	1.057 ± 0.008^{a}	1.038 ± 0.011^{a}	1.058 ± 0.023^{a}	1.051 ± 0.015^{a}	1.052 ± 0.009^{a}	1.045 ± 0.025^{a}	1.051 ± 0.021^{a}	1.076 ± 0.034^{a}	1.058 ± 0.036^{a}	1.058 ± 0.011^{a}	1.053 ± 0.016^{a}	1.049 ± 0.016^{a}	1.064 ± 0.017^{a}
Porosity (%)	67.9 ± 0.9^{a}	80.3 ± 1.0^{b}	75.4 ± 1.9^{c}	69.7 ± 1.2^{a}	68.7 ± 0.8^{a}	82.6 ± 1.6^{b}	75.5 ± 1.4^{c}	69.2 ± 2.5^{a}	67.9 ± 2.6^{a}	81.9 ± 0.8^{b}	75.0 ± 1.1^{c}	62.6 ± 1.2^{d}	61.6 ± 1.2^{d}
Circularity	0.884 ± 0.003^{a}	0.729 ± 0.004^{b}	0.732 ± 0.001^{b}	0.812 ± 0.002^{c}	0.875 ± 0.006^{a}	0.764 ± 0.001^{d}	0.746 ± 0.008^{e}	0.813 ± 0.001^{c}	0.885 ± 0.003^{a}	0.793 ± 0.009^{f}	0.767 ± 0.007^{d}	0.841 ± 0.007^{g}	0.893 ± 0.001^{h}
Convexity	0.965 ± 0.002^{af}	0.860 ± 0.002^{b}	0.868 ± 0.002^{c}	0.921 ± 0.002^{d}	0.961 ± 0.002^{a}	0.891 ± 0.003^{e}	0.880 ± 0.006^{e}	0.920 ± 0.001^{d}	0.967 ± 0.001^{f}	0.909 ± 0.009^{dg}	0.893 ± 0.007^{eg}	0.941 ± 0.004^{h}	0.972 ± 0.001^{i}
Elongation	0.233 ± 0.004^{a}	0.279 ± 0.007^{b}	0.295 ± 0.002^{c}	0.259 ± 0.000^{d}	0.253 ± 0.004^{ef}	0.285 ± 0.004^{b}	0.295 ± 0.005^{c}	0.255 ± 0.000^{e}	0.249 ± 0.003^{f}	0.270 ± 0.000^{g}	0.291 ± 0.004^{bc}	0.264 ± 0.002^{h}	0.249 ± 0.002^{f}

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

higher than 80%. This means the agglomeration process created granules with porous structures and large pores existed inside the powder material matrix. On the other hand, it is interesting to note that, though the coated WPI also had large particle size, their porosity had no significant improvement compared to standard WPI. The powders formed by 5% concentration lecithin solution even had the lower porosity values of about 62%.

Agglomeration processes use small liquid droplets as binding bridges to adhere primary particles and thus enlarges the granule size (Jacob, 2007; Litster & Ennis, 2013). Loose structures are usually achieved in fluidised bed agglomeration, which are motivated by air rather than mechanical agitation. In that case, thus the agglomerated WPI particles exhibited much lower loose bulk density and tapped density, as well as higher porosity caused by the large interstitial spaces. However, the Wurster coating process is different from agglomeration, as the liquid droplets are uniformly distributed on the surface of individual primary particles by layering (Dewettinck & Huyghebaert, 1999; Saleh, et al., 2007). Therefore, compared to ST, the coated particles had no significant difference in bulk density and porosity values, though some of them had bigger sizes. In addition, the higher concentration of liquid in the coating process results in the formation of thicker layers with high compactness. That is possibly the reason why 5% lecithin solution caused a slightly higher bulk density and lower porosity. However, no matter whether agglomeration or coating, the small amount of lecithin added had no significant effect on the true density of WPI powders.

3.1.2 Particle morphology

The results of three parameters to describe the morphology of particles (circularity, convexity and elongation) are also presented in Table 7-1. Firstly, ST had

values of 0.884, 0.965 and 0.233 for these three parameters, respectively. The agglomerated granules were shown to have the more irregular shape properties, which include the lower values of circularity and convexity as well as higher values of elongation. This indicates that the fluidised bed agglomeration process caused less rounded shape particles, with rougher surface and higher ratio of height and width (Ji, et al., 2015). Some large agglomerated particles (e.g. 0.5% A_1) can even have the smallest circularity and convexity values, which were approx. 0.73 and 0.86, respectively. The Wurster coating process also modified the shapes of powders, but the influences were less significant than those of agglomeration. In addition, comparing the effect of particle size, it is found that the larger size for coated particles was relevant to their lower circularity and convexity. It is interesting to see that the particles formed by lower concentration lecithin solution (e.g. 0.5%A & 0.5%C) had the comparatively more irregular shape properties. As it is shown in Table 7-1, high concentration solution used in both agglomeration and coating processes produced more spheroidal and smooth particles.

The standard WPI powder is spray dried from small liquid droplets; thus its particle shape is more like a circle with a flat surface (Sadek, et al., 2015; Sadek, et al., 2013). However, when these primary particles aggregated together by liquid, the new porous “raspberry” structures were formed (Christelle Turchiuli, Eloualia, El Mansouri, & Dumoulin, 2005). As shown in Fig. 7-2AB, the lecithin can be observed and it distributed among the particles, acting as binding bridges. Therefore, their shapes were modified irregularly. Meanwhile, as the small nuclei progressively grew during the agglomeration process, the intermediate agglomerates may adhere again, which caused the less rounded and rougher granules than the nuclei (C. Turchiuli, Smail, & Dumoulin, 2013). Some other studies reported that milk protein powders agglomerated by lactose or sucrose solution also had similarly shaped particles (Ji,

et al., 2015; Szulc & Lenart, 2013). The effects were more significant for those large milk protein agglomerates. However, in the coating process, lecithin was uniformly layered on the surface of WPI particles (Fig. 7-2CD). The shapes of new particles were less modified than the agglomerated particles, as they grew based on the shape properties of the primary particles (Teunou & Poncelet, 2002).

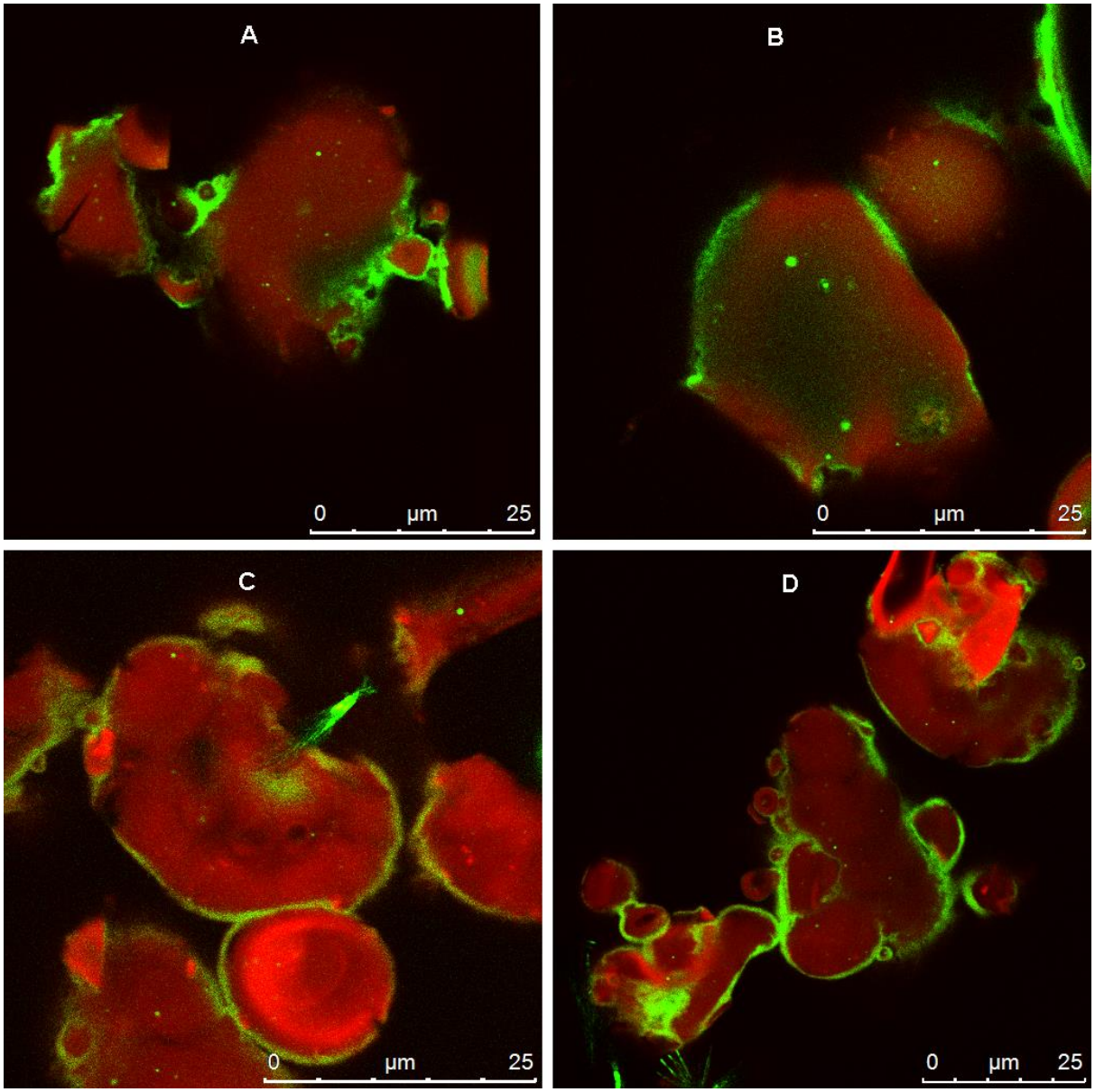

Fig.7-2 Confocal microscopy images of agglomerated and coated WPI powders by 5% (w/v) lecithin solution (**A&B:** agglomerated WPI; **C&D:** coated WPI). Green presents the lecithin and red is whey protein. Lecithin used as binding bridges in **A&B** while

more coverage can be observed on the surface of particles in **C&D**. The bars indicate 25 μm in length.

3.2 Effects on the wetting process of WPI powders

3.2.1 Wetting time by immersional wetting procedure

The wettability of WPI powders were assessed by wetting time in Table 7-2. It is clear to see that standard WPI was extremely difficult to be wetted by water. Even after 20 min, there were still a great number of particles floating on the surface of water. This is due to when particles contacted water, the materials quickly formed skins on the interface between the wetted particles and water, which can be observed in Fig.7-3AB. The skins were believed to prevent water from further penetrating into the powder matrix (Ji, Fitzpatrick, Cronin, Maguire, et al., 2016). The coating process seemed to play no significant beneficial role in decreasing the wetting time, as 0.5%C and 2%C present the same wetting time as standard powders. Only the coated powders by 5% lecithin required shorter time of about 7 or 8 min, which was still considered as the poor wettability. However, the agglomerated powders exhibited completely different results. Most agglomerated WPI, especially for those large agglomerates, needed much shorter wetting time. When their binding liquid for agglomeration contains enough lecithin (e.g. 2%A & 5%A), they only took less than 10 seconds to be fully wetted. This means they were very quickly penetrated by water, and they can be considered as instant powders. In addition, particle size also greatly influenced the immersional wetting behaviours, as A_1 powders were found to expend have significant less wetting time than A_2 powders. This effect was more obvious for the powders that were agglomerated by the higher concentration of lecithin solution (e.g. 2%A & 5%A).

Table 7-2 Wetting time of WPI powders by immersional wetting procedure

Sample	ST	0.5%A	0.5%C	2%A	2%C	5%A	5%C
Large size fraction	> 20 min	15 min ± 2.4 min	> 20 min	10 s ± 2 s	> 20 min	3 s ± 1 s	7 min ± 1 min
Small size fraction		> 20 min	> 20 min	12 min ± 4 min	> 20 min	4 min ± 1.5 min	8 min ± 2 min

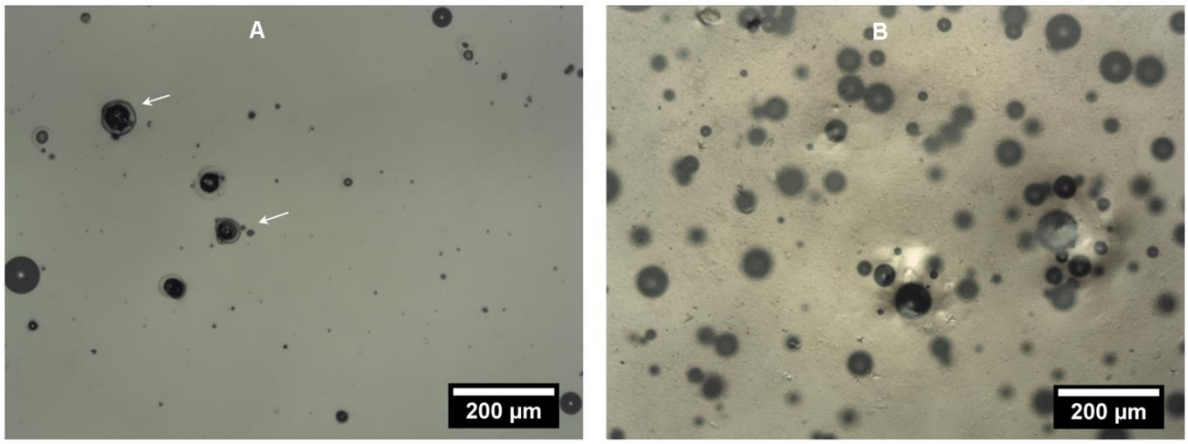

Fig.7-3 Optical microscopy images of WPI particles, showing the impermeable layers formed at the interface of particles / water, as white arrows indicated in **A**; the thicker films can be observed in **B** when more WPI particles were wetted by water. The particles were dispersed in water on glass slides before observation. (Scaled bars = 200 µm)

3.2.2 Contact angles by spreading wetting procedure

In Fig. 7-4A, for the 0.5%A and 0.5%C, water droplets took a long time to penetrate into the powder beds. They not only had the large initial contact angles, which were all higher than 130°; but also required more than 300 seconds to reach the angles of about 100°. Only the A_1 samples showed relatively quicker changes, as they needed 100 seconds to reduce the contact angle to 50°. However, when the concentration of lecithin increased to 2% (Fig.7-4 B), the agglomerated WPI, for

different particle sizes, were both immediately penetrated by droplets in just 2 or 3 seconds. The 2%C_1 also displayed much better wetting behaviour, while the 2%C_2 displayed a wettability as poor as ST. Even at the condition of highest concentration of lecithin (Fig.7-4 C), the 5%C_2 still had almost no changes for its contact angles, although its initial angle was much smaller than that of ST. But for the agglomerated or coated WPI with large sizes, the dramatic reductions of the penetration times were observed in Fig.7-4 C. Comparing the effect of particle size, it is clear to find that the larger particles corresponded to the quicker wetting by water droplets, especially for the coated particles using 2% and 5% lecithin solution. In addition, there were some notable phenomena for the coated WPI powders. Firstly, they displayed the smaller initial contact angles than other samples, including the agglomerates. Meanwhile, it is also interesting to see that the coated powders with large sizes (e.g. 2%C_1 & 5%C_1) had the different angle changes at the end of penetration process. Their angles stopped decreasing and even increased until the droplet reached an equilibrium state.

For the immersional wetting or spreading wetting procedures, both of agglomeration and coating processes using lecithin solution improved the wettability of WPI by different degrees. It is due to lecithin as a surface-active agent, which can effectively bind protein and water molecules together and thus reduce the surface tension at the interfaces of solids and liquid (Whitehurst, 2008). Some studies reported that agglomeration, using lactose or sucrose solutions as binding liquid, had no significant effect on the wetting of milk protein isolate and WPI powders (Ji, et al., 2015; Ji, Fitzpatrick, Cronin, Maguire, et al., 2016). Therefore, lecithin used in those processes is believed to positively influence the wetting behaviours of WPI powders. The influences are more significant if more lecithin is used, as higher surface energy

is achieved, which enhances wetting ability. However, lowering surface tension is not the only factor to control the wettability, as agglomeration was shown to play a much better beneficial role than coating, even though they both contain same amount of lecithin. The porous loose structures and large particle formed by agglomeration have more advantages for water to flow inside of powder particles (Depalo, et al., 2013; Forny, et al., 2011). In the other words, limited capillary flow may happen for the coated particles with relatively low porosity or small sizes, as shown in Fig.7-4D.

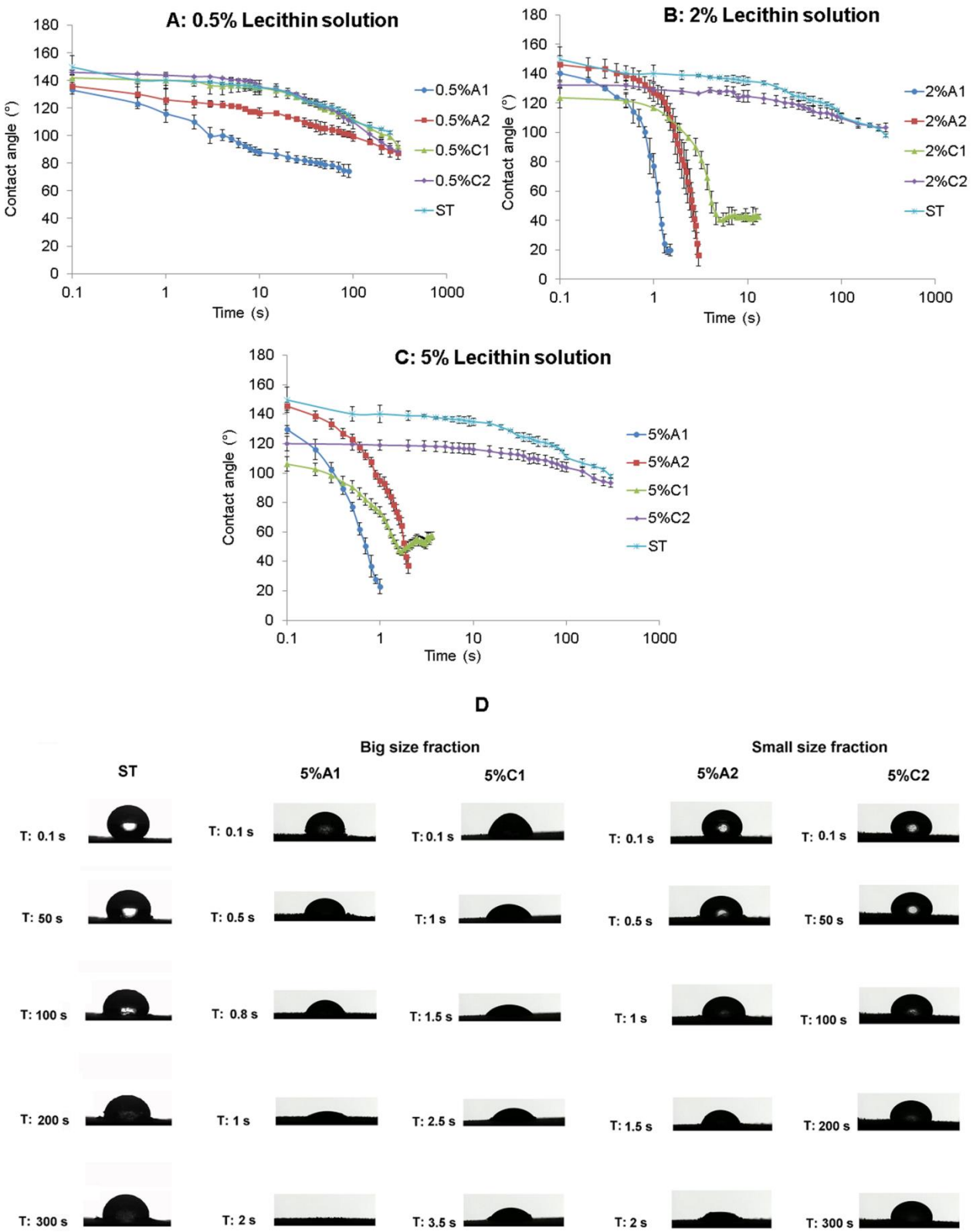

Fig.7-4 The change of contact angle (°) as a function of penetration time for ST, agglomerated and coated WPI powders using the sessile drop technique at approx. 20 ℃ temperatures. **A:** powders produced by 0.5% (*w/v*) lecithin solution; **B:** by 2%

(*w/v*) lecithin solution; **C:** by 5% (*w/v*) lecithin solution; **D:** example images of standard, agglomerated and coated WPI powders formed by 5% (*w/v*) lecithin solution to show how the water droplets penetrated into powder beds by the different time intervals.

3.3 Effects on the capillary flow and the film formation

As a prerequisite of good wettability of WPI, overcoming the barrier caused by the layers on the interface of WPI and water as well as accelerating the capillary flow become the two most important steps. Consequently, the effect of agglomeration and coating processes on the capillary flow behaviour and the formation of layers are necessary to investigate. This will help to explain why these processes facilitate water to wet the problematic WPI powders.

3.3.1 Capillary flow

As mentioned previously, capillary flow may be one of the rate-controlling factors for the wetting process of WPI powders. Thus, the results based on modified Washburn method are presented in Fig.7-5. It can be seen that ST only absorbed 0.05 g water in 10 min; the coated WPI powders all exhibited similar water absorption ability, regardless of the particle size or the lecithin solution used in the coating process. However, a significant increase was founded for the agglomerates, which gained more weight after 10 min water absorption. These influences were more obvious for the agglomerates with large size fractions (e.g. 0.5%, 2% and 5% A_1), as their additional weight can reach over 0.1 g. At the same time, the absorbed water also increased at the higher concentration of lecithin, as the agglomerates formed by 5% lecithin had the best capillary flow behaviours of all. This means water more easily penetrates into the matrix of large agglomerates with high porous

structures and more lecithin. It can be validated by Washburn capillary model (Washburn, 1921) as Eq.:

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

Where r is radius of pores; θ is the contact angle; l is the penetration depth; η is water viscosity; γ is the water surface tension and t is time for capillary flow. Thus, it is clear to see that the penetration behaviour of WPI are positively related to the radius of pores, which are influenced by the porosity of the powder and the particle size (Forny, et al., 2011). Therefore, this is the reason why agglomerated WPI showed better wetting behaviour than coated WPI, as the agglomerates had bigger pore radii to allow faster water penetration. In addition, more lecithin added to the powders may also lead to the smaller contact angle θ, and greater penetration depth.

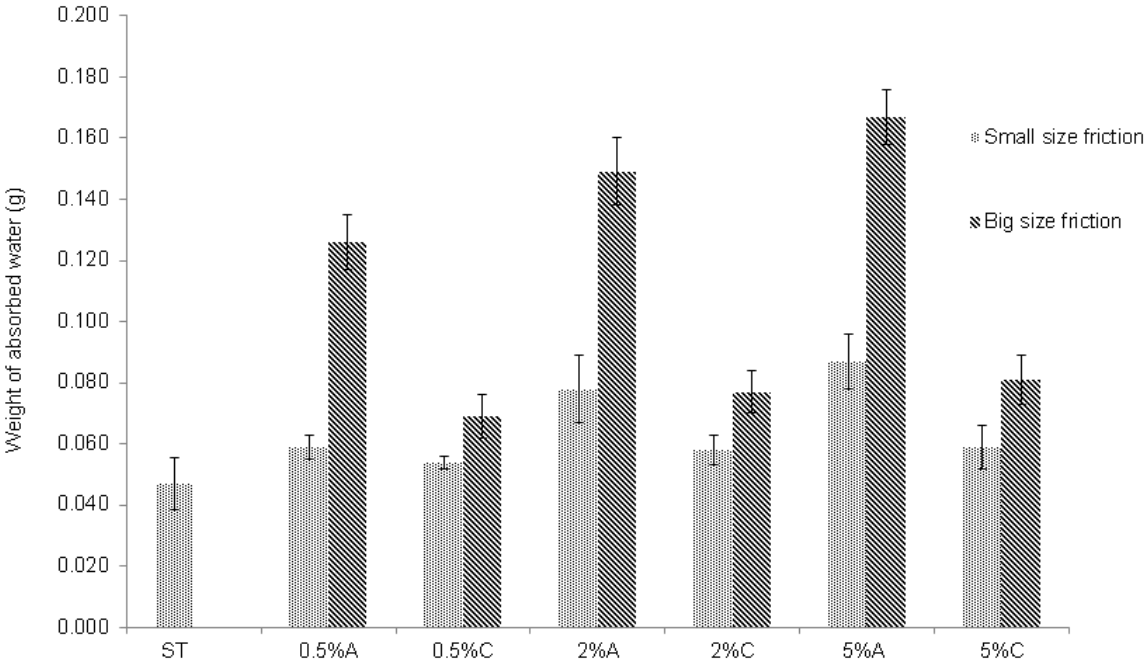

Fig.7-5 Weight of absorbed water by capillary flow for standard, agglomerated and coated WPI powders after 10 min.

3.3.2 The effects of agglomeration and coating on the film strength

The film formed by the hydration of WPI particles is believed to seriously impede and delay water penetration during the wetting process (Ji, Fitzpatrick, Cronin, Maguire, et al., 2016; Kim, Chen, & Pearce, 2002). The results of film strength formed by different samples at 2 and 10 min are presented in Table 7-3. The ST formed the strongest films for both 2 and 10 min contact times. The strength of films reached approx. 70 and 86 mN, respectively. All the agglomerated or coated WPI had significantly weaker films.

Table 7-3 Film strengths at WPI particles / water interface after 2 or 10 min contact times*

Sample	ST	0.5% A_1	0.5% A_2	0.5% C_1	0.5 %C_2	2% A_1	2% A_2	2% C_1	2% C_2	5% A_1	5% A_2	5% C_1	5% C_2
2 min (mN)	70 ± 4 ^{a*}	62 ± 3 ^{b*}	64 ± 1 ^{b*}	41 ± 2 ^{c*}	40 ± 4 ^{c*}	0	28 ± 2 ^{de*}	24 ± 3 ^{d*}	30 ± 3 ^{de*}	0	0	26 ± 1 ^{d*}	31 ± 2 ^{e*}
10 min (mN)	86 ± 6 ^{a**}	27± 7 ^{bd**}	41 ± 4 ^{c**}	28 ± 6 ^{bd**}	38 ± 3 ^{c*}	0	27 ± 2 ^{bd*}	25 ± 1 ^{b*}	30 ± 2 ^{d*}	0	0	28 ± 3 ^{bd*}	38 ± 3 ^{c**}

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

Considering the results for the coated powders, the addition of a small amount of lecithin, i.e. 0.5%C, had a significant impact on reducing film strength in comparison to the ST powder. Increasing the lecithin addition to 2% further reduced the film strength, especially at 2 min contact time. However, increasing further to 5% showed no significant improvement. Consequently, it was advantageous, in terms of reducing film strength, to add lecithin to somewhere in between 0.5 and 2%. There was no additional benefit to adding higher amounts because the particle surfaces were possibly saturated with lecithin from a wetting perspective. These results are

similar to the results of capillary flow shown previously, where the effect of different amount of lecithin on the coated powders was not significant.

