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Mechanical integrity and rehydration properties of agglomerated nutritional dairy ingredient powders

Thesis presented by
Ryan Hazlett
B.Sc. Food Science, University College Cork
for the degree of
Master of Science
in
Food Science and Technology
December 2019

Table of Contents

Abstract

Chapter 1 **2**
Introduction

Chapter 2 **8**
Approaches for improving the flowability of high-protein dairy powders post spray drying – a review

Chapter 3 **72**
Influence of mechanical integrity during pneumatic conveying on the bulk handling and rehydration properties of agglomerated dairy powders

Chapter 4 **115**
Modification of the physical, bulk handling and rehydration properties of milk protein isolate powders using agglomeration with novel protein-based binder solutions

Chapter 5 **158**
General discussion and suggestions for future research

Appendix **163**

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.

Signature:



Ryan Hazlett Date: 23/12/19

Dedication

I would like to dedicate this thesis to my parents, Laura and of course, Zara.

Your love and support were everything.

“Life and love go on, let the music play...”

Johnny Cash

Abstract

The functional properties of nutritional dairy powders are key in determining the ease at which they can be stored, handled and further applied in formulations or on direct consumer application. Powder agglomeration is a unit operation employed during the spray drying process, in order to obtain a greater control of the resulting powder's physical, bulk handling and functional properties. The studies presented in this thesis explore the importance of maintaining agglomerate integrity on powder handling (i.e., powder conveying) post-spray drying, while presenting novel research findings in the application of agglomeration for the modification of commercially important, high-protein content dairy powders (e.g., milk protein isolate; MPI). Initially, a custom fabricated pressure dispersion rig was utilised to achieve breakdown of agglomerated powder particles, similar to that occurring in industrial powder conveying systems (i.e., lean phase conveying). Analysis of the resulting powders showed that the significant alterations in both powder physical and bulk properties (i.e., decreased particle size, increased bulk density and increased surface free fat concentrations), occurring on agglomerate breakdown, significantly impaired the functionality (i.e., flowability and rehydration) of a range of commercially agglomerated nutritional dairy powders (i.e., whey protein concentrate, fat-filled milk powder and an infant formula powder). In addition, the agglomeration of MPI was researched, focusing on the utilisation of novel protein-based binders to achieve agglomeration. The results demonstrated that the use of novel protein-based binder solutions achieved a greater extent of agglomeration in comparison to more traditional binder solutions (i.e., water or lactose), ultimately improving the flowability and wetting properties of MPI powders. The conclusions of this thesis demonstrate the importance of maintaining the mechanical integrity of agglomerated dairy powders and the potential for the further application of agglomeration using novel protein-based binder solutions to tailor the functionality of high-protein dairy powders, such as MPI.

Chapter 1

Introduction

1.1 Background

The complex composition of milk, which makes it a key source of nutrition, also imparts numerous technological functionalities which result in the inclusion of milk and milk-derived ingredients in various formulated food products, such as nutritional beverages, cheese, bakery and dessert products (Haug et al., 2007; Hazlett et al., 2018). To economically store, transport and apply the volumes of milk solids required for these various applications, liquid milk is routinely dehydrated into powder form using spray drying, to increase shelf life and reduce the space required for, and costs associated with, storage and transport (Pisecky, 2012). The global dairy powder market reached a volume of 9.8 million tons in 2017 and has been forecasted to grow strongly to reach 13 million tons by 2023 (IMARC, 2017).

The continual growth of the dairy powder market has led to the development and application of numerous fractionation, enrichment and processing technologies which allow for the production of tailored dairy ingredient powders with modified composition and functional properties, thereby increasing the market opportunities and commercial values (Schuck, 2014). These added-value powders often have quite different compositional profiles, including for example, the high protein content of dairy protein concentrates and isolates and the high fat content in ingredient powders such as fat-filled and infant formula powders.

Dairy powders with high contents of protein or fat often exhibit characteristic powder physical and bulk handling properties (e.g., cohesiveness), which present challenges for the handling, storage and application of such powders. Poor powder flowability can significantly limit the ease at which dairy ingredient powders are stored in silos, conveyed through pipes, and applied during further formulation (Barone et al., 2019;

Crowley et al., 2014; Fitzpatrick et al., 2004). One approach to improve the flowability of powders is to use agglomeration to achieve powder particle size enlargement. Agglomeration is a unit operation often applied during the production of dairy powders, whereby numerous individual powder particles are combined into larger cluster-like structures, achieving an increase in mean particle size (Cuq et al., 2013). Commodity dairy powders, such as skim and whole milk powders are traditionally agglomerated to modify and control the resulting functional properties of these powders. Newer generation, high-value nutritional dairy ingredient powders, such as milk protein concentrates and isolates, are increasingly being agglomerated to increase the ease of storage, handling and application across various applications. However, limited scientific knowledge is currently available surrounding the design, control and optimisation of agglomeration processes for high-value dairy ingredient powders, and an increasing scientific knowledge gap exists around the mechanical integrity of such agglomerated variants of higher-value dairy ingredient powders.

1.2 Research aims and objectives

1.2.1 Aims

This thesis aims to develop a greater scientific understanding of the agglomeration of a range of high-value nutritional dairy powders and to determine the effects of agglomeration on powder physical, bulk handling and mechanical integrity properties.

1.2.2 Objectives

The objectives of this thesis were to:

1. Systematically assess the causes of poor flowability in high-protein dairy powders, in advance of critically evaluating selected options for improving flowability of high-protein dairy powders (Chapter 2).

2. Determine the mechanical integrity of selected commercially important, agglomerated nutritional dairy powders while systematically studying the causes and effects of agglomerate breakage on the resulting powder physical, bulk handling and rehydration properties (Chapter 3).

3. To develop and apply a process for agglomeration of milk protein isolate powders using novel protein-based binder solutions and determine the effects of binder type on key quality attributes of resultant powders (Chapter 4).

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Chapter 2

Approaches for improving the flowability of high-protein dairy powders post spray drying – a review

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Declaration

The relevant literature was critically reviewed by Ryan Hazlett (RH). The chapter was written by author RH and reviewed by all co-authors.

Table of contents

Chapter 2

2.1 Abstract 10

2.2 Introduction 11

2.3 Causes of poor flowability of high-protein dairy powders 16

2.3.1 Powder bulk composition 17

2.3.2 Powder particle and bulk physical properties 17

2.3.3 Environmental and processing conditions 19

2.3.4 Interparticle interactions 21

2.4. Approaches for improving the flowability of high-protein powders 25

2.4.1 Particle size enlargement 26

2.4.2 Surface modification 38

2.5 Emerging technologies for improving the flowability of high-protein powders 46

2.6 Conclusion and outlook 49

2.7 Acknowledgements 50

2.8 References 51

2.1 Abstract

Challenges are commonly encountered in the bulk handling and application of high-protein dairy powders, and are strongly influenced by their poor flowability. Powder flowability can be defined as the ability of a powder to flow under set environmental or processing conditions and is ultimately determined by the type and extent of interparticle interactions occurring in the bulk powder (e.g., van der Waals and electrostatic interactions). High-protein powders are particularly susceptible to the occurrence of interparticle interactions, resulting in increased cohesive forces being experienced in the bulk powder, thereby reducing powder flowability. This review summarises the major factors responsible for poor flowability in high-protein dairy powders and critiques traditional (e.g., agglomeration) and some of the more relevant novel approaches (e.g., dry- and wet-coating and roller compaction) available for improving the flowability of powders post spray drying. This review material will be of considerable interest to dairy scientists, technologists and engineers challenged with understanding, predicting and controlling the bulk handling and flowability of high-value dairy protein powders.

2.2 Introduction

Dairy powders are typically produced by dehydrating a liquid milk stream *via* a combination of evaporation and spray drying technologies in order to increase shelf life and to allow for easier and more economical handling, transport, storage and further application of large volumes of milk solids (Schuck, 2014). As of 2017, the global milk powder market had reached a volume of 9.8 million tons and global market forecasts have predicted this volume will continually increase to approximately 13 million tons by 2023. The continued commercial growth of dairy powders is attributed to their numerous applications, mostly, but not limited to, the food and beverage industries (IMARC, 2017).

Technological advancements have allowed for selective fractionation and enrichment of dairy proteins (caseins and whey proteins), mainly through centrifugal separation and membrane processing (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) of milk streams prior to spray drying. The concentration of dairy proteins, and subsequent depletion of milk serum phase (water, lactose and minerals) and fat constituents can yield a wide range of dairy protein ingredients (Figure 2.1). These ingredients can be categorised as either protein concentrates (35–89% protein), e.g., milk protein concentrates (MPC), whey protein concentrates (WPC), micellar casein concentrates (MCC), or as the respective protein isolates (≥90% protein), i.e., milk protein isolates (MPI), whey protein isolates (WPI) and micellar casein isolates (MCI) (Mulvihill and Ennis, 2003; Schuck, 2009; Schuck *et al*., 2016). For the purpose of this review, protein isolates (≥90% protein, low fat and lactose levels) will be the main dairy protein ingredient powder type in focus for further discussion.

High-protein dairy powders have notable nutritional and functional properties, leading to their use in high value commercial applications such as infant and sports

nutrition products (Hambræus and Lönnerdal, 2003; Hazlett *et al*., 2018; Kinsella and Morr, 1984; O'Regan *et al*., 2009). The value of the global dairy protein ingredient market is expected to reach 58 billion US dollars by 2022. The strong growth of the protein-enriched dairy ingredient market has been driven strongly by the recent consumer demand for high-protein label declarations on a wide range of food and beverage products (e.g., breakfast bars, yoghurts and coffee drinks). In the UK market alone, the appearance of "high-protein" claims has increased by ~500% between 2010 and 2015 (Bord Bia, 2018; Markets and Markets, 2018).

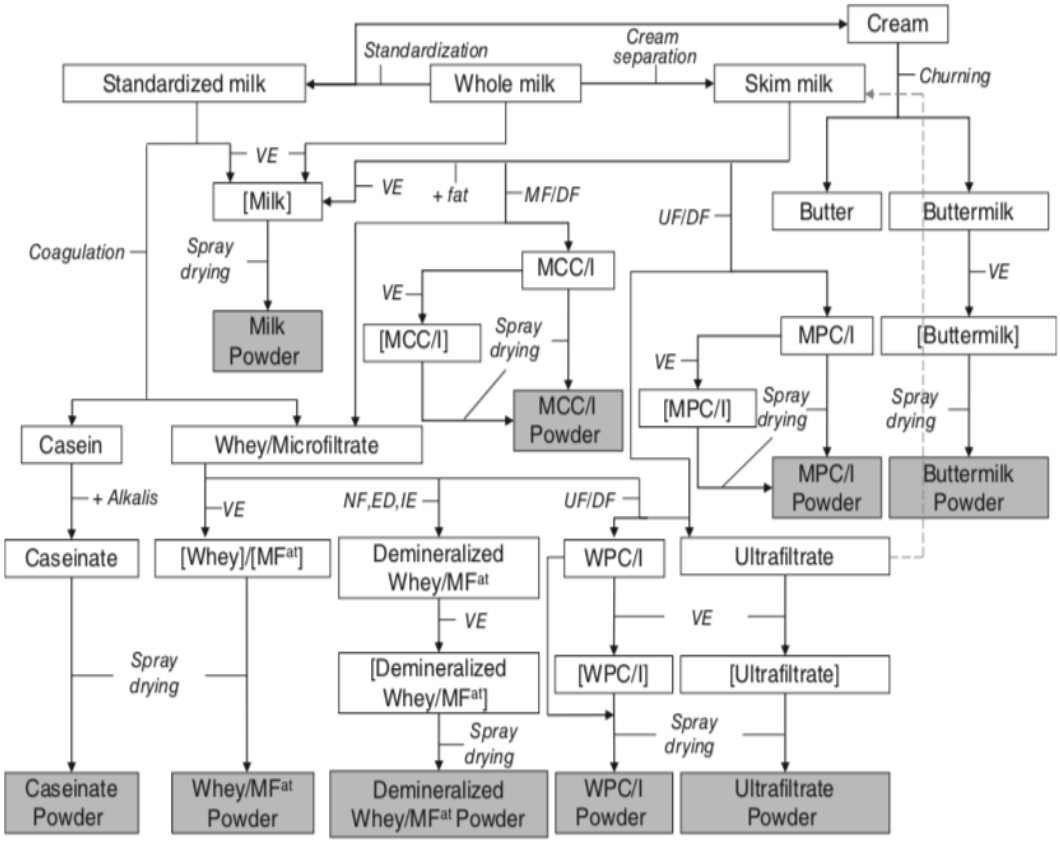


Figure 2.1 *Fractionation and concentration processes yielding a range of dried dairy powder ingredients (grey boxes) from a liquid whole milk stream.VE: vacuum evaporation, IE: ion exchange, ED: electrodialysis, MF: microfiltration, NF: nanofiltration, UF: ultrafiltration, DF: diafiltration, MFat: microfiltrate. WPC/I: whey protein concentrate/isolate, MPC/I: milk protein concentrate/isolate, MCC/I: micellar casein concentrate/isolate (Schuck, 2013b).*

The application of high-protein dairy powders requires these powders to be stored, in and discharged from, large silos, transported through pipes (pneumatic conveying) and further processed (e.g., rehydrated, dry blended) in an efficient manner in order to fully harness the beneficial nutritional and functional properties of the powders. The characteristics of these powders i.e., at particle (e.g., particle size, shape and density, surface energy and roughness) and bulk (e.g., cohesive strength, bulk density and interstitial air) levels will determine at what level of ease a powder can be handled and processed for application in varied formulations; this notably includes powder flowability (Kim *et al*., 2005).

Previously, powder flowability has simply been defined as "the ability of a powder to flow" (Li *et al*., 2004; Santomaso *et al*., 2003; Schuck, 2013). This definition suggests that flowability is an inherent powder property (i.e., a powder will either flow or not); however, literature has shown that the ability of a powder to flow is ultimately determined by the extent at which interparticle interactions (e.g., van der Waals, electrostatic, liquid/solid bridging) occur, which are heavily influenced by a combination of:

- Powder bulk composition (e.g., fat, protein and moisture contents)
- Powder physical properties (e.g., particle size, shape and distribution, bulk density)
- Environmental and processing conditions (e.g., temperature, pressure and relative humidity).

Studies have shown that even minor changes to the above factors have the ability to cause a marked change in powder flowability (Crowley *et al*., 2014; Iqbal and Fitzpatrick, 2006; Teunou and Fitzpatrick, 1999). Therefore, a more suitable definition of powder flowability is proposed here as "the ability of a powder to flow under set

environmental or processing conditions". High-protein dairy powders, such as isolates, are associated with poor flowability due to their highly cohesive nature, making the handling and further application of these powders, challenging for manufactures and end-users alike.

On silo storage, cohesive powders, such as dairy protein isolates, have the ability to form structures such as ratholes or arches, within the storage hopper, that may act to alter, limit or fully inhibit the flow patterns and discharge of these powders from silos (Figure 2.2). Ratholes occur when powder, interacting with surrounding silo walls and other powder particles, becomes stationary and thus creates areas of no-flow within the silo. On the formation of a rathole, powder will continue to flow through a central channel and discharge, although limited, is still possible. The discharge of powder from a silo is completely inhibited when stable arches are formed. Stable arches (also referred to as bridges) may form at the outlet of a hopper when the cohesive strength of a powder is sufficiently high to fully inhibit powder flow. This creates a non-flow regime whereby a discharge aid is needed to re-initiate powder flow from the silo. Routinely, high mechanical force is applied to the outlet of a hopper to encourage discharge of cohesive powders, normally leading to visible damage to the outside of the hopper outlet region (Iqbal and Fitzpatrick, 2006; Miccio *et al*., 2013; Schulze, 2008).

For efficient handling, powders must be easily conveyed between two points, even over long distances within a plant. Highly cohesive powders, such as dairy protein isolates, have the ability to build up at compact zones of conveying lines such as elbow bends (Figure 2.2). At these points, excessive powder build-up may cause blockages of powder conveying lines leading to process down times (Deng and Bradley, 2016; Klinzing, 2010; Wang *et al*., 2000).

Application of dairy protein isolate powders at industrial scale commonly involves rehydration of these powder ingredients in order to utilise their well-described and often tailored functional (e.g., gelation and surface activity) and nutritional (e.g., delivery of essential amino acids and bioactivity) properties. Efficient rehydration of dairy powders includes the wetting of powder particles, followed by their dispersion and solubilisation. Cohesive powders, such as dairy protein isolates, are prone to form clumps on initial wetting during their rehydration. The formation of these clumps may be attributed to their poor powder flowability as large clusters of cohesive powder particles make initial contact with the surface of the liquid. The subsequent wetting of these clusters occurs only at the surface, forming a gel layer which retards water from penetrating into the clumps of powder particles (Barbosa-Cánovas, 2005; Fitzpatrick *et al*., 2016, 2017). Laboratory-scale studies have confirmed that clump formation impedes further stages of rehydration (dispersibility and solubility) from occurring and therefore prevents the efficient rehydration of dairy protein isolates (Figure 2.2).

All the challenges outlined above are faced by industries that work with high-protein dairy powders and are, in part, caused by poor powder flowability (Figure 2.2) (Bouvier *et al*., 2013; Crowley *et al*., 2014; Schuck, 2011). The purpose of this review is to comprehensively describe why high-protein dairy powders exhibit poor flowability, as well as to outline the traditional, and to present novel, techniques that are, or may possibly be, utilised by the food industries to improve the flowability of these powders post-spray drying.

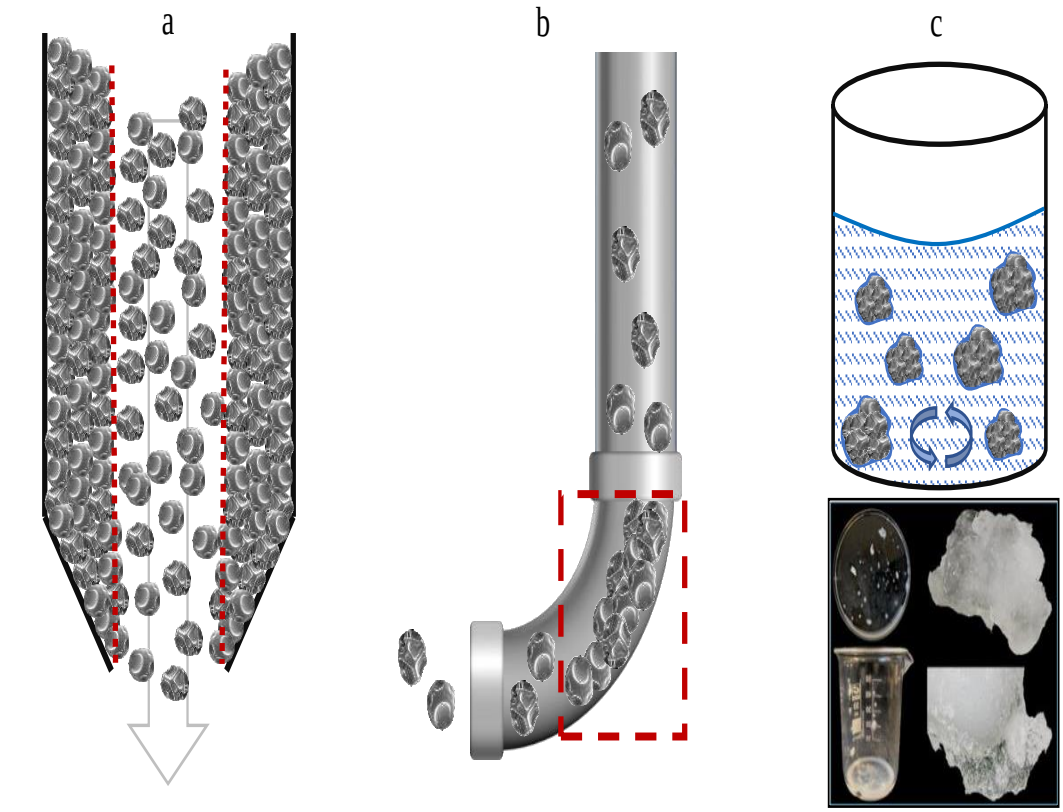


Figure 2.2 *Schematic representations of challenges arising on the storage (ratholing during silo storage - a), handling (build up on powder conveying line - b) and applications of high-protein dairy powders requiring rehydration (powder clumping on wetting - c).*

2.3 Causes of poor flowability of high-protein dairy powders

Ultimately, a powder will exhibit poor flowability when the combined cohesive forces between particles (interparticle interactions), and hence the cohesive force of the bulk powder, are greater than the force which is encouraging movement (e.g., gravity for silo discharge and compressed air pressure for pneumatic transport). The types and extent of interparticle interactions occurring are dependent on (i) powder bulk composition, (ii) powder physical properties and (iii) environmental and processing conditions experienced by that powder.

2.3.1 Powder bulk composition

The extent of interparticle interactions occurring in dairy powders is strongly influenced by these powders bulk composition (i.e., the constituents making up a powder particle), most notably the concentrations of fat (Fitzpatrick *et al*., 2004; Silva and O'Mahony, 2017) and protein (Barone *et al*., 2019). Bulk powder composition is ultimately determined by the combination of fractionation and enrichment processes utilised in the manufacture of these ingredients, pre-spray drying (Section 2.2). For high-protein dairy powders, unit operations such as membrane filtration are utilised to increase the proportion of protein in the bulk composition of the resulting powder (Figure 2.1, Table 2.1). A study by Crowley *et al*. (2014) showed that a significant decrease in powder flowability occurred as the bulk protein content increased for MPC powders with protein content ranging from 35 – 90%. The reduced flowability was attributed to an increased compressibility index on increasing protein content, as the powders with higher protein content could pack together into closer arrangements, thereby increasing the extent of interparticle interactions and cohesion.

2.3.2 Powder particle and bulk physical properties

The physical properties of a powder have a large effect on the number and intensity of interparticle interactions occurring between powder particles. These include particle (e.g., size and shape), surface (e.g., area, roughness and energy) and bulk (e.g., density, size distribution) properties (Ghoroi *et al*., 2013; Hou and Sun, 2008; Kaerger *et al*., 2004). These properties are mostly determined by the unit operations and processing parameters utilised during the production of a powder; of example, during powder spray drying, parameters such as atomisation pressure, atomiser type or feed viscosity can be controlled and used to form powders with very

different physical properties, leading to greatly different flowability performance (Maas *et al*., 2011; Nikolova *et al*., 2015; Pisecky, 2012).

High-protein dairy powders usually have smooth surfaced and spherical primary particles, of mean particle diameters less than 100 µm (Figure 2.3, Table 2.1). This results in a bulk powder in which particles can pack together tightly due to their uniform and spherical size and shape distributions, respectively. Also attributable to the small particle sizes is the large surface area per unit mass of powder (Table 2.1) (Crowley *et al*., 2014; O'Sullivan *et al*., 2017; Wu *et al*., 2019). Ultimately, these physical properties allow for many contact points between neighbouring powder particles, increasing the propensity for interparticle interactions and resulting in strong cohesive forces in the bulk powder, thereby reducing the overall powder flowability.

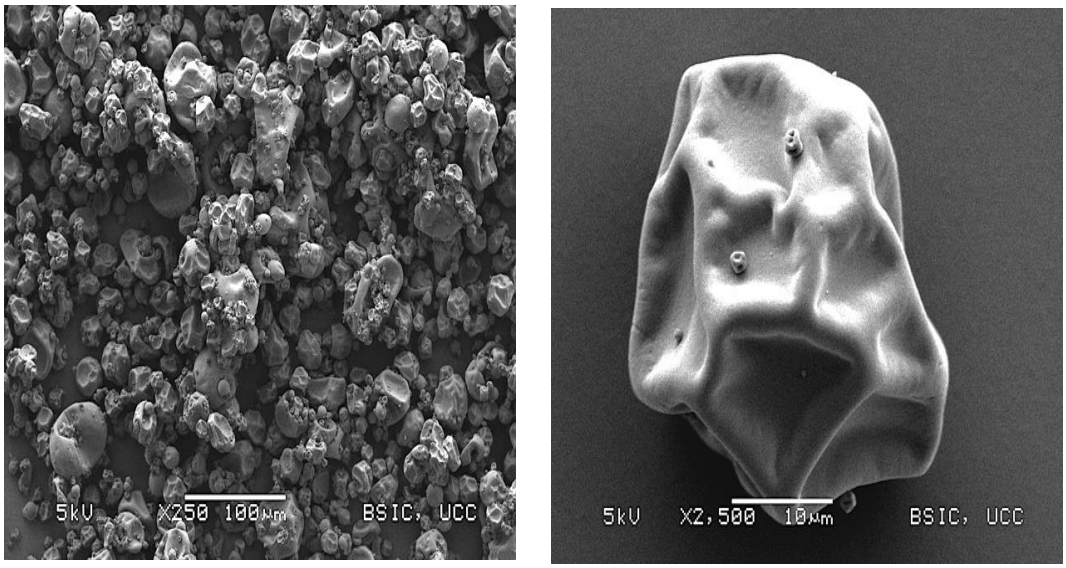


Figure 2.3 *Scanning electron micrographs (magnifications- X 250 and X 2500, scale bars of 100 µm and 10 µm included) of a representative milk protein isolate powder.*

Table 2.1 *Measured values for composition, particle and bulk properties of a representative milk protein isolate powder.*

Composition	Protein (%)	85.1 ± 0.8
	Carbohydrate (%)	5.67 ± 0.9
	Fat (%)	1.49 ± 0.0
	Moisture (%)	2.34 ± 0.0
	Ash (%)	5.47 ± 0.1
Physical properties	Particle size (μm)	
	Dv10[a]	11.9 ± 0.3
	Dv50[b]	31.7 ± 0.7
	Dv90[c]	64.7 ± 0.2
	Sphericity[d]	0.74 ± 0.0
	Specific surface area ($m^2 kg^{-1}$)	212 ± 4.4
	Particle density (g cm^{-3})	1.38 ± 0.0
Bulk properties	Bulk density (g cm^{-3})	0.27 ± 0.0
	Tapped density (g cm^{-3})	0.43 ± 0.0

[a] *Dv10* - Particle size below which 10% of material volume exists
[b] *Dv50* - Particle size below which 50% of material volume exists– median
[c] *Dv90* - Particle size below which 90% of material volume exists
[d] Sphericity - Unitless value representing sphericity of a particle (1- perfect sphere)

2.3.3 Environmental and processing conditions

The moisture content (and relative humidity) of the environment surrounding a high-protein dairy powder will impact the nature and extent of interparticle interactions occurring in the bulk powder. Studies have shown that at high relative humidity, the moisture surrounding powder particles condenses at the contact points and thus, through capillary action, creates a liquid bridge (Table 2.2). The reduction of flowability through liquid bridge formation is prominent in powders containing large amounts of hygroscopic materials (e.g., carbohydrates). Dairy protein isolates tend to contain low proportions of lactose (and other carbohydrates) and thus, a very high relative humidity (~ 80% RH) is needed in order to significantly reduce their

flowability through caking (Amidon and Houghton, 1995; Karde and Ghoroi, 2015; Podczeck *et al*., 1997, 1996; Price *et al*., 2002; Teunou and Fitzpatrick, 1999).

