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Impact of Moisture Content and Composition on Flow Properties of Dairy Powders

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IMPACT OF MOISTURE CONTENT AND COMPOSITION ON FLOW PROPERTIES OF DAIRY POWDERS

by

Katelynn Palmer

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ABSTRACT

Impact Of Moisture Content And Composition On Flow Properties Of Dairy Powders

by

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Utah State University, 2023

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Milk protein concentrate (MPC) and isolate (MPI), and milk permeate powder (MPP) are functional dairy powders that are used in many food applications. Protein-rich and lactose-rich milk powders can cake/clump during manufacture and storage due to extrinsic factors. This not only decreases powder quality, but also reduces process efficiency.

In the first study, a method was developed for objective and reliable assessment of dairy powder flow characteristics. Milk protein powder was subjected to three-point shear failure testing. Flow function coefficients (*ffc*) were obtained after Mohr circle analysis of pre-shear and shear-to-failure points. Due to the globular shape and larger particle size (50–70 μm), milk protein powders exhibited stick-slip phenomenon and lack of shear-to-failure points at higher pre-shear (>6 kPa) and shearing normal stresses than the flat-shaped, smaller size (<20 μm) cohesive calcium carbonate powder. Shear-to-failure points in milk protein powders were established by lowering pre-shear and shearing normal stresses, increasing data capturing interval and optimizing rotation speed. Based

upon reliable *ffc* values MPC 80 powder and MPI 85 were classified as easy flowing and cohesive respectively.

In the second study, we studied critical factors affecting flowability e.g. particle size, moisture content and temperature. Increase in powder moisture content resulted in reduced flowability for all samples. The *ffc* value increased with particle size. However, impact of particle size was most noticeable with the smallest (< 50 μm) and largest particles (> 250 μm), both of which had decreased flowability due to increased particle-particle interactions. Impact of test temperature was not significant on the flow characteristics of the powder samples.

In the third study, we studied the effect of storage time and temperature on the flow characteristics of protein-rich and lactose-rich powders. Throughout storage, MPP, MPC 80, MPI 85 low lactose and MPI 90 samples remained flowable, regardless of temperature variation. Storage temperatures of 35 and 42°C impacted the physicochemical changes the most, with MPI 85 low lactose the most sensitive to Maillard browning. This study forms a scientific basis for understanding factors affecting flowability of protein and lactose rich powders so that dairy industry can produce superior quality products.

(231 pages)

PUBLIC ABSTRACT

Impact Of Moisture Content And Composition On Flow Properties Of Dairy Powders

Katelynn Palmer

Milk protein concentrate (MPC) and isolate (MPI), and milk permeate powder (MPP) are functional dairy powder products that are used in food applications worldwide. It is critical that environmental factors and physical powder characteristics during production and storage are controlled. When dairy powders are exposed to non-ideal conditions (high moisture, varying temperatures,) they can quickly become very sticky, and clumpy. When powders become sticky, their ability to easily flow is reduced. As a result, processing and storing the powders effectively and sustainably becomes very difficult.

In the first study, an analysis method was created to test the general flow behavior of different milk powder samples with a powder rheometer. It was discovered that the shape and size of the powder particles plays a large role in how the flowability of these powders is recorded.

In the second study, the powder samples were modified with different environmental factors, moisture and temperature to determine if these changes would affect the overall flowability of the powder samples. Increased moisture reduced the overall flowability of the powders. Temperature variation had no significant impact on the flowability of the powders. The particle size in relation to flowability was also

analyzed to see if different particle sizes made powder flow more easily. It was discovered that the smallest size particles (< 50 μm) were the most cohesive (or least flowable) in nature.

The third study examined the impact of storage time (12 months) and temperature in relation to the powder's flowability. The color of the powder was also analyzed to see if the color changed over time in response to different temperatures. It was discovered that in general, each of the powder samples kept the same level of flowability at month 12 compared to the powder samples at the beginning of the study. From the color study, MPI 85 low lactose powder was discovered to have the highest amount of color change from a light, white powder to a darker, yellowish powder. This change in color occurred because the powder sample contained several types of sugar that tend to turn a product brown when exposed to heat for extended periods of time.