Considering the results for the agglomerated powders, the low lecithin, 0.5%A, showed only a small reduction in film strength at 2 min contact time, although it did reduce substantially at 10 min. The reduction in film strength at 2 min. is a much smaller than that for the corresponding coated powders (0.5%C). This is most likely because there is less lecithin on the particle surfaces in comparison to the coated particles because much of the lecithin is in the bridges. Increasing the lecithin content further had a major impact on reducing the film strength of the agglomerates. For agglomerates with higher lecithin contents (2%A and 5%A), there were no measureable film strengths, except for the small particle size fraction at 2% lecithin (2%A_2). The zero film strengths are simply because the powders had fully wetted by 2 min and there were no films remaining; the wettability of these powders had greatly improved in comparison to the ST powder. Particle size also played an important role on the formation of WPI films. Except for the agglomerates containing high amount of lecithin (5%A_1 & 5%A_2), the powders from large size fraction created the weaker films and the difference was more obvious after 10 min.

The film strength is believed to directly connect to the difficulty of water penetrating through the films. The higher strength of the films may result in the slower water penetration and thus prolong the wetting process. In that case, the lower strength of films formed by the hydration of coated WPI was believed to weaken the negative influence of films from acting as barriers to delaying of powder wetting (Kim, et al., 2002). The agglomeration and coating processes were found to contribute differently to the wetting behaviours of WPI. On the basis of the results presented, it is believed that the coated WPI powders allow water to more easily contact the powders at the beginning of the wetting process, as lecithin can be better distributed on the surface

of particles. More surface area of coated particles is covered by lecithin if compared to the agglomerated particles. Therefore, it results in smaller initial contact angles and weaker WPI films. Agglomeration process seems to contribute somewhat differently to improving the wettability of WPI. Lecithin addition does have a major impact; however the large volumes inside the particles and between particles formed by agglomeration allowed quicker water penetration into the powder by capillary flow. So, the change of contact angles and the decrease of film strength were more rapid than that of coated powders. The only challenge for the agglomerated WPI is to overcome the surface tension where there is little or no lecithin present.

4 Conclusion

The fluidised bed agglomeration and Wurster coating processes were believed to modify the physical and structural properties by different particle growth mechanisms. As binding liquid was used as bridges between primary particles, agglomeration produced large granules with lower bulk density and higher porosity; while the coating process created powders with comparatively higher bulk density and lower porosity. More irregular shapes by lower circularity and convexity as well as higher elongation were found for the agglomerated WPI. These kinds of structural modifications influenced the wetting process of WPI powders. Lecithin addition by those processes improved the wettability of WPI powders by different degrees. Even the distribution of lecithin on the surface of particles by coating gave them a more advantageous first step of wetting by lowering the surface tension and weakening the films. However, it was difficult for water to penetrate into the bed of coated particles because their low porosity leads to the slow capillary flow process. Agglomeration can be used as an effective method to solve the problems of capillary flow, due to the highly porous structures of the agglomerated powders. Large particle

size can also positively affect water penetration via increasing the radius of particle pores. Overall, the collaborative effects of lecithin addition (high coverage on the surfaces), high porosity and large particle size are all contributing to improving the wetting process of WPI powders.

Acknowledgements

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CHAPTER EIGHT

General Discussion

In the current study, it firstly investigated the effects of agglomeration and coating processes on the structural and physical characteristics of milk protein powders. Chapter 4 indicated the effect of different liquid binders (water, lactose solution, sucrose solution) used in fluidised bed agglomeration on the particle size, shape, density and porosity of milk protein isolate powder; while Chapter 5 present the influence of different granule growth processes. In addition, it also compared the difference between the physical properties of agglomerated MPI, which are produced by fluidised bed and high shear agglomeration, respectively. Chapter 7 focused on lecithin addition by fluidised bed agglomeration and Wurster coating, as well as their effects on the structural modification of whey protein isolate powder.

Furthermore, this study paid more attentions on the subsequent functionalities of high protein dairy powders, including rehydration behaviours (wetting, dispersing and dissolving), flowability and water adsorption. Chapter 2 firstly carried out the assessment of rehydration measurements of different milk protein powders, so as to find out the suitable methods to quantify the dynamic rehydration processes. After that, Chapter 3 investigated the effects of fluidised bed agglomeration on the wettability, dispersability and solubility of different kinds of milk protein powders (MPI, WPI, MC, SC, and CC). In addition, high shear mixer agglomeration was also used to try to improve the rehydration abilities of milk protein isolate powder in Chapter 5; Wurster coating was also used as an alternative method to add lecithin onto the difficult-to-wet WPI powders (Chapter 7). Moreover, the study of Chapter 6 reported the effects of agglomeration processes on the improvement of MPI powder flowability and also the influence on water adsorption behaviours.

1 The effects on the structural and physical properties

It was found that agglomeration and coating processes played critical roles in determining the structural and physical properties of milk protein powders. The effects are mainly influenced by different process types, granule growth and different liquid binders used as discussed below.

1.1 The effect of different process types

Based on Chapter 4, 5 and 7, the results show the fluidised bed granulator creates agglomerated MPI that is 2 to 4 times (100 mm - 200 mm) greater in size than that of the primary MPI powders. The formed agglomerated MPI powder is very irregular, showing with less rounded shapes and rougher surfaces than that of non-agglomerated particles. Meanwhile, large interstitial volume and internal pores are also found in the structures generated by fluidised bed, which means low bulk density and high porosity values for those agglomerates. However, MPI granules produced by HS can reach sizes of more than 1000 mm, which are ~20 times that of the primary powders. This is due to the binding bridges being comparatively weak in the agglomerates produced by fluidised bed; while the HS granules are consolidated by strong mechanical agitation, which lead to much stronger adhesive forces and thus tend to adhere more particles (Cuq et al., 2013). This kind of physical compaction results in the plastic deformation of agglomerates via a process of squeezing-out entrapped air, increased internal pore saturation and reduced porosity (Iveson et al., 2001; Reynolds et al., 2006). On the contrary, the Wurster coating process is different from agglomeration, as the liquid droplets are uniformly distributed on the surface of individual primary particles by layering (Saleh and Guigon, 2007). Therefore, compared to agglomerated WPI, the coated WPI had no

significant difference in bulk density and porosity values, though some of them may have bigger sizes based on their partial agglomeration.

1.2 The effect of granule growth

As it is mainly described in Chapter 4 & 5, the effects of different agglomerate sizes have been identified. For the agglomerated MPI produced by fluidised bed, the larger size is corresponding to more irregular shape properties, having lower circularity and convexity. This is believed to be caused by low deformation system that contributes to the steady growth behaviour. After the sprayed droplets wet the surface of MPI particles, the primary particles start to adhere to each other and form the nuclei agglomerates. Then the size continues to grow via the layering of the primary particles, where the phenomenon known as “snowballing” occurs, which finally forms the “raspberry” structures (Mörl et al., 2007). Bigger size agglomerates are usually found to have more porous structures, with more irregular shapes, lower bulk density and higher porosity. However, the high shear mixer agglomeration exhibits completely different behaviours in the granule growth process, as mechanical agitation tends to rapidly coalescence the MPI particles. Firstly, the nuclei agglomerates are solidified by the force of agitation, which resulted in the less air entrapped and the small interstitial spaces in the matrix. When the nuclei granules continued to grow, they coalesced together to create the bigger secondary agglomerates, based on the strong bridges that were produced by mechanical forces. This process produced the more irregular particles, which increased the void volumes among these particles. When the secondary agglomerates reached the critical size, the bonds were not strong enough to bind other particles (Hapgood et al., 2007; Litster and Ennis, 2013). In that case, the granules stopped growing and they were highly deformed again by the mechanical solidification. These are the reasons

why the granules from HS and FB present the different physical and structural characteristics, shown in Table 6-1**.**

1.3 The effect of different binders

The impact of liquid binders on the structural modifications of MPI agglomerates are not significant, compared to the factors of processing types and granule growth. The different binders including water, 5% lactose and sucrose solution, appeared to have no particular effect on bulk loose and tapped densities as well as porosity value. Only the small difference in the particle density was found for the agglomerated MPI using different liquid binders. In addition, water binding agglomerates had comparatively less similarity of a circle and lower convexity, due to higher binder liquid concentration resulted in the higher compactness of agglomerates (Szulc and Lenart, 2013). Similar results are also observed for agglomerated and coated WPI powders in Table 7-1, which shows the particles agglomerated or coated by lower concentration lecithin solution (0.5%) had the comparatively more irregular shape properties. At the same time, 5 % lecithin solution caused a slightly higher bulk density and lower porosity of WPI powders, as the higher concentration of liquid in the coating process results in the formation of thicker layers with high compactness.

2 The effects on rehydration behaviours

The influences of agglomeration and coating processes on the dynamic rehydration processes, including wetting, dispersing and dissolving, have been investigated. According to the study, different processes, granule growth and different binders (coating materials) are found to contribute differently to the rehydration behaviours of different milk protein powders.

2.1 The effect of different processes

The agglomerated casein-dominant powders (MPI & MC) exhibit the significantly better wettability, by needing much shorter wetting time, being quickly penetrated by water droplets and absorbing more water by capillary force (Chapter 3 & 4). The small particle size and dense structures are believed to be the rate-limiting factors to control the dynamic wetting process of the casein-dominant powders (Crowley et al., 2016). Thus, the increases of particle size and powder porosity, caused by fluidised bed agglomeration, play beneficial roles in the improving wettability. However, some other milk protein powders, e.g. WPI and SC, appear to form an impermeable layer at the powder/water interface when they are ready to contact water. This results in non-hydrated regions, where water is difficult to break through and then penetrate into the particles, due to the special water holding capacity for these milk proteins (Peters, 2016). Instead of particle size and porosity, the natural physicochemical characteristic of WPI and SC is the main factor that determines their wettability. In that case, the structural modifications induced by the agglomeration have no obvious influences on accelerating the disappearance of the gel-like skins surrounding the particles. On the other hand, as the much larger granules with bigger interstitial spaces are produced by high shear granulator, the MPI granules are found to be very quickly wetted by water. These granules with high particle density are very easily immersed below the water surface by their gravity and then water can also penetrate into the interstitial spaces between particles by capillary force.

However, when taking into consideration the solubilisation process, including dispersing and dissolving, the study in chapter 3 & 4 has shown that there was no significant difference, between the dispersibility and solubility of the agglomerated

and non-agglomerated MPI. It is not surprising, as the prolonged solubilisation process of milk protein powders are mainly determined by the casein micelles, which are very difficult to be collapsed and dispersed under the effect of water erosion (Fig.3-6) (Mimouni et al., 2010; Schuck et al., 2007). Therefore, the use of fluidised bed agglomeration does not influence the disintegration of micellar structures. Furthermore, the densely packed structures generated by high shear mixer agglomeration require much longer time to break down into small solids, before they are totally solubilised into water. Consequently, the agglomerated MPI makes the dispersibility even worse, especially for those primary aggregates of granules (nucleus), which led to the slowest release rate of materials.

2.2 The effect of granule growth

The effect of granule growth on the rehydration process is actually based on the different extents of the physical and structural modifications. According to the research in chapter 4 & 5, the larger FB agglomerates with higher porosity are related to the more water uptake by capillary rise. Similar results were also observed for the large HS granules, which absorbed the greatest amount of water, had the least wetting time, as well as caused quickest disappearance of water droplets. It can be explained by Washburn equation, as larger particle size combining with big interstitial pores resulted in greater mass of liquid by spontaneous intrusion (Lazghab et al., 2005; Washburn, 1921). However, as it is discussed previously, the impact of agglomeration on the solubilisation is not positive. In Fig.4-6, there is no clear relationship between the FB agglomerate size and the dispersibility of MPI. For high shear mixer agglomeration process, different granule growth processes delayed the release of materials by different degrees. Of these granules, the nuclei granules present the greatest granule strength that can resist the agitation force, as highest

mechanical energy is required to separate the primary aggregates and disperse them into the medium (Fig.5-4). 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. More adhesive forces are needed for the formation of larger granules, which thus are more easily to break down.

2.3 The effect of different binders

As the effect of different binders on the structures of milk protein powder is not significant, thus the subsequent influence on the rehydration process is also limited, which is reported by the study of chapter 4. In that case, the only possible approach is regarding to the chemical functionality of the added material itself. For example, as the most used food grade surfactant, lecithin can be potentially used to improve the rehydration of milk protein powders (Dashiell, 1989). In chapter 7, the study demonstrates that the addition of lecithin dramatically shortens the wetting time for WPI powder, which is believed to be one of the most difficult-to-wet milk protein powders (Schuck et al., 2012). Especially when adding lecithin solution by fluidised bed agglomeration, WPI powder only requires several seconds to be completely wetted. Meanwhile, the WPI coated by lecithin solution appear to form the weaker layers, where water more easily penetrates through and wets the particles. It is due to the ideal wettability of a powder depends on the particle size, porous structures and surface tensions (contact angles by water), which are all necessary factors to determine the dynamic wetting behaviour (Crowley et al., 2016). On the other hand, the effects of different binders on the dispersing and dissolving processes can be ignored, as the micelle structures are the main reason to delay the rehydration

process of casein-dominate powders. However, it will be also interesting to see if lecithin still plays a beneficial role on the solubilisation after powders are wetted. It may need further study in the future.

3 The effects on flowability and water adsorption

It is commonly believed that adhesive forces are usually the source of such flow problems for fine-grained dry bulk solids. The major adhesive forces are based on van der Waals interactions and the intensity of the forces mainly depend on the particle size as well as the distances between individual particles (Fitzpatrick, 2013; Schulze, 2007). When the distances are small or the surfaces of particles are in contact, van der Waals forces have a large influence. This can be the reason why the non-agglomerated MPI powders with small size have poor flowability. The FB agglomerates have large sizes and rough surfaces, which result in an increase in distance and thus a reduction of adhesive forces. The granules from HS also presented similar behaviours, as their adhesive forces were no longer dominant compared to the gravity force. The dense packed structures allow the granules to flow more freely. If considering the friction between bulk solids and solid surfaces, e.g. the wall of a hopper, the angle of wall friction as a function of stress is important for quantifying the wall friction during hopper design. Significant differences were observed for the HS granules associated with various sizes, presenting the large wall friction angles with different degrees. It is due to their high bulk density caused more force transferring through wall shear stress, which meant the large wall friction force and thus attained the big angles of wall friction.

Isotherms and kinetics are the two most used methods to evaluate the water adsorption behaviours of dairy powders. In Fig.6-3, the water adsorption isotherms all have a linear slope, regardless of the type of granulation process. There was no

significant difference between the non-agglomerated MPI and the FB agglomerates, which adsorbed almost the same quantity of water. The interior porous structures formed by fluidised bed had no significant effect on the rate and extent of hydration, and water molecules seemed to enter and exit as easily as that occurring in non-agglomerated MPI. However, the HS granules were found to adsorb less water from the surrounding environment, suggesting that moisture vapour is more difficult to penetrate into the structures and form layers on the surface of internal primary particles. On the other hand, the HS MPI granules had more compacted structures, restricting diffusion of water into the internal surface as a result of reduction of surface-binding sites for water to adsorb (Al-Muhtaseb et al., 2002). Therefore, the large particles with low specific surface area are believed to retard the moisture adsorption behaviour of milk protein powders.

4 Overall conclusion

- Based on the different agglomeration mechanisms, the MPI powders agglomerated by FB generally present a 2 to 4 times (100 mm - 200 mm) increase in size over the primary powders. The formed agglomerates have the most irregular morphology by showing the least spherical shapes and roughest surfaces. It also results in porous structures with lowest bulk density (both loose and tapped) and highest porosity values.

- MPI granules produced by HS can reach sizes of more than 1000 mm, which are ~20 times that of the primary powders. Under the effects of high shear agitation forces, the granule's shape is more like a sphere and its surface is comparatively smooth. In addition, the densely packed structures for those HS granules cause the highest bulk density and lowest porosity values.

- Poor wettability was the rate-limiting factor for WPI and SC rehydration, while poor dispersibility was the main problem for MC rehydration. Both MPI and CC displayed both poor wettability and poor dispersion. Special water holding capacity is the main reason for the poor wettability of WPI and SC, which tend to form an impermeable layer at the powder/water interface when contacting with water; while the prolonged solubilisation of MC and MPI are due to the strong interactions in micellar structures, where the casein micelles are difficult to be collapsed and dispersed under the effect of water erosion.

- Fluidised bed agglomeration has the beneficial role of improving the dynamic wetting process of MPI and MC powders, by requiring shorter wetting times, being more quickly penetrated by water droplets and absorbing more water by capillary force. The MPI granules based on high shear mixer agglomeration appear to be more easily wetted by water. The effects are more significant if the larger MPI granules are produced and bigger interstitial spaces are formed.

- When using lecithin solution as a liquid binder, the agglomerated WPI only requires several seconds to be completely wetted and also allows quick water penetration. However, high coverage of lecithin by coating process gives a more advantageous first wetting step. The ideal wettability of a powder depends on the particle size, porous structures and surface tensions (contact angles by water), which are all necessary factors to determine the dynamic wetting behaviour.

- Agglomeration processes showed no beneficial influence on the solubilisation process of different milk protein powders. In fact, the densely packed structures created by high shear mixer largely delayed the release of materials during the rehydration of MPI powders.

- The MPI with densely packed structures made by high shear mixer granulator adsorbed least moisture and showed the slowest adsorption kinetics during storage at different relative humidities. The agglomerated MPI with loose and porous structures by FB exhibited no significant difference, compared to the non-agglomerated powder.

- Large MPI granules have significantly better powder flow behaviours. Agglomeration processes can effectively reduce the minimum outlet diameters of hoppers for reliable flow from both mass-flow or core-flow hoppers. However, large wall friction angles caused by the HS granules (especially the smaller granules) may also require steeper hopper walls to discharge bulk solids and avoid them remaining at rest.

5 Future work

Based on the current research, it is found that agglomeration and coating processes play critical roles in modifying the structures and surface composition of dairy powders. They may be considered to link to other functionalities, e.g. caking, particle breakage (friability) or viscoelastic behaviour and thermo-mechanical transitions, which are also very important to the production of dairy powders in industry. For example, caking behaviour is the undesired phenomenon for lactose-based dairy powder, which often occurs by forming bridges between lactose particles. It is mainly

dependent on surface composition, particle size and shape as well as the consolidation environment with relative humidity and temperature. In that case, the post-dehydration process can not only increase the particle size and surface roughness (decrease contact area), but also change lactose distribution on the surface of particles. Therefore, it presents potential effects to reduce the caking behaviours of lactose-based dairy powders.

Relationships between the post-dehydration process and the final functionality of dairy powders are necessary to study by establishing statistical models, which enable the prediction and control of functionality. So far, a great number of statistical models have been set up for pharmaceutical powders, thus there is scope for application to food powders. At the same time, with the rapid development of 3D printing technology, the structural design for powders may become possible in the future. The unified particles with the controlled particle size distribution, shape, density and porosity can be designed and used to validate the models tailored for powder rehydration, water adsorption and other food powder functionalities. Consequently, it is believed to be a new opportunity for “smart process” in food technology.

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APPENDIX

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Assessment of measurement characteristics for rehydration of milk protein based powders

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ABSTRACT

Rehydration is an important powder property and is regarded as a critical issue by the dairy industry. Traditional powder rehydration measurements are relatively empirical with poor reproducibility. Thus, more reliable techniques tailored for dairy powders should be developed based on varied rehydration behaviours and applications. In this paper, a critical assessment to identify the measurement characteristics of milk protein powder rehydration is presented. Milk protein based powders were used as model systems. Four different wettability measurements (Immersion, Capillary rise, Condensation and Spreading) and four different dispersibility measurements (Dispersibility Index, Light scattering of particles in suspension, Light transmission and Conductivity of suspension) are compared and analysed. The results show that the method based on immersional wetting procedure is only appropriate for skimmed milk powder while the method for capillary rise wetting is more useful for the agglomerated milk protein powders with porous structures. Contact angle changes in the spreading wetting approach is found to be a straightforward technique to show the hydrophobicity or hydrophilicity of milk protein powders. If compared with traditional dispersibility measurements, light transmission of suspension is suitable to reflect optical properties of slow dispersion process. Light scattering methods can also be used to measure the dynamic size change of particles during the dispersion process. Furthermore, the conductivity of suspensions is a useful indicator to quantify the dispersibility indirectly by the release of minerals during rehydration. In summary, it is necessary to understand the specialities and applications of dairy powders before choosing the appropriate rehydration measurement methods.

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1. Introduction

Rehydration properties are considered as an important benchmark to determine the overall quality of powder products. In the dairy industry, powder rehydration is regarded as a critical issue as some powders exhibit poor wettability with the materials floating on the surface of solution and others dispersing very slowly accompanied by lump formation, which is especially the case for high-protein-containing powders (Anema, Pinder, Hunter, & Hemar, 2006; Havea, 2006). Traditional dairy powder rehydration measurements, which were often designed for the analysis of instant skimmed milk powder or whole milk powder, are thus relatively crude with poor reproducibility for other specialty milk protein products (i.e., micellar casein, whey protein or milk protein isolate powders). Therefore, more analytical approaches have been developed to observe each dynamic step and to find the methods to quantify the kinetics of powder rehydration process (Crowley et al., 2015; Fang, Selomulya, & Chen, 2010; Forny, Marabi, & Palzer, 2011; Freudig, Hogekamp, & Schubert, 1999; Gaiani, Scher, Schuck, Desobry, & Banon, 2009; Marabi et al., 2008; Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2009). However, it is a challenge to find a universal method to measure the rehydration abilities of varied dairy powders, as they present significantly different behaviours during the rehydration process. Recent studies have shown that whey protein isolate powder has poor wettability and that the wetting stage is the main limiting factor for whey protein rehydration. In comparison, the slow dispersion of micellar casein is responsible for its extended rehydration time. Whereas for milk protein isolate, both wetting and dispersing processes are rate-limiting steps (Gaiani, Schuck, Scher, Desobry, & Banon, 2007;

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Schuck et al., 2007). Consequently, it is necessary to examine the feasibility of the existing techniques for determination of the rehydration of milk protein powders and to validate the every typical powder and technique case by case in order to find the most appropriate one.

It is commonly believed that wetting is the critical step in powder rehydration process, as powder materials with poor wettability have limited access to contact with water which then causes the formation of non-hydration regions. In general, wetting behaviour can be assessed through different procedures including immersional wetting, capillary wetting, condensational wetting and spreading wetting in Fig. 1, which was modified and developed from the other researches (Israelachvili, 2011; Lazghab, Saleh, Pezron, Guigon, & Komunjer, 2005). The immersional wetting process uses the time required for a given mass of powder to submerge fully below the liquid surface as a measure of wettability. But it is mainly of practical use for dairy powders that are easy to wet whereas milk protein based powders tend to float on the surface of the liquid and so wetting time is no longer a useful measure. Thus, it is interesting to assess which kind of dairy powders will be suitable for characterisation by this traditional immersional wetting process. Secondly, capillary rise wetting is a process whereby the liquid penetrates into the solid porous structure by capillary force. For this case, the Washburn method is mostly used, which can be quantified by the mass of adsorbed liquid as a function of time (Ji, Cronin, Fitzpatrick, Fenelon, & Miao, 2015; Thakker, Karde, Shah, Shukla, & Ghoroi, 2013; Washburn, 1921). However, the feasibility of this approach for dairy powders is still not validated, as some researches have shown that spontaneous liquid penetration only occurs if the contact angle between the liquid and solid is lower than 90° (Yuan & Lee, 2013). Also the wetting behaviour by capillary rise is not only influenced by the actual wettability but also by the porous architectures of solids (Buckton & Newton, 1986). Thirdly, the condensational wetting process concerns the adsorption of moisture vapour on a solid surface and faster wetting usually corresponds to higher rates of vapour sorption (Israelachvili, 2011). The method uses different salts solution in desiccators to provide varied relative humidity environment for powder adsorption (Schuck, Jeantet, & Dolivet, 2012). Hence uptake of water vapour may represent totally different wetting behaviours for milk protein powders compared to wetting by liquid water where surface tension effects need to be considered. Finally, the spreading wetting process focuses on the contact angle when a given amount of a liquid spreads over a solid substrate (Israelachvili, 2011; Rouquerol, Rouquerol, Llewellyn, Maurin, & Sing, 2013). The method examines a single liquid drop penetrating into solids and thus evaluates the wettability by monitoring the changes in contact angles over time. In summary, all four methods corresponding to different wetting procedures have been widely used in pharmaceutical research, however few applied in dairy powder research. Therefore, it is important to identify whether the analytical methods based on these four wetting procedures are suitable for the typical milk protein powders.

Dispersibility is also believed to be an important step in the rehydration process, as it is necessary for particles to be dispersed into the liquid before dissolving (Galet, Vu, Oulahna, & Fages, 2004; Goalard, Samimi, Galet, Dodds, & Ghadiri, 2006). The dispersion process is accompanied by the transfer of particle mass, particle size and particle energy, which can be used as the indicators to quantify the process (Forny et al., 2011). The use of the dispersibility index is the traditional standard method to measure the amount of dry matter combining simple mixing in a liquid followed by sieving.