Environmental moisture also impacts the surface energy of powder particles, impacting bulk powder flowability. Dairy protein isolates, like other high-protein dairy powders are strongly hydrophobic due to the presence of protein and fat at the surface of the powder particles (Burgain *et al*., 2016; Felix da Silva *et al*., 2018; Fyfe *et al*., 2011). Previously, Karde *et al*. (2017) showed that while on increasing relative humidity, the surface energy of hydrophilic powders also increased, no change in surface energy was experienced on the same increase in relative humidity for ibuprofen which, like protein isolates, is highly hydrophobic.

The level of consolidating stress acting on powders is another well studied, environmental factor influencing powder flowability (Chen *et al*., 2010; Crowley *et al*., 2014). As discussed, large silos or hoppers are used for the storage of powders and in these vessels, varying (head) pressures will act on the powder depending on the powder's location in the silo, resulting in a bulk powder exhibiting differing levels of flowability. Above a specific pressure, a bulk powder will experience either deformation, which encourages flowability (e.g., low bulk density powders, such as MPI) or consolidation, which decreases flowability (e.g., high bulk density powders such as skim milk powder) (Valverde *et al*., 1998). The reduction in flowability through consolidation is caused by plastic deformation at contact zones between powder particles, resulting in increased number and strength of interparticle interactions thereby, increasing the cohesive bulk strength (Garg *et al*., 2018).

2.3.4 Interparticle interactions

The main attractive forces occurring between powder particles are van der Waals, electrostatic, liquid- (*via* capillary forces) and solid-bridging interactions, and are summarised in Table 2.2 (Shah *et al*., 2017). For dairy powders with large mean particle size (>150 μm), such as agglomerated powders, the forces acting upon these powders, such as gravity, usually outweigh these attractive forces and thus, such powders tend to flow well. For powders with smaller mean particle size (<100 μm), such as dairy protein isolate powders, the number and extent of the above attractive interactions may outweigh the effect of the acting forces, hence causing powder particles to adhere to each other, reducing powder flow (Li *et al*., 2004; Shah *et al*., 2017).

2.3.4.1 Van der Waals interactions

Van der Waals interactions are known to have one of the lowest adhesion strengths of those presented in Section 2.3.4. However, they are the predominant force causing adhesion in dry powder systems of small particle size, such as protein isolates, due to the large number of van der Waals interactions occurring at the particle level in these powders (Kendall and Stainton, 2001; Li *et al*., 2004; Simons, 1996). Van der Waals interactions occur as electrons are in constant movement in powder particles, leading to the continual formation of temporary dipoles at the surface of (and throughout) powder particles. A dipole is a set of charges, of equal magnitude, but opposite sign (Table 2.2), and thus, the adhesion of two (or more) powder particles occurs due to the attractive forces that exist between the dipoles of opposite powder particles (*via* ionic bonding) (Fowler and Stone, 1987; Shah *et al*., 2017). It is well established that the most influential powder particle and bulk properties for

determining the amount of van der Waals interactions occurring are particle size and interparticle spacing, respectively (Seville *et al*., 2000; Visser, 1989; Yu *et al*., 2003). Commercial dairy protein isolate powders are composed of primary particles of small particle size (<100 μm) which can pack together closely due to their spherical shape, and these features align closely to the conditions needed for van der Waals interactions to occur to a great extent in the powder bulk, thereby limiting flowability of high-protein dairy powders.

2.3.4.2 Electrostatic interactions

The forces associated with electrostatic charging (also termed "tribocharging") are, again, of low strength when compared to other interparticle forces (Simons, 1996). Like van der Waals interactions, electrostatic charging can also have a large effect on the flowability of high-protein dairy powders due to the extent to which they can occur (especially when combined with van der Waals interactions). During the production of dairy powders, particles frequently collide with solid surfaces (termed particle collisions) or with other powder particles (termed particle attrition), during processes such as pneumatic conveying, fluid bed processing and dry blending. On such collisions, the surface of dairy powder particles builds a charge, and due to the organic nature of dairy powders, insulation of this charge will occur, leading to a very slow dissipation of charge over time. Oppositely charged particles, if in a close arrangement (such as the case for dairy protein isolate powders), will create attractive forces that lead to the cohesion of the particles, limiting powder flowability (Matsusaka *et al*., 2010; Naik *et al*., 2016; Shah *et al*., 2017).

2.3.4.3 Liquid bridging

It is possible for physical bridges to form between two or more particles and the resulting interparticle interactive forces are strong. Initially, this occurs in the formation of liquid bridges between particles, which, in turn, could form physical bridges if certain environmental criteria prevail. These interactions can strongly reduce the ability of a dairy powder to flow (Shah *et al*., 2017; Simons, 1996). Similar to van der Waals and electrostatic interactions, the physicochemical properties of a dairy powder, such as particle size and shape, also play a role in the formation of these bridges. Another important influence on the formation and stabilisation of these physical bridges is the environmental conditions surrounding the powder such as the relative humidity and temperature (Podczeck *et al*., 1997).

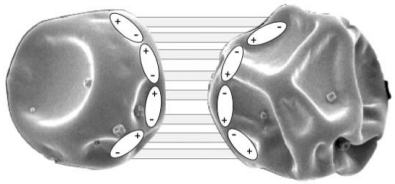
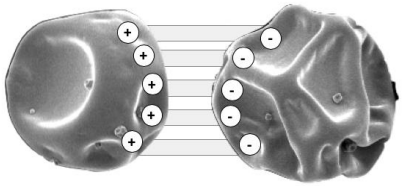
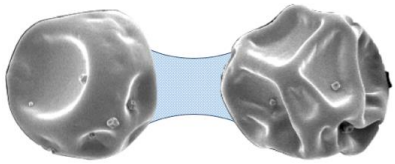
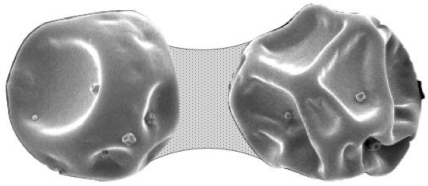
Liquid from within powder particles (moisture or liquid fat) or from the environment (environmental moisture) may condense at contact points of closely located particles. This condensate will create many cohesive liquid bridges (termed pendular bridges) between the two particles due to the presence of a strong attractive capillary force which is reported to be over 50-times stronger than van der Waals forces (Modugno *et al*., 2015; Rhodes, 1990; Simons, 1996). Liquid bridging is mostly associated with the presence of excess moisture surrounding, or within, powder particles due to the production or storage conditions; however, the reduction in dairy powder flowability caused by excess surface fat is also attributed to the formation of liquid bridges. At room temperature (~20°C), the majority of milk fat present in dairy powders is fluid-like (Kelly *et al*., 2014; Zychowski *et al*., 2016), and when present at the surface of powder particles, a liquid bridge will form through the attraction of capillary forces (Foster *et al*., 2005).

The occurrence of liquid bridging during the storage of dairy protein isolate powders is low compared to other commercial dairy powders (e.g., whole milk powder or skim milk powder), which may be attributed to the much lower level of hygroscopic carbohydrates present in dairy isolate powders due to the fractionation and protein enrichment (i.e., lactose reduction steps) in their production (Figure 2.1, Table 2.1).

2.3.4.4 Solid bridging

Under the necessary conditions (e.g., temperature and relative humidity), a liquid bridge may be further stabilised through transition into a solid bridge *via* evaporation, crystallisation, or solidification of the bridging material. This in turn increases the strength of the attractive forces between particles (Foster *et al*., 2005; Padmadisastra *et al*., 1994). If occurring in an un-controlled manner (caking), the formation of liquid or solid bridges will significantly reduce a dairy powders ability to flow and make the handling and storage of these powders much more difficult. In contrast, the controlled formation of a liquid and subsequent, solid bridge, is routinely utilised as a means of particle size enlargement in order to control powder flowability which will be the focus of later sections of this review (Section 2.4.1).

Table 2.2 *Summary of interparticle interactions occurring at particle level in high-protein dairy powders. Scanning electron microscopy micrographs of milk protein isolate powder particles used to represent powder particles.*

	Description	Illustration	Strength	Magnitude
Van der Waals	Temporary **dipoles** at powder particles interact *via* ionic bonding with dipole of **closely located particles**.		+	++++
Electrostatic	Opposite **charges** on surfaces of powders from **friction and attrition** lead to ionic bonding between particles.		++	+++
Liquid bridging	Surrounding or internal **moisture condenses** at contact points between particles. **Liquid capillary forces** cause adhesion.		+++	++
Solid bridging	**Solidification of liquid bridges** *via* evaporation or crystallisation cause large increase in strength of adhesion.		++++	+

2.4 Approaches for improving the flowability of high-protein dairy powders

Due to the growing market for high-protein dairy powders, there is a continual need to tailor and control the flow properties of such powders, in order to ensure easy storage, handling and further application. To increase a powder's flowability, actions must be taken in order to reduce the number and extent of the above interparticle

interactions from occurring at the bulk level. Traditional and more novel approaches to control a powder's flowability exist and are utilised by various industries handling powders such as the food, pharmaceutical and biochemical industries, and these approaches may be categorised as (i) particle size enlargement and (ii) surface modification of powder particles.

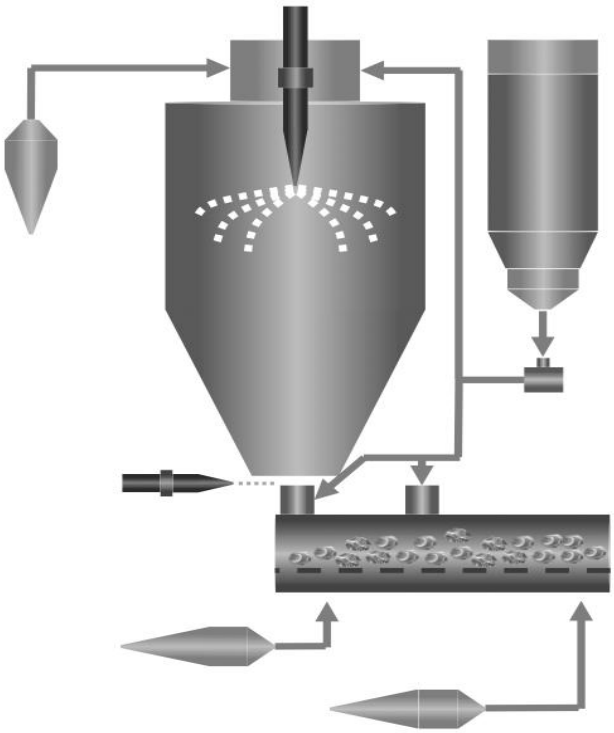
2.4.1 Particle size enlargement

The most traditional approach to increase a powder's flowability is to increase the size of the particles that make up a powders bulk, allowing the forces encouraging movement (such as gravity or pressurised air) to outweigh the forces of cohesion, thereby, allowing the powder particles to flow. Inversely, the extent of interparticle interactions will be reduced, serving to further improve powder flowability (Schulze, 2008). The terms agglomeration (mainly used within the food industry) and granulation (mainly used within the pharmaceutical industry) are both used to describe the processes of increasing the particle size of a powder by combining numerous individual primary powder particles together into large cluster-like structures where the individual particle may still be distinguishable. These clusters of particles are of a much greater size than that of the original particle, thus increasing flowability. Agglomerated particle structures contain increased volumes of interstitial air in the form in capillaries and pores, reducing the powder's bulk density and allowing for easier penetration and movement of water into and through the cluster structures through capillary action on rehydration (Cuq *et al*., 2013; Iveson *et al*., 2001; Pisecky, 2012). For the purpose of this review, the term agglomeration will be used to collectively describe the various methods for particle size enlargement that follow.

2.4.1.1 Spray dryer and fluid bed agglomeration

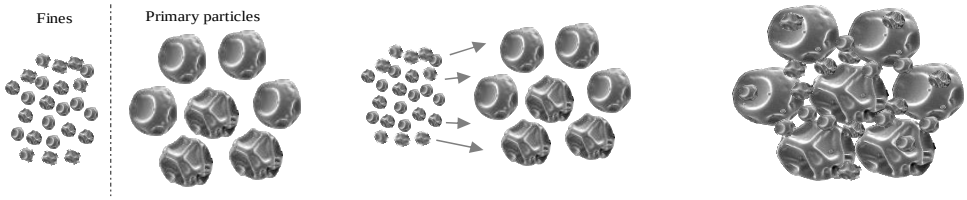
The process of agglomeration in the production of dairy powders generally occurs in the spray dryer chamber, and/or, in the external fluid bed located after the spray drying chamber (Figure 2.4) (Drake *et al*., 2009; Neff and Morris, 1968). In the spray drying chamber, agglomeration occurs through the collisions of either wet particles (primary agglomeration) or wet and dry particles (secondary agglomeration). To some extent, both primary and secondary agglomeration occur naturally in the spray chamber through random collisions of moving particles in the chamber (spontaneous agglomeration). However, by controlling the geometries and parameters of the spray drying process, both primary and secondary forms of agglomeration can be forced to occur to varying extents (forced agglomeration) (Drapala *et al*., 2017; Kumar *et al*., 2017; Pisecky, 2012). The most utilised form of agglomeration in the spray drying chamber occurs through the process of fines return. During production of powders by spray drying, powder material of a much smaller particle size than that of the target primary particle will be produced, this material being termed "fines" (usually <10 μm). Due to their small particle size, these fines are carried out of the spray chamber in the exhaust air and then collected in a filter system such as a cyclone, or bag filter. The fines may be then recirculated back into the top of the spray dryer main chamber and directed at the atomisation zone, where new primary particles are being formed, allowing the dry fines to collide and coalesce with newly formed, wet particles leading to the formation of large porous clusters of particles with channel spaces between the individual primary particles (Figure 2.4). The degree of agglomeration *via* fines return may be controlled by altering the amount of the fine powder particle material that is recirculated back into the dryer main chamber (Gianfrancesco *et al*., 2008; Schuck, 2013a, 2014).

a) Spray drying process



b) Agglomeration via fines return

1. Fines produced
2. Fines recirculated
3. Agglomerate formed



c) Agglomeration via rewetting

1. Binder addition
2. Wetting
3. Nucleation
4. Solidification

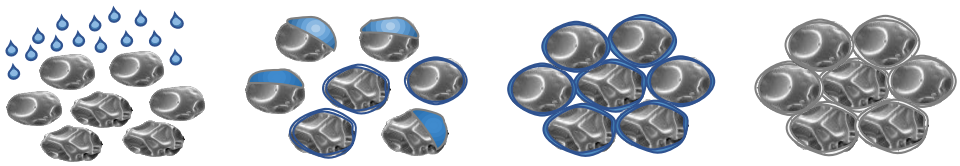


Figure 2.4 *Schematic representations of (a) the spray drying process used for dairy powders with external fluid bed drying and (b) agglomeration via fines return and (c) agglomeration via rewet processing.*

On leaving the spray drying chamber, powder particles generally enter into an external fluidised bed unit where heated and cool air pass upwards though the powder separately, at velocity, to complete drying and cooling of the powder, respectively. This high velocity air pushes powder particles upwards and disperses them into the chamber of the fluid bed, i.e., fluidising them in order to finalise their drying and facilitate subsequent cooling (Figure 2.4) (Seville *et al*., 2000). Particle size enlargement of the powder through fluid bed agglomeration can be achieved here by rewetting, i.e., applying a binding solution onto the particles as they enter into the fluid bed unit. The process in which the binder acts to agglomerate the powder particles has been well studied and is separated into four main stages: binder addition, wetting and spreading of the binder, nucleation and solidification (Figure 2.4) (Cuq *et al*., 2013).

a) Binder addition

The method of addition of the binding solution may vary from pouring to pumping, but studies have shown that the most uniform agglomeration process (large agglomerates of a narrow particle size distribution) is achieved by atomising the solution onto the powder particles as they enter the fluid bed unit (Reynolds *et al*., 2005a). A twin-fluid nozzle is routinely used to atomise the viscous binder solution using high air pressures to form a uniform spray of the solution in droplet form which can come into contact with the powder particles.

b) Wetting and spreading

When the binder first comes into contact with the powder particles, the binder will begin to wet the surface of the particles. Due to the fluidisation movement of the

particles, the binder will spread and coat the entire surface of the powder particles, which is important for the formation of agglomerates of a uniform particle size.

c) Nucleation

Initially, collisions of the now-wetted particles, cause the formation of liquid bridges (Section 2.3.4.3), which link two or more particles together through capillary forces. This initial particle growth acts as a nucleus for further consolidation and growth of the agglomerate structure.

d) Solidification

Due to the elevated temperatures (approx. 70°C) of the initial stages of the external fluid bed, the liquid bridges stabilising the agglomerate structures will be, partially or fully, evaporated, crystallised or solidified depending on the compositional make-up of the liquid bridge. Solidification of the liquid bridge leads to the formation of a strong, solid bridge between primary particles in an agglomerated structure.

The binding solution used for fluid bed agglomeration of powders can vary depending on the application, with binder characteristics such as composition, viscosity, rate of addition and surface tension all playing a vital role in determining the type, size and strength of the agglomerates formed. Water and sugar solutions are some of the binder solutions used by various powder handling industries during fluid bed agglomeration; however, for the dairy industry, lecithin, a natural, phospholipid-rich surfactant which has been traditionally used for coating agglomerates formed *via* fines return, has been identified as a potential binder for powder agglomeration due to its well established beneficial impact on the rehydration properties of the resulting agglomerated structures (sometimes termed lecithination/instantisation) (List, 2015;

Sharma *et al*., 2012). Lecithin, usually dispersed in a blend of vegetable oils, is highly viscous and can effectively bind numerous particles together in large cluster structures. Due to its high fat content, at the elevated temperatures of the external fluid bed, the lecithin blend can efficiently spread over the surface of the agglomerate structure, which is then solidified on further heating and cooling. The increase in particle size on agglomeration *via* lecithination improves the flowability and bulk handling of the powder but also, has a very beneficial impact on the wettability of the resulting agglomerates (Kinsella and Morr, 1984; Wu *et al*., 2020). As lecithin is rich in phospholipids, by coating the surface of an agglomerated powder particle it in turn increases the hydrophilic nature of the powder surface due to the presence of the amphipatic, phospholipid molecules (both hydrophobic and hydrophilic). Traditionally, powders such as whole milk powder (WMP) and fat filled milk powder (FFMP) are lecithinated (instantised) as the application of these powders requires these powders to fully wet on first contact with water (Schmidmeier *et al*., 2019).

The agglomeration of high-protein dairy powders *via* spray dryer and fluid bed agglomeration is not widely practiced by dairy industries. Although particle size enlargement has been clearly shown to improve the flowability of many dairy powders it must be noted that it does this by altering the physical and bulk properties of the original powder. For example, agglomerating a high-protein dairy powder with the aid of lecithin (or other binding solutions), will reduce concentrations of other constituents of that powder (Ji *et al*., 2016). This must be avoided in the production of high-protein dairy powders such as protein isolates (MPI, WPI) where strict requirements for protein content of the final powder ($\geq$ 90% protein) must be satisfied. Also, when high-protein dairy powder is agglomerated, the bulk density of that powder decreases, meaning that the same mass of the agglomerated powder will occupy a larger volume

than that of the non-agglomerated form. Ji *et al*. (2017) showed that for MPI, the initial low bulk density (0.30 g cm^{-3}) of the powder was further reduced (0.18 g cm^{-3}) on agglomeration by fluid bed processing. These effects of spray dryer and fluid bed agglomeration can be seen as a disadvantage for the dairy powder industry as it can lead to a reduction in product value and an increase in storage/transport costs, respectively.

Studies by Gaiani *et al*. (2007b) and Mimouni *et al*. (2010) have shown that casein- and whey-dominant powders (e.g., MPI and WPI, respectively) have different rate limiting steps in their rehydration processes and therefore, agglomeration of these powders may yield different effects on their rehydration behaviour. For whey-dominant powders, the initial wetting stage is the rate limiting step whereas, for casein-dominant powders, particle dispersibility limits the rehydration. As particle size enlargement *via* spray dryer and fluid bed agglomeration effects the wetting stage of rehydration, it can positively impact whey-dominant protein powders, such as WPI, whereas it can negatively impact the rehydration of MPI or MCI which are casein-dominant high-protein powders, due to its negative impact on powder dispersibility (Gaiani *et al*., 2007a). Ultimately, a more comprehensive approach to improve the flowability of high-protein dairy powders is required which minimises any negative effects on the compositional and rehydration properties of these powders.

2.4.1.2 Shear agglomeration

Shear agglomeration is a method of particle size enlargement, commonly used in the pharmaceutical industry. The process shares many similarities to that of fluid bed agglomeration (Section 2.4.1.1) as again, a binding solution is used to facilitate the agglomeration of primary particles into larger structures. The binder is added to a

mass of powder that is in constant movement and shear mixing in an agglomerating drum/vessel. On continual mixing in the presence of the binder solution, the powder particles form relatively large agglomerates (>1 mm in size) through surface wetting, nucleation and consolidation. Agitators in the agglomeration device mix at specific speeds to introduce shear forces which act to reduce the particle size of the formed agglomerates towards a smaller target agglomerate size through the forces of attrition and breakage (Arndt *et al*., 2018; Chirkot and Propst, 2005; Gokhale *et al*., 2005; Oulahna *et al*., 2003).

The level of shear used can vary (low or high shear) but most routinely high shear forces are used to treat the agglomerating powder particles. Litster and Ennis (2004) report that for high shear agglomeration, the mixing agitators will be rotating at 60-800 rpm, while the agitator provides high levels of shear by rotating at 500-3500 rpm typically. The shear forces experienced during agglomerate formation causes densification, whereby the particles that make up an agglomerate are further compressed, minimising interparticle channels and causing the entrapped binder to be squeezed out to the surface of the agglomerated structure, allowing for further nucleation and agglomeration to occur. The resulting agglomerates of shear agglomeration therefore, are quite often large, dense structures that are spherical in shape (Faure *et al*., 2001). The effect of agglomerate densification on the resulting powder bulk density during shear agglomeration processing was illustrated in a study by Chevalier *et al*. (2009). Here agglomerates of calcium phosphate were formed *via* low and high shear agglomeration. It was found that the agglomerates formed using high shear forces had a much higher bulk density (0.73 $g.cm^{-3}$) than that of the agglomerates formed using low shear forces (0.53 $g.cm^{-3}$).

For the agglomeration of high-protein dairy powders, shear agglomeration provides no clear advantages to that of the current dairy industry standard, fluid bed agglomeration. The formation of more dense agglomerates may alleviate the reduction in bulk density experienced on fluid bed agglomeration; however, this densification process acts to eliminate the interparticle channels and pore spaces between particles, with these components of agglomerated dairy powders being key in their efficient rehydration; interparticle channels allow the surrounding liquid to easily penetrate into inner primary particles of the agglomerated powder, facilitating solubilisation. Large, dense agglomerates of high-protein dairy powder particles could lead to further clumping issues on powder wetting (Figure 2.2) and overall reduced powder solubility, previously displayed by (Ji et al., 2016a).

2.4.1.3 Extrusion agglomeration

Extrusion technology is regularly used for the continuous agglomeration processing of pharmaceutical powders at commercial scale. Another form of wet agglomeration, extrusion agglomeration utilises water or a more complex binder solution to cause the agglomeration affect. For the agglomeration of hydrophobic or poor wetting powders, such as high-protein dairy powders, the adequate and efficient distribution of the binder, to allow for uniform nucleation and growth, is a limiting process step. Extrusion agglomeration exposes powders to high forces through intense mixing and kneading in the extrusion line which forces the spreading of the binders across the powder particles allowing the size of agglomerates to increase *(Iveson et al.*, 2001; Seem *et al.*, 2015).

In the extrusion agglomeration process, the powder drops, or is fed, into a barrel where screws counter-rotate at a set speed; the number of screws varies, with the most

common configuration being a twin-screw extrusion line. The counter-rotating motion of the screws transports the powder along the extrusion barrel and creates a mixing motion in the bulk powder. A liquid feed line is used to introduce the selected binder, at a pre-determined addition rate, into the extrusion line, and into contact with the powder forming liquid bridges. As the wetted powder particles pass through the barrel, they enter kneading zones where discs of specific geometries act to create zones of high shear forces. These forces, as in high-shear agglomeration, cause densification of the agglomerated particles and allow for further agglomerate growth. Each section of the extrusion agglomeration process allows for heating, drying and cooling of the agglomerated structures as the extrusion barrel is jacketed allowing for temperature control. Many process geometries (e.g., number of screws, screw length and diameter, kneading elements) and parameters (e.g., screw speed, liquid:solid ratio) may be utilised in order to control the extrusion agglomeration process and thus, tailor the physical properties of the resulting agglomerated powder, as discussed at length by Seem *et al*. (2015). The final step in the process is the shaping or milling of the formed agglomerate (extrudate) to the desired particle size/shape. In the pharmaceutical industry, the extrudate is commonly compressed directly into tablet form which is a widely used form of powder delivery. However, if implemented in the production of high-protein dairy powders, a milling step may be utilised to control the particle size of the agglomerates formed in the extrusion process (Figure 2.5) (Dhanalakshmi *et al*., 2011; Djuric and Kleinebudde, 2008; Thompson and Sun, 2010).