Dedicated in loving memory to my Grandpa, John W. Palmer for his constant love and support.

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LIST OF ABBREVIATIONS

ADPI= American dairy Product Institute

FFC = Flow function coefficient

kPa = kilopascals

MCR = Modular compact rheometer

MPC = Milk protein concentrate

MPI = Milk protein isolate

MPP = Milk permeate powder

PSA = Particle size analyzer

RC = Rennet casein powder

RH = Relative humidity

SEM = Scanning Electron Microscopy

NaCN = Sodium caseinate powder

WPC = Whey protein concentrate powder

LIST OF SYMBOLS

T_g = Glass transition temperature

α = angle of internal friction

σ = normal stress (kPa)

σ_1 = consolidation stress

σ_c = unconfined yield strength

σ_p = pre-shear point (normal stress kPa)

τ_1 = intercept of the linearized yield loci

τ = shear stress (kPa)

τ_p = pre-shear point (shear stress kPa)

τ_c = Cohesion (kPa)

CHAPTER 1

INTRODUCTION

The demand for dry milk powder has been on the rise for many years, and is likely to continue as the world population keeps increasing (Lagrange et al., 2015). There is a wide variety of milk powder and whey powder products currently available in the market. Common products include, whole milk powder, skim milk powder, nonfat milk powder, milk permeate powder, milk protein concentrates and isolates, and whey protein concentrates and isolates (Jana, 2017; Tehrany and Sonneveld, 2009).

Each powder type has specific compositional requirements. Whole milk powder must have more than 26% but no greater than 40% milkfat and cannot contain more that 5% moisture ("21CFR131.147," 2022). Milk protein concentrate (MPC) end-product must contain at least 40% protein by weight, and for milk protein isolate (MPI), the percentage of protein must be greater than, or equal to 89.5% protein on dry matter basis (ADPI, 2021a). The percentage of protein contained in these powders is typically designated by the number included in the name of the product, e.g., milk protein concentrate 80. Various compositions are achieved using different membrane filtration systems.

Dairy powders can be used in a wide variety food applications, with ingredient functionality being largely determined by the composition of the powder. For example, whole milk powder is commonly used in sauces and instant beverages to provide creaminess, whereas nonfat milk powder is used to fortify fluid milk products and frozen desserts, without the addition of extra fat (ADPI, 2021b). General functions of MPC and MPI include: gelling, emulsifying, and water binding (ADPI, 2021a). One study found that MPC could be successfully added as a component to bulk-starter for cheese making, and to yogurt as a stabilizing agent (Mistry, 2002). Milk protein concentrate powders also contain significant amounts of high quality proteins that are sought after in many food systems (ADPI, 2021a) such as, high protein nutrition bars, ice cream, beverages, bakery products, and nutrition products (Agarwal et al., 2015). Milk permeate powder does not contain protein, but still has value as a sucrose replacement in bakery items and can also be used for milk standardization purposes (ADPI, 2021c).

The majority of dairy powders are made using a spray drying process, and after spray drying is completed, the powder is pneumatically transported in pipes to storage silos and bins, or to hoppers where it can be packaged into bags or mixed into ingredient blends (Boiarkina et al., 2016; Schulze, 2008). Therefore, studying rheology of powders is important. Rheological testing can be done by several different methods, including: shear testing, flow cell testing, avalanching, compression tests, and cohesion tests (Schulze, 2008). Flow behavior of the powder during processing, conveying, ingredient blending, and product storage is dependent on physicochemical factors, as well as external environmental factors. Physicochemical characteristics of powders includes density, melting points of powder components, flowability, composition, and particle size

and structure (Decision et al., 2014; Saifullah et al., 2016). Environmental factors include relative humidity, temperature, time, and equipment type.

Some powders (e.g., lactose and fat rich powders) have a tendency to stick to walls or form a cake during transportation and storage. When moving powder to or from, silos, hoppers, or bins, these types of powders can become less flowable, stickier, and more difficult to transport. During powder conveying, higher air velocities can induce excessive flowability, which can lead to loss of powder fines to the atmosphere, therefore resulting in not only product losses but also environmental pollution. To overcome these problems, powder handling equipment must be optimized in design to ensure that powders do not stick to the wall of dryers, conveyors, and storage silos (Schulze, 2008).