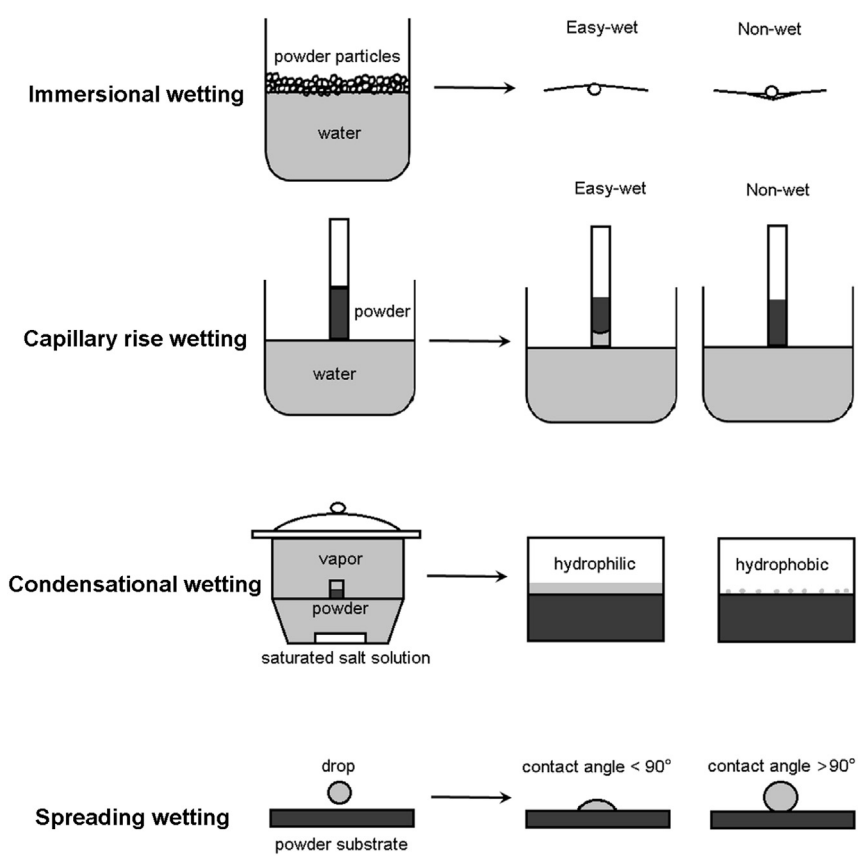

Fig. 1. Different wetting procedures.

Limitations of this method are that it cannot monitor the dynamic dispersing process and it is often influenced by the wetting behaviour of powders as they need to be wetted first. Therefore, more effective methods have been found for improved monitoring of the particles dispersibility. The most common method is the use of an optical fibre sensor to collect the intensity of light scattering of particles in suspension. Based on the principles of forward light scattering, it has been used to measure the particle size distribution over the mixing time and to monitor the dispersibility of powders in terms of the variation in particle size (Chen & Lloyd, 1994; Galet et al., 2004). Moreover, transmission of near-infrared light has also been used to exhibit the dynamic process of solids dispersing in the suspension during centrifugation (Crowley et al., 2015). Although some studies have shown light scattering and transmission to be reliable methods to monitor dispersion behaviour for food powders and milk protein powder (Crowley, Kelly, & O'Mahony, 2014; Fang, Selomulya, & Chen, 2007), it is still required to examine and investigate the selectivity of these methods with other dairy powders as they present completely different dispersion behaviours. Additionally, conductivity is another possible approach to express the kinetics of dispersing process via the release of minerals in suspension (Zhuang, Zhou, Nguyen, & Hourigan, 1997). Numerous studies reported that some minerals had approximately the same dissolution rate as micellar casein (Holt, 1997; Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2010). However, it is still not fully understood whether the conductivity method is capable of quantifying the dispersion of MPI or MC and other non-casein dairy powders.

In this paper, four wettability methods and four dispersion methods are applied to measure the rehydration behaviour of six milk protein powders, which are whey protein isolate (WPI), micellar casein (MC), sodium caseinate (SC), milk protein isolate (MPI), MPI agglomerate and skimmed milk powder (SMP). The objective is to evaluate the advantages, drawbacks and limitations of each of the methods and to identify which methods are more suitable for assessing the rehydration behaviour of milk protein powders.

2. Materials and methods

2.1. Materials

MPI, SC and SMP were supplied by Kerry Ingredients (County Kerry, Ireland). WPI was supplied by Davisco Food International (Le Sueur, MN, USA). MC was produced from skimmed milk powder by firstly microfiltration with 100 kDa molecular weight membranes. The retentate is concentrated by vacuum evaporation and the concentration process was performed at a temperature of 65 °C. The solid concentration of about 38% was then obtained by the water removal. Finally, the concentrated solution was spray dried to obtain the MC powders. The inlet and outlet temperatures were 180 °C and 85 °C, respectively, and the drying air-flow rate is 750 m^3 h^{-1}. The manufacture of agglomerated MPI powder was described in details in the study of Ji et al. (2015). Briefly, 100 g 15% lactose solution was used as the binding liquid which was progressively added to 200 g MPI powder (1 mL min^{-1}) in a top-spray fluidised bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Lowa, USA). The temperature of injected air was 50 °C and the air flow rate was 200 L min^{-1}. After the addition of lactose solution, the obtained powder was dried with hot air at 100 L min^{-1} flow rate and 50 °C temperature for a further 15 min. The compositions of the milk protein powders are shown in Table 1. All the powders were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 45 °C overnight to obtain the final moisture content of about 1.5%. They were kept in the desiccators before the wettability and dispersibility measurements.

2.2. Wettability measurements

2.2.1. Wetting time by immersional wetting procedure

This method is used to quantify the wettability of dairy powders by the time needed to achieve complete wetting of a given quantity of powder, when powder is gently dropped on the surface of water and immersed without any agitation (Schuck et al., 2012). In this study, 6 g powder samples were filled into a standard 400 mL beaker, which contained 100 mL of distilled water with 20 °C temperature. Powder was considered as wettable if wetting time was less than 60 s and non-wettable if wetting time was greater than 120 s (GEA Niro, 2005). All the measurements were repeated three times.

2.2.2. Modified Washburn method by capillary rise wetting

Washburn method is a common technique to measure the wettability of powders based on capillary rise wetting behaviour. It usually monitors the rate that a liquid penetrates into powders or granules by recording the penetration depth of the liquid inside the capillary as a function of time (Washburn, 1921). However, the method can be derived and developed into other forms, e.g. the depth of penetrated liquid is instead of mass. The principle of the instrument was described in the study of Ji et al. (2015). A 2 g powder sample was loaded into a cylindrical glass tube with an open base bottom covered by filter paper and gauze. The tube was set just above the surface of distilled water at 25 °C. The wettability of powder was quantified by the additional mass of the wetted powder in 10 min, which was the weight of adsorbed water by the powder. Each sample was measured five times.

2.2.3. Water adsorption by condensational wetting

Condensational wetting procedure can be considered as water vapour adsorption and was determined by static-gravimetric method. Triplicate 1 g powder samples of each dairy powder were stored in empty glass vials of known weight. The powders were kept in desiccators with a stable relative humidity, which ranged from 11% to 75%, until equilibrated. The hygroscopic environment (R.H.) was provided by different saturated salt solutions which were LiCl (11%), CH_3COOK (22%), $MgCl_2$ (33%), K_2CO_3 (43%), $Mg(NO_3)_2$ (53%), $NaNO_2$ (65%) and NaCl (75%). The desiccators were evacuated before they were stored in a 25 °C incubator. The weight

Table 1
Composition of dairy powders investigated in this study.

Dairy powder	Protein (%, w/w)	Moisture (%, w/w)	Lactose (%, w/w)	Fat (%, w/w)	Ash (%, w/w)
MPI	86.0	4.0	<1.0	1.5	6.0
Agglomerated MPI	82.0	5.0	6.2	1.4	5.6
WPI	90.0	5.0	<1.0	1.0	3.0
MC	84.0	5.0	2.0	1.0	7.5
SC	88.0	5.7	<1.0	0.7	4.7
SMP	36.0	4.0	51.0	0.8	8.2

of powder was measured for at least 96 h until it reached a constant value. The results were expressed as equilibrated moisture content as a function of water activity to show the water vapour adsorption isotherms.

2.2.4. Contact angles by spreading wetting

The measurement of contact angle is a direct method to measure the tangent angle at the contact point of three phases. Due to the dynamic process for the wetting behaviour, it is usually to monitor the rate of change of contact angle to quantify the wettability of powders (Crowley et al., 2015). Thus, an optical tensiometer (Attension Theta, Biolin Scientific Ltd., Espoo, Finland) was used to measure contact angle (θ) of 12 μL deionised water droplet by the sessile drop technique with dynamic live measurements at a temperature of 20 °C. Before measurement powders were loaded into an aluminium pan (ø = 100 mm, h = 7 mm) and a smooth surface was formed by passing a leveller across the surface. The volume of the remaining water droplet above the solids during the wetting process was also evaluated (Yuan & Lee, 2013). The measurements for each sample were repeated at least 5 times.

2.3. Dispersibility measurements

2.3.1. Dispersibility index

The Dispersibility Index (DI) is defined as the percentage (%) of dry matter that passes through a sieve after mixing for a short time with a spatula. The sieve with mesh size of 250 μm is used to separate the dispersed particles from the suspension based on the extent of dispersion (Schuck et al., 2012). In this study, 10 g powder was added into a 250 mL beaker with 100 mL deionised water at 25 °C and then mixed vigorously with a spatula for 15 s in order to make 25 complete circle stirring movements along the diameter of the beaker. After that, the reconstituted samples were then poured onto the 250 μm sieve to separate the dispersed particles in the suspension based on the extent of dispersion, and the samples that passed through the sieve were collected in a bottle for further drying at 105 °C temperature overnight in an oven. The extracted dry matter was weighed and used to calculate the DI as following Equation (1):

$$DI = \frac{W_d \cdot (100 + w)}{w \cdot \frac{100 - W_m}{100}} \quad (1)$$

where w is the weight of sample, W_d (%, w/w) is the dry matter after sieving, W_m (%, w/w) is the free moisture content of the powder. The measurements for each sample were repeated 3 times.

2.3.2. Particle size measurements by laser light scattering method

Laser light scattering method based on Malvern Mastersizer 3000 (Malvern Instruments Ltd, Worcestershire, UK), was used to quantify the powder dispersion process in term of decreasing rate of particle size. The detailed measurement principle of the machine was described in the study of Ji et al. (2015). In order to reach the ideal obscuration range of the machine, approximately 5 mg MPI, MC, SMP and 100 mg WPI and SC were added into dispersion unit with 120 mL distilled water at a temperature of 25 °C ± 2 °C and then agitated at 2000 rpm. Triplicate measurements were carried out for each powder. Particle size distributions were recorded every 2 min until D (50) reached ~1 μm (the diameter of 50% particles was just lower than 1 μm) (Ji et al., 2015; Mimouni et al., 2009).

2.3.3. NIR transmission measurements by Lumisizer

Lumisizer (L.U.M. GmbH, Berlin, Germany) is an analytical centrifuge, which was used to quantify the dispersibility of milk protein powders by measuring the intensity of transmitted near-infrared light in suspension. 1.5 g samples were rehydrated into 100 mL deionised water at a temperature of 25 °C. 1.5% (w/v) concentration suspension was then obtained through agitating by a magnetic stirring bar (length 2.5 cm) with a rate of 400 rpm for 30 min. After that, 400 μL suspensions were sampled by 16 gauge needles to fill into polycarbonate cells. The sampling positions always had a constant distance (approximate 1 cm) from bottom of the beaker. The measurements were carried out by two different centrifugations; firstly 36 g for 10 min and then followed by 168 g for further 10 min. The intensity of the transmission of NIR light was measured in the distinct regions of the sample cell and was related to the different phases of dispersion, including stable solution, initial sediment and compressed sediment, which created the varied optical densities. The transmission profiles were presented every 10 s for the first 10 min 36 g centrifugation and then every 60 s for next 10 min 168 g centrifugation. Integral transmission of each profile was calculated by software SepView 4.1 (L.U.M. GmbH, Berlin, Germany) and is shown as a function of time. Meanwhile, compressed sediment height under 36 g and 168 g of centrifugation was determined by the area of greatest optical density, which means the area of lowest transmission but subtracting the steady-state value caused by the cell bottom (Crowley et al., 2015).

2.3.4. Conductivity measurements during particles dispersing

Conductivity meter (FE30-Kit – FiveEasy™ conductivity, Mettler Toledo Ltd., Greifensee, Switzerland) was used to measure the release of minerals accompanied by the rehydration of powders and showed the ionic strength of reconstituted powders. Each sample weighting 8 g was poured into 400 mL deionised water and wetted by the vortex as rapidly as possible. A 2% w/v solid suspension was created and mixed at 500 rpm in a 25 °C water bath. Deionised water was used and had a conductivity value of 67 μs cm^{-1}. The probe was calibrated at 25 °C with a standard solution of known conductivity value of 1314 μs cm^{-1} before placed in the suspension. The values were recorded every 10 s for the first 2 min, followed by every 60 s for next 10 min and every 10 min for final 90 min. The measurements for each sample were repeated at least 3 times.

3. Results and discussion

3.1. Wetting behaviours of milk protein powders based on different wetting procedures

3.1.1. Wetting time by immersional wetting

As can be seen from Table 2, only the skimmed milk powder can be considered to be wettable with a wetting time of 22 s. The other powders required very long times in excess of 20 min (although the agglomerated MPI did have a time of 8 min). The result is not surprising because skimmed milk powder contains high content hydrophilic lactose, which allows water easily penetrating into the particles and thus sinking and dispersing quickly in the water. But for other high protein powders, there was an impermeable hydrophobic layer formed between the water surface and powders. This layer separated the water and the powder so that water had no access to penetrate into powder particles and caused the formation of non-hydration regions (Gaiani et al., 2007; Schubert, 1993). In that case, the interface of solid and gas was difficult to be replaced by the interface of solid and water due to the high content of hydrophobic milk protein powder with low porosity. Therefore, the traditional method based on immersional wetting procedure was not suited for the milk protein powders with poor wettability. Moreover, as powder wetting behaviour is a dynamic process, it is

Table 2
Wetting time of dairy powders by immersional wetting procedure.

	SC	WPI	MPI	Agglomerated MPI	MC	SMP
Wetting time	>20 min	>20 min	>20 min	8 min ± 2 min	>20 min	22 s ± 3 s

better to measure the kinetics of wettability, which usually can be quantified by the associated free energy change when the type of interface is transformed (Yuan & Lee, 2013).

3.1.2. Modified Washburn capillary rise wetting method

It is obvious to see that capillary rise wetting method is largely dependent on the inter-particle pores of powder samples and the choice of liquid, which determines the surface tension and viscosity (Forny et al., 2011). Hence, it is the reason why agglomerated MPI with porous structure showed the greatest wettability in Fig. 2, which absorbed more than 1 g water in 10 min (Ji et al., 2015). At the same time, MC powder also showed comparatively good wetting behaviour as it absorbed nearly 0.5 g water. But for SC and WPI powders, they were only slightly wetted by water because water cannot penetrate into a powder spontaneously if high contact angle ($\theta > 90°C$) and negative capillary pressure (Lazghab et al., 2005; Palzer, Sommer, & Hiebl, 2003; Yuan & Lee, 2013). Moreover, it is interesting to find that SMP powder only gained about 0.1 g weight after 10 min of the capillary wetting procedure, which should be wetted by water much more easily. However, SMP might dissolve quickly in the measuring water during measurement so that pure water was replaced by the drops of solution saturated with SMP. It caused the viscosity of liquid to increase, which decreased the rate of water uptake at the point at which the weight of water balances the capillary pressure (Stamm, Gissinger, & Boymond, 1984). Consequently, the modified Washburn method based on capillary effect was concluded to be sensitive to agglomerates with high porosity but not applicable for dairy powders that are easy-dissolved.

3.1.3. Water adsorption by condensational wetting

In Fig. 3, WPI and SC powders were found to adsorb the greatest mass of moisture at relative humidity value from 11% to 75%. It is inconsistent with the results measured by other wettability methods, which showed WPI and SC powders had extremely poor wettability. It is explained previously as the formation of an impermeable layer at the powder–water interface. However, for condensational wetting behaviour, the water vapour seemed to more easily penetrate into powdered solids and wetted them without creating any films or layers, although the vapour may condense into liquid droplets during the process (Depalo & Santomaso, 2013; Lazghab et al., 2005). Hence, WPI and SC may have the higher rates of vapour adsorption and better wettability by

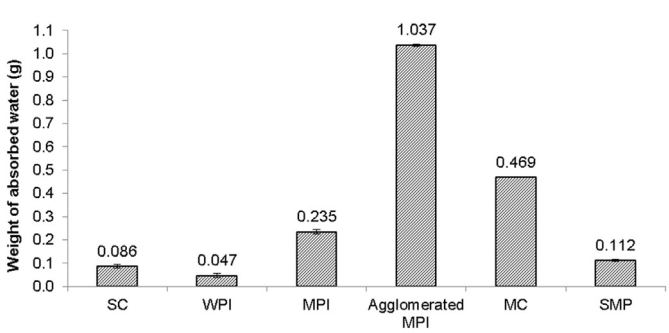

Fig. 2. Mean weight of absorbed water for samples (SC, WPI, MPI, Agglomerated MPI, MC and SMP) after 10 min.

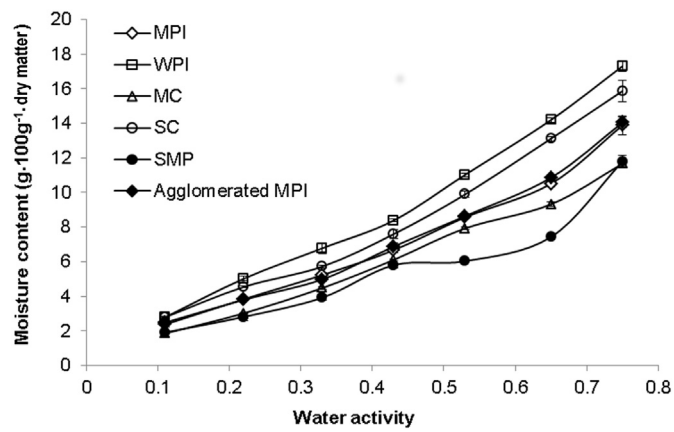

Fig. 3. Water vapour adsorption isotherms of dairy powders (MPI, WPI, MC, SC, SMP and Agglomerated MPI) at 25 °C environment.

the condensational wetting mechanism. Fig. 3 also illustrates that unagglomerated MPI and agglomerated MPI powders have no obvious difference in the isotherm data, which means that agglomeration process played no special role on MPI's water sorption behaviour. SMP exhibited different water adsorption isothermal behaviour from other powders, with no increase in moisture adsorption between the water activity values of 44% and 53%. This behaviour is consistent with previous reports that demonstrated lactose content in SMP reduced water adsorption due to crystallisation (Bronlund & Paterson, 2004; Jouppila & Roos, 1994; Shrestha, Howes, Adhikari, & Bhandari, 2007).

Water adsorption phenomenon of different milk protein powders has been discussed many times elsewhere (Berlin, Anderson, & Pallansch, 1968; Foster, Bronlund, & Paterson, 2005; Kinsella & Fox, 1986; Murrieta-Pazos et al., 2011). Few of them mentioned the adsorption properties as an indicator of powder wettability. Generally, wetting behaviour is evaluated as the critical first step of rehydration process of powders (Depalo & Santomaso, 2013; Hogekamp & Schubert, 2003). But in this study, condensational wetting was discussed as an exceptional issue due to solids being wetted by water vapour instead of contacting water or water droplets directly. This method is different from other three wetting methods (immersion, capillary rise and spreading) based on the contact angle of liquid phase and solid phase (Kwok & Neumann, 1999), while condensational wetting procedure focused on the adsorption of saturated vapour, where the interfacial effects are less pronounced. Therefore, though this static-gravimetric method for water sorption measurement could quantify the vapour wetting with high accuracy and good reproducibility, it is not able to assess the wettability regarding powder rehydration process. But vapour wetting may still provide some insights into general wettability of dairy powders.

3.1.4. Contact angles by spread wetting

Contact angle is usually used as a primary parameter to indicate the degree of wetting process with a small contact angle ($\theta < 90°$) representing good wettability and large angle ($\theta > 90°$) corresponding to poor wettability (Gao & McCarthy, 2006; Mittal, 2006). As the surface of liquid is exposed to wet the fresh surface of solid

after liquid drop and solid interact, it is important to monitor the rate of change of contact angle until reaching an equilibrium angle. It means wetting behaviour is dynamic procedure other than a static state (Link & Schlünder, 1996). Thus, in this study, it showed how the contact angle of samples changed and also the volume of droplets above the substrate decreased as a function of time.

According to Fig. 4A, B, the contact angle of SMP reduced dramatically in just 5 s with a final angle of 60° and 3.5 μL water volumes remained. MC powder was second fastest, which took about 15 s to reach the equilibrium. Meanwhile, agglomerated MPI was found to be more easily and quickly penetrated by water droplet than that of unagglomerated MPI, because of the significant effect of agglomeration process on improving the wettability of MPI (Ji et al., 2015). WPI and SC powders exhibited extremely poor wetting behaviours with contact angles changing only by about 40° and 10° in 5 min, respectively. This method showed advantages due to its simple operation, straightforward observation and high selectivity for dairy powders (Crowley et al., 2015). It only needs a small amount of liquid and a small powder contact surface area (Letellier, Mayaffre, & Turmine, 2007). However, there are still some limitations for the optical tensiometer method. Firstly, the dynamic contact angles were difficult to measure with high reproducibility and accuracy at high speed rate (Hunter, 2001), this was noted for the results of SMP, MC and agglomerated MPI. Also granule beds with rough surfaces can also pose problems in the assignment of the tangent line, as non-smooth surface is likely to cause variations of contact point along the contact line (Rotenberg, Boruvka, & Neumann, 1983). Although the limitations regarding of how flat the surface should be for measurements are unknown, there are a series of techniques for powder presentation to prepare the surface as smooth as possible, including solid compacts by a hydraulic press (Crowley et al., 2015), dip coating (Spelt & Vargha-Butler, 1996) and surface polishing (Vargha-Butler, Kashi, Hamza, & Neumann, 1986). Care should be taken to minimize alteration in the physical architecture of the powder particles during generation of a powder bed with a smooth surface.

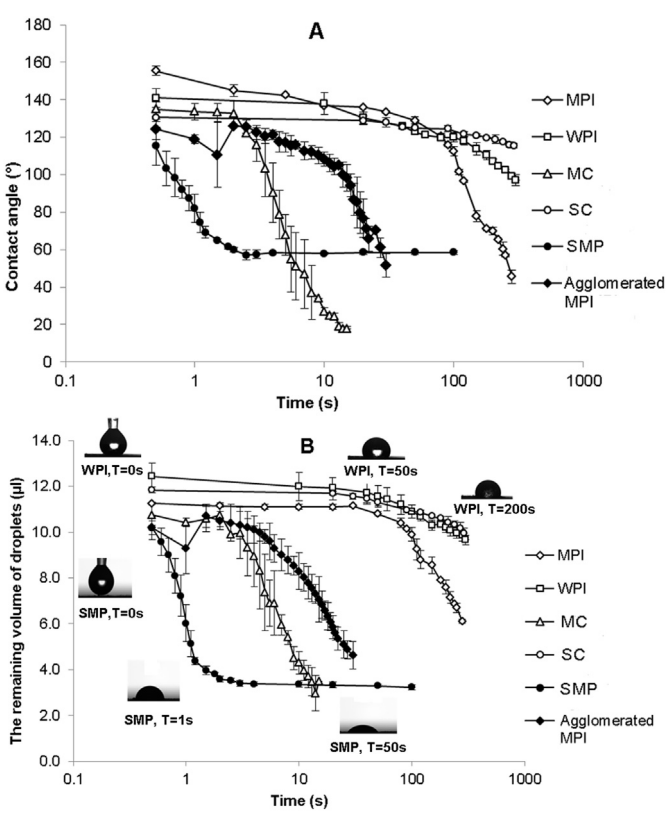

Fig. 4. AB. A: The change of contact angle (°) as a function of time using the sessile drop technique in approx.20 °C temperature. B: The change in the volume of droplet (μL) above the solids as a function of time during the wetting process in approx.20 °C temperature. The initial volume of water droplet was approx.12 μL.

3.2. Dispersing behaviours of typical dairy powders based on different measurements

3.2.1. Dispersibility index

DI is most widely used parameter to describe the dispersibility of powder particles by measuring the mass percentage of dry matter that pass through the sieve after simple stirring. This method is easy to operate and can quantify the dispersion behaviour of dairy powders directly with low-cost.

Fig. 5 shows the dispersibility of SMP and MC was the highest with 95% and 49% DI values, respectively. The result of SMP was similar to that reported by Schuck et al. (2012), but not for MC, which is only 24% DI value according to their research. It is due to some drawbacks in the selectivity of this traditional method as it is not suitable for other milk protein powders with poor wetting behaviour. The results in Fig. 5 show the DI values of WPI and SC were only 39.58% and 6.63% respectively, which were lower than expected. This was caused by samples not being properly wetted before they began to disperse in the suspension. The periphery of most WPI and SC particles were surrounded by impermeable layers during the simple stirring process which restrained materials from contacting with water. Therefore, the feasibility of the DI method is believed to be largely dependent on the wettability of dairy powders. Besides that, the reproducibility and accuracy of the measurements also rely on the consistency of multiple operators in treatment of stirring and transferring suspension into sieves, even if there are clear guidelines to follow. Furthermore, the DI parameter is not adequate to quantify the whole dispersion process as it only shows the final state of dispersed particles. Whereas, dispersion is a dynamic process accompanied by the release of materials and the transfer of particle size, particle mass and energy (Forny et al., 2011).