In a series of studies, Keleb *et al*. (2002, 2004) used pharmaceutical powders that exhibit poor flow and dissolution properties (i.e., α-lactose monohydrate and paracetamol), to evaluate the efficiency of an extrusion agglomeration process with (polyvinylpyrrolidone as binder), and without (water as binder), the use of complex

binding solutions, in direct comparison to a shear agglomeration process. The results showed that agglomeration was achieved for all powders without the use of complex binding solution (polyvinylpyrrolidone) for extrusion agglomeration (high agglomerate yield and over 60% of the agglomerates formed had particle size greater than 250 μm) while the agglomeration of these powders was not possible using shear agglomeration without the use polyvinylpyrrolidone as a binder. The possibility of agglomerating a difficult to handle powder, such as paracetamol, with only water suggests that this approach to particle size enlargement may be attractive in the processing of high-protein dairy powders.

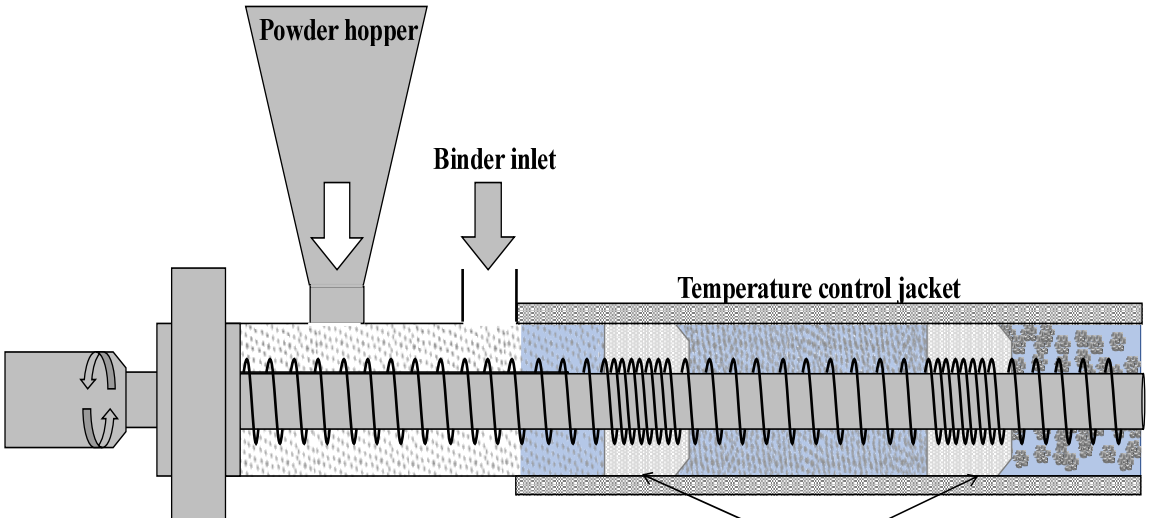


Figure 2.5 *Schematic representation of a typical extrusion granulation process.*

2.4.1.4 Roller compaction agglomeration

All approaches for particle size enlargement discussed thus far in this review have been forms of wet agglomeration, where binding solutions are used to facilitate the agglomeration of powder particles. On the other hand, roller compaction, is a form of dry agglomeration where particle size enlargement is achieved by applying very high levels of pressure which forces particles closer together and induces changes in the particle structures, yielding agglomerates. Dry granulation is routinely used in the agglomeration of powders that are sensitive to moisture and therefore cannot be processed *via* traditional wet agglomeration approaches. Roller compaction is the most studied, and applied, form of dry agglomeration, commonly used in the pharmaceutical industry to improve the flowability of various pharmaceutical powders. The clear advantages to dry agglomeration (e.g., no binder needed, no heating or drying steps required) highlights it as a method of particle size enlargement with potential in the production and control of difficult to handle high-protein dairy powders (Abu Fara *et al*., 2018; Dhanalakshmi *et al.*, 2011).

A typical roller compaction process involves feeding a powder, either *via* gravity (for powder with good flowability) or a screw feeder (for powder with poor flowability, such as high-protein dairy powders) into the contact zone of two large co-rotating rollers. At this point, termed the "nip region", large frictional shear forces will draw the powder down and between the two rotating rollers. Very large pressures begin to build up within the powder bulk which causes two main conformational changes in the powder particles. Firstly, particles are forced to rearrange into close arrangement, and then, as the pressure continues to build, a critical point for the particles is met, which either causes particle breakage (for fragile particles) or particle deformation (for stronger particles). As a result, the powder exits the rollers in the

form of heavily compacted ribbon-like structures that can be gently milled and screened to form agglomerated powder structures with desired particle sizes (Figure 1.6) (Omar *et al*., 2016; Reynolds *et al*., 2010; Wu *et al*., 2010).

2.4.2 Surface modification

The surface characteristics (e.g., surface energy and charge) and composition (e.g., surface fat) of dairy powders plays a key role in determining the number and extent of interparticle interactions occurring in the powder bulk, and thus, impacts the powder's flowability (Section 2.3.4). For high-protein dairy powders, due to their small and spherical size and shape, the surface properties of these powders allow for extensive van der Waals and electrostatic interactions to occur, leading to such

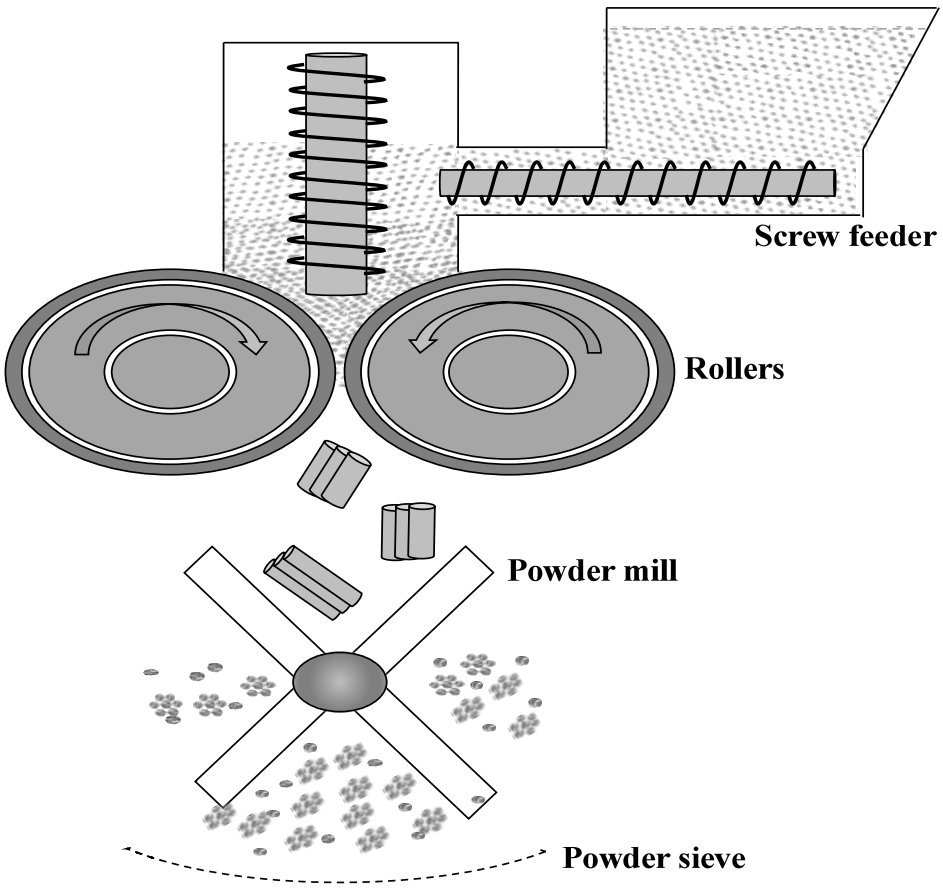


Figure 2.6 *Schematic representation of the roller compaction agglomeration process for dry powder followed by milling to achieve the desired powder particle size.*

powders having high cohesive strength. The presence of fat at the surface of powder particles is also attributed to reduced powder flowability. During production of dairy powders by spray drying, fat contained in the atomised droplet will be preferentially located at the powder particle surface on atomisation and subsequent drying, leading to an over representation of fat at the surface when compared to bulk of the powder (Fäldt and Bergenståhl, 1996; Foerster *et al*., 2017, 2016a, 2016b). Even in high-protein dairy powders, where fat usually contributes to a very small percentage of the total bulk composition (approx. 1-5% fat), the surface composition of these powders may be dominated by fat. Studies by Kim *et al*. (2002, 2005) focussing on the effect of surface composition on the flowability of spray dried dairy powders showed that for a WPC 80 powder (86% protein, 6% fat), over 50% of the exposed powder surface was comprised of fat, despite the fact that fat constituted only 6% of the bulk powder composition. This over-representation of fat at the surface of dairy powders, compared to the bulk, also occurs in casein dominant systems such as MPC, MPI and MCC (Crowley *et al*., 2018; Kelly *et al*., 2015). The presence of fat at the surface of powders is a strong factor influencing (generally adversely) their flowability and rehydration properties. In the case of high-protein powders, where small, spherical particles are in close arrangement, the presence of fat at powder surfaces may play a critical role in large cohesive strength experienced in the bulk powder, and ultimately act to limit their flowability.

Surface modification is a method of processing which acts to alter the surfaces of powder particles by creating a new powder surface or shell in order to improve the bulk handling characteristics of powders. By altering only the surface of a powder particle, changes in particle size and shape are minimised and thus, as are large changes to the bulk density of a powder. Minimising the decrease in bulk density (a

feature of particle size enlargement - Section 2.4.1), is desirable in the production of high-protein dairy powders for storage and transport costs. Two main methods of surface modification have been previously utilised by both food and pharmaceutical powder processing industries, and these are fluid bed coating and dry coating of powder particles.

2.4.2.1 Wet coating

Wet coating (also termed fluid bed coating) of powder particles *via* fluid bed processing utilises powder fluidisation and liquid atomisation to achieve a very thin layer of coating material on the surface of a powder. This newly formed layer is then dried rapidly and cooled in a manner that avoids particle agglomeration, creating a new powder boundary that alters the surface properties and composition to improve powder flowability. Surface coating has been utilised in food applications previously using biopolymers such as lactose, glucose, starch hydrolysates and alginate solutions as coating solution for food powders. Close control over the composition and viscosity of these coating solutions, as well as the addition level and rate is necessary to achieve uniformly coated particles while preventing unwanted agglomeration during fluid bed coating of powders. (Dewettinck and Huyghebaert, 1999; Szulc and Lenart, 2013; Werner *et al*., 2007).

Fluid bed coating utilises the same principles as fluid bed agglomeration (Section 2.4.1.1), where a liquid is atomised onto particles in fluidised motion. However, a different geometry of fluid bed, termed a "Wurster coater", is used for particle coating applications to avoid the unwanted agglomeration of particles in this process. Here, a central channel is inserted at the bottom of the fluid bed chamber which acts to accelerate and disperse the powder particles upwards and through an

atomisation zone where a thin layer of the coating solution is applied to the particle surface. The nozzle used for atomisation of the coating solution is loaded from the bottom of the fluid bed chamber (bottom-fed atomisation) and it sits in the central channel of the Wurster coater, spraying very fine, uniform droplets of the coating solution into the atomisation zone of the Wurster coater. As the particles become coated, the high velocity air continues to push them upwards into the fluid bed chamber in a fine dispersion. As the coated particles exit the Wurster coater's inner channel, they enter into the top of the fluid bed chamber where the elevated internal temperature rapidly acts to dry and solidify the newly formed particle coatings, before the particles are cooled and collected (Figure 2.7) (Hede *et al*., 2009; Jono *et al*., 2000; Rajniak *et al*., 2007).

For efficient particle coating while minimising unwanted agglomeration, each step of the above process must be carefully controlled, most notably, the fluidisation of particles into a fine dispersion where particle-particle interactions and collisions are avoided. Geldart (1973) developed a classification system to characterise the ease, or difficulty with which a powder can be fluidised, describing "Group C" powders (C – cohesive) as the most difficult to fluidise due to their characteristic low particle size and low particle density, both being important properties of high-protein dairy powders (Figure 2.8). This indicates that the efficient coating of high-protein powders may prove difficult due to improper fluidisation of high-protein dairy powders (e.g., channelling/ratholing in powder bed) (Wang *et al*., 1998). Chen *et al*. (2008) reported that unwanted agglomeration is unavoidable when coating powder particles with sizes ≤50 μm (typical of high-protein dairy powders) without prior modifications such as pre-treatment of powder *via* dry coating (Section 2.4.2.2) or though modified fluidisation (e.g., vibro-fluidisation) (Chen *et al*., 2008).

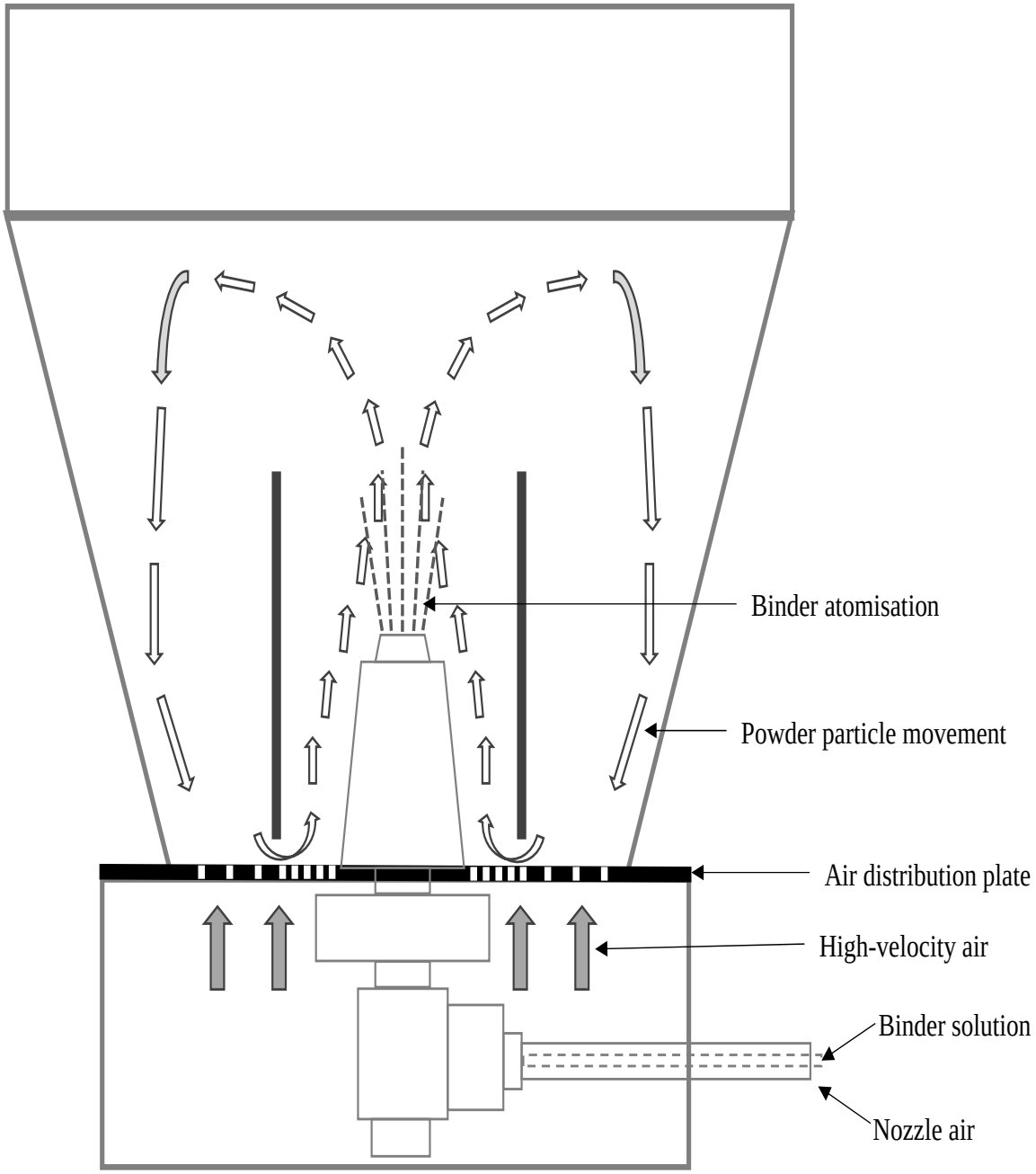


Figure 2.7 *Schematic representation of a fluid bed coating process achieved using a Wurster coater insert.*

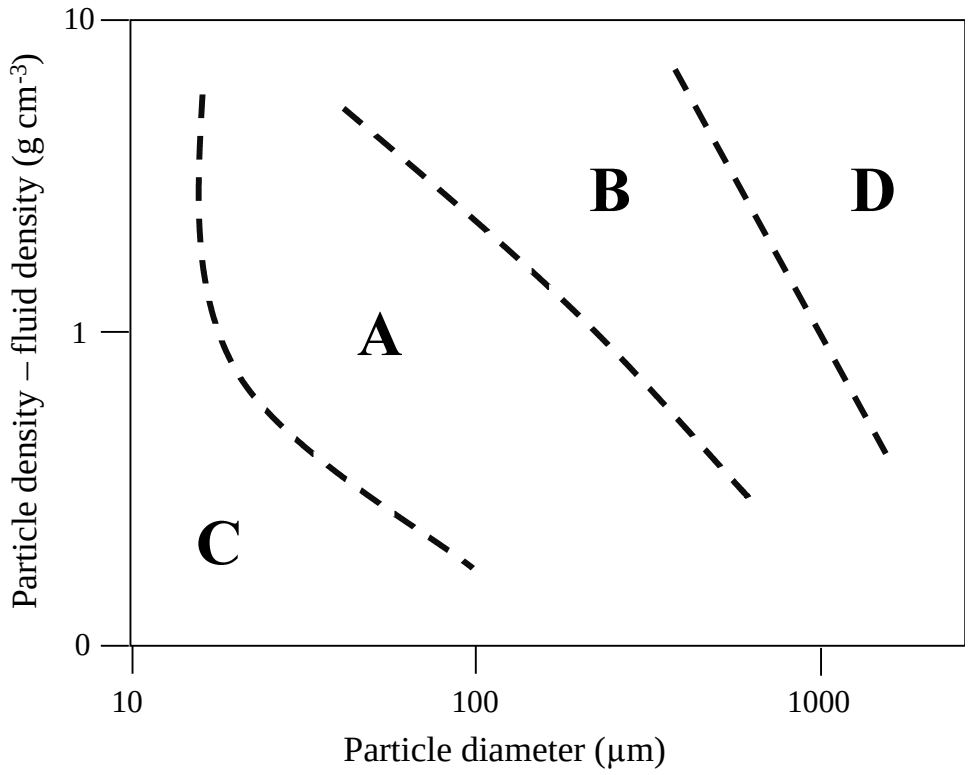


Figure 1.8 *Geldart classification chart for particle fluidisation: C- Cohesive, A- Aeratable, B- Sand-like and D-Spoutable.*

2.4.2.2 Dry coating

Traditionally, wet coating of powder particles was the standard procedure for surface alteration to tailor the flowability and fluidisation properties of powders. In more recent years, dry coating has emerged as a more efficient, sustainable and cost-effective method to modify powder surfaces. Wet coating, as well as other, previously discussed particle size enlargement processes, requires large energy and material input in various process steps such as binder atomisation, powder fluidisation and powder drying and cooling, whereas the dry coating process produces no organic waste streams and also has the potential to minimise energy input as no binder addition or drying steps are needed in this process. A reduction in energy and material input, in addition to minimising waste streams during processing is of increasing importance to

production industries as continuous improvements in environmental sustainability are desired (Bourhis *et al*., 2013; Pfeffer *et al*., 2001).

Dry coating is achieved by introducing very fine, submicron-sized material, termed "guest particles" into contact with larger micron-sized powder particles, termed "host particles". Through mixing and introduction of mechanical force, these guest particles (also termed "flow aids", "glidants" or "lubricants") will be dispersed, to some extent, on the surfaces of the much larger host powder particles. Due to the large differential in size, as well as the close arrangement between the host and guest particles, interparticle interactions will occur which lock the guest particles to the surfaces of the host powder particles. These particles stay locked onto the surface of the host as the force of attraction between the two particles is much greater than the force of gravity acting downwards on the submicron-sized guest particles (Ghoroi *et al*., 2013; Jallo *et al*., 2012; Karde and Ghoroi, 2014; Tomas and Kleinschmidt, 2009).

A review of previously published work shows that three main materials are used routinely as the guest particles for dry coating processing, these being, silica, silicate and stearate particles (Huie Liu *et al*., 2006; Yang *et al*., 2005; Zhou *et al*., 2010). The importance of the size of the guest particle was illustrated in a study by Yang *et al*. (2005), where silica particles of six different sizes (ranging from 20 nm to 2 μm) where introduced as guest particles in the dry coating of cohesive cornstarch particles (15 μm particle size). The results of this study showed that the improvement in flowability of the cornstarch was inversely proportional to the guest particle (silica) size, i.e., the smaller the particle size of the guest particle, the more effective it was for dry coating applications. The addition rate of the guest to the host particles is also noted as a key process parameter in dry coating. An increase in the flowability of the bulk host powder is experienced on increasing levels of guest particle addition. However, a

critical point is reached where further increasing guest particle addition level will lead to a reduction in powder flowability. This critical level varies dependent on the size of the guest and host particles but, for most studied powders and host particles, an optimal addition level of guest particles is typically 0.5–1.5% of the weight of the host powder bulk. At this optimal addition rate, full coverage of the host particles is typically achieved which improves the powders flowability. On exceeding this addition level, excess host particle build-up may occur at the powder particle surface which could lead to further interparticle interaction between neighbouring particles that may act to increase the cohesiveness of the powder (Chen *et al*., 2008; Morin and Briens, 2013; Schulze, 2008).

Due to the very small particle size of the guest particles (nm range), they have a very strong tendency to self-aggregate *via* van der Waals interactions. Therefore, when the guest particles are added to the host, the mixing step that acts to disperse the particles to the host's surfaces is a critically important step, which can limit the quality of particle coating that is achieved. Traditionally, depending on the scale, manual mixing or dry blending (v-shaped blender) have been used to disperse guest particles onto the surfaces of the host, although results for these methods have shown incomplete partial particle coating (porous coating) due to self-interactions of guest particles. Recently, high energy dispersion techniques have been used to achieve complete coatings (continuous coating) on the host particles and these include magnetic-assisted impaction coating (MAIC). In MAIC a coil structure creates an oscillating magnetic field that mixes and causes the fluidisation of host and guest particles which encourages particle-particle and particle-wall collisions leading to a uniform dispersion of guest particles at the surface of the host powder. Although mechanical force is used to disperse particles in MAIC, it is classified as a "soft"

coating process when compared to other high mechanical force dispersion techniques such as hybridizer coating which exposes particles to very large mechanical forces in order to achieve uniform coating. Although high mechanical force dispersion methods achieve very uninform and complete particle coatings, their application is limited for particles that are susceptible to breakage, such as high-protein dairy powders (Ghoroi *et al*., 2013; Pfeffer *et al*., 2001; Ramlakhan *et al*., 2000; Yang *et al*., 2005).

The flowability of very cohesive powders such as cornstarch (angle of repose (AOR) before dry coating: 50°, AOR after dry coating: 27°), ibuprofen (AOR before dry coating: 57°, AOR after dry coating: 48°), and lactose monohydrate (AOR before dry coating: 65°, AOR after dry coating: 38°) have been improved *via* dry coating in numerous studies (Han *et al*., 2013; Huie Liu *et al*., 2006; Jallo *et al*., 2012; Yang *et al*., 2005; Zhou *et al*., 2010). Combining this with a reduction in waste streams and energy consumption, dry coating represents a potentially suitable method for the improvement of high-protein dairy powders post-spray drying.

2.5 Emerging technologies for improving the flowability of high-protein powders

All approaches to improve powder flowability presented herein have been utilised, to some extent at industrial scale. Continually, novel technological approaches emerge for various applications that may be utilised and applied to achieve an improvement in powder flowability. The following section will highlight some emerging technologies studied mainly outside of the field of dairy technology that may offer potential to improve the flowability of high-protein dairy powders.

2.5.1 Steam jet agglomeration

Steam-jet agglomeration is a form of particle size enlargement involving rewet processing. In fluid bed and shear agglomeration-based processes, viscous binding solutions are atomised onto the surface of powder particles, whereas in steam-jet agglomeration, an aerosol jet of high temperature (greater than 100°C) steam is directed at free falling powder particles. As the steam-jet hits the powder particles, rapid condensation of the steam occurs, due to the large temperature difference between the particle and the steam jet. This condensation process forms water vapour at the surface of the primary powder particles which partially solubilises the components on the surface of the powder particles resulting in an increase in the surface viscosity and stickiness. The free-falling particles, now with increased surface viscosity, will adhere to each other on collisions *via* liquid bridging, forming an agglomerated structure which is then stabilised by drying the liquid bridges (Martins and Kieckbusch, 2008). Person *et al*. (2018a, 2018b) have shown that for skim milk powder (SMP), steam-jet agglomeration forms agglomerates of increased size (>400 μm) that also have higher mechanical integrity, and reduced breakage on handling and transport while still possessing an instant nature (wetted in <30 s) comparable to industrially produced agglomerated SMP (i.e., using fines return). It must be noted, however, that a low agglomerate yield (19-33% agglomerates) was reported in these lab-scale studies with all other material produced being too small (<400 μm) or too large (>4 mm).