3.2.2. Particle size measurements by light scattering

Light scattering method has been shown to be an applicable tool to measure the dispersibility of powders based on the change of particle size and the undissolved particle volume concentration (Chen & Lloyd, 1994; Ji et al., 2015; Mimouni et al., 2009; Richard et al., 2013). It is commonly believed, during the rehydration process, the size of dispersing particles is decreasing and thus the

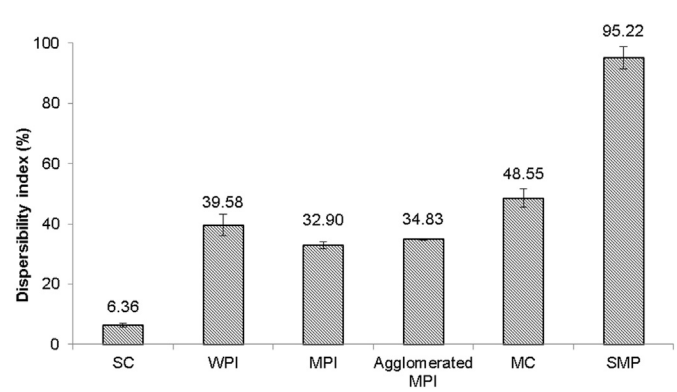

Fig. 5. Dispersibility index for samples. (SC, WPI, MPI, Agglomerated MPI, MC and SMP).

dispersibility can be quantified by the decrease rate of particle size. Meanwhile, it is necessary to evaluate the volume concentration due to powders consist of thousands of single particles. Thus, Fig. 6A showed how the volume concentration of undissolved particles decreased during the dispersion as a function of time. Using standard MPI powder as an example, the initial particle size of MPI was about 70 μm with high volume concentration (Single peak A) at the first stage of rehydration. As dispersion proceeds, the migration of peak and a bimodal distribution of particle size is observed, which results from the continuous release of particle materials into the surrounding aqueous phase (Fang, Selomulya, Ainsworth, Palmer, & Chen, 2011). With further rehydration, the volume concentration of small particles increased until another primary peak (Peak B) appeared and thus remained at a constant size of 0.3 μm at 60 min mixing time. The relationship of the particle size distribution of different dairy powders and the mixing time are present in Fig. 6B. Based on these results carried out by the light scattering, the migration of particles size of casein-dominant powders (MC, unagglomerated MPI and agglomerated MPI) with a slow-dispersion process can be clearly observed. MC powder took approximately 20 min to be mostly solubilised while MPI needed 40 min. There was no significant difference between agglomerated and unagglomerated MPI, which was previously explained in the study of Ji et al. (2015). At the same time, it was difficult to quantify the dispersibility of SMP by this method as it dispersed into water rapidly within less than 2 min. The same situation was found for SC, which formed lumps with big particle size initially but then collapsed quickly. Moreover, it is interesting to find that Mastersizer cannot detect any signals of scattered light from WPI suspension. It is because WPI particles had already dissolved in a very short time just after wetted by water entirely. Consequently, it was concluded that the static light scattering method was useful to monitor the slow-dispersing process of MC and MPI powders but it could not accurately quantify the quickness of the easy-dispersing dairy powders.

3.2.3. NIR transmission measurements by Lumisizer

In Fig. 7A, different regions of sample cell were identified based on the different light transmission properties of the suspension during a centrifugation process. For example, stable transmission value meant the stable supernatant, which was caused by dissolved small particles, while sediment formation of primary particles was explained by the low transmission value. Thus, it is possible to evaluate the dispersion behaviour of dairy powders by using the Lumisizer, according to the intensity of light transmission of different dispersion phases along the sample cell (Crowley et al., 2014). Meanwhile, the height of sediment under two different centrifuge speeds (36g and 168g) can also be calculated to show the final solubility of powders at the 30 min mixing time (Fig. 7B). It is not surprising to see that there was no sediment for WPI, SC and SMP powders, as they have good dispersibility and solubility. This was also shown by the previous results in Fig. 6B. Almost the same sediment height was observed for MPI and MC powders under the effect of 36 g centrifugation, while MC had slightly more compressed sediment when using 168 g centrifugation. In addition, when MPI powders were agglomerated by fluidised bed granulation process, there appeared to be a greater number of particles dissolved into water and less sediment was formed. But these results were only based on one specific time point, which was at 30 min mixing time. Dispersion and dissolution are kinetic processed and thus it is suggested to be advantageous to measure the sedimentation behaviour as a function of time until powders were completely solubilised (Fang et al., 2007; Hogekamp & Schubert, 2003; Ji et al., 2015). On the other hand, integral transmissions (%) were calculated and provided by the software of Lumisizer in Fig. 7C to evaluate the dispersion behaviour of powders. Each integral transmission value was used to stand for one transmission profile based on different centrifugation time. Fewer primary particles were found for the agglomerated MPI dispersion compared to the non-agglomerated MPI dispersion, due to higher transmission value showed in Fig. 7C. It meant agglomerated MPI particles were comparatively more easily to disperse into water at 30 min mixing time. Even though this method is regarded as a simple way to measure the dispersibility and solubility together, however, there is an important drawback that needs to be mentioned. The actual intensity of light transmission is largely dependent on the type of dairy powders. In other words, it is pointless to compare the disperse behaviours of dairy powders with different compositions, as they have different spectroscopy behaviour and NIR transmission in solutions. It is only of feasible to compare the non-agglomerated MPI and agglomerated MPI, which had very similar constituents. For this reason, the transmission values of WPI, SC and SMP were completely different, although they all dissolved within 30 min.

3.2.4. Conductivity measurements

The conductivity method is considered as a possible way to quantify the solubilisation process of casein-dominant powders. The primary species that contributed to conductivity were believed to be soluble minerals, while the contribution of proteins and

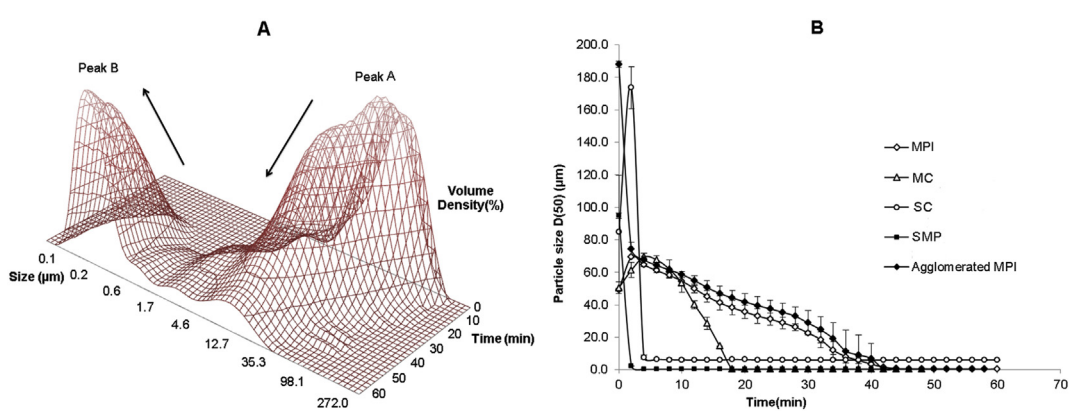

Fig. 6. AB. A: Volume density (%) based particle size distributions of dispersing MPI particles measured as a function of time (every 2 min for 60 min mixing time) during the rehydration process at 25 °C ± 2 °C and 2000 rpm. The size of initial large primary particles with large volume (Peak A) decreased with an increase in small dissolved particles (Peak B). B: Particle size D (50) measurements of dispersed particles of SC, MPI, Agglomerated MPI, MC and SMP. (WPI sample cannot be measured by Mastersizer as WPI dissolved rapidly and the dissolved solids is nanoscale).

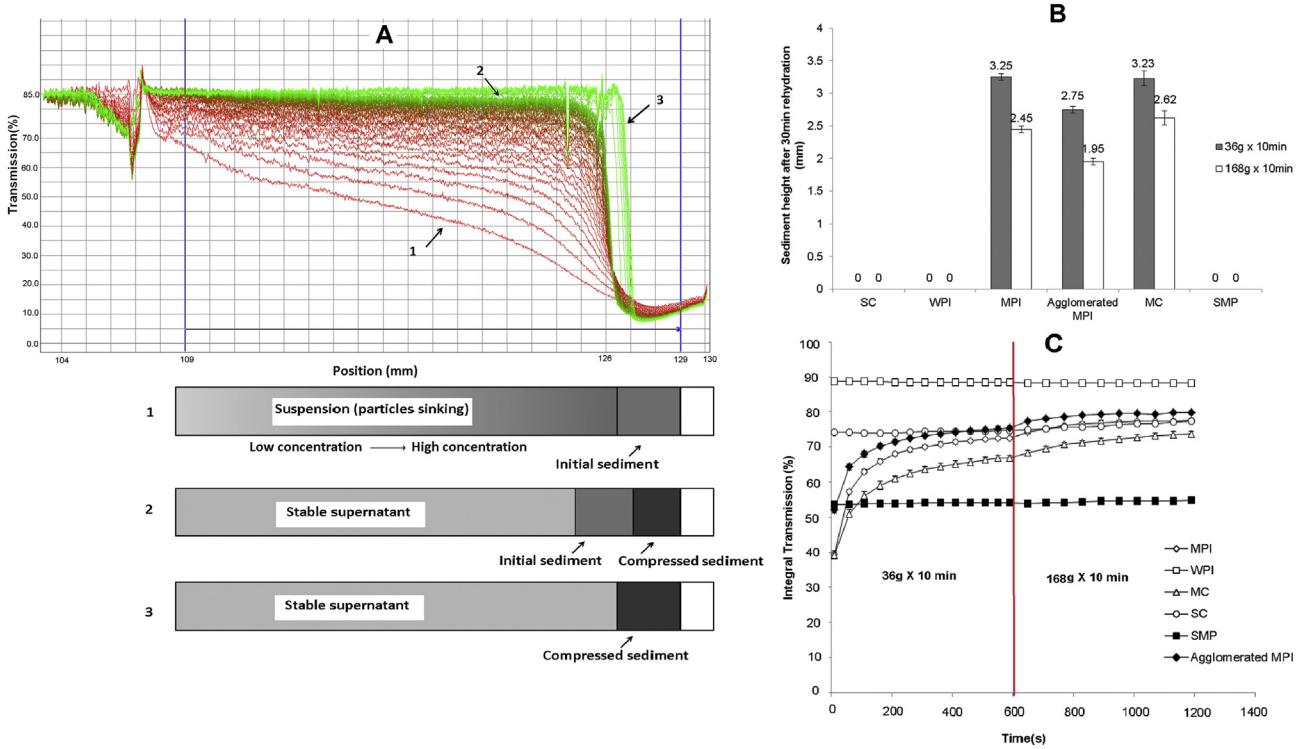

Fig. 7. ABC. A: A schematic illustration explaining the sedimentation behaviour of MPI suspension was showed by the transmission (%) of NIR light through the sample cells by centrifugation time. Profiles were measured every 10 s for first 10 min with 36g centrifugation and every 60 s for next 10 min with 168g centrifugation. Each measurement profile showed the distinct regions corresponding the different positions along the sample cell. The different transmissions represented the regions of dispersed particles and undissolved primary particles, which respectively formed stable supernatant, initial sediment and compressed sediment after centrifugation. Representative profiles based on different time (1: 10 s, 2: 10 min, 3: 20 min) were showed as examples. B: The sediment formed by 1.5% (*w/v*) sample suspension, which were rehydrated by 400 rpm stirring condition for 30 min at25 °C distilled water, after 36g and 168g centrifugation for both 10 min. The height of sediment was determined by the regions of low transmission subtracted the steady-state value that caused by cell bottom (from 129 mm). C: Integral transmission was calculated by the software of SepView 4.1 (L.U.M. GmbH, Berlin, Germany). Each integral transmission value (%) represented the overall transmission through the sample cell (from 109 mm to 129 mm) by a function of centrifugation time.

lactose can be ignored due to big molecular size or uncharged material respectively (Mucchetti, Gatti, & Neviani, 1994; Zhuang et al., 1997). At the same time, some studies believe that calcium, phosphorus, magnesium together with caseins all belong to the slow-dissolving fraction (Mimouni et al., 2010) because most of them come from the casein micelle structures and exist as colloids in typical milk (Holt, 1997). These slow-dissolving salt constituents also exhibited similar kinetics of solubilisation with caseins (Mimouni et al., 2010). Therefore, this is the reason why the conductivity of MPI and MC suspension increased slowly but continuously over time just as the solubilisation progress (Fig. 8). The conductivity meter was used to monitor the dispersion process of particles by measuring the release of slow-dissolving salts in suspension. It is thus, possible to compare the kinetics of solubilisation of these two dairy powders based on the changes in conductivity. At the same time, the conductivity of agglomerated MPI was found to increase faster than unagglomerated MPI at first 80 s while for the next 90 min, they present the almost same kinetics. It is because agglomerated MPI is more easily wetted and thus fast-dissolving salts are more quickly dissolved into water than that of unagglomerated MPI. SMP and WPI powders, which also belong to fast-dissolving samples, reached the individual steady conductivity values in very short time (less than 10 min) as shown in Fig. 8. It is not possible to evaluate their dispersion process corresponding to the conductivity values because there is no proof yet to show the relationships of salts and these fast-dissolving dairy constituents, even though Marabi et al. (2008) reported that the final steady-state conductivity meant the complete rehydration of these powders. Besides that, it is obvious to see that the initial conductivity of all samples increased quickly at first, which was considered to be caused by the release of fast-dissolving salts in suspension, e.g. sodium and potassium, when samples were wetted by water progressively (Mimouni et al., 2010). Furthermore, it is remarkable that the specific conductivity values of these dairy powders depend on how much salts remain in the powders during the manufacturing process. Consequently, conductivity methods for casein-dominant powder dispersion should only focus on the kinetics of conductivity instead of the value itself, which are always determined by varied membrane processes and different batches (de la Fuente, 1998).

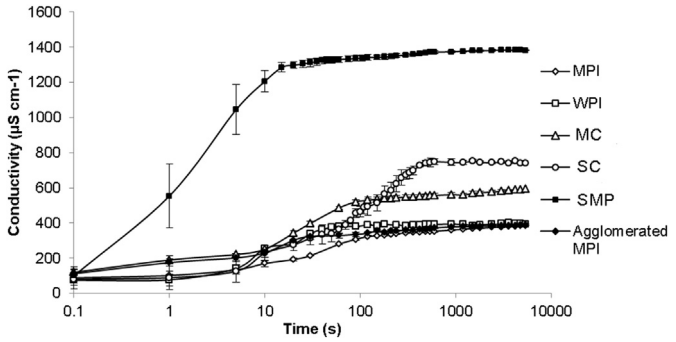

Fig. 8. The change of conductivity by a function of mixing time for the 2% (*w/v*) concentration sample suspension, with 500 rpm stirring condition at 25 °C. (Distilled water was used in suspension, which had conductivity value of 67 μs cm^{-1}.)

Table 3
Summary of the methods characteristics of dairy powders wettability and dispersibility[a].

Method	Accuracy?	Speed?	Reproducible?	Dynamic method?	Suitable dairy powders?	Application limits	Industrial setting?	Equipment	Potential benefits
Immersional wetting method	1	3	2	No	SMP or other easy-wet milk protein powders	Not be able to distinguish the wetting behaviour of poor wetting powders	Yes	Beaker and slide	Cheap; fast measuring
Washburn method	3	3	3	No[b]	MC, MPI and agglomerates	Used for Newtonian liquids only and not suitable for easy-solubilising powders	Yes	Cylinder glass tube	Quantitative method; fast measuring
Water adsorption static method	3	1	2	Yes	No dairy powders[c]	Moisture vapour wetting by different mechanism	Yes	Desiccators and incubators	Automotive; no operator-dependent
Contact angle	3	3	2	Yes	All milk protein powders	Need the surface of powdered samples as smooth as possible	Yes	Optical tensiometer	Direct method; fast measuring; small sample amount
Dispersibility Index	2	1	1	No	Easy-wet dairy powders without lump formation	Bad reproducibility with multiple operators and not capable for poor-wetting powders	Yes	Spatula and sieve	Cheap; easy to operate
Light scattering	3	3	2	Yes	Slow-disperse milk protein powders	Difficult to measure fast-disperse milk protein powders	Yes	Online measuring equipment	Direct method; automotive; small sample amount
Light transmission of suspension	2	3	2	No	Slow-disperse milk protein powders	Not suitable for fast-disperse milk protein powders	Difficult	NIR light equipment	Automotive; quantitative method
Conductivity of suspension	3	3	2	Yes	Only casein-dominant powders	Only useful with the premise of same release rate of salts and protein particles	Yes	Online measuring equipment	Automotive; quantitative method

[a] 1: low level; 2: medium level; 3: high level.
[b] It could be developed into a dynamic method.
[c] Not suitable for the wettability of powder rehydration.

4. Conclusion

The measurement characteristics of wettability and dispersibility of milk protein based powders were discussed in this paper. Due to the different potential use for the dairy powders, such as, MPI and WPI can be used in nutritional beverages or infant formula while MC and SC are the important materials in cheese making, an overall assessment of the methods based on these dairy powders was summarized in Table 3 with their advantages, drawbacks and limitations.

For the wettability measurements, the traditional method with immersion wetting process may be used as an initial screening and can differentiate between powders that wet reasonably well from those that are poor wetting. Contact angle methods are believed to be very useful for quantifying and comparing the wettability of milk protein powders. But it still needs to ensure the surface of powdered sample is as smooth as possible so that more accurate contact angles can be observed. Washburn method based on capillary rise wetting is also capable of assessing the wettability of some dairy powders. The major problem with this approach is with powders that readily solubilise when contacted with water, as they may form a solubilised viscous layer at the water–powder interface that inhibits capillary rise. This can lead to misleading results, for example, SMP is a good wetting powder but has a low capillary rise in the Washburn test.

For the dispersibility measurements, particle size measurements by light scattering method is suitable for all the powders tested, especially for slow-dispersing milk protein powders, e.g. MC and MPI powders. One problem with this approach is it cannot accurately measure how quickly the fast dispersing powders are dissolving, such as SMP, because of the time required to do the measurement. The poor dispersibility of some powders at a specific stirring time is also possibly described by the light transmission of the suspension using an analytical centrifuge. However, once again the fast-dispersing dairy powders, like SMP, WPI or SC, are difficult to quantify their dispersing process in water as they dissolve quickly once wetted completely. The DI method is only useful for assessing powders that wetted well and dispersed fairly quickly, such as SMP. It is not suited for powders that wetted poorly because they form lumps and disperse slowly because of poor wetting. For example, WPI has poor DI, due to its poor wettability, even though it is a good dispersing powder. Conductivity method is believed to have potential for casein-dominant dairy powders due to the similar release rate of colloidal salts and micellar casein.

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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.

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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 (Oftedal, 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, no matter what 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).

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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 simultancously 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), and 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.

2. Materials and methods

2.1. Materials

The composition of the milk protein powders used in this study is showed in Table 1. MPI and SC were supplied by Kerry Ingredients (County Kerry, Ireland). WPI was supplied by Davisco Food International (Le Sueur, MN, USA). CC was produced by Teagasc (County Cork, Ireland). Skim milk (Kerry Ingredients, County Kerry, Ireland) was used to produce MC by a pressure driven process with 100 kDa molecular weight membranes and then the obtained retentate was vacuum evaporated to increase the solid content to approximately 38%. The concentration process was performed at 65 °C. Finally, the MC powders were obtained by a spray drying process, where the inlet and outlet temperatures were 180 °C and 85 °C, and the drying air-flow rate was 750 m^3 h^{-1}. Before the measurements, all the powders were dried in a vacuum oven (Jeiotech, Seoul, Korea) at 45 °C overnight to obtain the final moisture content of about 1.5% and then kept in the desiccators.

2.2. Agglomeration process

The agglomeration process of all these milk protein powders was carried out by a top-spray fluid bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Lowa, USA). 50 g of each model powder was fed into the product vessel. As different milk powders have different fluidisation behaviours in the fluidised bed, the appropriate upward flowing air streams from 30 L min^{-1} to 250 L min^{-1} were adjusted for the 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 min 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 immersional 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 s is usually considered easy to wet while powder which takes longer than 120 s 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 cm^2. Wetting time was 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

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.

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 min. 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 & Lee, 2013). A small contact angle ($\theta < 90°$) represents good wettability for the solid, and a large contact angle ($\theta > 90°$) 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 °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 °C ± 2 °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 min intervals as the particles were mixed, until D (50) reached approx.1 μm (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 °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 min, 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 min and then followed by 168 g for a further 10 min. The measurements were performed every 10 s for the first 10 min 36 g centrifugation and then every 60 s for next 10 min 168 g centrifugation.

2.5. Scanning electron microscopy

2 g of standard MPI powder were added to 100 mL distilled water to create the 2% (*w/v*) suspension. Stirring was performed by an overhead mixer (Eurostar 40 digital, IKA, Staufen, Germany) and a 4-bladed stirrer of 50 mm diameter (R 1342, IKA) for different rehydration time at 25 °C (60 min, 90 min and 150 min). One or two drops of each MPI suspension was deposited for 5 min on the silicon substrates, which were rinsed by 100 mM phosphate buffer (pH = 7) in advance. 3% glutaraldehyde solution was used to fix the chemical structures of rehydrated milk protein for 15 min (Mimouni, Deeth, Whittaker, Gidley, & Bhandari, 2010a). After that, distilled water was used to wash the samples to remove the fixing chemicals. The samples were dehydrated by graded ethanol, which were 50%, 70%, 90% and 100% (Dalgleish, Spagnuolo, & Goff, 2004), and then they were further dried in a desiccator with P_2O_5 until they were suitable to be observed by scanning electron microscopy in a vacuum environment (~5 × 10^{-6} mbar). A field emission

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.

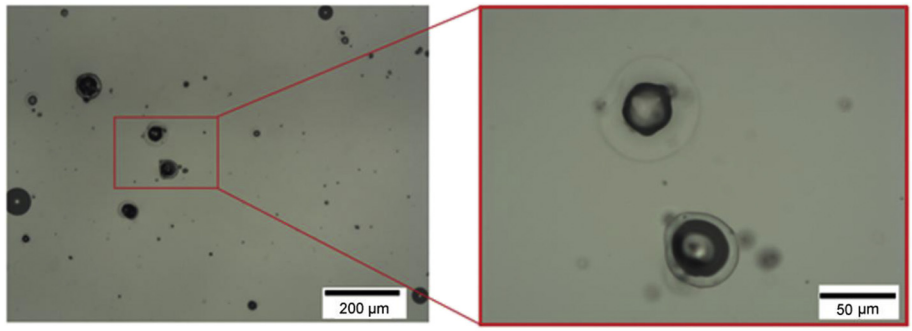

Fig. 1. Optical microscopy images of WPI particles, upon which formed the impermeable hydrophobic layers when wetted by water. The particles were dispersed in water on glass slides. (Left: scale = 200 μm; Right: scale = 50 μm).

scanning electron microscope (Zeiss Supra, Carl Zeiss Microscopy GmbH, Jena, Germany) was used for imaging at 1.5 kV.

3. Results and discussion

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 min. 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 min because water cannot penetrate into these powders spontaneously under the high contact angle ($\theta > 90°$) 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 s, which showed the best wetting behaviours of all powders. However, for MPI powder, the water droplet took a much longer time (280 s) 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 s 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.

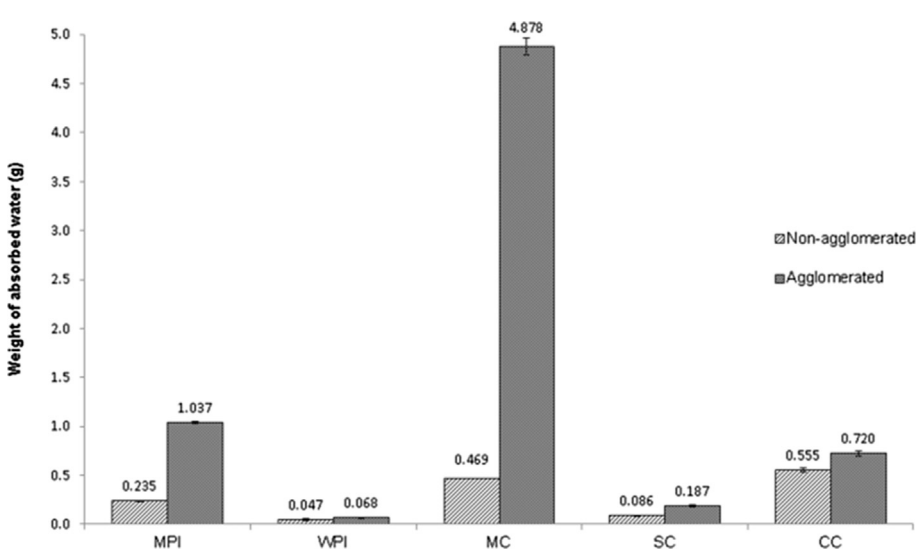

Fig. 2. Weight of adsorbed water for samples (MPI, WPI, MC, SC, CC and their agglomerates) by capillary rise wetting after 10 min.

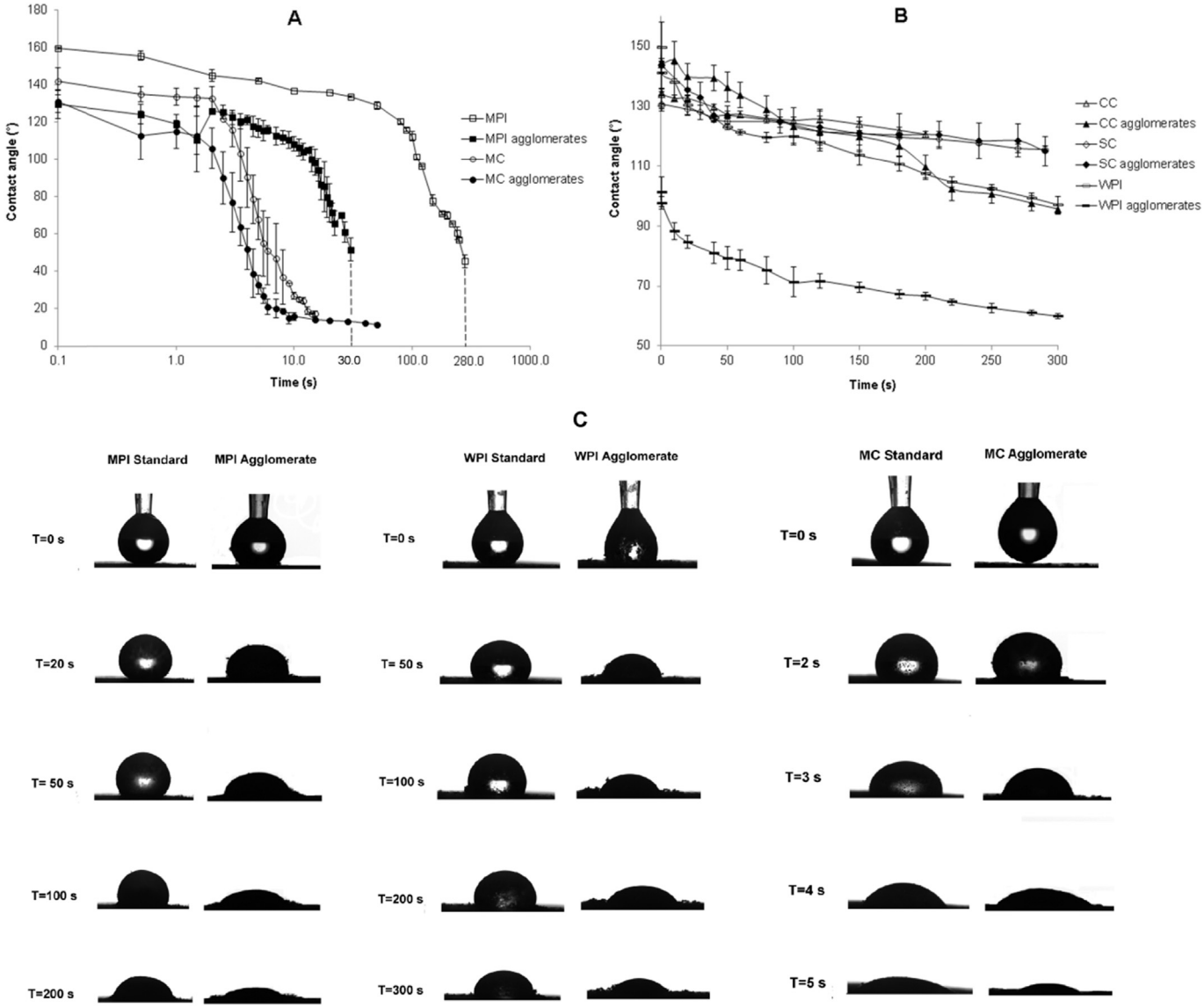

Fig. 3. **A**: The change of contact angle (°) as a function of time for MPI, MC and their agglomerates using the sessile drop technique in approx. 20 °C temperature. **B**: The change of contact angle (°) as a function of time for WPI, SC, CC and their agglomerates. **C**: Images of MPI, WPI and MC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

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 min to reach an equilibrium size while MPI needed 40 min 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 min. In Fig. 4B, SC exhibited very good dispersion behaviour as its particle size decreased dramatically below a size of 1 μm within just 6 min. WPI disappeared very quickly within 2 min, as the machine did not detect any signals of particles after 2 min mixing. (The dissolved WPI are nanoscale, which is out of detecting range.) At the same time, it is interesting to see that the particle sizes 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 min 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

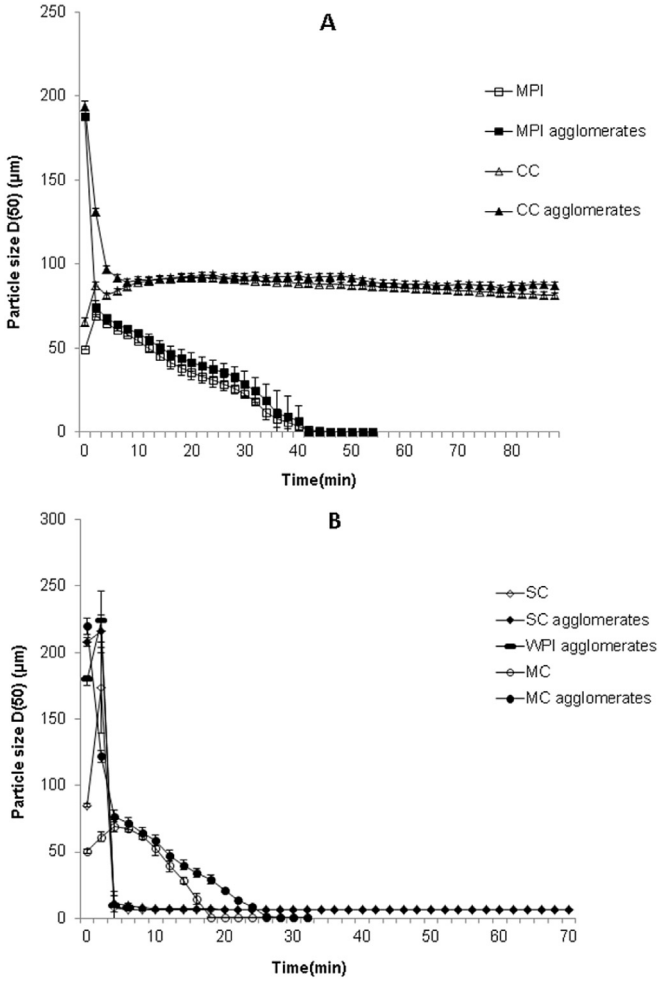

Fig. 4. **A**: Particle size D (50) measurements of dispersed particles of MPI, CC and their agglomerates for every 2 min in 25 ± 2 °C water. **B**: Particle size D (50) measurements of SC, MC and their agglomerates. (WPI quickly dispersed into water and Mastersizer cannot detect its particle size. Even agglomerated WPI can only be measured for the first 4 min).

and about 2.5 mm height under the 168 g centrifugation, after 30 min 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, & Velev, 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 min. The agglomerated MPI also showed an increase of about 0.8 g. The agglomeration process not only largely increased the sizes 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 s 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 s 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 s, 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 & Lee, 2013), Table 2 shows that most of the agglomerated powders still needed longer than 20 min for completely wetting (only agglomerated MPI and MC had significantly shorter wetting times of about 480 s and 320 s, 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

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

		MPI		WPI		MC		SC		CC	
		NA	A	NA	A	NA	A	NA	A	NA	A
Sediment height (mm)	36 g × 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 × 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.

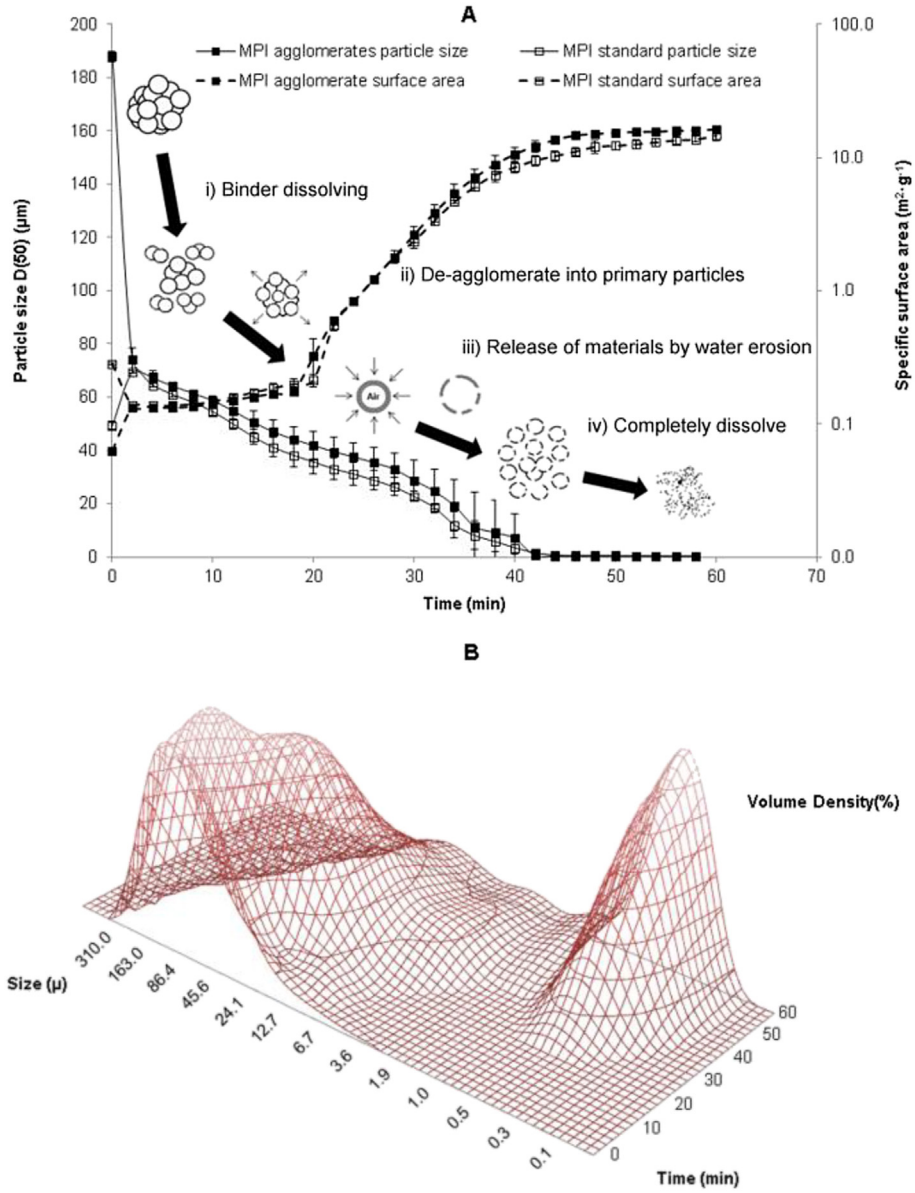

Fig. 5. A: Schematic of MPI and agglomerated MPI particles rehydration in water, based on the change of particle size D (50) and specific surface area as a function of time. **B**: Volume density (%) based size distributions of dispersing MPI particles measured as a function of time. It showed the volume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

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 min 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

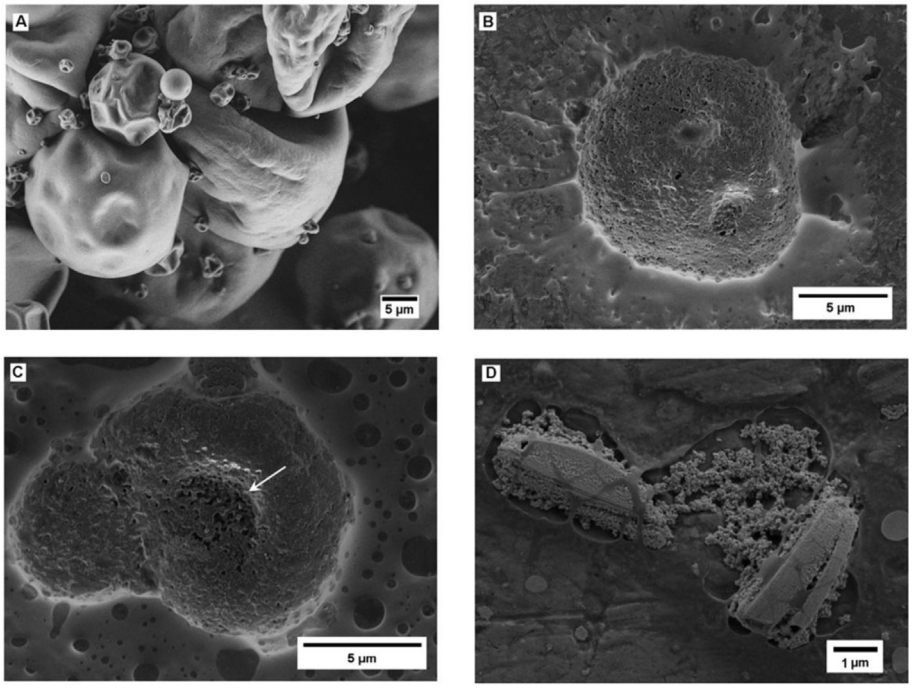

Fig. 6. SEM images of MPI particles after different rehydration time. **A**: spray-dried particles before rehydration (1.4 kV); **B**: particles after 60 min rehydration (1.5 kV); **C**: particles after 90 min rehydration (1.5 kV); **D**: particles after 150 min rehydration (1.5 kV). The white arrow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

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 min but it is followed by dramatic growth for the next 40 min. 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 min 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 non-agglomerated MPI particles with different sizes for the different stirring time. Similarly, the volume of large particles decreased slowly at first 20 min but decreased sharply due to the collapse of the structures. Therefore, the dissolved small particles appeared from 20 min 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 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 non-agglomerated 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.

4. Conclusion

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

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Effects of fluid bed agglomeration on the structure modification and reconstitution behaviour of milk protein isolate powders

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Fluid bed agglomeration
Binders
Wettability
Solubilisation
Morphology
Density

ABSTRACT

The effects of agglomeration on the density, morphology and subsequent reconstitution behaviours of milk powders were investigated. In this study, milk protein isolate, as a model system, was agglomerated in a fluid bed granulator with three different binders: water, lactose and sucrose solution (*15% w/v*). Morphology was quantified by circularity, convexity and elongation. Wettability was measured by the modified Washburn method. Powders solubilisation was quantified by dynamic particle size measurement and the kinetics of dissolved solids concentration in solution. The results showed that granules with water as the binder produced significantly lowest circularity and convexity and highest elongation. An increase in the size of the agglomerated MPI corresponded with an increase in the wettability but a decrease in the ability of solubilisation in water. Granules agglomerated with hydrophilic sugars were found to contribute differently which improved the wettability significantly but no improvement for the kinetics of dissolution.

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1. Introduction

Fluidized bed agglomeration, as one of the most used granulation methods, is a process by which granulated particles are obtained by spraying a binder as solution, suspension, or melt onto a fluidized powder bed (Rajniak et al., 2007a; Turchiuli et al., 2013; Weber et al., 2007). In the food industry, powders are usually required to have good handling properties (dust-free, good flowability and easy to rehydrate). Milk protein isolate powder (MPI), as a widely used dairy ingredient, not only has fine particles and dense structures but is also difficult to rehydrate (Gaiani et al., 2007). The process of fluid bed agglomeration is applied to optimise the physical and structural properties of dairy powers, such as, particle size, densities, porosity, shape (Szulc and Lenart, 2013) and subsequently the reconstitution behaviour (Knight, 2001). Because there is strong interaction between the fluid bed process and the properties of obtained powders (Knight, 2001), controlling the process conditions is a potential way to improve the quality of MPI powders.

The use of binders in fluid bed agglomeration is one of the most frequent methods to modify the structure of agglomerates. They form solid bridges adhering primary particles and create new structures with pores and voids. Therefore, they affect the rate of particles size enlargement, densities and morphology of the granules (Keningley et al., 1997; Mills et al., 2000). However, different binders have different bonding efficiency due to varied chemical compositions, mechanical properties, concentration, viscosity and inter-particular interactions between the particles and the binders. For example, sucrose or glucose usually produces hard and brittle bridges while gelatin and acacia gum provide slow disintegration and high hardness to the agglomerates (Barbosa-Cánovas and Juliano, 2005). In food systems, aqueous solutions of lactose and sucrose are the most used binders in fluid bed agglomeration. Thus, the relationship between types of binders and agglomerates structural properties needs to be clearly identified. Although some pharmaceutical research related to agglomerate behaviour in fluidized beds has been published (Abberger et al., 2002; Chua et al., 2011; Parveen et al., 2013; Rajniak et al., 2007b; Seo et al., 2002), less attention has been given to milk powder systems, especially high protein-based powders which also present great potential for improvement to the quality of dairy powder structures.

The reconstitution ability of milk protein powders is an essential attribute as most of them are dissolved before use. It is commonly believed that the whole reconstitution process mainly consists of three sequential stages which are wetting, dispersing and dissolving phases (Forny et al., 2011; Gaiani et al., 2007; Hogekamp and Schubert, 2003; Richard et al., 2012). Each stage is affected by the

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different physical properties. Generally, wettability depends on large particles with large pores in between and also small contact angles (Hogekamp and Schubert, 2003); dispersibility is influenced by particle size, porosity and density (Goalard et al., 2006); dissolution is favoured by the presence of small hydrophilic molecules on the surface (Lillford and Fryer, 1998). Using sugar solutions as binders in agglomeration modifies the powders' structure and surface composition and influences the interaction with water. Consequently, the performances of different binders on the reconstitution ability should be investigated. Furthermore, as the reconstitution process is dynamic and powders with high protein content have relatively poor wettability and dispersibility (Gaiani et al., 2007; Richard et al., 2012), it is impossible to quantify the total process according to traditional standard methods. Moreover, different reconstitution stages often overlap (Fang et al., 2007) and it is a challenge to observe each stage independently, particularly dispersing and dissolving stages. Hence new methods were developed to better quantify the reconstitution ability of powders in this study. For example, the modified Washburn method, as a dynamic wettability measurement, was found to describe the ability of the powder particles to overcome the surface tension between themselves and the liquid (Depalo and Santomaso, 2013). Meanwhile, particle size measurement by static light scattering was used to monitor the solubilisation (both dispersing and dissolving) of powders during rehydration process (Richard et al., 2012). Final solubility was expressed as the kinetics of dissolved solids concentration (w/w%) in water.

The overall aim of this study was to acquire a better understanding of the influence of fluid bed agglomeration of milk protein isolate (MPI) powder, using three different binders and two agglomerate size fractions, on improving the reconstitution ability of MPI. Within this study, the influence of the three binders on the physical properties of the agglomerates, including powder densities, porosity and morphology, was also investigated.

2. Materials and methods

2.1. Materials

Milk protein isolate (MPI) was supplied by Kerry Ingredients (County Kerry, Ireland). The composition of MPI is 86% protein, 1.5% fat, 6% ash and <1% carbohydrate. The binding liquids used in the fluid bed agglomeration were: distilled water; aqueous solutions of lactose, 15% w/v (Arla Food Ingredients, Viby J, Aarhus, Demark) and aqueous solutions of sucrose, 15% w/v (Sigma Aldrich, USA).

2.2. Fluid bed agglomeration

A top-spray fluidised bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Lowa, USA) was used to carry out the agglomeration of MPI. 200 g MPI powder was fed into the bottom of product vessel and fluidised by upward flowing air stream. The temperature of injected air was 50 °C and the air flow rate was 200 L min^{-1}. 100 g binding liquid was injected from the top of vessel by a peristaltic pump (1 mL min^{-1}) and sprayed into small droplets by a two-fluid spray nozzle. The air pressure on the nozzle was 1 bar. When the binding solution had been used up, the product was dried for 15 min at 50 °C and the air flow was reduced to 100 L min^{-1}.

2.3. Powder characterisation

Three different samples were obtained based on three different binders in the fluid bed granulation (A_1: Water binding, A_2: Lactose solution binding, and A_3: Sucrose solution binding). The 106 μm, 180 μm and 300 μm level sieves (Endecotts, London, UK) were used to obtain two different agglomerate size fractions (P_1: 106 μm ~ 180 μm and P_2:180 μm ~ 300 μm). Including unagglomerated MPI standard powder (MSP), a total of 7 powders (MSP, A_1P_1, A_1P_2, A_2P_1, A_2P_2, A_3P_1, and A_3P_2) were investigated in this study. The obtained samples were dried overnight in the vacuum oven (Jeiotech, Seoul, Korea) at 60 °C temperature and then kept in the desiccator to cool down into room temperature.

2.4. Density and porosity

Loose and tapped bulk densities were measured using a graduated cylinder and a tapped machine (Funke Gerber, Berlin, Germany). The volume occupied by a given mass of powder (50 g) after 100 taps was measured three times to calculate the tapped bulk density. Gas Pycnometer (AccuPyc II 1340, Micromeritics Instrument Corporation, Georgia, USA) was used to measure the apparent density of samples, which were placed in the sample cell and purging with a flow of helium to degas the cell by ten pressurisation cycles. Furthermore, porosity (ε) was calculated using tapped bulk density ρ_T and apparent density ρ_A. The relation shows as Eq. (1):

$$\varepsilon = (\rho_A - \rho_T)/\rho_T \times 100 \quad (1)$$

2.5. Particle shape

The shape properties were described by Malvern Morphology G3 (Malvern Instruments Ltd, Worcestershire, UK). 15 mm^3 volume samples were placed in the dispersion unit to be dispersed into single layer on the glass plate so that they can be observed by the microscope. Generally, three parameters were used to quantify and indicate the shape properties of powders (Fig. 1). Firstly, the circularity value between 0 and 1 was defined as the ratio of the perimeter of the surface equivalent disc (P_e) to the real perimeter of the particle silhouette (P_r). The bigger value means the more alike to the equivalent circle. Secondly, the convexity describes the compactness of a particle. The maximum theoretical convexity is 1 that means the surface of particle is very smooth. Finally, elongation stands for aspect ratio of particles and a needle shape has a high value which is close to 1. These indicators were usually expressed as average value for bulk population distribution. Each sample was measured five times to obtain the average value.

2.6. Reconstitution properties

2.6.1. Wettability

Dynamic wettability measurement was based on the Washburn method (Washburn, 1921) which applied the capillary force to wet the powder (Fig. 2). In this study, 2 g samples were added into a glass tube without bottom (powder holder), and covered by filter paper and a piece of gauze at the bottom of the tube to prevent the powders falling down. Then the tube was fixed just above the distilled water (24 °C) surface. After 10 min, an analytical balance was used to measure the additional mass of wetted powder. Each sample was measured five times.

2.6.2. Solubilisation

Due to it is difficult to observe the dispersing and dissolving phases independently, solubilisation ability of the powders, including dispersibility and dissolution, was expressed as the reduction rate of particle size in dispersant based on granule erosion and break-up (Chen and Lloyd, 1994; Goalard et al., 2006; Richard et al., 2012). An optical fibre sensor (Fig. 3) (Galet et al., 2004; Larsen et al., 2003), which collected the light backscattering of

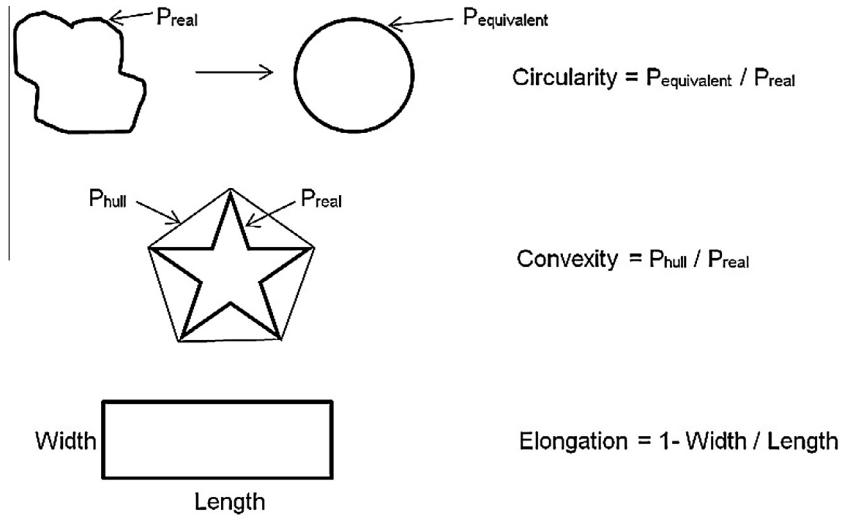

Fig. 1. Definition of the shapes factors: circularity, convexity and elongation measured by Malvern Morphology G3.

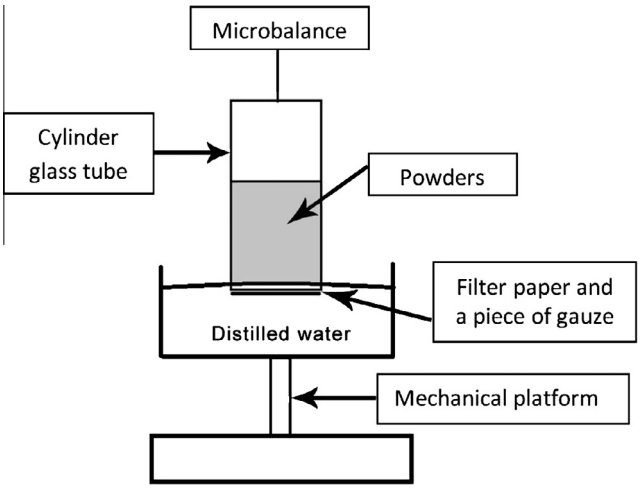

Fig. 2. Scheme of modified Washburn method to quantify the wettability of MPI powders by measuring the weight of adsorbed water (24 °C) in 2 g powders after 10 min.

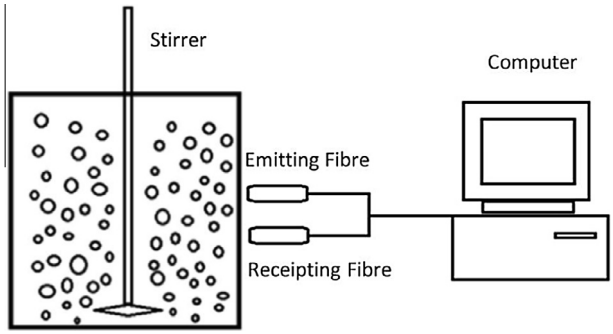

Fig. 3. Scheme of Light scattering method to quantify the solubilise ability of MPI powders to monitor the particle size of dispersed particles every 2 min in 25 ± 2 °C water at mixing condition of 2000 rpm.

the particles, was used to determine the kinetics of solubilisation and reflect the quality of powder's reconstitution behaviour. Another used method to quantify the solubility of powder was the measurement of the concentration of dissolved powder (w/w%) in distilled water by time under the stirring.

2.6.2.1. Particle size measurement of dispersed particles. Particle size measurement of dispersed particles was measured by laser light scattering using Malvern Masterszier 3000 (Malvern Instruments Ltd, Worcestershire, UK) equipped with a 4 mW He–Ne laser operating at a wavelength of 632.8 nm. Samples were diluted into 120 ml dispersion unit with distilled water to reach obscuration of 8%. Refractive indexes for solvent, particle and adsorption were set as 1.33, 1.45 and 0.01, respectively. In this study, in order to be within the ideal obscuration range of machine, a constant mass of samples (approximate 5 mg) were introduced into dispersion unit with 2000 rpm agitation and 25 °C ± 2 °C temperature range. The solid in liquid concentration was set at 0.004%. During the triplicate measurements, samples were detected every 2 min until D (50) reached ~1 μm (the diameter of 50% particles was just lower than 1 μm). The average results were used to monitor the particle size reduction as powders dispersed and dissolved.

2.6.2.2. Dissolved solids measurement. For dissolved powder concentration measurement, samples weighing 1 g were added into 50 ml water in the beakers and slightly mixed by a spoon to make the powders wet completely and sink below the surface of water. Then samples were placed in 24 °C water bath and stirred by 3-pitched-blade impellers (impeller diameter: 4 cm) at a rate of 300 rpm for different mixing time (30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min, 240 min). After that, the suspensions were put into 50 ml centrifuge tubes and centrifuged at 3000 g and 24 °C for 10 min (Eppendorf Centrifuge 5810R, Hamburg, Germany). 2 ml supernatant was taken and analysed by solid analyser machine (Smart System 5, CEM, North Carolina, USA), to evaluate the concentration of solids (w/w%) in the solution. All the results were repeated three times.