The clear advantage of steam-jet agglomeration, over the previously discussed particle size enlargement methods, is the use of steam instead of a viscous binding solution to achieve an increase in particle size. This minimises changes to the composition of the powder being processed, which is desirable in the production of

high-protein dairy powders. However, this process is reliant on the efficient condensation of water vapor at the surface followed by the subsequent imbibing of the water droplets into the powder particle surface leading to an increase in surface viscosity. Contact angle measurements efficiently characterise the initial contact and imbibing of a water droplet at a powder surface, with a low contact angle indicating good powder wetting properties. O'Sullivan *et al*. (2017) measured the contact angles of both SMP and MPI, with SMP (highly agglomerated using steam-jet agglomeration) having a low initial contact angle measurement (approx. 40°). The high-protein MPI powder showed a much higher contact angle (approx. 120°) indicating its poor surface wetting properties which may act to restrict the effectiveness of steam-jet agglomeration for high-protein dairy powders.

2.5.2 Static elimination

The build-up of charge on the surface of powder particles during conveying and further treatments (such as milling) acts to reduce the flowability of high-protein dairy powders through the occurrence of electrostatic interactions between oppositely charged powder particles (Section 2.3.4.2). Due to the danger of excessive charging of powders, and their contribution to dust explosions, research has been conducted to develop methods to dissipate charge from the surface of powder particles.

Static eliminators have been developed in nozzle form to reduce the surface charge of powders. These nozzles are constructed using ionizing needle electrodes, a power supply and a compressed air source, and generate ions, causing the surrounding environmental air to become ionised before the compressed air forces the ionised air away from the nozzle and into contact with a powder surface. When in contact with the charges present on a powder surface, the ions (formed by the static eliminator) will

neutralise the surface of the powder particles. Multiple nozzle static eliminator configurators have been implemented and studied in powder conveying lines and storage silos in order to avoid excess charge build up due to safety concerns (Kodama *et al*., 2002, 2000; Revel *et al*., 2003). A study by Pingali *et al*. (2009) has identified, and focused on the use of a static eliminator (and a slowly rotating drum) for the improvement of powder flowability. A series of pharmaceutical blends where initially tumbled in a rotating drum before the introduction of a static eliminator which acted to dissipate the charge on the powder particle surfaces within the drum. The effect on the flowability of the powder was analysed by measuring the expansion of the powder bed within the drum (*via* digital image analysis), which is linearly related ($R^2 = 0.979$) to the powder's flow index, i.e., powder flowability. Results from this study showed an increase in the flowability of all pharmaceutical powder blends tested due to the reduction in particle charge (e.g., the flow index of a milled pharmaceutical grade lactose powder increased by 41% on use of the static elimination process).

2.6 Conclusion and outlook

To ensure the forecasted growth of high-protein dairy ingredient powders is realised, actions must be taken to allow for improved tailoring of their physical and bulk properties. Currently, challenges associated with storage, handling and application of these powders, caused largely by their poor flowability, are acting to limit the commercial growth of these ingredients. The flowability of high-protein dairy powders is limited mainly by the occurrence of van der Waals and electrostatic interparticle interactions and therefore, an intervention which acts to reduce the occurrence and strength of these interactions is needed to improve their flowability. The current industry standard for improving the flowability of dairy powders is *via*

agglomeration during spray and fluid bed drying steps of their production. Although many studies have clearly illustrated the improvement in flowability of high-protein dairy powders using this approach, undesirable consequences are also experienced, such as decreased powder bulk density and decreased particle dispersibility on rehydration (in particular for casein-dominant powders). Several of the alternative approaches discussed in this review are actively used in other industries (e.g., pharmaceutical and biochemical) to improve powder flowability and offer potential to the food industry to allow for greater ability to tailor and modify the particle, bulk and functional properties of future generations of high-protein dairy powders.

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Chapter 3

Influence of mechanical integrity during pneumatic conveying on the bulk handling and rehydration properties of agglomerated dairy powders

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Declaration

This chapter was written by author Ryan Hazlett (RH) and reviewed by all co-authors. RH co-designed the study with co-authors and performed all of the experimental work.

Table of contents

Chapter 3

3.1 Abstract 74

3.2 Introduction 75

3.3 Materials and methods 77

3.4. Results and discussion 84

3.4.1 Quantification of agglomerate breakage 84

3.4.2 Influence of agglomerate breakage on powder properties 90

3.4.3 Influence of agglomerate breakage on powder flowability 99

3.4.3 Influence of agglomerate breakage on powder rehydration 100

3.5 Conclusions 105

3.6 Acknowledgements 105

3.7 References 107

3.1 Abstract

Dairy powders are routinely agglomerated during their manufacture to tailor their bulk handling and rehydration properties. However, agglomerated powder particles are susceptible to breakdown on further handling, most notably, during powder conveying. In this study, three agglomerated dairy powders (a whey protein concentrate, WPC, fat-filled milk powder, FFMP and an infant formula powder, IF) were conveyed through a custom-fabricated, pilot-scale pressurised powder dispersion rig to understand the causes and effects of agglomerate breakdown on dairy powder handling and application. All samples displayed significant breakdown on pressure dispersion, evident by a reduction in particle size and a subsequent increase in powder specific surface area and bulk density. These changes led to reductions in powder flowability for all samples (flow index: WPC: 9.3 to 5.1, FFMP: 5.7 to 4.9 and IF: 16 to 10) *via* increased particle-particle interactions. The initial stages of rehydration were impeded by agglomerate breakage (42.9–47.0% reduction in wettability and 7.22–16.4% reduction in dispersibility), while final powder solubility remained relatively unchanged. For FFMP and IF samples, these reductions align with increased concentrations of free fat on powder surfaces which become exposed on agglomerate breakage, increasing powder hydrophobicity. For the WPC sample, a reduction in the volume of interstitial air on breakage acts to reduce capillary movement of water into particles, preventing efficient wetting and dispersion on rehydration. The results of this study provide new insights into the alterations occurring to the physical and bulk-handling properties of agglomerated dairy powders on agglomerate breakdown, while also identifying the negative effects these alterations can have on the functional properties of these powders.

3.2 Introduction

The production of dairy powders, *via* spray drying, concentrates the numerous nutritional and functional properties present in a dairy system in a solid form that allows for more economical storage and transport (Schuck, 2013). In order to fully utilise the functional and nutritional properties of these ingredients on further application these powders need to be both easy to handle (i.e., possess good flowability) and to rehydrate. Certain dairy powder types display challenges with handling and rehydration, attributable mainly to their bulk composition and/or physical properties (Fitzpatrick *et al*., 2016, 2007) and for such powders, agglomeration may be utilised to overcome these challenges.

Powder agglomeration is a process of particle size enlargement that is routinely utilised in the production of spray dried dairy powders, whereby numerous individual primary particles are combined together into cluster-like structures where individual primary particles may still be distinguished (Cuq *et al*., 2013; Iveson *et al*., 2001). The increase in particle size achieved on agglomeration has been shown to alter the powder physical and bulk-handling properties, ultimately increasing their flowability, by reducing the extent of interparticle interactions (e.g., van der Waals forces) occurring between individual powder particles (Barkouti *et al*., 2013; Ji *et al*., 2017; Szulc and Lenart, 2013). The improvement of powder rehydration in the initial stages (i.e., wettability) on agglomeration is another, well established, beneficial effect of agglomerating dairy powders. By forming agglomerated structures, an increased volume of interstitial air is incorporated into the powder bulk through the presence of numerous capillaries and pores within and surrounding the agglomerated structures which allow the rapid penetration and movement of liquid into and throughout the agglomerated structures, thereby improving the wetting properties (Dacanal and Menegalli, 2010; Forny *et al*., 2011; Gaiani *et al*., 2007; Ji *et al*., 2016).

The industry standard agglomeration process utilised commercially during the production of dairy powders occurs in the spray dryer main chamber (Pisecky, 2012); however, on exiting the spray dryer, transport of the now agglomerated powder, to other locations in the processing plant *via* conveying lines is required for further handling, storage, packaging or application. During conveying, powder particles have the propensity to collide with other powder particles (i.e., attrition) and solid surfaces (i.e., collision) to an extent that is dependent on the type of conveying system used (i.e., dilute or dense phase). The attrition and collision forces experienced by the agglomerated particles can cause a breakdown in particle structure, which has the ability to negatively affect the bulk and functional properties of the powder.

Numerous studies have been completed in the area of pharmaceutical sciences to study the breakage of granulated powder material, including understanding the causes, mechanisms and means of measurement (Iveson *et al*., 2001; Reynolds *et al*., 2005; Simons, 1996; Subero and Ghadiri, 2001). Granulation, although another form of powder particle size enlargement, forms particles that are very different to agglomerated dairy powder particles. The particles formed *via* granulation are usually relatively large (~ 1 mm), spherical and dense, with high mechanical integrity (Faure *et al*., 2001). These properties contrast with those of agglomerated dairy particles which are generally associated with low mechanical integrity. Therefore, it proves challenging to extend any correlations between the breakdown of granulated pharmaceutical powders and agglomerated dairy powders.

This study was designed with the aim of identifying both the overarching mechanisms responsible for dairy powder agglomerate breakdown, as well as to assess the subsequent effects that this breakdown has on selected key quality attributes (i.e., bulk handling and rehydration properties) of the resultant powders. Three representative agglomerated dairy powders were chosen (i.e., whey protein concentrate, fat filled milk powder and infant formula

powder) which had diverse bulk composition, physical properties and intended applications in order to generate inter-relationships between these properties applicable to many different forms of agglomerated dairy powders (e.g., high protein content and high fat content powders). The powders were dispersed through a custom-fabricated dispersion rig with analysis before and after dispersion used to develop a deep understanding of the causes and effects of agglomerate breakdown, ultimately providing new insights to allow for greater control of the functional and physical properties of agglomerated dairy powders during conveying.

3.3 Material and methods

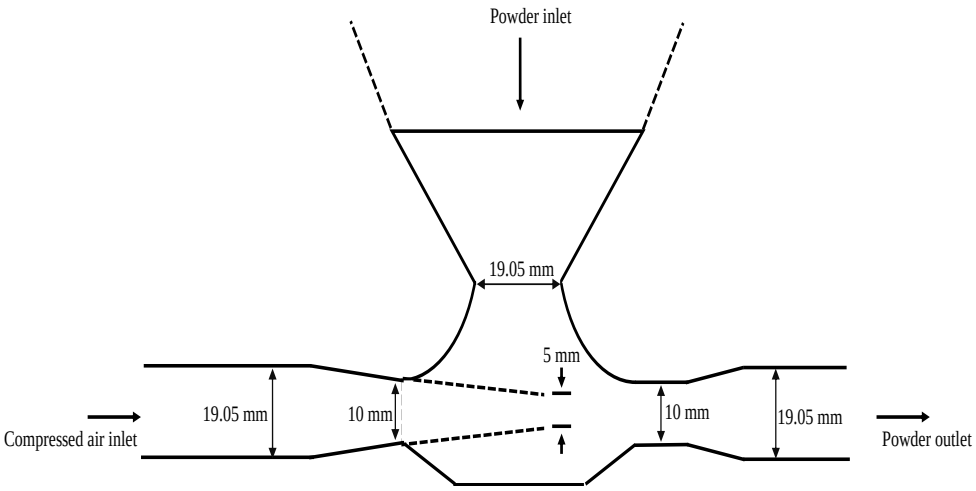
3.3.1 Materials and composition

Three commercially significant agglomerated dairy powders were used in this study. Agglomerated whey protein concentrate (WPC) and agglomerated fat-filled milk powder (FFMP) ingredients were kindly donated by Carbery Ingredients (Ballineen, Cork, Ireland) and Lakelands Dairies (Bailieborough, Cavan, Ireland) respectively, while a first-stage, whey-dominant, infant formula (IF) powder was sourced from a local commercial outlet. Data for composition was provided by the suppliers of the WPC (protein: 80.0% and fat: 8.50%) and FFMP (protein: 26.4% and fat: 28.7%) ingredients and was calculated from the product packaging for the IF powder (protein: 8.52% and fat: 25.6%). In addition, moisture content of the powders was analysed according to International Dairy Federation (IDF) standard 26:2004 (IDF, 2004). All chemicals and reagents, unless otherwise stated, were sourced from Sigma-Aldrich (Wicklow, Ireland) and were of analytical grade.

3.3.2 Powder dispersion process for agglomerate breakdown

A pressure dispersion rig was custom fabricated by Liam A. Barry Ltd. (Little Island, Cork, Ireland) to achieve controlled breakage of agglomerated dairy powders in a simulated lean phase pneumatic conveying configuration. The rig was composed of a compressed air source, an eductor (Figure 3.1), a powder hopper and stainless steel and flexible tubing. Compressed air, at 1 and 3 bar, was passed through the rig, creating a venturi effect as the compressed air accelerated through the narrowing orifice of the eductor. The agglomerated powder was slowly poured into the powder hopper to avoid bridging or arching at the exit of the hopper and the venturi in the eductor component created a vacuum that drew the powder in the hopper downwards, into the compressed air stream. The powders, on exiting the eductor, entered stainless steel tubing (20 mm in length) where particle-particle and particle-wall collisions occurred causing the agglomerated powder structures to break down further, before sample collection. On collection, the powders were transferred to, and stored in, two (double bagged) zip-lock, low density polyethylene bags (VWR, Belgium) at room temperature (20°C) and protected from light until analysis. One kilogram of each powder was dispersed at 1 and 3 bar dispersion pressure yielding three samples for each agglomerated powder: a control, which had not been dispersed through the rig (C), and a 1 bar (1b) and 3 bar (3b) sample. Cleaning of the rig was completed by dissembling, washing (warm water) and drying (50°C) the rig's components in between each dispersion run to avoid cross-contamination between samples.

Figure 3.1 *Schematic representation of the eductor component of the custom-fabricated pressure dispersion unit.*



3.3.3 Powder physical properties

3.3.3.1 Agglomerate size and morphological analysis

The particle size distribution (PSD) and specific surface area (SSA) analysis of the powders was measured using a Mastersizer 3000 equipped with an automated Aero S dry powder disperser cell (Malvern Instruments, Worcestershire, UK). Approximately 4 g of each sample was placed in the feed hopper of the Aero S cell, set at a height of 4 mm. A feed rate of 45% was used to ensure a standard obscuration level was achieved for each powder. The lowest possible dispersion pressure of 0.2 bar was used to minimise additional breakage on

dispersion during all PSD analysis. Background and measurement durations of 20 s were used, and the particle refractive and absorption indices were set at 1.45 and 0.01, respectively. The particle size of the agglomerated dairy powders was reported as the volume-weighted median particle diameter (i.e. Dv50 value) and this data was used in later calculations such as agglomerate breakage (see Section 3.3.3.2).

The morphology of the powder samples was analysed *via* scanning electron microscopy (SEM). Each sample was applied to double-sided, adhesive carbon tape and fixed to aluminium SEM stubs. A coating (10 nm) of 20:80 palladium:gold was applied to the stubs using a sputter coater (Emitech K550X, Ashford, UK) to avoid charging on analysis. The stubs where then transferred to the SEM (JSM – 5510, Joel Ltd, Tokyo, Japan) where micrographs were taken (5 kV) for each sample to assess the impact of breakage on the morphology of the agglomerated powder particle structures. Magnifications varied from 150 – 400 X due to the different particle sizes of the three different agglomerated powders.

3.3.3.2 Powder agglomerate breakage

The extent of agglomerate breakage following dispersion at 1 and 3 bar, as described in Section 3.3.2, was calculated for each sample following the method described by Schuck *et al*. (2012a), utilising the following calculation:

$$\text{Agglomerate breakage (\%)} = \frac{\text{Ctrl d50 (µm)} - \text{d50 @ X bar (µm)}}{\text{Ctrl d50 (µm)}} . 100$$

The breakdown of agglomerated powder particles was associated with an increase in the quantity of fine powder material in the bulk powder. To quantify the fine material generated

on agglomerate breakdown, the Dv10 value (i.e., the particle size value below which 10% of the material volume exists) was used as a threshold and all material smaller than this was termed 'fine material'; this was quantified by calculating the area (utilising the Trapezoidal rule) under the volume distribution curve (from PSD analysis) for each sample, at each dispersion pressure.

3.3.3.3 Distribution of fat in powder particles

The surface free fat content of each powder sample was quantified post breakage using the GEA Niro analytical methods No. 10a (GEA Niro, 2006a) with minor modifications previously described by Schmidmeier *et al*. (2019). Confocal laser scanning microscopy (CLSM) was used to visualise the distribution of fat throughout the powder particles and to observe any changes occurring as a result of breakdown of agglomerated powders containing high bulk fat levels following a method previously described by Drapala *et al*. (2017).

3.3.4 Powder bulk-handling properties

3.3.4.1 Particle density, bulk density, occluded and interstitial air

The particle density of the samples was measured using the Micromeritics Accupyc II 1340 gas pycnometer, using helium gas as described by per GEA analytical methods No. 11a (GEA Niro, 2006b). The bulk and tapped density of the agglomerated powders were measured as per GEA methods No. A2a and b, respectively, using a STAV 2003 Stampf-volumeter (J. Engelsmaan Apparatebau, Ludwigshafen, Germany) to assess tapped density. The volumes of interstitial (Via) and occluded (Voa) air of the samples were then calculated using the method described by Schuck *et al*. (2012b).

$$V_{ia}\ (ml\ 100g^{-1}) = \left(\frac{1}{bulk\ density\ (g\ cm^{-3})}\right) - \left(\frac{1}{tapped\ density\ (g\ cm^{-3})}\right).10000$$

$$V_{oa}\ (ml\ 100g^{-1}) = \left(\frac{1}{tapped\ density\ (g\ cm^{-3})}\right) - \left(\frac{1}{particle\ density\ (g\ cm^{-3})}\right).10000$$

3.3.4.2 Powder flowability

The flow index (*i*) of each sample was determined using a Brookfield Powder Flow Tester (PFT) (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) using a method previously described by Crowley *et al*. (2014).

3.3.5 Rehydration properties

3.3.5.1 Wettability

Initially, the IDF wettability standard method 87:2014 (IDF, 2014) was used to assess the impact of agglomerate breakdown on the wetting properties of the powder samples. For powders that took longer than 60 min to wet (i.e., WPC and FFMP), a modification to the IDF standard procedure, previously described by Fitzpatrick *et al*. (2016), was employed. In brief, this modification includes carefully removing any powder particles that have not migrated below the water surface (i.e., have not been wetted) 60 min after addition of powder to the water surface. The removed, un-wetted particles were then transferred to a pre-weighed moisture dish before drying at 103°C overnight after which the samples were removed from the moisture oven and allowed to cool to room temperature in a desiccator before being weighed using an analytical balance. The weight of the un-wetted particles is used to determine the amount of wetted particles by difference from the starting weight. The mass of wetted particles is then used to determine wettability of each sample using the following calculation:

$$Wettability\ (\%) = \frac{mass\ of\ wetted\ particles\ (g)}{mass\ of\ inital\ powder\ (g)}. 100$$

2.3.5.2 Dispersibility

A modified version of the IDF dispersibility method 87:2014 (IDF, 2014) was utilised whereby powder (10 g) was added to the surface of 250 ml of ultrapure water in an 80 mm diameter beaker. Once added, the solution was stirred for 30 s using a metal spatula, allowing one motion across the diameter of the beaker per s. A full 360° rotation of the beaker was achieved in the 30 s period by slowly rotating the beaker while stirring. After stirring, the beaker was left to stand undisturbed for a further 30 s. Following this, the contents of the beaker were passed through a 150 μm analytical sieve into a receiver beaker. The sieved solution (10 ml) was pipetted, in duplicate, into pre-weighed moisture dishes and dried at 103°C for 2 h. Following drying, the dishes were cooled in a desiccator and weighed to calculate total solids (TS) of the sieved material. This value was incorporated in a calculation as described in the IDF method to calculate the percent dispersibility of samples.

3.3.5.3 Solubility

To asses powder solubility a 10% (w/w) powder suspension was formed by adding 30 g of sample to 270 g of ultrapure water (~22°C) in a beaker of 80 mm internal diameter. The suspension was stirred at 400 RPM, using an overhead stirrer (Eurostar 100 Control; IKA-Werke GmbH & Co. KG, Staufen, Germany) equipped with a three-blade impeller (diameter-50 mm) for 60 min. Following this a method previously described by McCarthy *et al*. (2014) was used to quantify the solubility of the suspensions using the following calculation:

$$Solubility\ (\%) = \frac{total\ solids\ of\ supernatant\ (\%)}{total\ solids\ of\ suspension\ (\%)}. 100$$

3.3.6 Statistical data analysis

All experimental analyses were conducted in triplicate with the data generated being subjected to one-way analysis of variance (ANOVA) using SPSS version 25 (SPSS Inc., Chicago, IL, USA). A Tukey's paired-comparison post-hoc test was used to determine statistically significant differences ($P < 0.05$) between mean values for different samples, with mean values deemed to be significantly different from each another at a 95% confidence level. Unless otherwise stated, results are expressed as mean ± standard deviation from triplicate analysis, with statistically significant differences identified using superscript letters.

3.4 Results and discussion

3.4.1 Quantification of agglomerate breakage

Initially, all three powders had significantly ($P < 0.05$) different particle sizes before pressure dispersion, with the IF formula sample having the largest Dv50 value of 252 μm, followed by the WPC and the FFMP samples with Dv50 values of 209 and 120 μm, respectively (Table 3.1). Powder particle size analysis, before and after pressure dispersion at 1 and 3 bar, was utilised to quantify the extent of agglomerate breakage occurring in each sample. The results, presented in Table 3.1, indicate that significant ($P < 0.05$) agglomerate breakage occurred for all samples; with the Dv50 value for each sample being reduced significantly as the samples were conveyed through the dispersion rig at both 1 and 3 bar dispersion pressures. The WPC and IF samples, which had highest initial Dv50 values, displayed the greatest reductions in particle size on dispersion at 1 and 3 bar. The reduction in Dv50 value for the FFMP sample, although significant ($P < 0.05$), resulted in less of a reduction

in particle size, attributable to the smaller initial Dv50 value of the sample in comparison to the WPC and IF samples (Table 3.1). These results indicate that agglomerated dairy powders, of larger initial particle size, are more susceptible to reduction in particle size during powder conveying due to a greater extent of attrition and collisions occurring between other particles and solid surfaces, respectively. This finding is in agreement with results presented by Boiarkina *et al*. (2016) in a study comparing the extent of agglomerate breakage from different infant formula powder conveying systems (pneumatic and bucket elevator conveying).

Although larger agglomerates are more susceptible to a reduction in particle size during powder conveying; the initial size of the powder must be considered when reporting agglomerate breakage. The percentage of agglomerate breakage was calculated for each sample after 1 and 3 bar dispersion and the results (Table 3.2) show that relatively similar levels of agglomerate breakage were displayed by all samples at each dispersion pressure. At 1 bar dispersion, the WPC and FFMP samples were broken down by 8.12 and 8.56%, respectively, whereas, the IF samples showed a lesser extent of agglomerate breakage at this dispersion pressure, as only 5.29% agglomerate breakage occurred. At 3 bar dispersion, the FFMP sample showed the lowest level of agglomerate breakage (21.7%) followed by the IF (23.1%) and WPC (26.3%) samples. These results indicate that although larger agglomerates are more susceptible to a reduction in particle size during conveying, the resulting levels of agglomerate breakage for small (FFMP) and large (WPC and IF) agglomerated powders are relatively similar

Table 3.1 *Powder physical properties, including particle size distribution parameters, specific surface area (SSA) and particle density (ρp) of whey protein concentrate (WPC), fat filled milk (FFMP) and infant formula (IF) powders before (C) and after pressure dispersion at 1 (1b) and (3b) 3 bar.*

		Dv10	*Dv50*	*Dv90*	*D[4,3]*	*D[3,2]*	*SSA*	ρ_p
		----------µm----------					kg m^{-2}	g cm^{-1}
	C	95.6 ± 0.52[a]	209 ± 1.15[a]	365 ± 4.73[a]	221 ± 1.53[a]	165 ± 0.58[a]	27.3 ± 0.12[a]	1.25 ± 0.01[a]
WPC	*1b*	87.6 ± 0.06[b]	192 ± 0.58[b]	336 ± 2.52[b]	203 ± 1.00[b]	152 ± 0.58[b]	29.7 ± 0.08[b]	1.24 ± 0.01[b]
	3b	67.1 ± 0.15[c]	154 ± 1.53[c]	269 ± 4.73[c]	162 ± 1.53[c]	118 ± 0.58[c]	38.3 ± 0.15[c]	1.25 ± 0.01[a]
	C	43.7 ± 0.35[a]	120 ± 1.15[a]	231 ± 3.51[a]	130 ± 1.53[a]	83.7 ± 0.71[a]	53.9 ± 0.46[a]	1.23 ± 0.01[a]
FFMP	*1b*	40.0 ± 0.23[b]	110 ± 1.15[b]	213 ± 6.35[b]	120 ± 2.31[b]	76.3 ± 0.59[b]	59.2 ± 0.44[b]	1.22 ± 0.01[b]
	3b	34.5 ± 0.10[c]	94.5 ± 0.45[c]	183 ± 3.00[c]	103 ± 0.88[c]	65.2 ± 0.26[c]	69.2 ± 0.26[c]	1.23 ± 0.01[a]
	C	109 ± 0.58[a]	252 ± 2.65[a]	492 ± 6.66[a]	280 ± 3.06[a]	193 ± 1.53[a]	23.5 ± 0.17[a]	1.26 ± 0.01[a]
IF	*1b*	99.2 ± 0.71[b]	239 ± 3.79[b]	455 ± 9.17[b]	259 ± 0.10[b]	178 ± 2.65[b]	25.4 ± 0.35[b]	1.26 ± 0.01[a]
	3b	76.1 ± 0.15[c]	194 ± 1.53[c]	352 ± 4.16[c]	205 ± 2.08[c]	139 ± 0.58[c]	32.5 ± 0.16[c]	1.26 ± 0.01[b]

Values followed by different superscript letters in the same column, for each sample, are significantly different ($P < 0.05$).

[a] *Dv10* Particle size below which 10% of material volume exists

[b] *Dv50* Particle size below which 50% of material volume exists

[c] *Dv90* Particle size below which 90% of material volume exists

[d] D[4,3] volume-weighted mean particle diameter

[e] D[3,2] surface-weighted mean particle diameter

Table 3.2 *Agglomerate breakage, bulk density (ρ_{bulk}), tapped density (ρ_{tapped}), volume of interstitial air (V_{ia}), volume of occluded air (V_{oa}) and flow index (i) of whey protein concentrate (WPC), fat filled milk (FFMP) and infant formula (IF) powder before (C) and after pressure dispersion at 1 (1b) and 3 (3b) bar.*

		Agglomerate breakage	ρ_{bulk}	ρ_{tapped}	V_{ia}	V_{oa}	*i*
		%	----------g cm^{-3}----------		----------ml $100g^{-1}$----------		-
WPC	*C*	n.a.	0.25 ± 0.01[a]	0.36 ± 0.01[a]	198 ± 2.17[s]	11.0 ± 0.19[a]	9.32 ± 0.64[a]
	1b	8.12 ± 0.79	0.26 ± 0.01[b]	0.38 ± 0.01[b]	184 ± 4.17[b]	11.6 ± 0.23[b]	7.50 ± 0.29[b]
	3b	26.3 ± 0.76	0.27 ± 0.01[c]	0.42 ± 0.01[c]	156 ± 3.00[c]	11.2 ± 0.23[ab]	5.07 ± 0.67[c]
FFMP	*C*	n.a.	0.39 ± 0.03[a]	0.54 ± 0.01[a]	103 ± 1.98[a]	5.13 ± 0.04[a]	5.58 ± 0.18[a]
	1b	8.56 ± 0.92	0.40 ± 0.03[b]	0.58 ± 0.01[b]	91.0 ± 4.21[b]	5.34 ± 0.06[b]	5.42 ± 0.60[a]
	3b	21.7 ± 0.44	0.44 ± 0.09[c]	0.60 ± 0.01[c]	84.0 ± 1.09[c]	5.03 ± 0.09[a]	4.93 ± 0.28[a]
IF	*C*	n.a.	0.43 ± 0.03[a]	0.56 ± 0.01[a]	99.3 ± 1.13[a]	4.77 ± 0.05[a]	16.1 ± 0.68[a]
	1b	5.29 ± 1.00	0.45 ± 0.03[b]	0.58 ± 0.01[b]	92.6 ± 1.98[b]	4.73 ± 0.04[b]	12.9 ± 1.39[b]
	3b	23.1 ± 0.23	0.49 ± 0.09[c]	0.63 ± 0.01[c]	78.9 ± 2.00[c]	4.52 ± 0.01[ab]	10.2 ± 0.30[c]

Values followed by different superscript letters in the same column, for each sample, are significantly different ($P < 0.05$).

n.a = not applicable

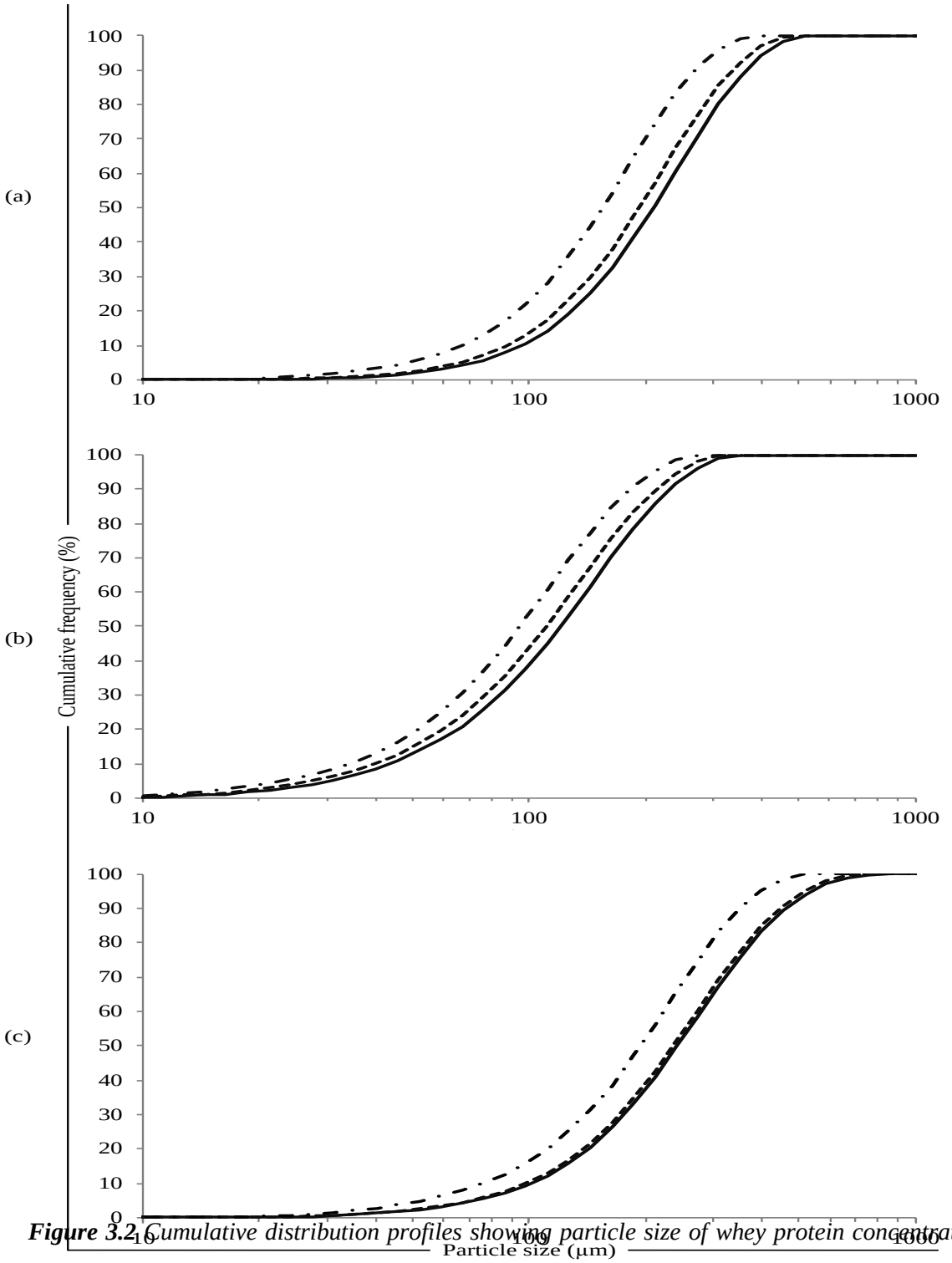


Figure 3.2 *Cumulative distribution profiles showing particle size of whey protein concentrate (WPC; a), fat filled milk (FFMP; b) and infant formula (IF; c) powder before (—) and after pressure dispersion at 1 (- - -) and 3 (- ·-) bar.*

3.4.2 Influence of agglomerate breakage on powder properties

3.4.2.1 Powder physical and bulk properties

Clear changes to the powder particle properties for all samples were measured on increasing dispersion pressure. A reduction in particle size resulted in a subsequent and significant ($P < 0.05$) increase in the SSA of each sample (WPC; 27.3 to 38.3 kg m^{-2}, FFMP; 53.9 to 69.2 kg m^{-2} and IF; 23.5 to 32.5 kg m^{-2}) (Table 2.1). As powder particles break down, and the particle size is reduced, the exposed surfaces of the now broken down particles will be of a much greater area, allowing for increased magnitude and number of interparticle interactions occurring at the powder bulk level (Crowley *et al*., 2014; Han *et al*., 2019).

The reduction in particle size and subsequent increase in the appearance of fine materials in all samples, led to a further significant increase ($P < 0.05$) in the bulk density of each sample, a key quality parameter for further application of powder e.g., transport costs and dosage control (Schulze, 2008). The WPC sample showed an 8% increase in bulk density at 3 bar dispersion while the bulk density of the FFMP and IF samples increased by 13 and 14% respectively, at the same dispersion pressure (Table 2.2). The increase in bulk density occurring on agglomerate breakage is a consequence of the broken down agglomerates packing together into closer arrangement due to their decreased size and increased uniformity, therefore taking up a smaller volume in a given space. These results are in agreement with work completed by Hanley *et al*. (2011a) who also showed an increase in bulk density occurred in a range of IF sample after lab-scale powder conveying.

Although the WPC sample showed the lowest increase in bulk density, it conversely experienced the greatest increase in tapped density on agglomerate breakage, which is another key physical property used to predict the bulk handling properties of a powder, post production

in processes such as transport and storage (Abdullah and Geldart, 1999). The tapped density of the WPC sample increased by 17% after 3 bar dispersion, whereas the increase in the tapped density of the FFMP and IF was 11 and 13%, respectively (Table 3.2). These results suggest that although the agglomerates of the WPC sample were considerably broken down, the agglomerate structures still present in the bulk required further energy to encourage them into a closer arrangement, whereas for the FFMP and IF samples the agglomerate structures were broken down in a manner that allowed for this close arrangement of particles to occur in the bulk powder before further energy input (i.e., tapping).

Gas pycnometery analysis employed here showed that the WPC sample had over twice the amount of occluded air (11.0 ml 100 g^{-1}) than that of the FFMP and IF samples (5.13 and 4.77 ml 100 g^{-1}, respectively). This is attributable to its higher bulk protein content which causes hollow primary powder particles, with large amounts of entrapped air, to be formed during spray drying (Bouman *et al*., 2016) (Table 3.2). A similar finding was reported by Crowley *et al*. (2014) in a study where the content of occluded air increased on increasing protein content over a range of milk protein concentrate powders. The presence of occluded air is clearly evident in the scanning electron micrographs where the WPC powder particles seem to be agglomerates of hollow primary particle shells with large amounts of entrapped occluded air, also present, but to a lesser extent in the FFMP sample (Figure 3.3). However, the IF samples had the appearance of more compact, dense agglomerated powder particle structures. It is hypothesised here that these hollow particle shells, of which the WPC agglomerates (and to some extent the FFMP sample) were composed of, acted as fragile points in the agglomerate structures, allowing for extensive breakage to occur at these points during the impacts experienced during pressure dispersion. This hypothesis is reinforced by the significant

increase ($P < 0.05$) in the presence of fine material present in the powder bulk of the WPC sample, which was the highest of all three samples, which easily breaks off of the friable, hollow powder particles present in the WPC powder bulk (Figure 3.4).

A significant reduction ($P < 0.05$) in the volume of interstitial air was experienced for all samples, with the WPC sample, which had the largest initial volume, again, experiencing the largest loss on agglomerate breakdown, reducing from 198 to 156 ml 100 g^{-1} on pressure dispersion at 3 bar. The IF sample had a decrease from 99.3 to 78.9 ml 100 g^{-1} while the volume of interstitial air on in the FFMP was reduced from 103 to 84.0 ml 100 g^{-1}, at the same dispersion pressure (Table 3.2). The presence of interstitial air located between agglomerates and between neighbouring powder particles within an agglomerate structure, is one of the key quality characteristics desired from the agglomeration process. This interstitial air contributes to the improvement of powder flowability and wettability associated with powder agglomeration, acting to reduce the magnitude of interparticle interactions and to encourage the movement of water through the powder bulk *via* capillary action, respectively (Forny *et al*., 2011; Shah *et al*., 2017).

2.4.2.2 Fat distribution

Initially, all samples had relatively similar concentrations of surface free fat present at the agglomerated powder particles (WPC; 0.57 g 100 g^{-1}, FFMP; 0.53 g 100 g^{-1} and IF; 0.66 g 100 g^{-1}) (Figure 3.5) even though large variations in the bulk fat concentrations were present between the samples. Both the FFMP and IF samples contained high concentrations of bulk fat (28.7 and 25.6% fat, respectively) while the WPC sample in comparison, contained a much lower concentration (8.50% fat). The similar levels of surface free fat, before pressure

dispersion, is attributed to the over-representation of fat occurring at the surface of spray dried dairy powders, caused by the atomisation step of the spray drying process. Here, the spray dryer feed is preferentially dispersed into discrete droplets at the presence of fat globules (lowest point of cohesion in the liquid stream), therefore arranging fat globules at the surface of the droplet where they are stabilised on subsequent spray drying (Foerster *et al*., 2016a, 2016b).

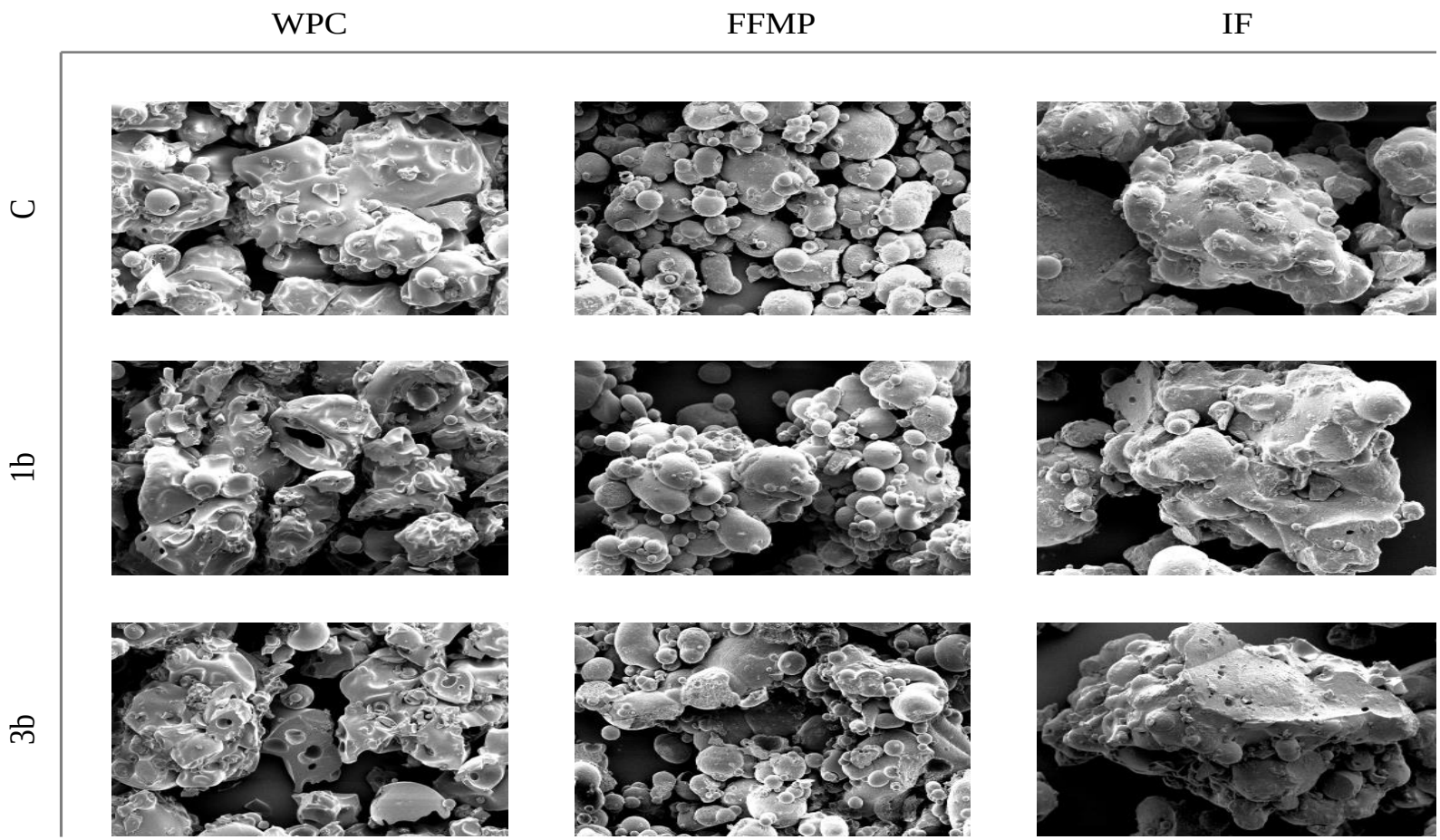


Figure 3.3 *Scanning electron micrographs of whey protein concentrate (WPC) – 370 X magnification, fat filled milk powder (FFMP) – 400 X magnification and an infant formula (IF) powder sample – 150 X magnification; before (C) and after pressure dispersion at 1 (1b) and 3 (3b)*

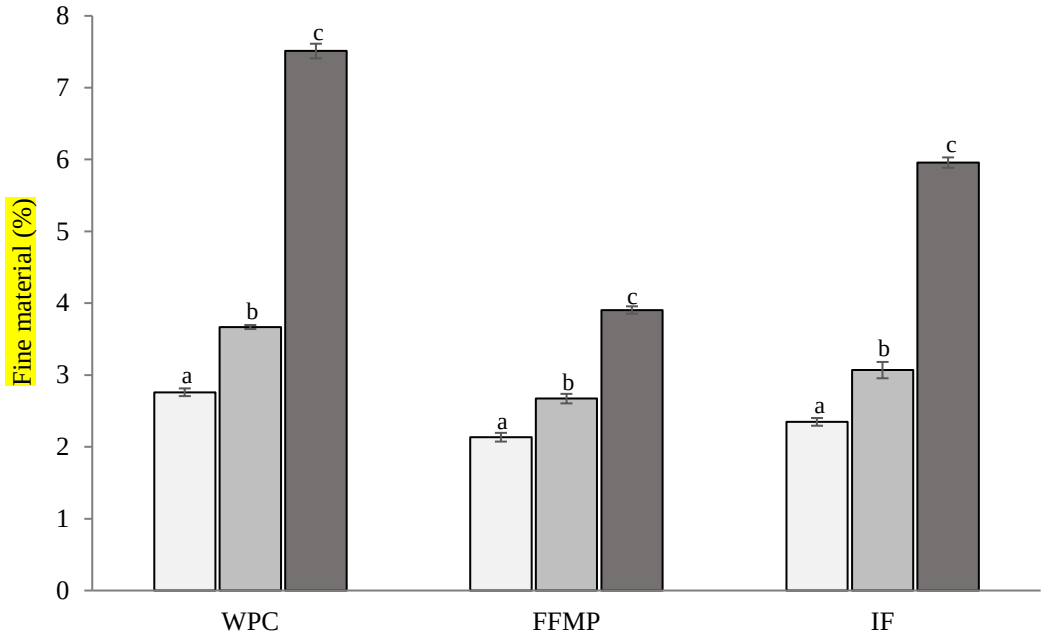


Figure 3.4 *Proportion of fine material in the whey protein concentrate (WPC), fat filled milk (FFMP) and infant formula (IF) powder before (C;□) and after pressure dispersion at 1 (1b;* ▫*) and 3 (3b;* ■*) bar.*

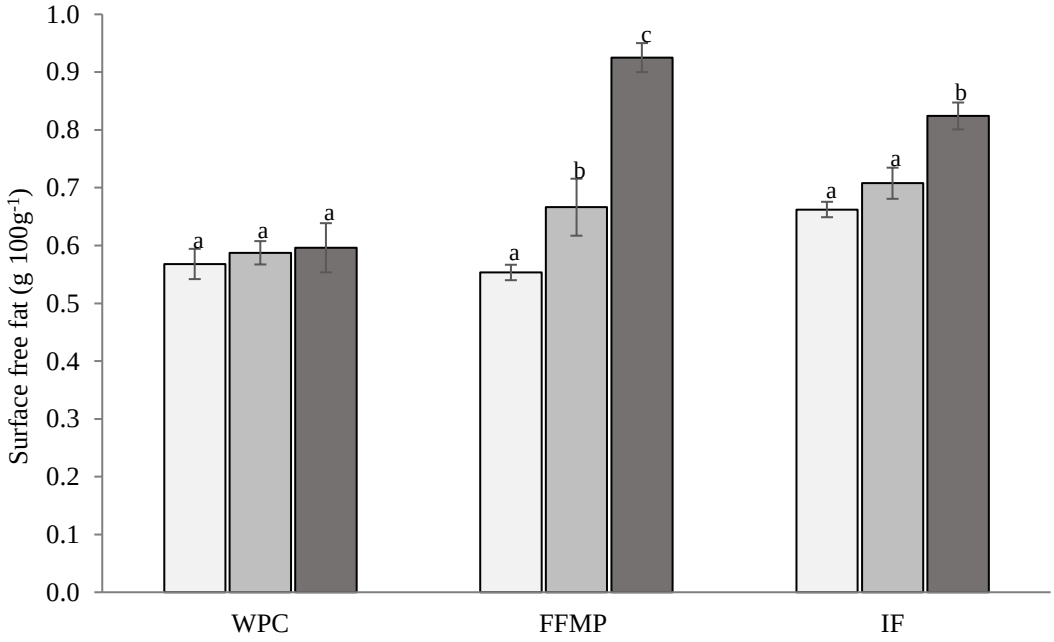


Figure 3.5 *Concentrations of surface free fat present on the surface of whey protein concentrate (WPC), fat filled milk (FFMP) and infant formula (IF) before (C;□) and after pressure dispersion at 1 (1b;* ▫*) and 3 (3b;* ■*) bar.*

Although all samples had similar initial surface free fat contents, a significant increase ($P < 0.05$) in the concentration of free fat on the powder surfaces was only distinguishable in the FFMP (0.55 to 0.93 g 100 g^{-1}) and IF (0.66 to 0.82 g 100 g^{-1}) samples on increasing dispersion pressure (Figure 3.5). As these powders contained much higher concentrations of fat, a homogenisation step is utilised during their production in order to stabilise the fat by reducing fat globule size before spray drying (Drapala *et al*., 2017; O'Sullivan *et al*., 2018). On agglomerate breakdown however; new surfaces, once hidden within the interior of the powder particles, become exposed, leading to increases in the concentrations of free fat on the particle surfaces for the FFMP and IF samples. This increase in surface free fat was significant ($P < 0.05$) at both the 1 and 3 bar dispersion pressures for the FFMP sample, whereas, for the IF sample, the increase was only significant after dispersion at 3 bar due to increased breakage at this pressure (Figure 3.5). These results are in agreement with previous finding by Hanley *et al*. (2011b) who also reported an increase in surface free fat on breakdown of an IF sample.

CSLM analysis was conducted on the FFMP sample which showed the greatest increase in the concentration of surface free fat occurring on agglomerate breakdown. The resulting micrographs (Figure 3.6) showed a distribution of small fat globules, dispersed through the particle's bulk structure. However, also present in the CSLM micrographs were large pools of coalesced fat globules which were primarily located along the pockets of occluded air, within the powder particle. During spray drying, fat migrates through the atomised droplet, towards air/water interfaces, including any pockets of occluded air that form during the spray drying process (Fäldt and Bergenståhl, 1996; Kim and Pearce, 2009). As previously stated, the presence of occluded air pockets provides weak points in powder particle structures, therefore,

agglomerate breakage at these points caused large pools of coalesced fat to become exposed at the newly altered powder surface. Now exposed, at surface level, fat acts to strongly influence (generally inversely) the resulting bulk handling and rehydration properties of a powder. Increasing surface free fat leads to an increase in the surface hydrophobicity of the bulk powder and contributes to increased interparticle interactions, critical to the wettability and flowability properties, respectively (Fitzpatrick *et al*., 2017; Kim *et al*., 2005).

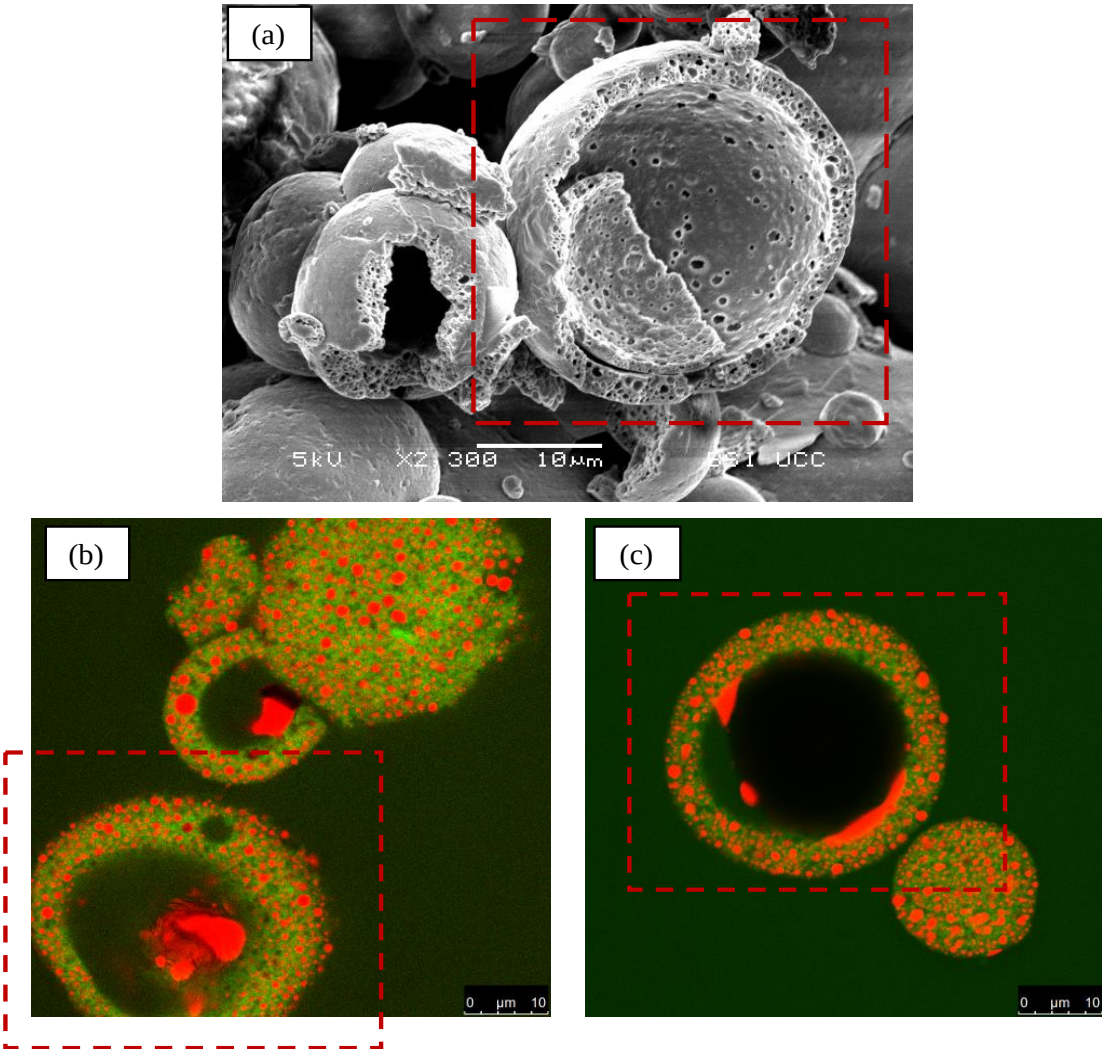


Figure 3.6 *(a) Scanning electron micrograph of fat filled milk powder sample (2300 X magnification) displaying a fragmented particle containing a large air vacuole and (b and c) confocal scanning laser micrographs of the same sample illustrating large pools of exposed coalesced fat (stained red), exposed due to agglomerate breakdown post pressure dispersion.*

The WPC sample showed no significant increase ($P > 0.05$) in the concentrations of surface free fat on pressure dispersion suggesting that the surfaces, exposed by agglomerate breakdown, contained negligible amounts of fat. This may be attributed to the low bulk fat content of this powder, meaning that a homogenisation step was not utilised during its manufacture (Schuck, 2013). Therefore, a very high proportion of the bulk fat can be expected to be over-represented at the surface of the powder particles with very low amounts dispersed within the interior bulk structure, which become exposed on agglomerate breakage (Figure 3.5). Similar results were presented in a study by Kelly *et al*. (2015) for a milk protein concentrate powder with a similar protein:fat ratio.