2.7. Statistical analysis

Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was carried out by SPSS software (PASW, Statistics 1.8). It was used to perform statistical differences 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. Influence of binders on physical properties of agglomerates

3.1.1. Density and porosity

Bulk density is defined as the mass of powders divided by the total volume occupied by them. The total volume includes particle volume, inter-particle void volume, and internal pore volume. Tapped density corresponds to the occupied volume after packing by tapping the container, which means voids between particles are reduced (Turchiuli and Castillo-Castaneda, 2009). It is commonly believed that agglomeration creates granules with lower bulk density due to the formation of voids structures (Kowalska and Lenart, 2005; Szulc and Lenart, 2010). Same trends were observed in Table 1, where loose and tapped bulk density of unagglomerated MPI powders were 0.298 g/cm^3 and 0.356 g/cm^3 respectively, which were significantly ($p < 0.05$) higher than those of agglomerated MPI powders. Furthermore, if compared with the bulk densities of six agglomerated samples, an increase in the size of the agglomerate was found to correspond to a decrease of bulk density. But the different binders appeared to have no particular effect on bulk loose and tapped densities for both particle size fractions. The loose bulk densities of samples were all about 0.21 g/cm^3 and 0.18 g/cm^3 for small and large size fractions respectively. And the tapped bulk densities were about 0.26 g/cm^3 and 0.20 g/cm^3 respectively. For apparent density, the agglomerates formed by distilled water were similar to that of MSP while those formed by lactose and sucrose had lower apparent densities, which were lower than 1.3 g/cm^3. Similar results were shown by Szulc and Lenart (2013), where values of apparent density were influenced by the type of binder liquid and the composition of samples. Besides that, Jinapong et al. (2008) also reported that agglomerated soymilk powders resulted in the lower apparent density than the standard unagglomerated ones.

Porosity is defined as the ratio of void volume to total volume of the powder and void volume is the difference between the total volume and particles volume (Turchiuli and Castillo-Castaneda, 2009). Thus, porosity is largely dependent on the measurement of total and particles volumes. Generally, an increase in porosity of the agglomerated powders was observed in comparison with the primary ones (Werner et al., 2007). In this study, the porosity values of MPI samples showed in Table 1 can reach around 80% based on the low bulk density. Agglomerated skim milk powders (Hogekamp and Pohl, 2003) and agglomerated soymilk powders (Jinapong et al., 2008) were also reported the similar porosity values. As the same trends to bulk density, agglomerated MPI samples also had significantly higher porosity than unagglomerated ones and larger particle size corresponded to higher porosity. Meanwhile, there was no big difference among the agglomerates with different binders in the same particle size fraction.

3.1.2. Morphology

The effect of the binders in fluid bed agglomeration on the morphological properties of powders was also investigated. Three morphological descriptors (Circularity, Convexity, and Elongation) followed by Malvern Morphology G3 identified the bulk shape properties. Examining Table 2, compared to the unagglomerated MPI powders, it is clear to find that agglomerated granules had significantly ($p < 0.05$) lower circularity and convexity but higher elongation, which means the particles had less rounded shape, rougher surface and lower ratio of width/length. As it is seen in Fig. 4, more irregular shapes were observed in agglomerates with larger particle size. It is due to initial primary particles (Fig. 4A) rapidly aggregated into intermediate structures to create small agglomerates (Fig. 4B) and then progressively grew to the big porous agglomerates (Fig. 4C). Thus, the shape factors of particles were significantly changed. If focusing on the effect of different binders, water binding agglomerates had least similarity of a circle and most surface area among the three for both small and large particle size fractions. Even for the sugars binders, there still was significant difference between them in convexity and elongation. It is not surprised to the results because the higher binder liquid concentration resulted in the high compactness of agglomerates (Szulc and Lenart, 2013). Thicker bridges or layers were formed on the surface of agglomerates obtained by higher binder concentrations. Same tendency was found in soymilk powders (Dacanal and Menegalli, 2010; Jinapong et al., 2008) and also in other agglomerated spray-dried powders (Fuchs et al., 2006; Turchiuli et al., 2005). However, morphology of agglomerates is very difficult to predict because it also depends on the droplet deposition, droplet spreading, bridge breakage and the amount and the way that binders are introduced (Werner et al., 2007).

3.2. Influence of binders and agglomerate size on reconstitution behaviour

3.2.1. Wettability

Wettability is the ability of the powder particles to imbibe a liquid and overcome the surface tension between them based on capillary force. Generally, the GEA Niro method is used to measure the

Table 1
Bulk density, apparent density and porosity of powders.[a]

Samples	MSP	A_1P_1	A_1P_2	A_2P_1	A_2P_2	A_3P_1	A_3P_2
Particle size D(50) (μm)	49.4 ± 0.2^a	106.2 ± 0.5^b	199.0 ± 1.2^c	102.5 ± 0.3^d	188.7 ± 1.0^e	103.4 ± 0.3^f	191.2 ± 1.4^e
Bulk Loose density (g/cm^3)	0.298 ± 0.007^a	0.206 ± 0.009^b	0.184 ± 0.006^c	0.221 ± 0.006^b	0.179 ± 0.005^c	0.215 ± 0.007^b	0.181 ± 0.004^c
Bulk Tapped density (g/cm^3)	0.356 ± 0.001^a	0.262 ± 0.000^b	0.198 ± 0.000^c	0.265 ± 0.001^b	0.199 ± 0.000^c	0.252 ± 0.001^d	0.207 ± 0.000^e
Apparent density (g/cm^3)	1.311 ± 0.004^{ab}	1.335 ± 0.020^a	1.302 ± 0.016^{bc}	1.282 ± 0.024^{bc}	1.278 ± 0.003^{cd}	1.254 ± 0.035^{de}	1.246 ± 0.027^e
Porosity (%)	72.85 ± 0.12^a	80.37 ± 0.30^b	84.79 ± 0.23^c	79.33 ± 0.32^d	84.43 ± 0.10^c	79.90 ± 0.41^{bd}	83.39 ± 0.34^e

[a] 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.[a]

Powder morphology	MSP	A_1P_1	A_1P_2	A_2P_1	A_2P_2	A_3P_1	A_3P_2
Circularity	0.826 ± 0.015^a	0.642 ± 0.006^b	0.592 ± 0.014^c	0.669 ± 0.008^{de}	0.630 ± 0.015^{bc}	0.688 ± 0.004^d	0.668 ± 0.002^e
Convexity	0.937 ± 0.008^a	0.796 ± 0.005^b	0.728 ± 0.010^c	0.814 ± 0.005^d	0.761 ± 0.017^e	0.829 ± 0.005^f	0.789 ± 0.007^b
Elongation	0.262 ± 0.010^a	0.317 ± 0.004^b	0.293 ± 0.003^c	0.301 ± 0.001^d	0.266 ± 0.001^a	0.309 ± 0.001^e	0.281 ± 0.005^f

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

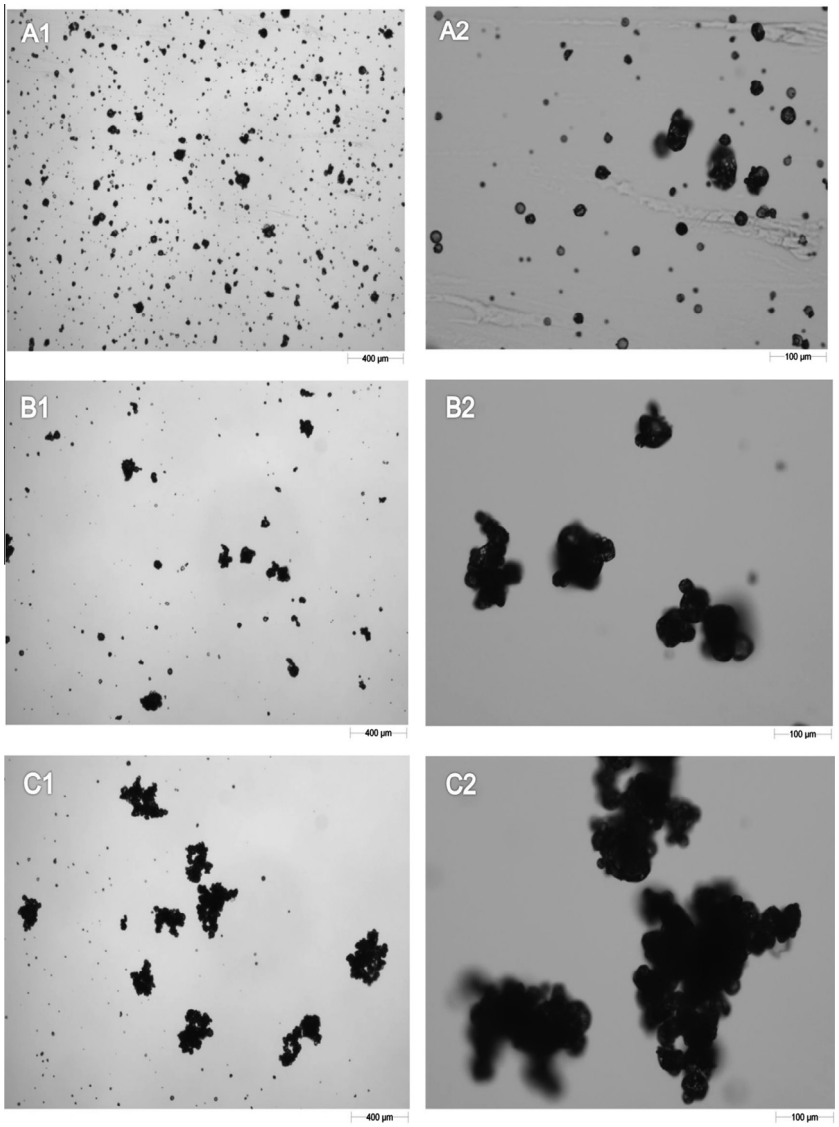

Fig. 4. Comparison of images obtained by Malvern Morphology G3. (×25, scale = 400 µm; ×100, scale = 100 µm) (A1 & A2: MPI standard powders; B1 & B2: small size fractions of agglomerates binding with water; C1 & C2: large size fraction of agglomerates binding with water.).

wettability of "easy-wet" powders. However, for some powders with poor wetting ability, such as high protein powders in this study, it can be determined by the additional weight of powder after absorbing liquid in a specified time.

Wettability results are illustrated in Fig. 5 for MSP and the six agglomerated powders. Agglomeration had a major improvement on the wettability of MPI, as the agglomerated powders absorbed significantly more water than that of MSP in 10 min. A major reason for this improvement was due to the increase in particle size, as presented in Table 1. Good wettability was generally favoured by the presence of large particles, resulting in larger voids between the particles which allowed water to penetrate more easily into the powders (Freudig et al., 1999; Hogekamp and Pohl, 2003). And also for each binder, the larger particle size fraction produced the highest wettability.

Fig. 5 also shows that binder type has an influence on wettability. The 15% lactose solution binder had the best wettability for both size fractions. For the smaller size fraction, the 15% sucrose solution binder was slightly better than the distilled water but worse for the larger size fraction. It is because the influence of binder composition on wettability is complex. The chemical nature of

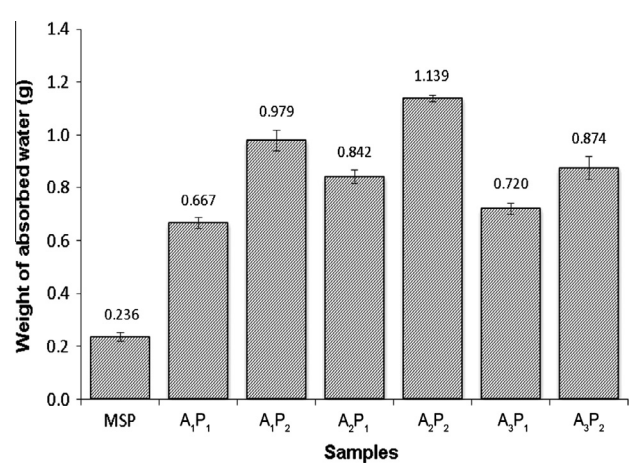

Fig. 5. Mean weight of absorbed water for samples (MSP, A_1P_1, A_1P_2, A_2P_1, A_2P_2, A_3P_1 and A_3P_2) after 10 min.

composition plays an important role, e.g. hydrophilic and hydrophobic nature (Fang et al., 2007; Freudig et al., 1999). Powders agglomerated with lactose and sucrose solution contain hydrophilic carbohydrates that results in the development of more hydrophilic bridge surfaces that make powder wetting by water more easy. The binder composition will also influence the morphology of agglomerates produced, as seen in Table 2, and this in turn will influence how water penetrates into the powder.

It is commonly believed that particles with rounder and rougher surfaces lead to higher wettability whereas smoother and elongated powders have lower wettability (Gaiani et al., 2011; Perea et al., 2009; Yekeler et al., 2004). This is due to the lower roundness and higher elongation which result in a higher wetting angle than equivalent round particles; longer contact lines also cause stronger adhesion force of prismatic particles (Oliver et al., 1977). Comparing the hydrophilic lactose and sucrose binders, samples agglomerated with lactose showed rounder (lower elongation) and rougher (lower convexity) which may in part explain the better wettability. However, due to a complex influence on wetting behaviour, the precise explanation of the effect of morphology is still unknown and needs further study in the future.

3.2.2. Solubilisation

3.2.2.1. Particle size measurement of dispersed particles. This approach measured the evolution of particle size of wetted particles over time (as described in materials and methods). Figs. 6ABC illustrate the influence of initial particle size on the solubilisation of particles over time (as illustrated by the decrease in D(90), D(50) and D(10) size values). Figs. 6ABC show an initial rapid decrease in particle size of the larger sized agglomerates. This is due to water easily penetrating into the agglomerate pore network, solubilising the solid bridges between the primary MPI particles and releasing them into solution. After this initial period of about 4 min, the particles attained a similar size, independent of initial agglomerated size fraction. This provides further evidence that the agglomerates have been broken down into their primary MPI particles.

This initial time period was followed by much slower solubilisation and it took around 60 min for the particles to mostly

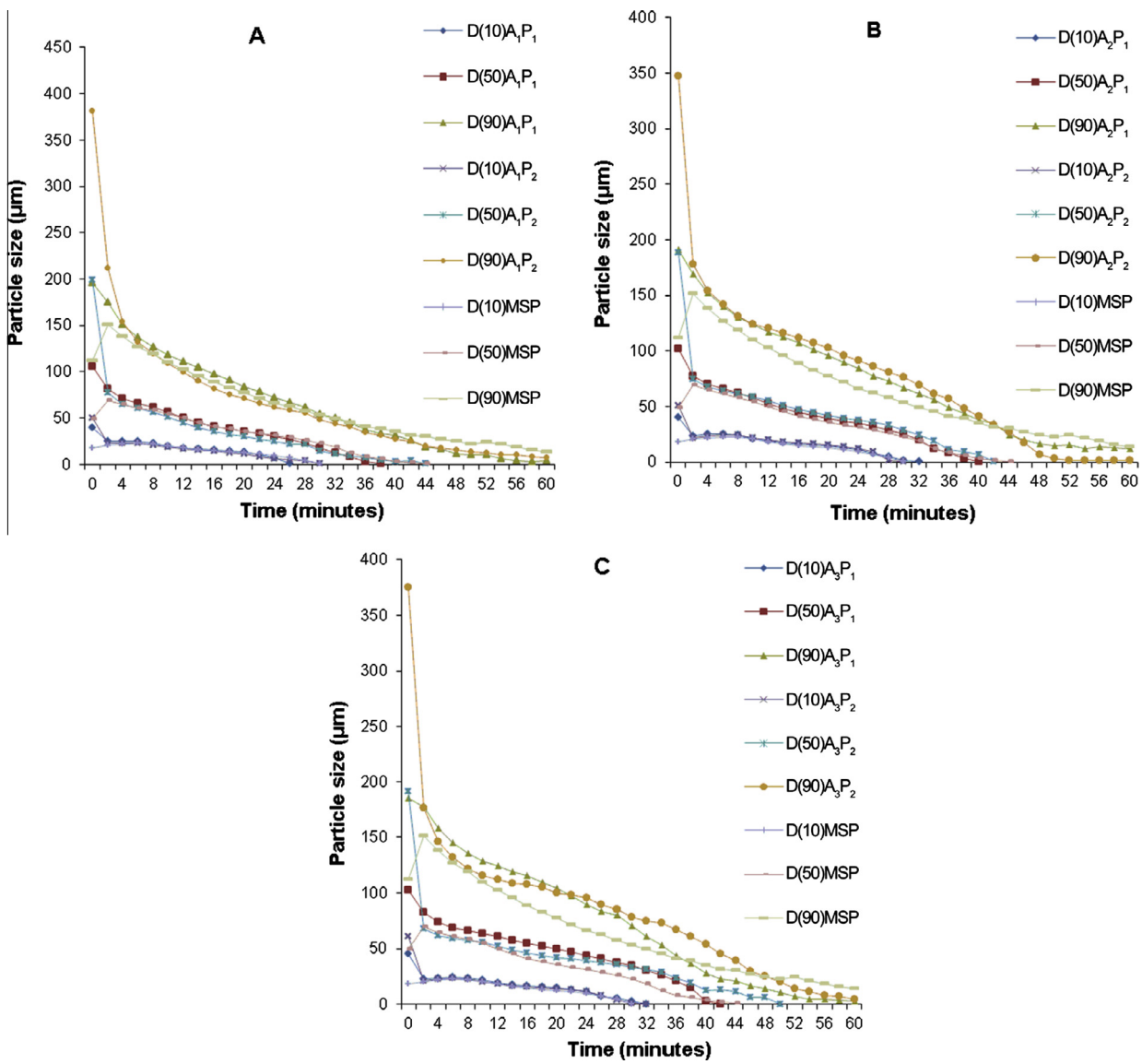

Fig. 6. Particle size measurement of dispersed particles versus time (every 2 min) in 25 ± 2 °C water at mixing condition of 2000 rpm (A = water binding agglomerates and MSP; B = lactose solution binding agglomerates and MSP; C = sucrose solution binding agglomerates and MSP.).

solubilise, as evidenced by the D90 values approaching zero. Figs. 6ABC show that agglomeration with any of the binders had no significant beneficial impact on the solubilisation rate of MPI. This appears to be due to the solubilisation rate being controlled by the solubilisation of the primary MPI particles (Mimouni et al., 2009). This suggests that the primary MPI particles solubilise very slowly, possibly due to strong attractions between casein micelles within the powder. In fact, it may marginally increase the solubilisation time, because a few minutes may be required to break down the agglomerates into MPI primary particles. In addition, there also appears to be some differences based on the type of binder used, however it is not of major significance. Overall, the solubilisation of the MPI powder was insensitive to agglomeration and the choice of binders.

In Figs. 6ABC, it is interesting to see that the particle sizes of MSP increased over the first 4 min. This is because particles usually sorb water following the wetting stage and this behaviour is called swelling. Same phenomenon was founded in others' papers (Gaiani et al., 2009, 2007; Goalard et al., 2006). On the other hand, Figs. 6ABC do not show swelling with the agglomerates as they had much shorter swelling time due to their quicker penetration by water (Gaiani et al., 2009). Furthermore, swelling of agglomerates and primary particles occurred when the agglomerates were disintegrating, so any increase in size due to swelling was counteracted by the large reduction in agglomerate size.

3.2.2.2. Dissolved solids measurement. Solubilisation is also expressed as the amount of solids that are dissolved into solution over time. As with Figs. 6ABC, Fig. 7 shows that agglomeration did not have a significant beneficial impact on the solubilisation rate of MPI. In fact, agglomerate solubilisation was slower than that of MSP when using distilled water as a binder. This is in agreement with the work by Schuck et al. (2007) and Gaiani et al. (2007). They found that granulation increased the solubilisation time of native phosphocasein powders. This is due to casein micelles interacting strongly within the primary particles and developing attractions that are difficult to break down (McKenna, 2000). Thus, water takes a long time to solubilise the powder particles and results in the slow solubilisation rate. In relation to agglomeration, water has to first penetrate into the agglomerates to release the primary MPI particles and this takes some additional time. Agglomerates formed by lactose and sucrose binders showed a somewhat similar progression to MSP, with similar dissolved solids concentrations above 200 min. The presence of lactose and sucrose on the surface of protein particles is believed to inhibit the interaction between casein micelles because they are more hydrophilic. Consequently, MPI powders agglomerated with lactose and sucrose solution are comparatively more easily dissolved into water than that agglomerated with water, as evidenced in Fig. 7.

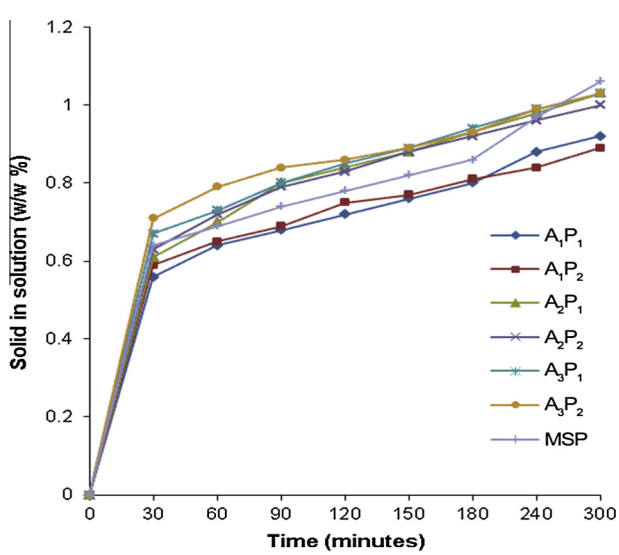

Fig. 7. Solubilisation as measured by dissolved solids concentration (w/w%) versus time (every 30 min) after 10 min 3000 g centrifugation.

It is interesting to observe that there is a big increase in dissolved solids content of the MSP and agglomerates over the initial 30 min where it increased form 0% to around 0.6%, whereas for the following 300 min, solids concentration continued to reach only 1%. This is most likely due to mass transfer considerations where at the beginning, the concentration gradient between particle surface and water is greatest and the particle size, surface area and influence of turbulence are greatest. Meanwhile, the results in Fig. 7 showed that it took 300 min to reach 1% solids concentration, which represented about 50% of the initial mass of particles added. But in Figs. 6ABC the dissolution took about 60 min to totally dissolve the particles as the D90 value were nearly at zero. The huge difference is due to the different agitation speeds which it is commonly believed to significantly influence the rehydration time (Richard et al., 2012; Schober and Fitzpatrick, 2005). This may be a potential factor that can improve the reconstitution properties of MPI powders.

4. Conclusion

In summary, fluid bed agglomeration with different binding liquids was found to modify the structures and physical properties of MPI powders. Agglomeration significantly decreased the bulk density; increased the porosity of powders; and formed particles with lower circularity and convexity but higher elongation values. The type of binder also influenced the shape factors of agglomerates. Using water as binder created more irregular particles than using the other two sugar binders.

Both the agglomerate size and the binder type had significant influences on the improvement in wettability. Overall, the larger agglomerate size fraction produced with the lactose binder provided the best wettability. In relation to solubilisation of the wetted particles, agglomeration had no beneficial effect with any of the binders used. This low rate of solubilisation is because it is controlled by the solubilisation of the primary MPI particles, which appears to be very slow due to the strong interaction between casein micelles in the primary particles. Consequently, it would be interesting to explore how the size of these primary particles influences the rehydration behaviour and if this could be manipulated to greatly improve the solubilisation rate in particular.

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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 larges 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, 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 solution was added into the bowl by droplets at the dosing speed of 4 mL 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 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, Lowa, USA), which provided the air with a temperature of 50 °C and the flow velocity of 200 L min^{-1}, 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 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 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 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 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) (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	425 μm – 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	180 μm – 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	106 μm – 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 $P < 0.05$.

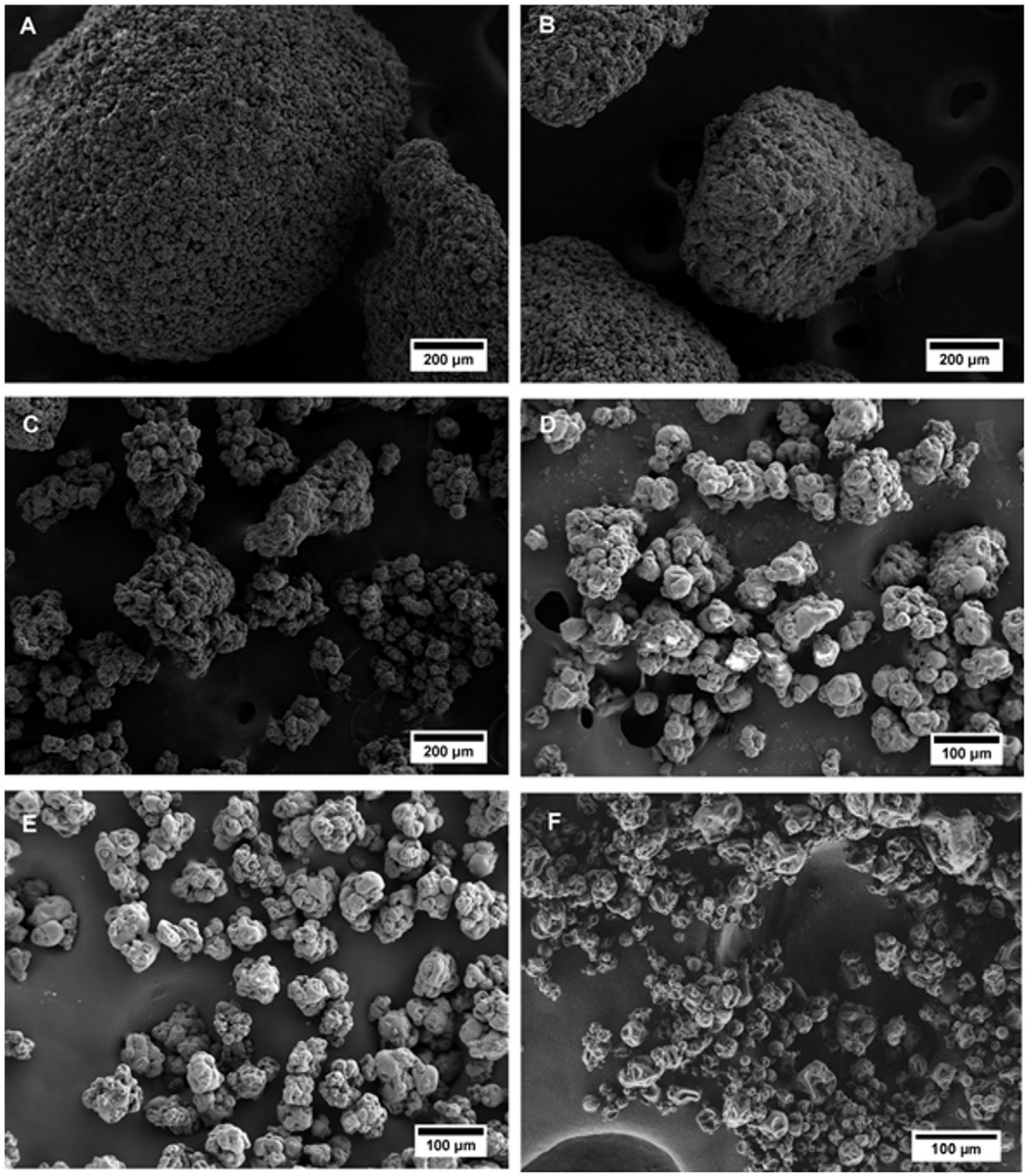

Fig. 1. SEM images of MPI granules with different particle sizes by granule growth processes. (**A**: S1; **B**: S2; **C**: S3; **D**: S4; **E**: S5; **F**: standard MPI).