2.4.3 Influence of agglomerate breakdown on powder flowability

Agglomerate breakage, led to a reduction in the flow index (i) value for all samples (Table 3.2). This reduction was significant ($P < 0.05$) for the WPC and IF samples, as these samples experienced the greatest reduction in particle size after dispersion, whereas for the FFMP sample, the reduction was not significant ($P > 0.05$). The WPC sample, which showed the greatest extent of agglomerate breakage, also displayed the greatest reduction in powder flowability, with the i value reducing from 9.32 to 5.07 after dispersion at 3 bar (45.6% reduction). This may be attributed to the significant ($P < 0.05$) increase in powder bulk density and SSA, as well as the significant ($P < 0.05$) decrease in the volume of interstitial air (Tables 3.1 and 3.2). In combination, this acts to bring the powder particles into closer arrangement, resulting in a greater number and strength of interparticle interactions (e.g., van der Waals and electrostatic interactions) occurring at bulk powder level, which reduces powder flowability through increased cohesive bulk strength (Zafar *et al*., 2017). A

considerable reduction in the flow index also occurred in the IF sample (16.1 to 10.2 i.e., 36.6% reduction) due to the same resulting effects of a reduction in particle size as described above for the WPC sample. Additionally, the increase in surface free fat occurring in the FFMP and IF samples on agglomerate breakdown may contribute to the reduction in powder flowability (Figures 3.5 and 3.6). Once exposed on a powder particle surface, fat has the propensity to form liquid bridges between neighbouring particles, causing a further increase in the cohesive forces in the powder bulk; this is particularly problematic in dairy products such as FFMP and IF which contain high concentrations of fat in their bulk composition (Foster *et al*., 2005). Although the reduction in the flow index of the FFMP sample was not significant ($P > 0.05$) (5.58 to 4.93 i.e., 11.6% reduction), it must be noted that the flowability of the control FFMP (non-dispersed) form was considerably lower than that of the WPC and IF samples, due to the smaller size of the initial agglomerated powder particles and therefore, even a minor reduction in flowability could have a considerable effect on further application.

3.4.4 Influence of agglomerate breakdown on powder rehydration

3.4.4.1 Wettability

For the IF sample, due to its instant nature, the standard IDF method was appropriate for measuring the sample's wettability and the results showed that the control sample wetted within 18.7 s. The time required for wetting increased significantly ($P < 0.05$) after dispersion at 1 and 3 bar pressure with wetting times of 21.3 and 35.0 s, respectively (Table 3.3).

Analysis of the wettability of both the WPC and FFMP samples required a modification of the IDF method (Section 3.3.5.1), due to their non-instant nature

(Schuck, 2012c). The results showed that both samples also displayed a significant ($P < 0.05$) impairment in their wettability on agglomerate breakdown. The WPC sample had a wettability of 68.7% but this was reduced to 59.4 and 39.2% on pressure dispersion at 1 and 3 bar respectively. Similarly, the FFMP initially had a wettability level of 65.9% with reductions to 46.6 and 34.9% when dispersed at 1 and 3 bar, respectively.

The impairment to powder wettability, resulting from agglomerate breakdown can be attributed to two major causes, firstly; the reduction in the volume of interstitial air, and secondly, the increase in concentrations of surface free fat. The presence of interstitial air between agglomerates and between neighbouring powder particles within an agglomerate structure encourage rapid wetting, as they act as channels allowing water to more freely penetrate the powder bulk *via* capillary movement. A reduction in the volume of interstitial air will cause the wetting to occur at a much slower pace, such as seen in the WPC sample (Table 3.2). The increase in concentration of free fat at the surface of powder particles, caused by agglomerate breakdown, also acted to inhibit efficient wettability by causing an increase in the hydrophobicity of the surfaces of the powder particles, which contributed to the impairment of wettability of the FFMP and IF samples (Figure 3.5 and 3.6).

Table 3.3 *Rehydration properties of whey protein concentrate (WPC), fat filled milk (FFMP) and infant formula (IF) powder before (C) and after pressure dispersion at 1 (1b) and 3 (3b) bar.*

		----------Wettability----------		Dispersibility	Solubility
		s	*%*	*%*	*%*
WPC	*C*	> 1 hr	68.7 ± 4.41^{b}	89.4 ± 0.95^{b}	95.8 ± 0.39^{a}
	1b	> 1 hr	59.4 ± 2.71^{b}	87.9 ± 0.80^{b}	94.4 ± 0.48^{a}
	3b	> 1 hr	39.2 ± 3.88^{a}	82.8 ± 1.28^{a}	92.8 ± 0.34^{a}
FFMP	*C*	> 1 hr	65.9 ± 3.64^{b}	75.2 ± 1.90^{c}	73.8 ± 0.73^{a}
	1b	> 1 hr	46.6 ± 4.02^{b}	69.8 ± 3.38^{b}	72.1 ± 0.17^{a}
	3b	> 1 hr	34.9 ± 3.20^{a}	62.9 ± 3.14^{a}	71.0 ± 0.63^{a}
IF	*C*	18.7 ± 0.61^{a}	100	91.4 ± 0.31^{c}	99.5 ± 0.27^{a}
	1b	21.3 ± 1.24^{b}	100	89.4± 1.27^{b}	99.0 ± 0.38^{a}
	3b	35.0 ± 1.02^{c}	100	84.8 ± 0.39^{a}	98.6 ± 0.34^{a}

Values followed by different superscript letters in the same column, for each sample are significantly different ($P < 0.05$).

3.4.4.2 Dispersibility and solubility

As the rehydration process continues, and in most cases, increased energy input is provided (i.e., through shear or heat) it was expected that the adverse effects of agglomerate breakage on rehydration may be diminished. However, a decrease in the dispersibility was also displayed by all samples, meaning that the agglomerated powder particles broke apart and became dispersed in the rehydration liquid to a lesser extent post pneumatic conveying. This reduction in dispersibility was significant ($P < 0.05$) for both the FFMP and IF samples at each dispersion pressure (1 and 3 bar), with reductions in the levels of dispersibility from 65.9 and 91.4% to 62.9 and 84.8%, respectively (Table 2.3). The reduction of WPC dispersibility was not significant ($P > 0.05$) between the control and 1 bar sample (89.4 to 87.9%), but at the 3 bar dispersion level, where further agglomerate breakdown occurred, this reduction in powder dispersibility (82.8%) was significant ($P < 0.05$) (Table 2.3). The more significant loss of dispersibility in the FFMP and IF samples than that of the WPC sample, suggest that the increase in surface free fat, caused by agglomerate breakdown (considerable increase in FFMP and IF samples), has a greater impact on the latter stages of rehydration then losses in the volume of interstitial air (considerable decrease in WPC sample) (Table 3.2 and Figure 3.5).

At the final stage of the rehydration process (i.e., powder solubility), enough time and energy had been provided to overcome the negative effects of agglomerate breakdown as there was no significant decrease ($P > 0.05$) in the solubility at each dispersion pressures for all samples.

2.5 Conclusion

In conclusion, the results from this study indicate that the initial size of agglomerated dairy powder particles is a determinant of the extent to which particle

size reduction occurs on powder conveying, i.e., larger agglomerate structures experience a greater reduction in particle size. The resulting effects of this breakage were displayed on analysis of the physical and bulk-handling properties of the samples, with significant decreases measured in particle size, specific surface area and volumes of interstitial air and concomitant increases in bulk and tapped density of each sample on pressure dispersion. The significant adverse effects agglomerate breakage can have on both the flowability and rehydration properties of the powder samples were demonstrated through this study. Powder flowability was decreased for all samples, attributed to increased particle-particle interactions, as broken-down agglomerates could pack together into closer conformations. The initial stages of rehydration (i.e., wettability and dispersibility) were significantly impeded by agglomerate breakdown though a combination of increased surface free fat (for the FFMP and IF samples) and a reduction in the volumes of interstitial air, both of which limit the movement of water through the powder bulk on rehydration. Although partial agglomerate breakdown is inevitable on powder conveying, the new insights provided here may be utilised to improve exiting industrial powder handling processes and final powder functionality.

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Chapter 4

Modification of the physical, bulk handling and rehydration properties of milk protein isolate powders using agglomeration with novel protein-based binder solutions

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Declaration

This chapter was written by author Ryan Hazlett (RH) and reviewed by all co-authors. RH co-designed the study with co-authors and performed all of the experimental work.

Table of contents

Chapter 4

4.1 Abstract 117

4.2 Introduction 118

4.3 Materials and methods 120

4.4. Results and discussion 127

4.4.1 Binder properties 127

4.4.2 Agglomeration of milk protein isolate 129

4.4.3 Powder composition 136

4.4.4 Bulk handling properties and powder flowability 137

4.4.5 Powder rehydration properties 143

4.5 Conclusions 147

4.6 Acknowledegments 148

4.7 References 14

4.1 Abstract

Milk protein isolate (MPI) is a commercially important dairy ingredient powder which is highly enriched in milk proteins. Due to this high protein content, MPI often displays both poor handling (e.g., powder flowability) and rehydration properties, which serve to limit its applications. In this study, agglomeration was investigated as a means of modifying the physical, bulk handling and rehydration properties of MPI. The binder solutions used ranged from traditional, such as water (B-H_2O) and lactose (B-Lac), to more novel, protein-based binders (B-MPI, B-MPI_{heat} and B-MPI_{TSC}), which have the potential to limit the unwanted compositional changes incurred with the use of traditional binders. Particle size analysis demonstrated that not only were the novel binders capable of achieving agglomeration, the extent of agglomeration achieved was greater than for the traditional binders (B-H_2O and B-Lac); most notably the B-MPI_{TSC} solution, with relatively high viscosity (12.5 mPa.s), facilitated the most extensive agglomeration of MPI (D[4,3] increased from 36.9 to 136 μm). Furthermore, the application of these novel binders resulted in minimal compositional changes, with protein content reducing from 85.1 to 82.8-83.8%. The flowability of MPI was significantly improved on agglomeration, with B-MPI_{TSC} showing the greatest improvement, as evident from flow index increasing from 4.73 to 6.17. Wettability of MPI was also improved significantly using all binders, due to the densified nature of the agglomerates; however, these dense structures restricted the latter stages of rehydration. These novel findings will underpin the development of next-generation MPI-type powder ingredients with tailored physical, bulk-handling and rehydration properties.

4.2 Introduction

Milk protein isolate (MPI) is a high protein dairy ingredient which is produced commercially by enriching all of the proteins present in milk (*via* centrifugal separation and membrane filtration) before spray drying into powder form. The resulting ingredient contains a high proportion of milk proteins (≥ 90%) which are associated with notable functional, nutritional and bioactive properties in a form that allows for easier storage and transport than liquid milk for more efficient further application (Hazlett *et al*., 2018; Schuck, 2013; Zayas, 1997). Continual growth has been displayed by the high-protein dairy ingredient market, driven strongly by their inclusion in numerous high-value commercial applications, such as infant and elderly nutritional formulations, as well as products where a "high protein" label declaration is desired; including, but not limited to, yogurts, breakfast bars and coffee drinks. The latter market, in particular, has displayed a ~500% increase between 2010 and 2015 in the UK, and the continual forecasted growth of these ingredients has motivated additional requirements for improved and diversified functional properties (Bord Bia, 2018; Markets and Markets, 2018).

MPIs (and other high-protein ingredients) often have poor bulk-handling (e.g., powder flowability) and rehydration properties (e.g., clumping on wetting and poor solubility) which restricted applications of this ingredient. These challenges are normally manifested during storage and discharge from silos, transportation through pipes (i.e., powder conveying) and further powder processing operations (e.g., rehydration and dry blending) (Fitzpatrick *et al*., 2017, 2007). In recent years work has been completed to improve the handling and rehydration properties of these ingredients in order to ensure that such ingredients can align with their forecasted commercial growth (Ji *et al*., 2017, 2016).

Traditionally, dairy powders (such as skim and whole milk powder) are agglomerated during their production in order to improve their functional properties- notably their flowability and wettability. Agglomeration of powder is a process of particle size enlargement whereby numerous individual primary powder particles are combined together into cluster-like structures, where the individual primary particles may still be distinguished (Cuq *et al*., 2013; Iveson *et al*., 2001). Agglomeration of powder particles may be achieved through a combination of fines return and application of binder solutions, such as lecithin, during spray and fluid-bed drying in order to combine numerous primary powder particles into larger clustered structures (Pisecky, 2012). This agglomeration process is rarely utilised at commercial-scale during the production of MPI (or other high protein ingredients) as it has the propensity to yield unwanted changes in the resulting bulk powder such as a decrease in the already low bulk density (due to the incorporation of interstitial air) and decreases in the overall protein content of the final powder (due to the application of binder solutions). Recent research has been conducted on the agglomeration of high protein powders; Palmer *et al*. (2018) previously established a method whereby protein solutions are used as a binder solutions, in place of lecithin, to agglomerate a whey protein isolate ingredient during fluid bed drying. The resulting powder had improved functional properties (i.e., flowability and wettability) without alterations to the final protein concentration, allowing the ingredient to still be classified as a protein isolate.

The current study was designed with the aim of improving the flowability and rehydration properties of an MPI powder *via* agglomeration with an emphasis on the application and assessment of novel protein-based binder solutions to achieve powder agglomeration. Here, two traditional binder solutions (i.e., water and lactose) and three

MPI solutions with varying pre-treatments (i.e., native, heated and dissociated) were applied to an MPI powder in order to increase particle size and bring about improvements in flowability and rehydration properties of the powder, respectively. The effectiveness of each binder solution was measured through direct analysis of the binder solutions, followed by analysis of the treated powders (post-agglomeration) compared to an untreated control in order to assess the extent of agglomeration achieved.

4.3 Material and methods

4.3.1 Materials and compositional analysis

The MPI ingredient used in this study was kindly provided by Kerry Ingredients (Tralee, Co. Kerry, Ireland) and was used both as the bulk powder in which agglomeration occurred and for the formation of protein containing binder solutions used in the agglomeration process. Trisodium citrate (TSC), used to achieve casein micelle dissociation, was provided by Citrique Belge (N.V., Tienen, Belgium); while all other chemicals and reagents, unless otherwise stated, were sourced from Sigma-Aldrich (Wicklow, Ireland) and were of analytical grade. Compositional analysis of the MPI powder, before and after the agglomeration process, was conducted to investigate the impact of agglomeration on the bulk composition of the powder. The total nitrogen was determined using the Kjeldahl method (using a nitrogen to protein conversion factor of 6.38) (AOAC, 1994), while the moisture content of the powders was determined using the standard IDF method (IDF, 2004).

4.3.2 Binder preparation

Five binder solutions were used for agglomeration of the MPI powder: ultrapure water (B-H_2O), a 15% (w/v) lactose solution (B-Lac), an 8% (w/v) protein MPI solution (B-MPI), an 8% (w/v) protein MPI solution heated to 95°C (B-MPI_{heat}) and an 8% (w/v) protein MPI solution containing 15 mM TSC (B-MPI_{TSC}). The B-lac solution was prepared by rehydrating the required amount of lactose powder (150 g) in approximately 80% of the total required volume of ultrapure water using overhead stirring at 500 RPM, followed by making up to final volume of 1 L. The batches of 8% protein MPI solutions were formed by dispersing the required amount of MPI powder (94 g) in approximately 80% of the total required volume of ultrapure water using overhead stirring at 300 RPM. After a total of 6 h overhead stirring, the solutions were magnetically stirred, at a low speed, for 14 h at 4°C to allow for casein micelle rehydration. Following overnight rehydration at 4°C, the samples were made up to final volume (1 L) using ultrapure water. Static light scattering using a Mastersizer 3000 unit (Malvern Instruments, UK) was employed as previously described by Crowley *et al*. (2015) in order to confirm that complete solubilisation of MPI occurred on rehydration, with the particle size and the native pH of the solutions being reported in Table 3.1. For the B-MPI_{TSC} binder solution, the required amount of 1 M TSC stock solution (15 mL) required to achieve a final concentration of 15 mM TSC, was added to the binder solution prior to overnight storage at 4°C to allow the TSC adequate time to chelate colloidal calcium phosphate (CCP) from the casein micelles, causing micelle dissociation. For the B-MPI_{heat} binder solution, 28 g aliquots of the 8% protein MPI solution were subjected to a lab-scale heat treatment using a TA Instruments AR-G2 controlled-stress rheometer (Crawley, West Sussex, UK), equipped with a starch pasting cell geometry, as previously described by Crowley *et al*. (2016), with minor

modifications. The solution was heated to 95°C and held for 2 min before cooling to 15°C and holding for a subsequent 10 min. Each aliquot was combined in a single batch, forming the B-MPI_{heat} binder solution.

4.3.3 Analysis of binder solutions

4.3.1 Viscosity analysis

The apparent viscosity of the binder solutions were measured using a rotational viscometer (HAAKE RotoVisco 1, Thermo Fisher Scientific, MA, USA) following a method previously described by France *et al*. (2020).

4.3.2 Surface hydrophobicity

Surface hydrophobicity was determined using the method of Alizadeh-Pasdar and Li-Chan (2000) with some minor modifications. The hydrophobic probe, 1-anilinonaphthalene-8-sulphonic acid ammonium salt (ANS), was used. Samples were diluted to 5 different protein concentrations in a sample buffer (0.1 M citric acid/0.2 M Na_2HPO_4) as follows: 0.003, 0.006, 0.009, 0.012 and 0.015% (v/v). Aliquots (100 µL) of each protein solution were added in duplicate to a black, flat-bottomed 96 well plate and 50 µL of $8x10^{-5}$ M ANS (in 0.1 M phosphate buffer) was added to one half of the wells. The plate was gently rocked for 15 min in the dark using a plate shaker after which the fluorescence intensity was measured using a Varioskan Flash plate reader (Thermo Fisher Scientific Oy, Finland) with excitation and emission wavelengths of 390 and 470 nm respectively. The slope value (where in all cases r^2 values were 0.97-0.99) was used to express the surface hydrophobicity in each sample.

4.3.3 Turbidity

The turbidity of the protein containing binders (i.e., B-MPI, B-MPI_{heat} and B-MPI_{TSC}) was measured following a method described by De Kort *et al*. (2011), with minor modifications. The turbidity of the binder solution was measured using a Cary 300 Bio UV-visible spectrophotometer (Agilent Technologies Inc., Santa Clara, CA, USA) set at a wavelength of 600 nm with no prior dilution of the binders.

4.3.4 Powder agglomeration process

The lab-scale agglomeration process involved adding 200 g of MPI powder to the mixing bowl of a Thermomix food processor (Vorwerk, Wuppertal, Germany) equipped with a whisk attachment to allow for heterogenous powder mixing. The powder was then mixed, using the 4 central blades, at a speed of 500 RPM, at 55°C, for 2 min to allow for equilibration of the powder bulk to the internal vessel temperature. Following this, a flexible, medical atomisation device (LMA MADgic, Teleflex, Westmeath, Ireland) was lowered into the mixing vessel in order to atomise 50 ml of the specified binder directly onto the powder, over 2 min, achieving a 20% total binder addition level. After binder addition, the wetted powder was allowed to mix for a further 2 min to allow for further agglomerate formation and solidification. After a total mixing time of 6 min, the wetted agglomerates were removed from the vessel and spread on a drying sheet before drying at 55°C using an oven, for 2.5 h. The agglomerated powder was removed from the oven every 30 min and mixed manually in order to achieve adequate and uniform drying. The dried agglomerates were then transferred to zip-lock, low density polyethylene bags (VWR, Belgium) and cooled in a desiccator overnight at 22°C. The next day, the agglomerated powders were passed through a 710 μm analytical sieve in order to separate any oversized

agglomerated material. This oversized material was then processed with an ultra-centrifugal mill (ZM 200, Retsch GmbH, Haan, Germany), equipped with a 500 μm screen, in order to reduce the particle size of the material to ≤500 μm. The milled and sieved fraction were then recombined (hereafter termed "treated powders") and were passed through an antistatic gate (PRX U SET, Haug GmbH, Leinfelden-Echterbingen, Germany) in order to eliminate excess charge at the surface of the agglomerated powder particles before storage in two (double bagged) zip-lock, low density polyethylene bags (VWR, Belgium) located in a desiccator 22°C.

4.3.5 Powder particle size, specific surface area and morphological analyses

The particle size distribution (PSD) and specific surface area (SSA) of the control and treated samples were measured using a Mastersizer 3000 equipped with an automated Aero S dry powder disperser cell (Malvern Instruments, Worcestershire, UK). Approximately 4 g of each sample was placed in the feed hopper of the Aero S cell, set at a height of 4 mm and a feed rate of 45% was used to ensure a standard obscuration level was achieved for each powder. The lowest available dispersion pressure of 0.2 bar was used to minimise agglomerate breakage on dispersion during all PSD analyses. Background and measurement durations of 20 s were used, and the particle refractive and absorption indices were set at 1.45 and 0.01 respectively. Powder particle morphology was assessed for the control and treated samples using scanning electron microscopy (SEM). Each sample was applied to double-sided, adhesive carbon tape and fixed to aluminium SEM stubs. A coating (10 nm) of 20:80 palladium:gold was applied to the stubs using a sputter coater (Emitech K550X, Ashford, UK) to avoid charging on analysis. The stubs where then transferred to the

SEM (JSM – 5510, Joel Ltd, Tokyo, Japan) where micrographs were taken (5 kV) for each sample at 500 X magnification.

4.3.6 Powder bulk handling properties

The flow index (*i*) of each sample was determined using a Brookfield Powder Flow Tester (PFT) (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) using a method previously described by Crowley *et al*. (2014). The particle density of each sample was measured using the Micromeritics Accupyc II 1340 gas pycnometer, using helium gas as described in GEA analytical methods No. 11a (GEA Niro, 2006). The bulk and compressed density (i.e., powder density before and after the application of consolidating stress) of each powder sample was extracted from the PFT analysis. The volumes of interstitial and occluded air present within each sample was then calculated using the particle, bulk and compressed density values following the method described by Schuck *et al*. (2012).

4.3.7 Rehydration properties

4.3.7.1 Powder wettability

The wettability of the control and treated samples were analysed using the standard International Dairy Federation (IDF) method 87, with minor modifications. Briefly, 2.5 g of each sample was distributed, in a standard manner, on the surface of 250 ml of ultrapure water at 22°C located in a glass beaker of internal diameter 80 mm. The time required, in seconds, for all powder to disappear beneath the surface of the water was measured using a stopwatch. Contact angle (θ) analysis was conducted using an optical tensiometer (Biolin Scientific Holding AB, Stockholm, Sweden) following a method previously described by Silva and O'Mahony (2017), with minor

modifications. Modifications included using a lower compression force (1000 kg) to minimise changes to the powder particle morphology and using a larger droplet volume of 13 µl. Values of θ were collected for 30 s, and images were extracted from the PGX software at 5 and 30 s intervals.

4.3.7.2 Powder solubility

To assess powder solubility, 100 ml of a 3.5% powder (w/w) solution was prepared *via* magnetic stirring, at 500 RPM for 3 h, for each sample. The extent of powder solubility was then quantified flowing a method previously described by McCarthy *et al*. (2014)

4.3.8 Statistical data analysis

All experimental analyses were conducted in triplicate with the data generated being subjected to one-way analysis of variance (ANOVA) using SPSS version 25 (SPSS Inc., Chicago, IL, USA). A Tukey's paired-comparison post-hoc test was used to determine statistically significant differences ($P < 0.05$) between mean values for different samples, with mean values deemed to be significantly different from each another at a 95% confidence level. Unless otherwise stated, results are expressed as mean ± standard deviation from triplicate analysis, with statistically significant differences identified using superscript letters.

4.4 Results and discussion

4.4.1 Binder properties

A series of binders were prepared for this study with varying properties (Table 4.1), related to their ability to bind powder particles during powder agglomeration, most notably their viscosity, which is established as a key binder property for powder agglomeration (Mills *et al*., 2000). The viscosity of the lactose (B-Lac) and protein-based binders (i.e., B-MPI, B-MPI$_{heat}$ and B-MPI$_{TSC}$) were measured and the results showed that the B-lac solution had the lowest viscosity value of 3.77 mPa.s. Although the lactose solution had the lowest measured viscosity, it must be noted that lactose solutions are generally considered as "sticky" and atomisation of such solutions forms droplets with high tensile strength lending to their use as binder solution in agglomeration (Adhikari *et al*., 2007; Szulc and Lenart, 2013).

The B-MPI solution had a significantly higher ($P < 0.05$) viscosity (5.73 mPa.s) than the B-Lac solution (3.77 mPa.s) due to the presence of casein micelles with strong ability to bind water (previously reported voluminosity value of 3.5–4 ml g^{-1}) (Huppertz *et al*., 2017). Heating at 95°C caused the viscosity of the MPI binder to be reduced, although not significantly ($P > 0.05$), from 5.73 mPa.s (B-MPI) to 5.36 mPa.s (B-MPI$_{heat}$). This may be attributed to the denaturation of heat labile whey proteins, occurring during thermal processing, whereby whey proteins present in the milk protein isolate system will begin to unfold, exposing hydrophobic domains (Anema and Li, 2003); causing a significant increase ($P < 0.05$) in the surface hydrophobicity (from 591 to 601) and pH (from 6.63 to 6.71) of the B-MPI$_{heat}$ solution.

The viscosity of the B-MPI$_{TSC}$ solution was significantly higher ($P < 0.05$) than the other two MPI-based binder solutions (12.5 mPa.s). This increase in viscosity on the addition of TSC is caused by casein micelle destabilisation and further dissociation

which has been shown to occur at this level of TSC addition (McCarthy *et al*., 2017). TSC is a calcium chelator, and when present in solution with casein micelles, acts to solubilise CCP from the interior structure of the casein micelles. CCP is known to be critical to the physical stability of casein micelles, acting to stabilise the casein proteins within the micelle structure (de Kruif *et al*., 2012). Depletion of CCP initially causes the micelles to swell, resulting in an increase in casein micelle voluminosity, and a considerable increase in the viscosity of the solutions (5.73 to 12.5 mPa.s). More extensive CCP depletion causes further dissociation of the micelle occurs whereby the micelles break apart into smaller micelle fragments (De Kort *et al*., 2012, 2011).

The dissociation of casein micelles within the B-MPI$_{TSC}$ binder was confirmed through turbidity analysis which showed that the turbidity of the B-MPI$_{TSC}$) (0.85) was significantly lower ($P < 0.05$) than either the B-MPI or B-MPI$_{heat}$ solutions (3.72 and 3.81, respectively) as the now-dissociated micelles, could no longer scatter light at the same intensity as the B-MPI and B-MPI$_{heat}$ solutions, both of which contained intact casein micelles. The results for both the viscosity and turbidity of the dissociated B-MPI$_{TSC}$ solutions were in alignment with previous studies conducted by De Kort *et al*. (2011, 2012). The dissociation of the casein micelles on addition of TSC also caused a significant reduction ($P < 0.05$) in particle size and surface hydrophobicity, and increase in the pH, of the solution when compared to the other MPI binder solutions (Table 4.1). The alterations achieved through TSC addition, bring the MPI solution closer to a desirable binder solution for agglomeration applications due to its high viscosity, allowing for increased particle incorporation during powder agglomeration (Dhenge *et al*., 2012; Tardos *et al*., 1997).

4.4.2 Agglomeration of milk protein isolate powder

The results (Table 3.2) showed that a significant increase ($P < 0.05$) in powder particle size (for all size parameters measured i.e., Dv10, Dv50, Dv90 etc.,) occurred on the application of each binder solution during the agglomeration process. For example, the mean particle size (D [4,3] value) increased significantly ($P < 0.05$) from the control sample on agglomeration; the B-H_2O showed the least increase in D[4,3] value (from 36.9 to 85.8 μm), followed by the B-Lac and B-$MPI_{heat,}$ which showed similar significant increases ($P > 0.05$) from 36.9 to 106 and 102 μm, respectively. The most significant increase ($P < 0.05$) in particle size was measured on application of both the B-MPI and B-MPI_{TSC} binder solutions which caused an increase in the D[4,3] value to 126 and 136 μm, respectively. These results illustrate that, although all binders were capable of achieving MPI agglomeration, the extent to which the agglomeration occurred varied due to differences in the properties of the binder solutions (Section 4.4.1).

To quantify the effectiveness of each binder solution, in terms of their ability to agglomerate MPI, the proportion of fine (<10 μm) and agglomerate (>100 μm) material present within the bulk powder was quantified for each treated powder and compared to the untreated control. The results (Table 4.2) show that when the B-H_2O binder was applied, the resulting powder was the closest to the original untreated control, containing 4.79% fines and 20.3% agglomerates. This result indicates that although primary particles are being combined into larger agglomerate structures, the water was unable to sufficiently incorporate the fine material, present in MPI, into these structures. The poor binding performance of the B-H_2O may be attributed to a combination of its low viscosity as well as the high contact angle exists between water

and the powder particles of MPI, both acting to limit the interactions between the B-H_2O binder and the MPI powder (Korson *et al*., 1969; O'Sullivan *et al*., 2017).

Application of the B-MPI_{heat} binder showed an increase in the ability to form agglomerates, when compared to the B-H_2O binder (B-H_2O; 20.3% and B-MPI_{heat}; 34.9% agglomerates present), attributable to the significantly higher ($P < 0.05$) viscosity of the B-MPI_{heat} sample. However, similar to the B-H_2O sample, a proportion of fine material was still present in the bulk powder after the application of the B-MPI_{heat} binder (1.29% fines present). This suggests that the interaction between the B-MPI_{heat} binder and the fine material in the MPI bulk powder was limited, potentially attributable to the high surface hydrophobicity displayed in this sample, ultimately resulting in both the B-H2O and B-MPI_{heat} possessing poor binding capacity for agglomeration of MPI. This hypothesis is supported by results presented in Table 4.2 for the PSD span of these samples, with both the B-H_2O and B-MPI_{heat} having significantly higher ($P < 0.05$) span values (6.51 and 5.37, respectively) then all other treated powders (3.62 – 4.72), suggesting that the resulting bulk powder contains a combination of fine material, unaffected primary powder particles and agglomerated material. The presence of fine material in a bulk powder has been shown to limit powder functionality, most notably flowability, with powders having wide particle size distribution (i.e., high span values) typically displaying poor flow properties (Liu *et al.*, 2008).

Greater binding capacity was displayed by the B-Lac solution, measured though a reduction of the fine MPI powder material during agglomeration to a level less than 1%, which can be attributed to the "sticky" nature of this binder (Section 4.4.1). However; it must be noted, that the percentage of agglomerate material is lower in the B-Lac sample (26.5%) then all of the protein-based binders, confirming that binder

viscosity plays a key role in the formation of agglomerated MPI structures, with the B-Lac solution having the lowest viscosity of all of the measured binder solutions (Section 4.4.1).

Finally, the B-MPI and B-MPI$_{TSC}$ displayed the highest binding efficiency of all binders tested during MPI agglomeration, with both of the resulting powders displaying a pronounced reduction in presence of fine material (0.10 and 0.02%, respectively) paired with a large increase in the presence of agglomerates (34.9 and 43.8%, respectively). The B-MPI$_{TSC}$ solution, in particular, outperformed all other binders tested, with the resulting powder containing both the lowest level of fine and highest level of agglomerate material, respectively. These results align with the hypothesis outlined in Section 4.4.2, where this binder was highlighted as the most optimal binder due to its significantly ($P < 0.05$) higher viscosity and relatively low surface hydrophobicity.

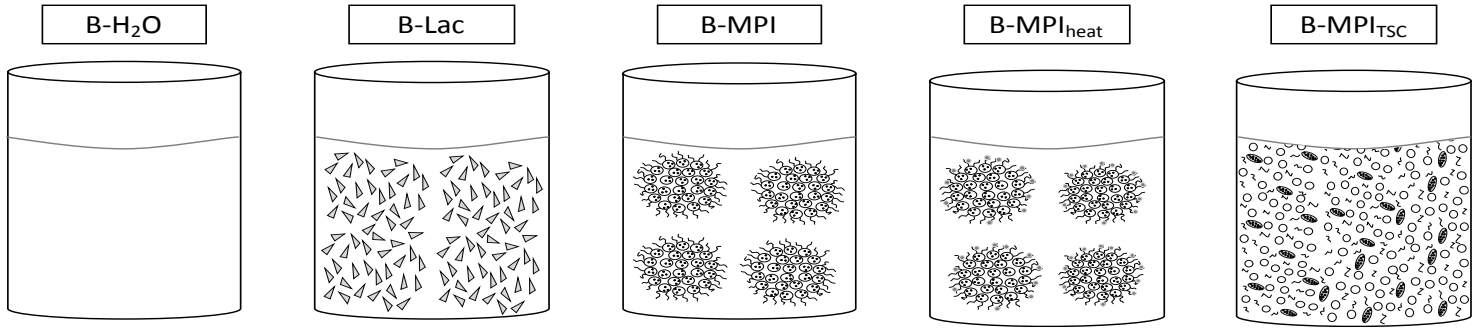


Figure 4.1 *Schematic representation of the agglomeration binder solutions; lactose molecules (⌂), micellar casein particles (○), κ-casein (ʖ), colloidal calcium phosphate (✿) and trisodium citrate molecules (⬭).*

Table 4.1 *Physical properties of binder solutions, including viscosity, particle size (D [4,3]), surface hydrophobicity, turbidity and pH*

Property	**Unit**	**B-H_2O**	**B-lactose**	**B-MPI**	**B-MPI_{heat}**	**B-MPI_{TSC}**
Viscosity	mPa.s	n.a.	3.77 ± 0.12^{a}	5.73 ± 0.24^{b}	5.36 ± 0.09^{b}	12.5 ± 0.31^{c}
D[4,3]	μm	n.a.	n.a.	1.22 ± 0.05^{a}	1.30 ± 0.06^{a}	0.73 ± 0.15^{b}
Surface hydrophobicity	slope	n.a.	n.a.	591 ± 1.53^{ab}	601 ± 1.72^{b}	558 ± 1.97^{a}
Turbidity	(-)	n.a.	n.a.	3.72 ± 0.20^{a}	3.81 ± 0.71^{a}	0.85 ± 0.29^{b}
pH	(-)	n.a.	3.75 ± 0.04^{a}	6.63 ± 2.31^{b}	6.71 ± 0.08^{bc}	6.77 ± 0.03^{c}

Values followed by different superscript letters in the same column are significantly different ($P < 0.05$).
n.a. = not applicable

Table 4.2 *Powder physical properties, including particle size distribution parameters and fine and agglomerate powder particle yield values for a milk protein isolate control (Ctrl) and agglomerated samples (B-H_2O, B-Lac, B-MPI, B-MPI_{heat} and B-MPI_{TSC}).*

	d_{10}	d_{50}	d_{90}	D [4,3]	Span	Fines[A]	Agglomerates[B]
	----------µm----------				-	%	%
Ctrl	11.9 ± 0.71[a]	31.7 ± 0.34[a]	64.7 ± 0.51[a]	36.9 ± 0.24[a]	1.75 ± 0.03[a]	9.17	1.86
B-H20	15.0 ± 0.21[b]	37.8 ± 0.47[b]	261 ± 19.0[b]	85.8 ± 5.69[b]	6.51 ± 0.43[d]	4.79	20.3
B-Lactose	23.8 ± 0.01[c]	55.7 ± 0.58[c]	287 ± 12.3[b]	106 ± 3.51[c]	4.72 ± 0.18[c]	0.13	30.4
B-MPI	26.8 ± 0.21[d]	65.3 ± 1.06[d]	341 ± 10.7[d]	126 ± 4.01[d]	4.81 ± 0.10[c]	0.10	26.5
B-MPI_{heat}	21.7 ± 0.10[c]	51.6 ± 0.20[c]	293 ± 1.53[b]	102 ± 0.58[c]	5.27 ± 0.01[c]	1.29	34.9
B-MPI_{TSC}	30.3 ± 0.15[e]	81.3 ± 1.46[e]	325 ± 15.7[d]	136 ± 5.51[d]	3.62 ± 0.13[b]	0.02	43.8

Values followed by different superscript letters, in the same column, are significantly different ($P < 0.05$).

Dv10 Particle size below which 10% of material volume exists

Dv50 Particle size below which 50% of material volume exists

Dv90 Particle size below which 90% of material volume exists

D[4,3] volume-weighted mean particle diameter

D[3,2] surface-weighted mean particle diameter

[A] % of volume distribution less than 10 µm

[B] % of volume distribution greater than 100 µm

Table 4.3 *Bulk handling properties, including bulk density (ρ_{bulk}), compressed density ($\rho_{compressed}$), volume of interstitial air (V_{ia}), volume of occluded air (V_{oa}), flow index (i) and compressibility index (CI) for a milk protein isolate control (Ctrl) and agglomerated samples (B-H_2O, B-Lac, B-MPI, B-MPI_{heat} and B-MPI_{TSC}).*

	ρ_{bulk}	$\rho_{compressed}$	V_{ia}	V_{oa}	*i*	CI
	----------g cm^{-3}----------		----------ml 100 g^{-1}----------		-	%
Ctrl	0.26 ± 0.01^{a}	0.43 ± 0.01^{a}	158 ± 0.23^{a}	1.32 ± 0.23^{a}	4.73 ± 0.19^{a}	38.2 ± 0.43^{a}
B-H_20	0.30 ± 0.01^{b}	0.44 ± 0.01^{ab}	148 ± 1.86^{b}	2.67 ± 0.04^{b}	4.91 ± 0.21^{a}	31.5 ± 0.66^{b}
B-Lac	0.34 ± 0.01^{d}	0.49 ± 0.01^{d}	129 ± 4.66^{c}	2.52 ± 0.11^{b}	5.85 ± 0.23^{bc}	29.4 ± 1.85^{bc}
B-MPI	0.32 ± 0.01^{c}	0.46 ± 0.01^{bc}	142 ± 1.15^{b}	2.68 ± 0.22^{b}	5.69 ± 0.16^{b}	29.0 ± 0.91^{c}
B-MPI_{heat}	0.31 ± 0.01^{b}	0.45 ± 0.01^{b}	143 ± 0.79^{b}	2.73 ± 0.03^{b}	5.57 ± 0.13^{b}	31.6 ± 0.53^{b}
B-MPI_{TSC}	0.34 ± 0.01^{d}	0.47 ± 0.01^{cd}	133 ± 0.65^{c}	2.79 ± 0.08^{b}	6.17 ± 0.15^{c}	28.7 ± 0.29^{c}

Values followed by different superscript letters, in the same column, are significantly different ($P < 0.05$).

4.4.3 Powder composition

Application of the various binder solutions required to achieve agglomeration, did cause alterations to the bulk composition of the MPI powder, resulting in a decrease in the overall protein content and an increase in the moisture content of all samples, as expected. The MPI control powder had a protein content of 85.1%, and this was reduced in a manner that was dependent on choice of binder solution. The B-H_2O and B-Lac binders caused the greatest reduction in overall protein content with the values reducing to 80.4 and 80.1%. respectively; aligning with results previously reported by Ji *et al*. (2016a) where MPI was similarly agglomerated using a 15% lactose solution.

The application of protein-based binders, in this study, did cause a reduction in the protein content of the resulting agglomerated MPI powder, but it must be noted that the reduction was of a much lower magnitude than experienced when using the more traditional binder solutions (i.e., B-H_2O and B-Lac). The protein contents of the B-MPI, B-MPI_{heat} and B-MPI_{TSC} samples were 83.2, 82.8 and 83.8%, respectively, and this higher protein content, relative to the other agglomerated forms of MPI, is attributed to the protein present in the binder solutions. The moisture content of the MPI increased on agglomeration from 2.34% (w/v) to 6.36-6.98% (w/v). This increase is attributed to the method of drying utilised in the agglomeration process (i.e., oven drying); traditionally, agglomeration is associated with a fluid-bed drying step which encourages rapid drying to a desired moisture content, usually within 2-5% (w/v) moisture. It is hypothesised that a more efficient drying process (e.g., fluid bed drying) would achieve a lower moisture content in the agglomerated MPI samples, resulting in a concomitant increase in protein content.

4.3.4 Bulk handling properties and powder flowability

All treated powders displayed a significant increase ($P < 0.05$) in bulk density on agglomeration, when compared to the untreated MPI control powder (Table 3.3). Initially, the MPI control had a bulk density of 0.26 $g.cm^{-3}$ which increased significantly ($P < 0.05$) on addition of each binder solution during agglomeration, with values ranging from 0.30 to 0.34 $g.cm^{-3}$ post-agglomeration The greatest, and most significant ($P < 0.05$) increase in bulk density was measured on application of the B-Lac (0.34 $g.cm^{-3}$), B-MPI (0.32 $g.cm^{-3}$), and B-MPI_{TSC} (0.34 $g.cm^{-3}$) binders, which were the most effective binders for MPI agglomeration (Section 4.4.2). Similarly, the B-H_2O and B-MPI_{heat} binders, which achieved limited agglomeration, also resulted in a lesser increase in bulk density although, still significant ($P < 0.05$), with bulk density values increasing from 0.26 to 0.30 and 0.31 $g.cm^{-3}$, respectively.

Traditionally, agglomeration of dairy powders is associated with a decrease in powder bulk density, which can be seen as a negative effect of the agglomeration process, acting to increase required storage space and associated transportation costs. In this study, conversely, an increase in bulk density was measured post-agglomeration, attributed here to the occurrence of process termed “densification”, which occurred during the agglomeration process. Densification (routinely utilised in other powder handling industries, e.g., the pharmaceutical industry) is a process that occurs when agglomerates are exposed to high shear forces during their formation, initially causing the individual powder particles, of which the agglomerate is composed, to be forced into a much closer arrangement; these particles can undergo further conformational changes, ultimately forming large dense agglomerate structures (Johansen and Schafer, 2001; Uniyal *et al*., 2020) The agglomeration process utilised in this study, exposed the forming MPI agglomerates to four blades,

each rotating at 500 RPM for a total of 6 min, which, as reported by Litster and Ennis (2004), is sufficient shear force to achieve powder densification.

Densified MPI agglomerate structures were present in all treated samples (i.e., on application of all binders) as visible through SEM analysis (Figure 4.2), indicating that the densification process was caused by the agglomeration and was independent of the binder selection. Additional microscopy analysis using SEM allowed clear visualisation the internal structures of these densified powder agglomerates (Figure 4.3). These micrographs were used to confirm that MPI primary powder particles experienced deformational changes on densification; which caused the levels of interstitial air, introduced initially on agglomeration, to be forced out of the agglomerate structure, yielding dense agglomerates for all treated powders, which has been previously reported to occur on agglomerate densification (Schæfer, 2001). This finding was supported by the results, presented in Table 4.3, where a measured, significant decrease ($P < 0.05$) in the volume of interstitial air was experienced on agglomeration of MPI; whereby the volume of interstitial air within the control MPI powder (158 ml 100 g^{-1}) was reduced to within 129–148 ml 100 g^{-1} on agglomeration of MPI.

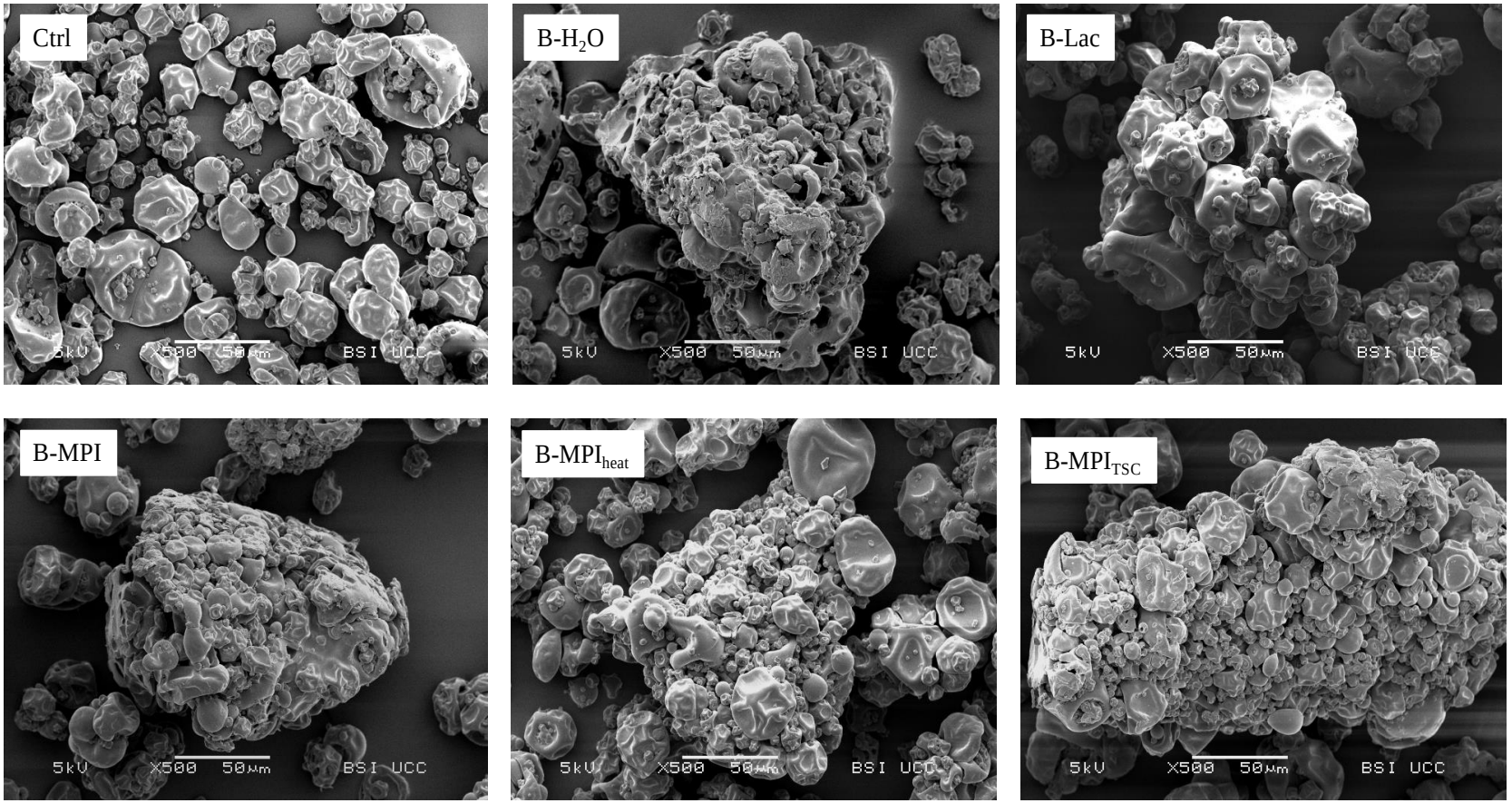


Figure 4.2 *Scanning electron micrographs of a milk protein isolate control (Ctrl) and agglomerated (B-H_2O, B-Lac, B-MPI, B-MPI_{heat} and B-MPI_{TSC}) samples. Level of magnification (500 X) and scale bars (50 µm) included*

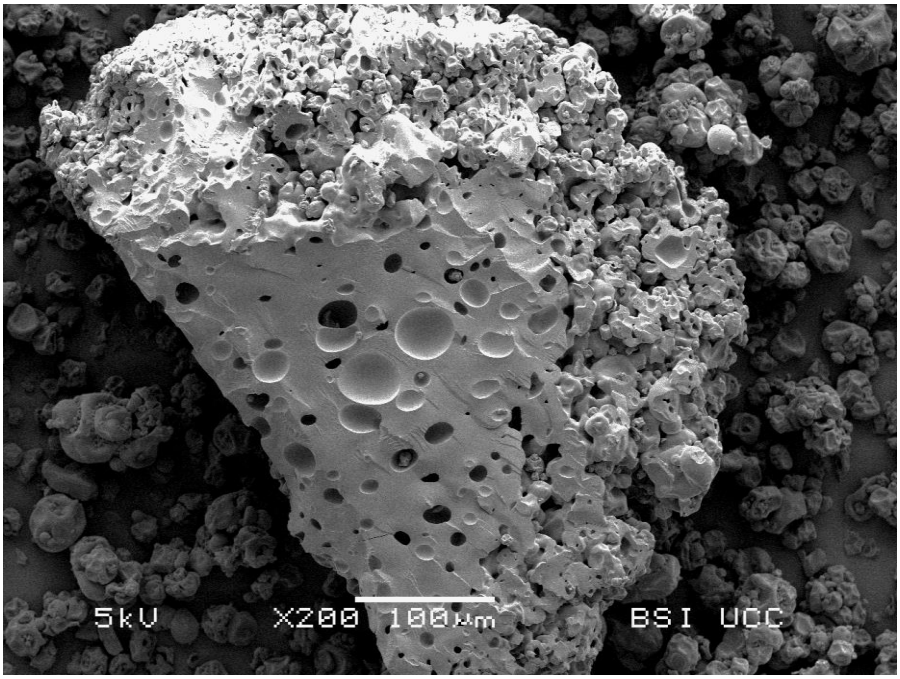


Figure 4.3 *Scanning electron micrograph capturing the interior of a densified milk protein isolate agglomerate structure present within the B-MPI$_{heat}$ sample. Magnification (200 X) and scale bar (100 µm) included.*

The increase in bulk density of MPI, achieved *via* agglomerate densification, has the propensity to yield a new form of this high-value ingredient, now requiring less storage and transport space, potentially reducing transportation costs. However, the associated reduction in interstitial air may impact on further applications, such as reducing final powder solubility, which is an already well-established challenge for rehydration of casein-dominant powders (Gaiani *et al*., 2007).