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 μm, 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).

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 $P < 0.05$.

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):

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

where l is the penetration depth of the liquid, η is liquid viscosity, γ is the liquid surface tension, r is radius of pores, θ 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 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 with a 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 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 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

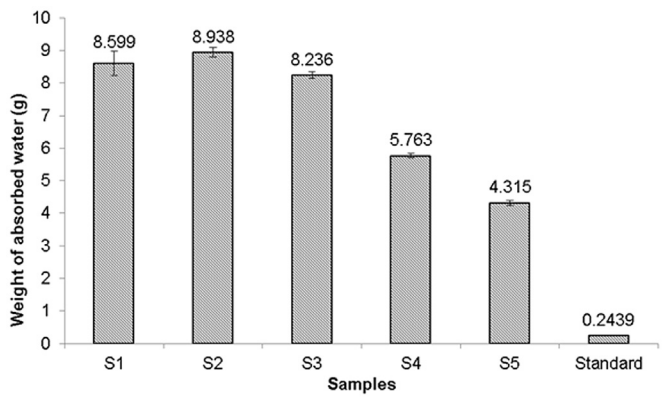

Fig. 2. Mean weight of absorbed water for samples (the agglomerated MPI granules S1, S2, S3, S4, S5 and standard MPI) after 10 min.

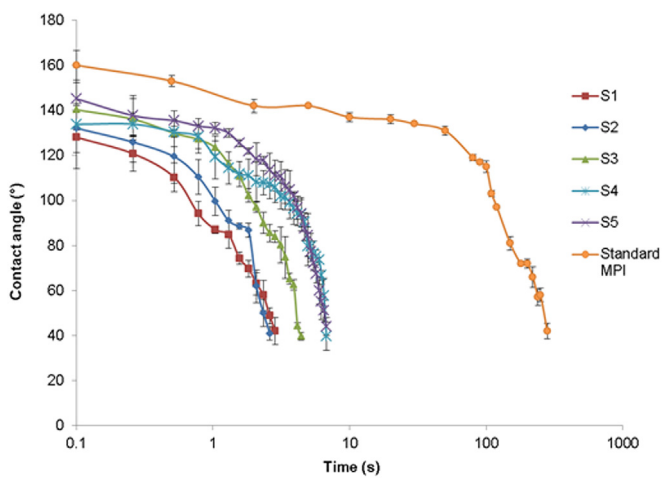

Fig. 3. The change of contact angle (°) as a function of time using the sessile drop technique in approx.20 °C temperature.

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

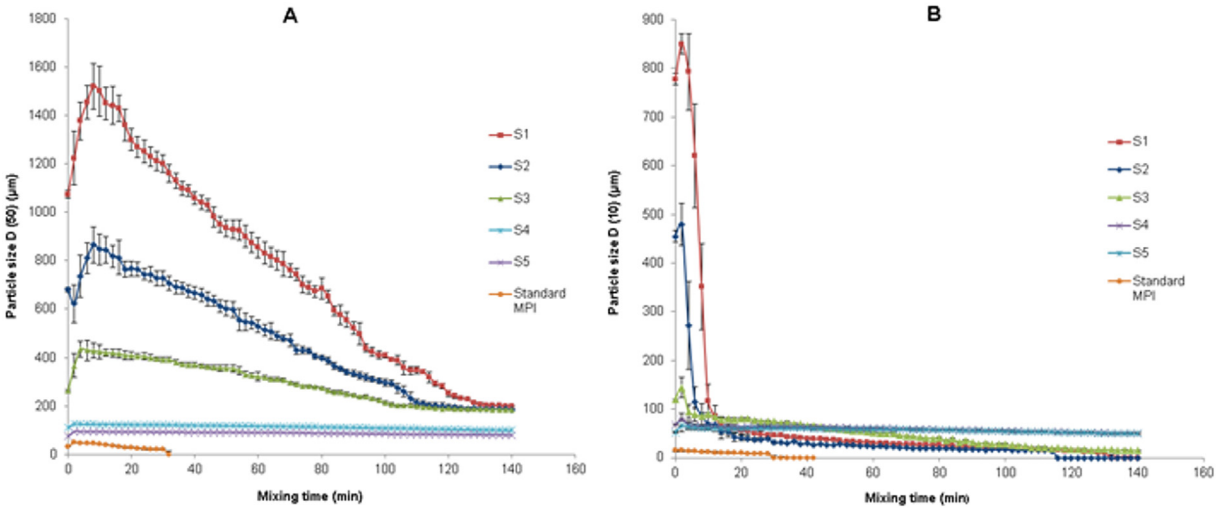

Fig. 4. Particle size measurements of dispersed particles of the agglomerated granules S1, S2, S3, S4, S5 and standard MPI, as a function of mixing time (every 2 min) **A**: D (50); **B**: D (10).

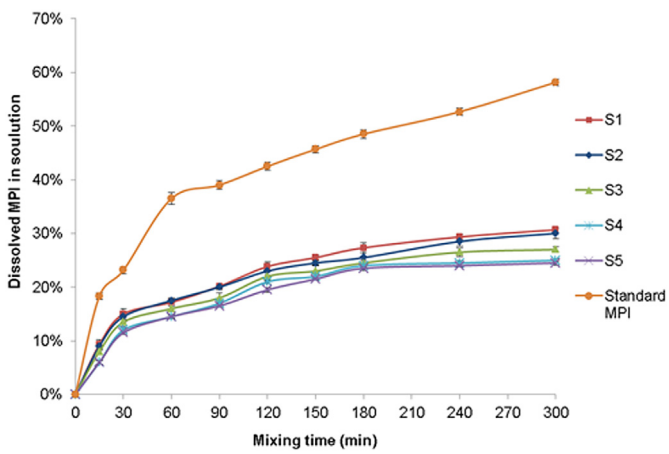

Fig. 5. Solubilisation as measured by dissolved MPI percentage (%) versus different mixing time.

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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The effects of fluidised bed and high shear mixer granulation processes on water adsorption and flow properties of milk protein isolate powder

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ABSTRACT

The effects of fluidised bed (FB) and high shear mixer (HS) granulation processes on water adsorption and flow properties of milk protein isolate powder (MPI) were investigated and compared. The agglomerated granules were characterised by different size fractions. It was found that granules produced from the HS process adsorbed less moisture, with slower adsorption kinetics, compared to those produced from using the FB. Granulation reduced the cohesiveness of the MPI powder, with HS having a significant greater impact due to the formation of the particles with higher bulk density and larger size. Particle size played a critical role that influenced water adsorption and flowability. Granulation processes contributed to different degrees to reducing the minimum outlet diameters of hoppers based on either mass-flow or core-flow discharges. HS granules had large wall friction angles, suggesting a need for steeper hopper walls for effective discharge.

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1. Introduction

Milk protein concentrates, manufactured from ultrafiltered skim milk, are widely used in nutritional beverages, sports nutrition bars and other dairy based products due to their high nutritional values. These powders provide a supply of milk solids in a stable and convenient form, especially for preservation and transportation (Ann Augustin and Clarke, 2011; Selomulya et al., 2013). However, milk protein based powders usually have fine particle size and dense structures, causing poor flow behaviour during conveying (Crowley et al., 2014; Ilari, 2002) and susceptibility to moisture adsorption during storage (Foster et al., 2005; Kinsella and Fox, 1986). Granulation is a size enlargement process that results in the formation of large granules with modified physical structures. Thus, it can be used as a potential process to improve the flow behaviour of bulk solids and influence the water adsorption behaviour (Szulc and Lenart, 2010, 2012).

Fluidised bed and high shear mixer agglomeration are the most widely used wet granulation processes (Jacob, 2007). Due to the different mechanisms of granule growth, the use of binders and intensity of solidification, the granules produced by these two processes have the completely different structures (Barrera-Medrano et al., 2007; Litster and Ennis, 2013). Generally, using a fluidised bed, binding liquids are atomized and converted into free-flowing solids, which then coalesce and agglomerate together by creating bonds between primary particles (Cuq et al., 2013). Granules, thus formed, without mechanical consolidation, usually have more irregular shape and high porosity, including large interstitial space and also internal pores inside single granules (Ji et al., 2015). In comparison, a high shear mixer granulation process provides strong agitation forces through an impeller with compacts particles so that the created granules are highly-packed, increasing bulk density and reducing porosity (Ji et al., 2016a; Reynolds et al., 2006). Furthermore, even granule growth processes during the granulation process are also believed to influence physical characteristics (Hapgood et al., 2007). Generally, wetting and nucleation, as the first step of granulation, wets the powders by binders and forms nuclei aggregates with loose structures; the subsequent coalescence process produces secondary agglomerates from the nuclei, which have the comparatively less spherical shape and rougher surface; finally, consolidation compresses the agglomerates uniformly to squeeze out entrapped air and decreases

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the pore volume and porosity (Cuq et al., 2013; Litster and Ennis, 2013). However, fluidised bed granulation exhibits different granule growth mechanisms. As the binding liquid is sprayed as small droplets (which are much smaller than primary powders), coalescence mostly occurs by layering of materials on the surface of wet particles (Barkouti et al., 2013). The resulting particles are less consolidated due to their motion in air, and not by mechanical agitation (Jacob, 2007). Consequently, granules formed using a fluidised bed is often more porous than those from high shear mixer granulators. For these reasons, the different structures modified by these two processes are believed to contribute to the different functionalities of the bulk solids.

Moisture adsorption refers to a phenomena occurring at the physical interface between the bulk solids and their surrounding humid environment. It contributes to moisture content during storage and thus has an important role to play in physical and chemical stability of powders. The behaviour depends to a large extent on the powder particle surface area, i.e., sorption area, composition and porosity; these factors affect the rate and extent of entry and exit of water molecules into the solid matrix (Al-Muhtaseb et al., 2002). Commercial dairy powders, especially high protein powders, typically have small particle size and large surface area (Schuck et al., 2012). Hence, they are prone to adsorb moisture during storage, handling and processing, which can easily cause the undesired caking, crystallization and loss of production (Fitzpatrick et al., 2008). Granulation can influence the water diffusion process by increasing particle size and modifying powder structures (Barrera-Medrano et al., 2007), altering storage and handling characteristics.

Flowability is another important parameter of milk protein powders and it has been suggested that small powder particles are generally regarded as less flowable compared to larger particles (Crowley et al., 2014). It is reported that materials with small particles and dense structures form cohesive arches by consolidation and interparticle adhesive forces, which can restrict discharge from silos (Schulze, 2007), effecting throughput and product quality. In general, there are two patterns for the flow of a powder out of a silo: 1) mass flow and 2) core flow (Fitzpatrick et al., 2004b). Mass flow is the desirable flow pattern where all the solids are in motion to give a first-in and first-out discharge regime. However, for a cohesive powder, 'arching' may still occurs at the hopper outlet, where a stable powder arch forms across the outlet, blocking the exit funnel. In addition, most flow problems happen in the core flow pattern, as cohesive powders will move out through a central funnel, which is formed by the no-flow particles remaining at the internal walls of hopper. This phenomenon may give rise to the formation of a stable rat-hole (Schulze, 2007). Thus, in order to make powders flow smoothly and discharge reliably, it is desirable to design for mass flow pattern. While studies (Fitzpatrick, 2007; Fitzpatrick et al., 2004a) report that particle size is a key determinant affecting flowability of powders, others claim particle shape and densities are also potential factors as they influence physical properties of surface contacts between particles (Cleary, 2008; Schulze, 2007). Thus, as an effective technique to modify these physical properties, the effect of granulation on the flowability of powders is important to investigate. So far, studies reporting granulation are mainly about pharmaceutical materials (Ennis, 2010; Gao et al., 2002; Iveson et al., 2001; Palzer, 2011); very few focus on dairy protein powders.

The objective of this study was to investigate the effects of two granulation processes, fluidised bed and high shear granulation, on water adsorption and flowability of milk protein powders. Powder granules formed by these two processes were analysed and their data was compared. The flow function and wall friction results were used to specify appropriate hopper outlet dimensions and hopper wall angles for both mass and core flow discharges.

2. Materials and method

2.1. Materials

In this study, Kerry Ingredients (Kerry, Ireland) supplied milk protein isolate powder (MPI) as a model powder, which consists of 86% milk protein, 5.2% moisture, 1.5% fat, 6% ash and less than 1% lactose. The lactose used as binders in fluidised bed and high shear mixer granulation, was purchased from Food Ingredients (Viby J, Aarhus, Demark).

2.2. Methods

2.2.1. Fluidised bed granulation

The agglomeration process of MPI was performed in a top-spray fluidised bed granulator (VFC-Lab Micro flo-coater, Vector Corporation, Iowa, USA). Each batch comprised of 200 g powder which was fluidised in the product vessel by upward flowing air stream from the bottom, at a flow rate of 200 L min^{-1}. The powders were preheated by a 50 °C air stream for 10 min, before 15% (w/v) lactose solution was introduced as a binding liquid. The liquid was injected via a peristaltic pump (1 mL min^{-1}) and sprayed as small droplets by a two-fluid spray nozzle, located on the top of the vessel. The air pressure on the nozzle was 1 bar. After addition of 150 g of lactose solution, drying was continued for 20 min at a reduced flow rate of 100 L min^{-1}. Three batches of MPI granules were produced as replicates.

2.2.2. High shear granulation

A high shear granulator (4M8, Procept, Zelzate, Belgium) was also used in this study to agglomerate the MPI powders. As in 2.2.1, 200 g MPI powder for each batch was fed into a glass bowel, where an impeller and a chopper were both used to agitate the powders at a speed of 300 rpm and 500 rpm, respectively. The binding liquid in this granulation process was also 150 g 15% *w/v* lactose solution, which was injected into the bowel as droplets with a dosing speed of 4 mL min^{-1}. The impeller and chopper continued to mix the products at the same speed for 10 min. Finally, the fluidised bed in 2.2.1 was again used to dry the granules with air (50 °C) at a flow rate of 100 L min^{-1} (Ji et al., 2016a). Three batches samples were prepared for the repeated measurements.

2.3. Powder characterisation

As different granule growth mechanisms occur in the fluidised bed and high shear mixer granulation processes, variations in particle size, shape and porosity of the formed granulated MPI are expected. Therefore, prior to comparison, the agglomerates were sieved into different size fractions. Two size fractions for agglomerates from fluidised bed granulation were prepared by 106 μm, 180 μm and 300 μm level sieves (Endecotts, London, UK) (FB_1: 180 μm–300 μm and FB_2: 106 μm–180 μm). Five size fractions for agglomerates from high shear mixer granulation were prepared by 75 μm, 106 μm, 180 μm, 425 μm, 850 μm and 1000 μm level sieves (HS_1: 850 μm–1000 μm; HS_2: 425 μm–850 μm; HS_3: 180 μm–425 μm; HS_4: 106 μm–180 μm and HS_5: 75 μm–106 μm). The particles that were not in these fractions were removed. The non-agglomerated standard MPI (ST) used as the controlled samples. All the samples were further dried in a vacuum oven (Jeiotech, Seoul, Korea) at 60 °C for 24 h and cooled down in desiccators to ambient temperature before measurements. The final moisture content of the powders can influence water adsorption and flow behaviour and therefore a value ranging between 2 and 3% was

targeted. The measurement was carried out in the preliminary study (Ji et al., 2016a). Malvern Masterszier 3000 (Malvern Instruments Ltd, Worcestershire, UK), which applies laser light scattering technique, was used to measure the particle size of the samples. Three repetitions were carried out; D(10), D(50) and D(90) parameters were used as a measure of particle size.

2.4. Water adsorption analysis

Water adsorption isotherms were carried out by the static gravimetric method. Approximately 1 g powder was weighed into small glass vials of known weight. Triplicate samples for each powder were firstly dried in a vacuum oven at 50 °C for 24 h to remove the residual moisture. The measurement was carried out in the preliminary study to make sure the residual moisture as low as possible (Ji et al., 2016a). Powders were kept in desiccators containing P_2O_5, equilibrated at room temperature, before placing in the desiccators with a stable relative humidity, which ranged from 11% to 65%. Different saturated salt solutions: LiCl (11%), CH_3COOK (22%), $MgCl_2$ (33%), K_2CO_3 (43%), $Mg(NO_3)_2$ (53%), and $NaNO_2$ (65%) were used to provide varied hygroscopic environments, respectively. During the equilibration, the desiccators were stored in two 25 °C incubators. The weight of powder was measured for at least 96 h until it reached a constant value. The results were expressed as equilibrated moisture content as a function of water activity to show the adsorption isotherms. At the same time, the sorption kinetics was also conducted by continuous measurement of mass increase (Schuck et al., 2012). The weight of powder was measured at 0, 3, 6, 9, 12 and 24 h, and then at 24 h intervals until equilibration. The results were exhibited as the moisture content for every 100 g dry matters as a function of time.

2.5. Powder flow analysis

The flowability of powders were quantified and analysed by a powder flow tester from Brookfield (Brookfield Engineering Laboratories, Middleboro, MA, USA). Flow functions and angles of wall friction were both measured to assess the flow behaviours of milk protein powder and its agglomerates. During the measurements, axial and torsional speeds for the tester were 1.0 mm s^{-1} and 1 rev h^{-1} (approx. 0.0167 rpm). The aluminium trough (230 cm^3, 15.2 cm internal diameter) of the annular shear cell was filled by the samples, which were levelled by different shaping blades (curved- and flat-) to create the smooth powder surface. The mass of solids based on the different bulk densities were recorded. Vane- or flat-profiled lids with 15.2 cm external diameter were attached to the compression plate of the tester for flow function and wall friction tests, respectively. All the measurements were repeated three times.

2.5.1. Flow function test

The flow function test is the primary measurement of powder flowability, which gives a measure of the strength of the bulk solids retained at a stress free surface following consolidation to a given stress level (Teunou et al., 1999). Hence, in this study, the unconfined failure test was carried out and five normal stresses between 0.2 and 4.8 kPa were applied to calculate the unconfined failure strength and major principle consolidation stress, based on Mohr circles from specific yield locus. The flow function was then constructed by plotting the failure strength versus the consolidation stress, which can be quantified as the flow index (ff_c) (Schulze, 2007). Normally, the standard classification of this index is: 1) if $ff_c < 1$, powder is non-flowing; 2) if $1 < ff_c < 2$, powder is very cohesive; 3) if $2 < ff_c < 4$, powder is general cohesive; 4) if $4 < ff_c < 10$, powder is easy to flow; 5) and if $ff_c > 10$, powder is very free flowing. Meanwhile, bulk density curve is also evaluated to describe bulk density changes as a function of stress acting on the powder. The compressibility index (CI) was calculated as follows:

$$CI\% = \frac{\rho_c - \rho_b}{\rho_c} \times 100$$

where ρ_b is loose bulk density without compressing (kg m^{-3}); ρ_c is compressed bulk density at 4.838 kPa major principle consolidation stress (kg m^{-3}).

2.5.2. Wall friction test

Wall friction is the friction between materials surface (e.g. the wall of a bin or silo) and bulk solids (powders). The angle of wall friction represents the angle to which a wall surface must be inclined to cause powder to slip (Teunou et al., 1999). It is an important index for silo design for flow, which also can be considered as chute angle. In this study, a flat plate of stainless steel AISI 304 attached in the tester was used to measure the angles. In total 10 normal stresses (0.48, 0.97, 1.45, 1.93, 2.41, 2.89, 3.37, 3.86, 4.34, 4.82 kPa) were applied. Finally, the angles were obtained from the slope of a line drawn from the origin to a point on the maximum wall yield locus at a normal stress of 4.82 kPa.

2.5.3. Two forms of flow obstructions for conical hopper design

There are two forms of flow obstruction problems for bulk solids that may occur in a silo: arching in mass-flow pattern and rat-holing in core-flow pattern, which are illustrated in Fig. 1. Hence, a hopper is usually designed for reliable flow aiming to avoid arching in mass-flow silos and rat-holing in core-flow silos. Critical arching diameter and hopper half angle are commonly used parameters to determine the outlet size of mass-flow silos. The critical arching diameter $D_{arching}$ (m) was calculated as follows (Chen et al., 2012; Crowley et al., 2014):

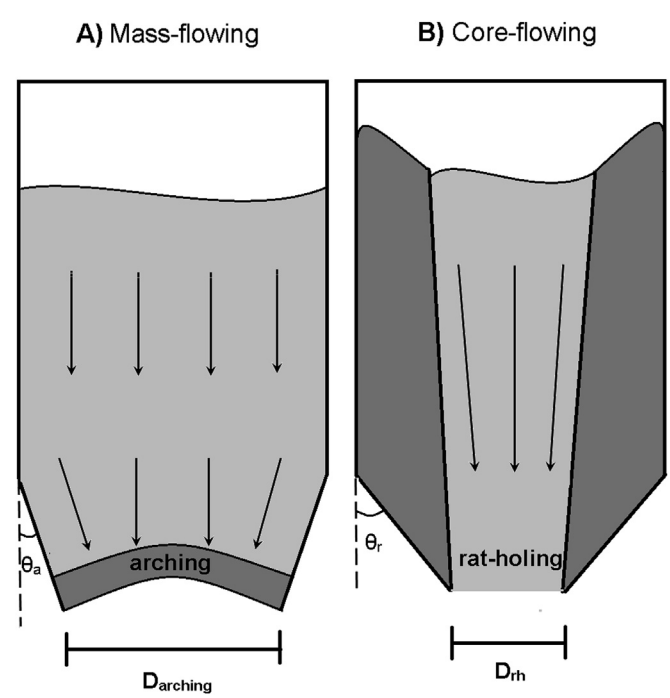

Fig. 1. Schematically illustration of arching and rat-holing problems in hoppers during **A**: mass-flowing discharge pattern and **B**: core-flowing discharge pattern, respectively ($D_{arching}$: minimum outlet diameter to prevent arching; θ_r: critical hopper half-angle to prevent arching; D_{rh}: minimum outlet diameter to prevent a stable rat-hole; θ_r: critical hopper half-angle to prevent a stable rat-hole).

$$D_{arching} = \frac{2 \times \sigma_a \times 1000}{\rho_a \times g}$$

where σ_a is critical arching stress (kPa); ρ_a is critical arching bulk density (kg m^{-3}); g is gravity acceleration (m s^{-2}).

The critical hopper half angle (θ_a) can be derived from the effective angle of internal friction ($\varnothing_e$) and the angle of wall friction ($\varnothing_w$) for a conical hopper (Schulze, 2007):

$$\theta_a = \frac{1}{2}\left[180^\circ - \cos^{-1}\left(\frac{1 - \sin\varnothing_a}{2\sin\varnothing_a}\right) - \varnothing w - \sin^{-1}\left(\frac{\sin\varnothing_{wa}}{\sin\varnothing_a}\right)\right]$$

where $\varnothing_a$ is the critical angle of internal friction at the corresponding critical consolidation stress for arching (°); $\varnothing_{wa}$ is critical angle of wall frictions at the corresponding critical consolidation stress for arching (°).

For core-flow silos, the critical rat-hole diameter (D_{rh}) and the maximum inclination of the hopper walls to the vertical (θ_r) were used to design the conical hopper dimensions (Schulze, 2007). D_{rh} can be obtained for a conical silo, assuming a silo diameter of 2 m and a height of 8 m:

$$D_{rh} = \frac{G(\varnothing) \times \sigma_r \times 1000}{\rho_r \times g}$$

where $G(\varnothing) = 0.7771 \times e^{0.0381\varnothing_r}$; $\varnothing_r$ is critical angle of internal friction for rat-holing (°); σ_r is critical rat-holing stress (kPa); ρ_r is critical rat-hole bulk density (kg m^{-3}).

Also, θ_r was assessed by $\varnothing_{wr}$:

$$\theta_r = 65^\circ - \varnothing_{wr} \quad \text{(If bulk solids are poorly flowing)}$$

$$\theta_r = 90^\circ - (\varnothing_{wr} + 10^\circ) \text{ (If bulk solids are easy – flowing, i.e. granules)}$$

where $\varnothing_{wr}$ is critical angle of wall frictions at the corresponding critical consolidation stress for rat-holing (°).

2.6. Statistical analysis

All the measurements were repeated three times and results were showed as mean ± standard deviations. One-way analysis of variance (ANOVA) was conducted by SPSS software (PASW, Statistics 1.8, 2009). The least significant difference (LSD) test, in relation to the applied variable using F-test, was used to compare the statistical differences of values relating to flow properties and hopper design. Significantly differences were considered when $P < 0.05$.

3. Results and discussion

3.1. Structural characteristics

The physical and structural properties of the different granules, including particle size, density, porosity and morphology parameters are shown in Table 1. It can be seen that independent of granulation process used, injecting binders to promote adherence of primary particles, produces significantly ($p < 0.05$) larger particles. As milk protein powders are cohesive, high air velocity was required during FB agglomeration resulting in granules only 2 to 4 times (100 μm–200 μm) in size of the primary powders. However, granules produced by HS can reach sizes of more than 1000 μm, which are ~20 times that of the primary powders. At the same time, the FB granules had lower bulk density and higher porosity than the HS granules. They also exhibited less rounded, rougher surface and higher ratio of length to width shapes based on the significantly lower values of circularity, convexity and higher values of elongation (Table 1). It can be more clearly observed from SEM images in Fig. 2. The primary particles were highly-packed in the granule structures that formed by HS process while FB process created irregular agglomerates containing large interstitial pores resulting in larger specific volumes. It is commonly believed that the granules without consolidation will grow progressively by layering materials on the surface, while consolidation supplied by strong mechanical agitation will lead to plastic deformation of granules via a process of squeezing-out entrapped air, increased internal pore saturation and reduced porosity (Cuq et al., 2013). These significant differences in physical and structural properties can be attributed to different granule growth mechanisms as influenced by process type and equipment used (Jacob, 2007).