The alterations to the MPI powder physical (e.g., particle size) and bulk (e.g., bulk density) properties on agglomeration yielded subsequent changes to the flowability of the powder. Shear cell analysis was utilised to measure these changes and the results show that agglomeration of MPI caused a significant improvement ($P < 0.05$) in powder flowability (Figure 4.4). The MPI control had a flow index of 4.73, and agglomeration resulted in this index increasing to within 4.91–6.17, depending on

the binder solution applied. The B-MPI_{TSC} binder (most effective binder solution) displayed the most significant increase ($P < 0.05$) in powder flowability (flow index value increased from 4.73 to 6.17). Additionally, the B-H_2O binder (least effective binder solution) resulted in no significant ($P > 0.05$) change in MPI flowability. The compressibility index (CI) of a powder is closely related to flowability, such that powders which can be easily compressed (i.e., having high CI values) generally displays poor flowability (Abdullah and Geldart, 1999). In this present study, the control MPI powder had the highest CI value (38.2%) and this was reduced significantly ($P < 0.05$) on agglomeration to 28.7–31.6%. Aligning with the flowability results, the B-MPI_{TSC} and B-H_2O, which had the highest and lowest flow indices, also had the highest and lowest CI values, respectively (Table 4.3).

The greater flowability of agglomerated MPI was attributed to the increase in particle size, and associated depletion in fine powder material on agglomeration, which acted to reduce the extent of interparticle interactions (e.g., van der Waals and

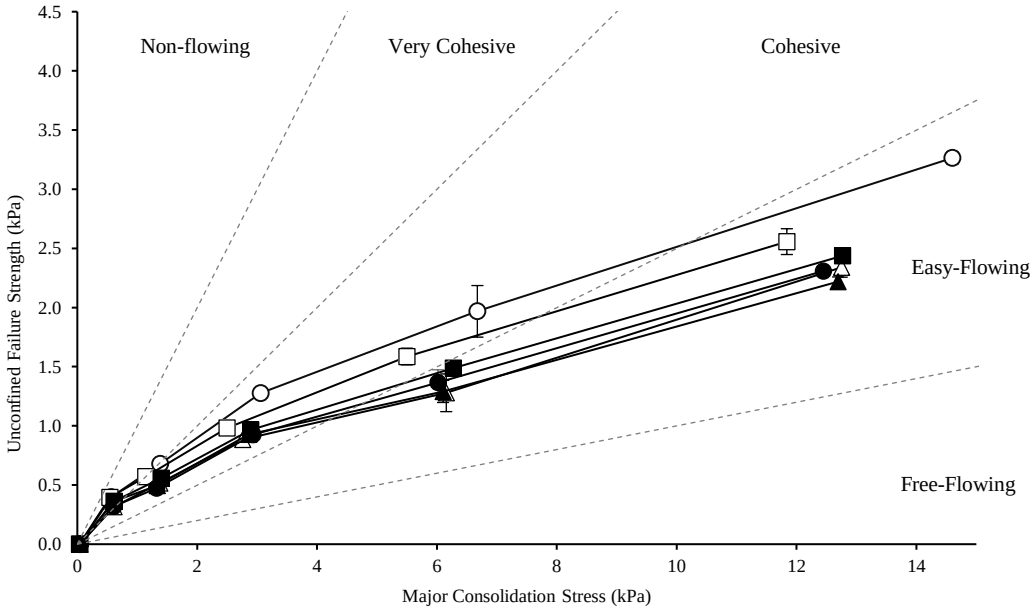


Figure 4.4 *Flow function profiles as a function of major principal consolidating stress (kPa) for a milk protein isolate control (Ctrl), (—○—) and agglomerated samples; B-H_2O (—□—), B-Lac (—Δ—), B-MPI (—●—), B-MPI_{heat} (—■—) and B-MPI_{TSC} (—▲—).*

electrotactic interactions) occurring between neighbouring powder particles, with similar findings being reported by Crowley *et al*. (2014) and Ji *et al*. (2017). To confirm this reduction in interparticle interactions on agglomeration of MPI, the angle of internal friction was measured for each powder and the results (Figure 4.5) show that the MPI control and B-H_2O displayed the highest angles of internal friction (53.1 and 51.8°, respectively) indicating that these samples displayed the greatest extent of particle-particle interactions. Furthermore, all treated powders that displayed a significant increase ($P < 0.05$) in flowability (i.e., B-Lac, B-MPI, B-MPI_{heat} and B-MPI_{TSC}), also displayed a significant reduction ($P < 0.05$) in their angle of internal friction, with values for the latter parameter ranging from 47.2-49.8°. For MPI powder, the increase in flowability, and reduction in compressibility, achieved in this study has the potential to significantly improve the ease of handling and application of such ingredient powders in numerous industrial unit operations such as storage (e.g., improved discharge from silos), conveying (e.g., reduced powder build-up on conveying lines) and packaging (e.g., less dust).

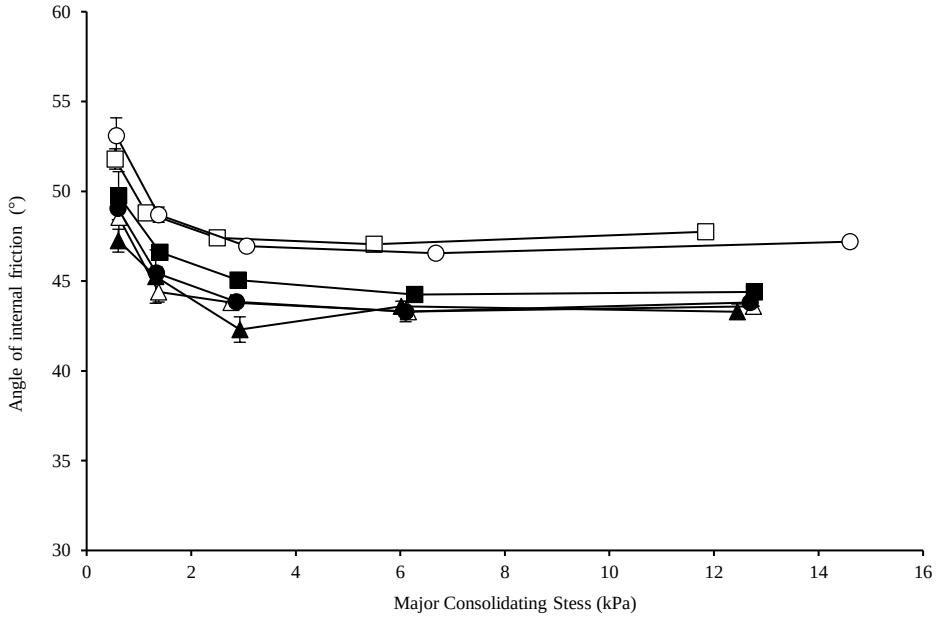


Figure 4.5 *Angle of internal friction as a function of major principal consolidating stress (kPa) for a milk protein isolate control (MPI Ctrl), (—○—) and agglomerated MPI samples; B-H_2O (—□—), B-Lac (—Δ—), B-MPI (—●—), B-MPI_{heat} (—■—) and B-MPI_{TSC} (—▲—).*

4.3.5 Powder rehydration properties

4.3.5.1 Powder wettability

As expected, the agglomeration of MPI caused a significant improvement ($P < 0.05$) in the wettability of the resulting agglomerated powders (Figure 4.6). The MPI control powder required 38.2 min to achieve complete wetting whereas the agglomerated forms of MPI were fully wetted within 3.50-9.97 min. This significant improvement in MPI wettability, displayed by all agglomerated powders, is attributable to the significant increase in particle size and increased bulk densities achieved on the agglomeration process. The formation of large, dense agglomerated structures in each bulk powder ensured that on wetting, gravitational force encouraged the particles to submerge below the water surface (i.e., become wetted), whereas in the MPI control, the particles were too small and light for gravity to have the same

effect. The B-Lac and B-MPI$_{TSC}$ had the lowest measured wetting times of all powders, and for the B-MPI$_{TSC}$ sample this is due to the extent to which agglomeration occurred in this sample. For the B-Lac sample, the presence of lactose in the powder bulk, and more notably at the surfaces of the agglomerated particles may also have acted to improve the wetting properties of this sample, due to it highly hydrophilic nature.

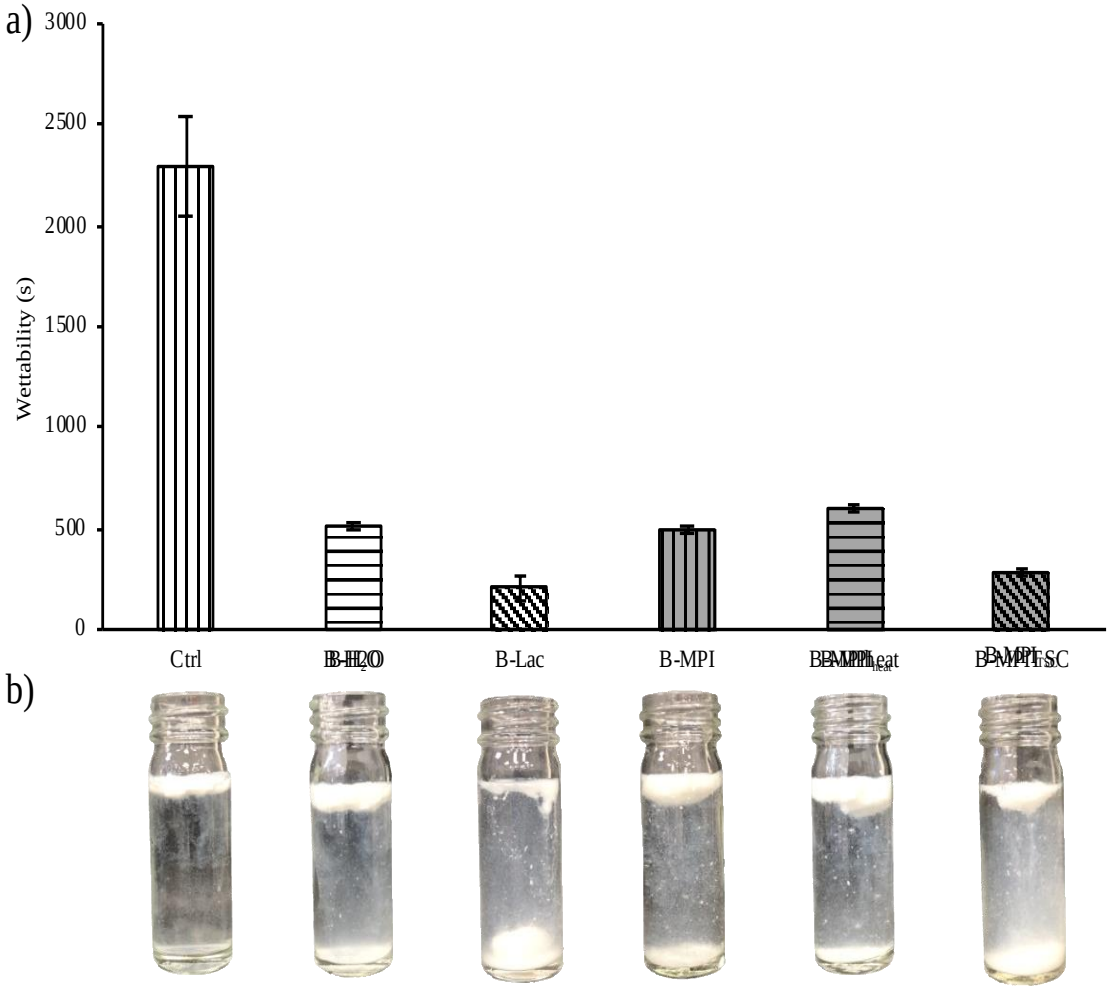


Figure 4.6 *(a) Wetting times for a milk protein isolate control (MPI Ctrl), ( ) and agglomerated MPI samples; B-H_2O ( ), B-Lac ( ), B-MPI ( ), B-MPI$_{heat}$ ( ) and B-MPI$_{TSC}$ ( ). (b) Images of powder wetting taken 3 min after powder incorporation (t=180 s) during wettability analysis.*

Contact angle analysis was carried out to further analyse powder wettability, more specifically, the initial contact occurring between water and the MPI powder samples. The results (Figure 4.7) indicate that the MPI control powder had a high initial (t=0) contact angle value of 90.5°, which aligns with results presented by O'Sullivan *et al*. (2017). This value remained relatively unchanged over the analysis run with a final (t=30) contact angle value of 88.5°, indicating that the water droplet was unable to penetrate into the bulk powder, attributable to the compact, hydrophobic MPI powder particle surfaces. The analysis of the agglomerated powders showed that all binders were capable of achieving a reduction in the initial contact angle (t=0), with values ranging from 81.2 to 87.2°. Although a reduction in the initial contact angle was measured for the B-H_2O and B-MPI_{heat} samples, these values remained relatively unchanged, similar to the MPI control, as the water droplet could not migrate further into the powder bulk, explained by the limited agglomeration achieved by these binders, as discussed in Section 3.4.2. The B-Lac, B-MPI and B-MPI_{TSC} samples, which were previously established as the most effective binders, not only caused a reduction in the initial contact angle, but also allowed the water droplet to migrate rapidly into the powder bulk, as evident by a sharp decrease in final contact angle values which were 65.4, 57.3 and 46.1°, respectively; indicating improved wetting properties of these powders. The final measured contact angle for each powder was in agreement with the trends in CI (Section 4.4.2), such that a sample with high CI value inhibited the migration of water into the bulk powder during this analysis. The improvement in wettability achieved through agglomeration is a key functional improvement that could act to increase processing efficiency, most notably through the reduction in wet blending times required for adequate MPI wetting on rehydration.

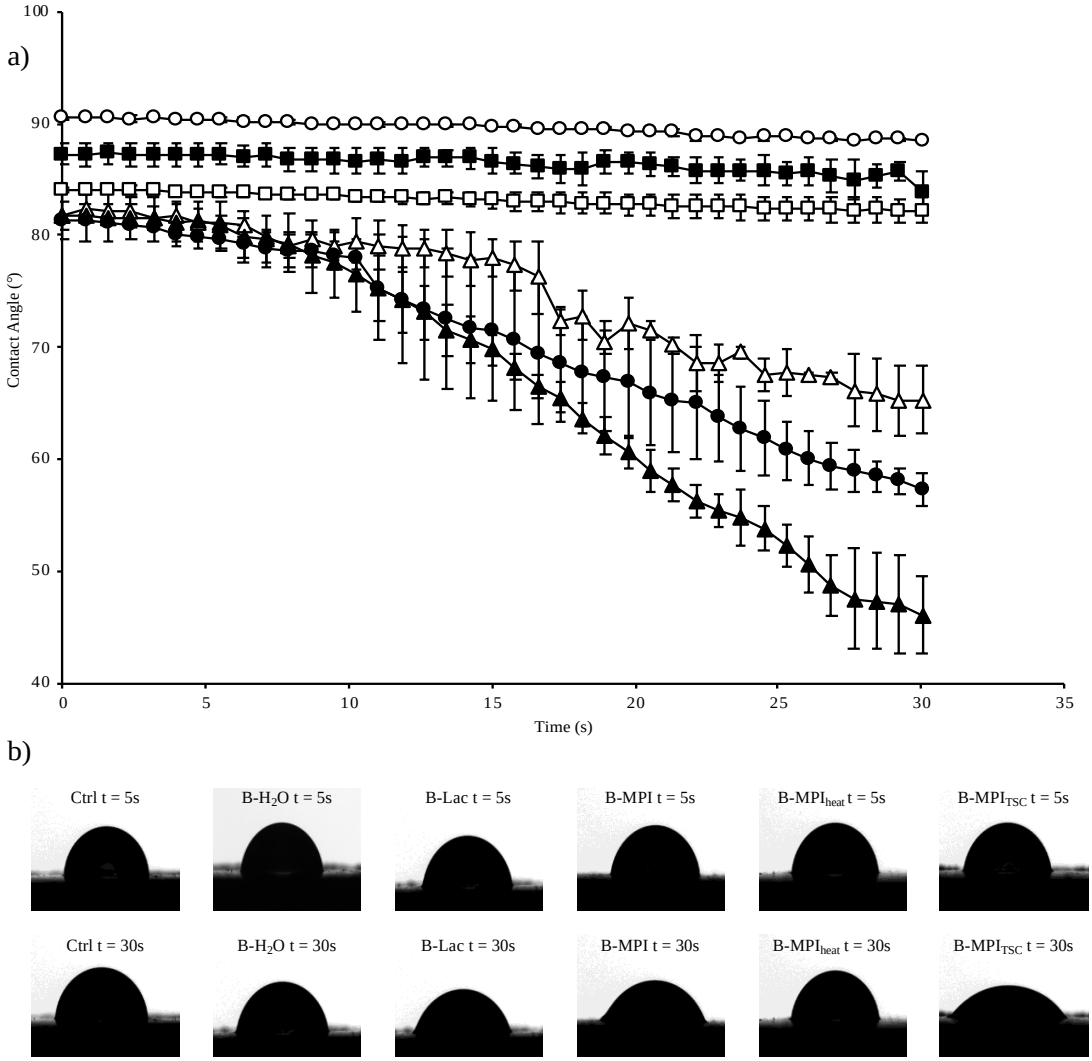


Figure 4.7 *(a) Contact angle developed between a droplet of ultrapure water and the compressed powder surface of a milk protein isolate control (MPI Ctrl), (—○—) and agglomerated MPI samples; B-H_2O (—□—), B-Lac (—Δ—), B-MPI (—●—), B-MPI_{heat} (—■—) and B-MPI_{TSC} (—▲—). (b) Representative images of contact angle analysis captured at 5 and 30 s into each analysis run.*

4.3.5.2 Powder solubility

For casein-dominant powders, such as MPI, the final stage of rehydration (i.e., powder solubility) has been established as the rate limiting step (Gaiani et al., 2007). The results show that the agglomeration of MPI significantly reduced ($P < 0.05$) its solubility, independent of the binder solution applied. Utilisation of a standard

rehydration process indicated that the MPI control had solubility of 56.3%, while the solubility of the agglomerated MPI samples ranged from 35.6 to 37.4%, with no significant differences ($P > 0.05$) between the agglomerated powders. This reduction in powder solubility is caused by the presence of large dense powder agglomerates (formed *via* particle densification; Section 4.4.2) in the bulk powders. For efficient solubility, liquid needs to be able to migrate into the interior of primary powder particles where it can act to solubilise the various constituents within the powder structures. The dense particle structures present in the agglomerated MPI powders inhibited this migration of water to their interior, therefore limiting powder solubility. A similar reduction in powder solubility was reported on agglomeration of a native phosphocaseinate (another type of casein-dominant dairy protein ingredient) by Gaiani *et al*. (2007) and of MPI by Ji *et al*. (2016b).

4.5 Conclusion

In conclusion, MPI was successfully agglomerated through the application of all binder solutions, as evidenced by a significant increase in particle size, while the extent to which agglomeration occurred was dependent on the properties of the individual binder solutions applied, most notably, viscosity. The results illustrate that the novel protein binder solutions were capable of not only achieving a similar extent of agglomeration as the more traditional binder solutions (i.e., water and lactose), but in most cases, outperformed them. Modification of an MPI solution, through TSC addition, significantly improved the properties critical to binding performance on agglomeration *via* casein micelle dissociation. A significant improvement in the flowability of MPI was achieved through agglomeration, as evident by increased flow index and concomitant decrease in powder compressibility, caused by the increasing

particle size and reduction of fine material on agglomeration, acting to reduce interparticle interactions. Improved wetting properties were also achieved on agglomeration of MPI, attributed to densification of agglomerates during the process, which yielded large dense agglomerated structures in all samples, with an ability to wet rapidly. Conversely, the formation of these dense structures restricted the latter stages of rehydration (i.e., solubility) which may limit the industrial application of such a process. The B-MPI$_{TSC}$ binder displayed the greatest extent of agglomeration and improvement in powder flowability and wettability however it must be noted that agglomeration of MPI caused a significant reduction in powder solubility, regardless of binder solution applied. Ultimately, the results from this study scientifically underpin the recent commercial interest in agglomerating high-protein dairy powders through the application of protein-based binder solutions, thereby achieving agglomeration with minimal reduction in the overall protein content of the resulting powder, while improving selected functional properties.

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Chapter 5

General discussion and suggestions for future research

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5.1 General discussion

Agglomeration is a long-established approach for modifying and controlling dairy powder functionality, with the key beneficial effects on both powder flowability and wettability being well established at both industrial and academic level (Gaiani *et al*., 2007; Pisecky, 2012). Key to powder agglomeration is the formation of powder structures of increased particle size, formed by combining numerous individual primary powder particles into enlarged, cluster-like structures (Cuq *et al*., 2013). This is mainly achieved by recirculating fine powder material, produced during spray drying and collected from exhaust air, back into the main spray chamber where they can combine with primary powder particles, ultimately forming agglomerated powder structures. Furthermore, complex solutions, such as lecithin, may be applied to these agglomerates (i.e., lecithination), achieving surface modification, acting to further improve powder wettability (Sharma *et al*., 2012). Although dairy powder agglomeration is well studied, and routinely utilised in the production of commodity dairy powders (e.g., whole and skim milk powder), the study of how these agglomerates react on further handling (i.e., during powder conveying) as well as the applicability of agglomeration for more high-value dairy powders (such as high-protein powders) is considerably more limited. Therefore, the objectives of this thesis initially focused on understanding how commercial, agglomerated, nutritional dairy powders change on further handling, before assessing the applicability of an agglomeration process for the modification of milk protein isolate (MPI) through the application of novel, protein-based binder solutions.

In **Chapter 3,** a custom-fabricated pressure dispersion rig was employed to facilitate the breakdown of agglomerates for a range of commercially available, nutritional dairy powders (i.e., a whey protein concentrate powder, a fat-filled milk

powder and an infant formula powder). The powders were dispersed through the rig at both 1 and 3 bar air pressures, allowing particle-particle (attrition) and particle-wall (collision) impacts to occur, with these forces acting to break down the agglomerates present within each bulk powder to an extent dependent on their overall mechanical integrity. Analysis of the powders, pre- and post-pressure dispersion showed not only, the extent of agglomerate breakdown, but also the more influential and detrimental effects these alterations can have on final powder functionality. Most notably, all powders, independent of the extent of agglomerate breakage, showed significant reductions in powder flowability, wettability and dispersibility properties, which are key functional considerations for further application. The results from this study provide new findings, illustrating the importance of maintaining the mechanical integrity of agglomerated dairy powders and further highlights the requirement for a greater level of control during the subsequent handling of these powders (i.e., during powder conveying) at industrial scale.

The clear improvement in powder functionality achieved through agglomeration, which was further distinguished in Chapter 2, led to development of an objective in **Chapter 4** to assess the ability of powder agglomeration to modify the functionality of MPI, while minimising unwanted changes associated with powder agglomeration (i.e., decreasing bulk density and altering the resulting powder composition). The approach to achieve this involved the use of novel protein-based binders in agglomeration, instead of the more traditional binders such as lactose or lecithin (Palmer *et al*., 2018). In this study, a lab-scale agglomeration process was established to assess the effectiveness of a range of MPI binder solutions (modified through various pre-treatments i.e., thermal processing and casein micelle dissociation) in comparison to more traditional binder solutions which have been

previously used for agglomeration i.e., water and lactose (Szulc and Lenart, 2013). The results presented in this study showed that the novel MPI binder solutions were capable of not only matching the traditional binders in terms of agglomeration ability, but in most cases, outperformed them. Furthermore, all agglomerated forms of MPI displayed significantly improved flowability and wettability characteristics, attributed to the increase in particle size achieved through agglomeration. As it was a key criteria when designing the study, it must be noted that the agglomeration of MPI did not cause a decrease in the resulting powder bulk density; conversely, a significant increase in bulk density was achieved, attributable to agglomerate densification. Additionally, although a reduction in the overall protein content was measured on application of the various binder solutions, use of the novel protein-based binder solutions resulted in the least dilution of the protein component in the resulting agglomerated MPI powders. These findings are of significance in the production of high protein powders, acting to scientifically underpin ingredient innovation and highlighting the applicability of powder agglomeration to enhance the functional properties of high-protein powders such as MPI.

5.2 Suggestions for future research

Considerable research in the field of dairy powder agglomeration is still required and a series of follow-up studies, complementary to the work presented in this thesis, could begin to address this. These studies may include:

Assessment of optimal agglomeration level for the production and handling of agglomerated dairy powders

Further scope exists to understand the optimal level of agglomeration required for specific dairy powder types, which could act to alleviate the inevitable breakdown that will occur during further handling (i.e., powder conveying). It is proposed here to utilise the same experimental approach as used in **Chapter 3** (i.e., powder analysis pre- and post-agglomerate breakdown); however, in this study, analysis of a singular dairy powder, agglomerated to varying extents, should be employed. By clearly setting an end target in terms of product functionality (e.g., complete wetting in ≤ 60 s) the maximum level of agglomerate breakage may be established that still allows for the functionality target to be met, therefore identifying the optimal agglomeration level for ta specific type of agglomerated dairy powder.

Impact of lecithin type and treatment on the surface modification of agglomerated high-protein dairy powders

Although the application of lecithin solutions, post-agglomeration, may cause unwanted alterations to composition of high-protein powder, as discussed in **Chapter 4**, the substantial improvement in powder wettability highlights it's potential to address the poor rehydration performance of various high-protein dairy powders (e.g., clumping on powder wetting). The influence of lecithiniation on the rehydration properties of MPI and whey protein isolate has been studied but it must be noted that these studies involved the application of dilute lecithin solutions (approximately 2% lecithin solution) to achieve agglomeration and surface modification, respectively (Ji et al., 2017, 2016). These lecithin solutions are not representative of the lecithin blends that are atypically used at industrial scale (40-50% lecithin in carrier oil), acting to

inhibit the scale-up of these findings to an industrial powder production setting. The need to assess the effect of lecitination, and lecithin modification, on the rehydration properties of high-protein powders still remains, with an emphasis on applying lecithin in a manner similar to that used at industrial scale (e.g., atomisation of highly concentrated lecithin solutions in lab-scale fluid bed drying scenarios).

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Appendix