3.2. Water adsorption

Fig. 3 displays water adsorption isotherms of MPI powder and its granules made using the FB and HS processes, under different humidly controlled environments. For the water activity range of 0.11–0.65, the isotherms all had a linear slope, regardless of the type of granulation process used, including the non-agglomerated MPI. There was no significant difference between the standard MPI (ST) and the granules from fluidised bed (FB1 & FB2), which adsorbed almost the same quantity of water. However, the granules from high shear mixer (HS1 to HS5) were found to adsorb less water from the surrounding environment, suggesting that moisture vapour is more difficult to penetrate into the structures and form layers on the surface of internal primary particles. In Fig. 4, the water adsorption kinetics at varying humidity are given; FB1 and FB2 exhibited similar adsorption behaviour as standard MPI, which all equilibrated at about 12 h. In comparison, the HS granules took longer time to reach constant weight and an effect that is more pronounced at the lower relative humidity environment (Aw: 0.22, 0.33 and 0.44). HS1 and HS2 powders, which had largest particle sizes (Table 1), adsorbed the least amount of water but continued to increase in weight until at least 24 h, especially at the low relative humidity e.g. 0.22, 0.33 and 0.44 (Fig. 4). It is interesting to note that HS3 and HS4 adsorbed more water than HS1 and HS2, and required shorter time to reach equilibrium. This effect was again more evident at the lower relative humidity environment.

As shown previously, FB granules have high porosity, which is suggested to facilitate penetration of water into the granule matrix (Hapgood et al., 2007). The interior porous structures had no significant effect on the rate and extent of hydration, and water molecules seemed to enter and exit as easily as that occurring in non-agglomerated MPI. On the other hand, the agglomerated MPI produced from by the HS process had more compacted structure, restricting diffusion of water into the internal surface as a result of reduction of surface-binding sites for water to adsorb (Al-Muhtaseb et al., 2002), compared to those granules which are less compacted. In this case, the large particles with low specific surface area were believed to retard the moisture adsorption behaviour, which was the reason why HS1 and HS2 exhibited the prolonged process. However, granule size does not always correlate with total sorption area, e.g., FB2 was not different from FB1, even though it had a smaller particle size. Furthermore, HS3 and HS4 had different results, where more moisture content was adsorbed by them rather than HS5, but they had large sizes on the contrary. It can be explained by the granules produced by coalescence process, with comparatively rougher surface and porous structures than other granules from high shear mixer (Fig. 2), which may cause the larger surface area to contact the water molecules (Murrieta-Pazos et al., 2011). The nuclei granules HS5 after solidification had higher

Table 1
Physical and structural properties of powders.

Samples	Particle size D_{10} (μm)	Particle size D_{50} (μm)	Particle size D_{90} (μm)	Bulk density (g/mL)	Porosity (%)	Circularity (0.5)	Convexity (0.5)	Elongation (0.5)
ST	18.1 ± 0.2[a]	49.4 ± 0.2[a]	112 ± 2.1[a]	0.298 ± 0.0[a]	72.85 ± 0.1[a]	0.816 ± 0.023[a]	0.931 ± 0.009[a]	0.301 ± 0.012[a]
FB1	50.8 ± 0.3[b]	188.7 ± 1.0[b]	346.5 ± 3.5[b]	0.179 ± 0.0[b]	84.43 ± 0.1[b]	0.630 ± 0.015[b]	0.761 ± 0.017[b]	0.266 ± 0.001[b]
FB2	40.1 ± 0.2[c]	102.5 ± 0.3[c]	190.5 ± 1.5[c]	0.221 ± 0.0[c]	79.33 ± 0.3[c]	0.669 ± 0.008[c]	0.814 ± 0.005[c]	0.301 ± 0.001[a]
HS1	778 ± 11.2[d]	1075 ± 15.7[d]	1565 ± 35.1[d]	0.538 ± 0.0[d]	51.8 ± 0.2[d]	0.862 ± 0.018[d]	0.931 ± 0.015[a]	0.262 ± 0.000[c]
HS2	456 ± 10.1[e]	681 ± 9.6[e]	1029.5 ± 20.9[e]	0.500 ± 0.0[e]	53.0 ± 0.2[e]	0.870 ± 0.004[d]	0.933 ± 0.001[a]	0.258 ± 0.004[c]
HS3	119.6 ± 1.5[f]	263 ± 5.2[f]	482 ± 8.0[f]	0.431 ± 0.0[f]	61.0 ± 0.1[f]	0.767 ± 0.015[e]	0.866 ± 0.013[d]	0.262 ± 0.010[bc]
HS4	67.6 ± 0.2[g]	111 ± 2.1[g]	178.5 ± 0.5[g]	0.450 ± 0.0[g]	60.3 ± 0.1[g]	0.820 ± 0.006[a]	0.908 ± 0.005[e]	0.263 ± 0.002[bc]
HS5	52.2 ± 0.3[h]	75.0 ± 1.0[h]	107.5 ± 0.5[h]	0.526 ± 0.0[h]	53.8 ± 0.1[h]	0.891 ± 0.001[f]	0.965 ± 0.001[f]	0.263 ± 0.006[bc]

[a] Adapted from Ji et al. (2015 & 2016a).
[b] Data are expressed as mean ± standard deviation; values followed by a different superscript letter in the same line are significantly different at $P < 0.05$.

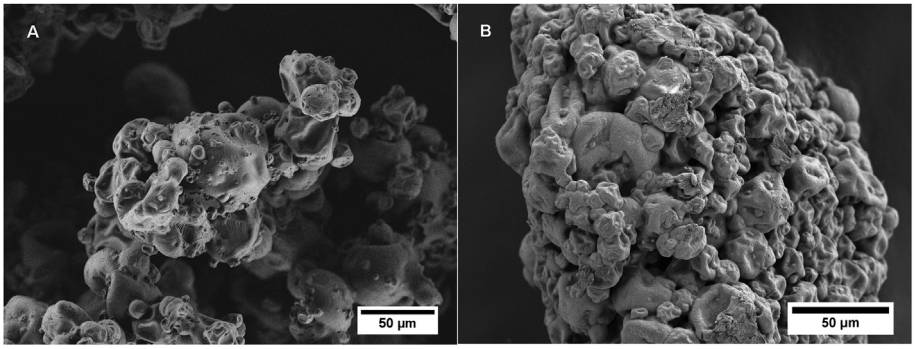

Fig. 2. SEM Images of MPI granules produced from fluidised bed and high shear mixer granulation, **A**: Fluidised bed (FB); **B**: High shear mixer (HS).

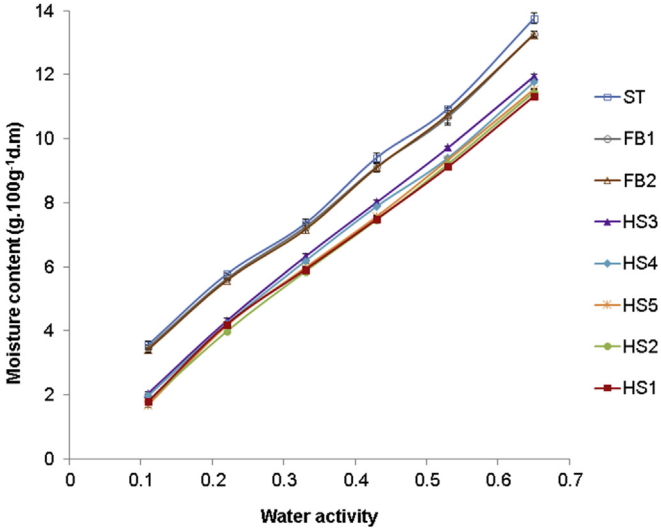

Fig. 3. Water vapours adsorption isotherms of powders (ST, FB & HS) at 25 °C environment.

granule strength and more dense structures. Therefore, it may be more difficult for water molecules to access all internal primary particles, particularly those towards the centre of a granule. It is interesting to see that the kinetics of water adsorption were also influenced by the gradient of different hygroscopic environments. When the equilibrium relative humidity was increased, additional water was progressively adsorbed by the protein powders. Condensational wetting may occur if relative humidity is higher than 0.5 and moisture may diffuse into these interior sites via capillary force (Ji et al., 2016b; Mathlouthi and Roge, 2003). Consequently, the difference of moisture content within HS granules was not significant and the difference between FB and HS was also reduced.

3.3. Flow properties

3.3.1. Flow function

The powders in a hopper are usually consolidated by stress, which is based on their own self-weights and varied from their positions in different regions of hopper or at different fill heights. Thus, the flowability of powders is often stress-dependent (Teunou et al., 1999). Fig. 5 illustrates that the standard MPI powder was a poor-flowing powder and it was very cohesive when consolidating stress was lower than 1.2 kPa. Even if the stress increased to 13 kPa, the standard MPI was still considered as a cohesive powder. However, the applied granulation processes, i.e., FB and HS, were found to significantly improve the flow behaviour of milk protein powders. Firstly, FB1 and FB2, produced from fluidised bed, had a lower unconfined failure strength at the same consolidating stress, indicating they had comparatively better flowability and can be classified as easy-flowing powders. Particle size also displayed a beneficial role as is demonstrated when FB1 and FB2 are directly comparing at higher stresses than 3.2 kPa. The granules formed by the HS process were all free flowing in the annular shear cell, regardless of size fraction or the stresses that consolidated them. Only HS3 exhibited slightly higher unconfined failure strength than other HS granules.

It is commonly believed that adhesive forces are usually the source of such flow problems for fine-grained dry bulk solids. The major adhesive forces are based on van der Waals interactions and the intensity of the forces mainly depend on the particle size as well as the distances between individual particles (Fitzpatrick, 2007; Schulze, 2007). When the distances are small or the surfaces of particles are in contact, van der Waals forces have a large influence. Therefore, plastic deformation and rearrangement occurring at contact points may cause an increase in adhesive forces (Aarons

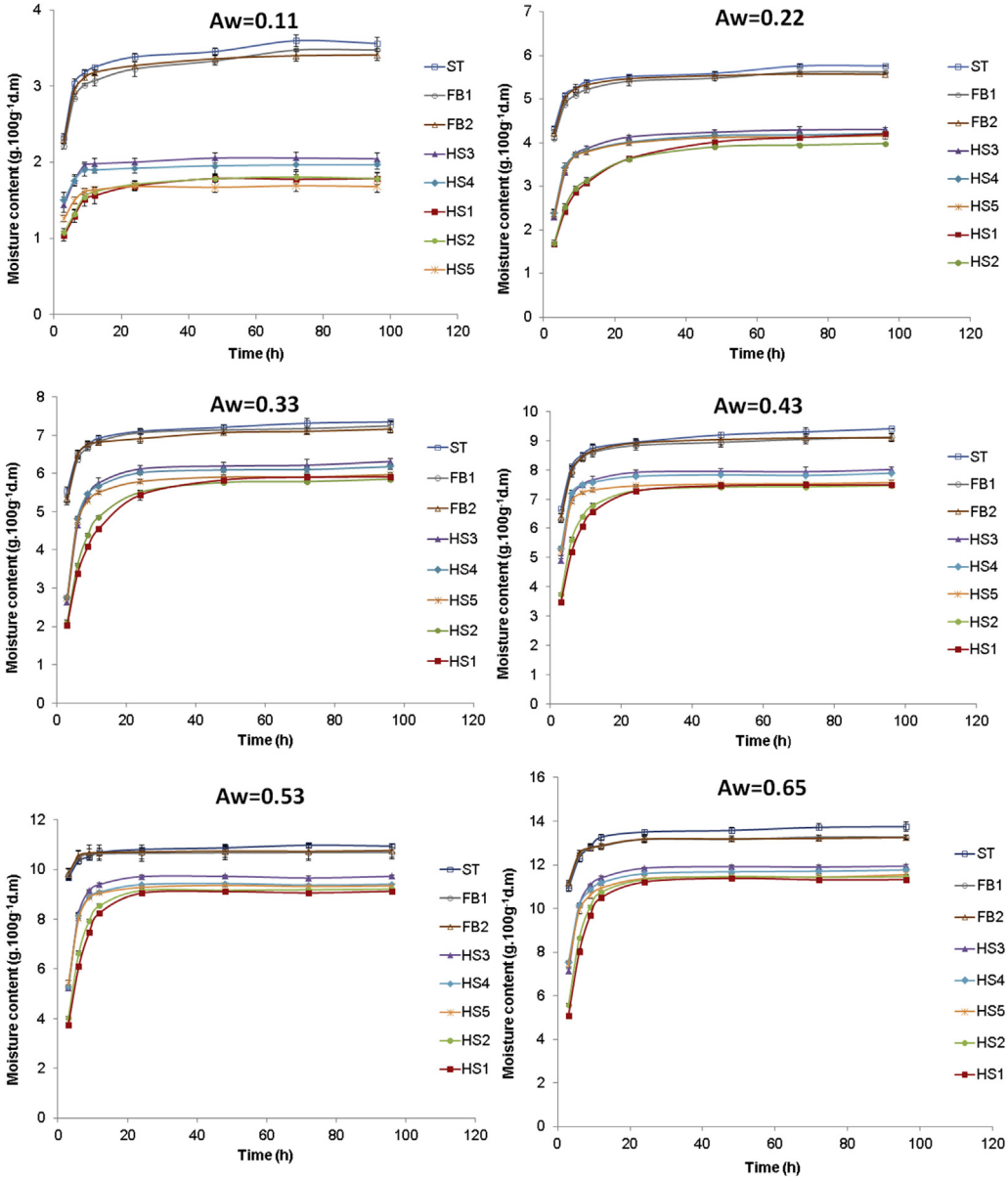

Fig. 4. Kinetics of water vapour adsorption for the powders (ST, FB & HS) at six different hygroscopic environments (aw: 0.11; 0.22; 0.33; 0.43; 0.53; 0.65).

and Sundaresan, 2006). This can be the reason why standard MPI powders with small size have poor flowability. For FB1 and FB2, their large sizes and rough surfaces resulted in an increase in distance and thus a reduction of adhesive forces. The granules of HS1 to HS5 also presented similar behaviours, as their adhesive forces were no longer dominant compared to the gravity force. The dense packed structures allowed the granules to flow more freely (Schulze, 2007). In addition, smooth and spherical particles usually flow better than rough and non-spherical particles (Cleary, 2008) which may explain why HS3 showed the slightly poorer flowability than the other HS granules.

3.3.2. Bulk density

Different from solid density, bulk density is determined by the voids that exist between or within the individual particles, which also depends on the magnitude of the consolidation stress acting on them. The results of bulk density in Fig. 6 showed that FB1 and FB2 had the lowest bulk density due to their significantly ($p < 0.05$) higher porosity compared to the other powder granules (Table 1). Their densities were lower than 200 kg m^{-3} when no stress was applied. In contrast, the granules of HS1 to HS5 showed much higher values of at least 400 kg m^{-3}, as their structures were consolidated by agitation forces in the high shear mixer. For compressibility indexes, shown in Table 2, a significantly ($p < 0.05$) higher value (39.5%) was observed for standard MPI powders compared to the granules. FB1 and FB2 were prone to be compressed by stresses, while HS1 to HS5 displayed the least plastic deformation. For example, for the HS1 and HS2 treatments, which had the largest granule size, their compressibility indexes were less than 10%, which indicates comparatively higher bulk strength. It is believed that the index is closely related to the volume of interstitial air as well as the internal occluded air (Bhandari et al., 2013). Therefore, the porous structures are considered as the major reason to influence the compressibility of powders. Meanwhile, high index

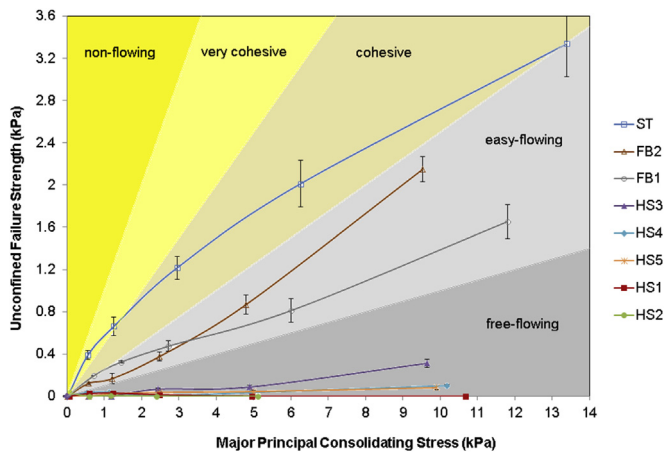

Fig. 5. Flow function curves for unconfined failure strength as a function of major principle consolidation stress for the powders (ST, FB & HS).

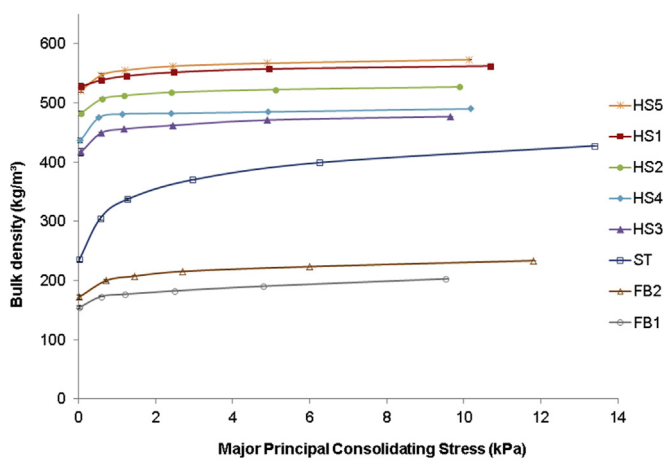

Fig. 6. Bulk density as a function of major principal consolidating stress for the powders (ST, FB & HS).

Table 2
Values for compressibility index and flow properties for conical hopper design, derived from shear cell testing.

Sample	*CI* (%)	θ_a (°)	$D_{arching}$ (m)	θ_r(°)	D_{rh} (m)
ST	39.5 ± 4.8[a]	18.7 ± 4.1[a]	0.26 ± 0.03[a]	43.2 ± 0.7[a]	1.49 ± 0.20[a]
FB1	18.9 ± 2.4[b]	34.4 ± 5.7[b]	0.12 ± 0.02[b]	65.9 ± 0.1[b]	0.75 ± 0.07[b]
FB2	21.5 ± 2.1[b]	32.7 ± 5.3[b]	0.10 ± 0.00[c]	65.4 ± 0.1[c]	0.83 ± 0.11[b]
HS1	5.3 ± 0.2[c]	Free flow	0.01 ± 0.00[d]	55.4 ± 0.3[d]	0 ± 0.00[c]
HS2	7.7 ± 0.4[d]	Free flow	0.03 ± 0.01[e]	51.9 ± 0.3[e]	0 ± 0.00[c]
HS3	11.5 ± 0.9[e]	Free flow	0.03 ± 0.01[e]	47.3 ± 0.9[f]	0.20 ± 0.03[d]
HS4	10.0 ± 0.7[e]	Free flow	0.02 ± 0.00[de]	40.1 ± 1.0[g]	0.04 ± 0.00[e]
HS5	8.1 ± 0.4[d]	Free flow	0.02 ± 0.00[de]	37.8 ± 0.8[h]	0.02 ± 0.00[f]

*Values followed by a different superscript letter in the same line are significantly different at $P < 0.05$.
***CI*: compressibility index; θ_a: critical hopper half-angle to prevent arching; $D_{arching}$: minimum outlet diameter to prevent arching; θ_r: critical hopper half-angle to prevent a stable rat-hole; D_{rh}: minimum outlet diameter to prevent a stable rat-hole.
***Rathole diameter was derived for a conical silo, assuming a diameter of 2 m and a height of 8 m.

values indicate that those powders were more likely to be compressed by self-weight in hoppers during storage, which may cause the altered bulk density and also subsequently affect the handling properties (Crowley et al., 2014; Schulze, 2007).

3.3.3. Wall friction angle

If considering the friction between bulk solids and solid surfaces, e.g. the wall of a hopper, the angle of wall friction as a function of stress is important when quantifying the wall friction during hopper design. In Fig. 7, FB1 and FB2 kept a constant angle of approximately 15° under the effect of different normal stresses. Standard MPI powder had a higher angle of 25° at the beginning of a 0.5 kPa stress and then followed by a slight decrease with increasing stress. Significant changes were observed for the granules of the HS process, which not only present large wall friction angles, but also varied as granule size changed. It is clear that decreasing particle size resulted in increased wall friction angles, regardless of the normal stresses applied. HS4 and HS5 had the greatest angles of all, due to their high bulk density caused more force transferring through wall shear stress, which meant the large wall friction force and thus attained the big angles of wall friction (Aarons and Sundaresan, 2008; Artoni et al., 2009). Meanwhile, comparing with other granules from the HS granulation process, the smaller sizes of HS4 and HS5 had increased specific surface areas, which may produce stronger particle-wall interactions. There is a greater tendency for the granules with high wall friction angles to undergo deposition or segregation in a hopper, as the particles near the hopper walls move slower than that in the centre. Thus high wall friction may lead to the materials near the walls discharging finally (Schulze, 2007).

3.3.4. Conical hopper design

The outlet diameter of conical hoppers and the inclination of the hopper wall to the vertical are very important parameters to determining bulk solids discharge from hoppers (Fig. 1) (Fitzpatrick et al., 2004b). As shown in Table 2, the minimum outlet diameters for preventing both arching in mass-flow discharge or rat-holing in core-flow discharge were compared for the different granules. The $D_{arching}$ values of granules were significantly lower than that of the standard powder, which had at least 0.26 m to avoid the occurrence of an arch at the outlet. The HS granules required the smallest hopper outlet diameters while the granules from fluidised bed needed slightly bigger diameters of about 0.1 m. In addition, the corresponding maximum hopper half angle of standard MPI that ensured mass-flow was 18.7°, which was lower than the values present by FB1 and FB2 with 34.4° or 32.7° respectively. However, there seemed no special requirements on half angles for HS granules, as they already displayed free flowing behaviours in the hopper. Similarly, for the core-flowing, HS granules needed a

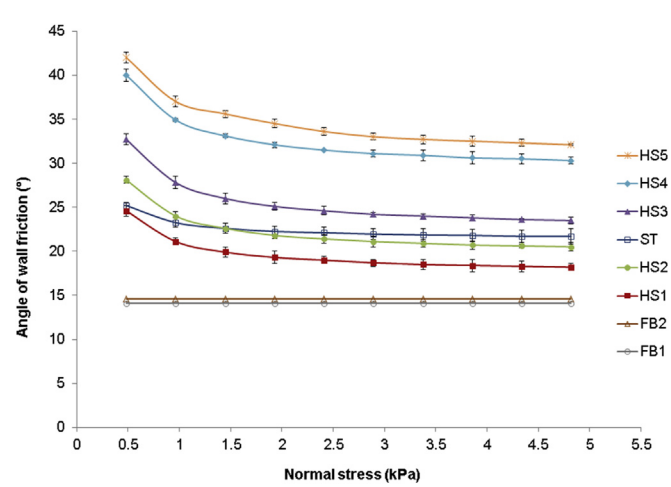

Fig. 7. The angles of wall friction as a function of normal stress for the powders (ST, FB & HS).

hopper with smallest outlet diameter (0.2 m or even less) to ensure discharge smoothly. On the other hand, 0.75 m and 0.8 m diameters were calculated for FB1 and FB2, respectively, which were still significantly lower than that of standard powder (1.5 m). The results were consistent with the previous flow function results, which indicated that the free flowing granules could discharge completely by gravity alone due to the strength of bulk solids being too weak to achieve a stable rat-hole. Therefore, comparatively smaller outlet dimension can be designed to support the ideal mass flow for those free- or easy-flow bulk solids (Fitzpatrick et al., 2004b). However, for maximum inclination of the hopper walls to vertical, the granules of fluidised bed showed the largest angles of 65°, while HS5 needed the steepest wall for the hopper, which had smallest angle. It is believed that the maximum inclination of hopper can be estimated based on Jenike's methodology as a function of wall friction angle (Schulze, 2007). Likewise, it is not surprising to see that the granules with high bulk density led to lower inclination because of their large angles of wall friction.

4. Conclusion

In summary, both methods produced MPI granules with significantly large particle sizes. High shear mixer granulator made granules with densely packed structures, which adsorbed least moisture and showed the slowest adsorption kinetics during storage at different relative humidity. The granules with loose and porous structures created by fluidised bed granulation, exhibited no significant difference in water adsorption measurements when compared to the non-agglomerated powder. Large MPI granules were found to have significantly better powder flow behaviours. Besides the effect of particle size, bulk density and shape properties may both play important roles in flowability of powders, however further studies are needed to validate their individual influences on flowability. Overall, granulation processes can effectively reduce the minimum outlet diameters of hoppers for reliable flow from both mass-flow or core-flow hoppers. However, large wall friction angles caused by the HS granules (especially the smaller granules) may also require steeper hopper walls to discharge bulk solids and avoid them remaining at rest.

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Nomenclature

MPI	Milk protein isolate
FB	Fludised bed granulation
HS	High shear mixer granulation
ST	Non-agglomerated standard MPI
D(10)	Particle size below which 10% of material volume exists (μm)
D(50)	Particle size below which 50% of material volume exists (μm)
D(90)	Particle size below which 90% of material volume exists (μm)
CI	Compressibility index (%)
ff_c	Flow index
ρ_b	Loose bulk density without compressing (kg m^{-3})
ρ_c	Compressed bulk density (kg m^{-3})
ρ_a	Critical arching bulk density (kg m^{-3})
ρ_r	Critical rat-hole bulk density (kg m^{-3})
$D_{arching}$	Critical arching diameter (m)
D_{rh}	Critical rat-hole diameter (m)
g	Gravity acceleration (m s^{-2})
σ_a	Critical arching stress (kPa)
σ_r	Critical rat-holing stress (kPa)
θ_a	Critical hopper half angle for arching (°)
θ_r	Critical hopper half angle for rat-holing (°)
$\varnothing_e$	Effective angle of internal friction (°)
$\varnothing_w$	Angle of wall friction (°)
$\varnothing_a$	Critical angle of internal friction for arching (°)
$\varnothing_{wa}$	Critical angle of wall frictions for arching (°)
$\varnothing_r$	Critical angle of internal friction for rat-holing (°)
$\varnothing_{wr}$	Critical angle of wall frictions for rat-holing (°)

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