The overall objective of this study is to utilize rheological testing with the shear cell and flow cell method to gain a comprehensive understanding of the intrinsic flow behavior and the impact of environmental factors on protein-rich and lactose-rich powders. This research will provide an additional benchmark for flowability standards for protein-rich and lactose-rich powders, which is necessary to be able to continue to produce high quality dairy powders and increase their usability in the ingredient industry. Additionally, the use of powder rheometer with a controlled environmental chamber to stabilize or modify samples during shear testing is particularly novel for protein-rich and lactose-rich dairy powders.

Research Hypothesis

Hypotheses of this study are:

1. Protein-rich and lactose-rich powder flowability is impacted by the relative humidity and temperature of the environment, storage time, and storage temperature
2. Protein-rich and lactose-rich powder flow properties are affected by the powder composition and particle size of the respective powder types
3. Shear cell methodology is able to differentiate between flow characteristics obtained for protein-rich and lactose-rich powder with different treatments

Objectives

1. To determine the critical moisture content and optimum flow, or shear conditions needed to ascertain the flowability of protein-rich and lactose-rich powders
2. To determine the impact of particle size on flowability of the protein-rich and lactose-rich powders, and to analyze the physicochemical characteristics of these powders
3. To determine the impact of storage in relation to three factors: flowability, powder particle structure, and microbiological counts

CHAPTER 2

LITERATURE REVIEW

2.1: Background

Milk protein concentrates (MPC) and milk protein isolates (MPI) are high protein powders made by ultrafiltration and diafiltration technology. These filtration membranes are used to fractionate the milk and remove fat, lactose and minerals and condense both casein and whey proteins (Maidannyk et al., 2020). To be considered as milk protein concentrates, the powder must contain at least 40% protein and milk protein isolate must contain at least 89.5% protein. Both products typically contain less than 3% fat, approximately 5% moisture, and have a low amount of lactose.

Milk permeate powder (MPP) is obtained from the by-product stream of MPC processing and is the end-product after ultrafiltration removes the majority of protein and fat from the milk. The remaining permeate is spray-dried into a powder that contains a minimum of 75% lactose, with approximately 3% of protein (as non-protein nitrogen), and 8.5% ash remaining. This high lactose powder contains only trace amounts of fat (<1%) (ADPI, 2021c). Lactose can be in either its amorphous or crystalline form, depending on the powder processing conditions.

Flowability in food powders such as tea, flour, whole milk powder, skim milk powder, high fat powder, lactose powder, milk protein concentrate powders, and whey

permeate powder have been previously studied by several groups (Crowley et al., 2014; Fitzpatrick et al., 2004; Juliano and Barbosa-Cánovas, 2010; Kamath et al., 1994; Teunou et al., 1999; Teunou and Fitzpatrick, 2000). However, the focus of this research will mainly revolve around milk protein concentrate and isolate powders and milk permeate powder.

Powders are considered bulk solids, consisting of individual particles of varying size with the presence of occulated and interstitial air (Schulze, 2008). Thus, when powders are processed, there must be consideration of how the flowability of the bulk powder mass is effected by the individual particles and the amount of entrapped air. Controlling the powder composition and particle size can affect the flowability of the bulk mass during processing and storage.

Rheology, the study of how matter flows, can be employed to determine the individual flow behavior of powders. Rheological properties of powders will impact the extent to which powders can cake or stick together, or how well the powder is able to flow without the addition of excessive force. If powders easily cake or become less flowable under certain conditions, it is beneficial to determine what those conditions are. Each rheological test employs a specific measurement to describe flowability. Shear cell testing specifically subject powder to normal forces and shear normal forces to determine flowability, and flow cell tests are similar, except with the addition of air flow**.** To our knowledge, shear cell and flow cell research on milk protein concentrates and isolates has not been widely completed.

2.2: Flowability problems during manufacture

The production of dairy powders follows a standard procedure of modifying the fluid milk composition using membrane filtration, removing water and concentrating the milk solids via evaporation, heating the concentrated product, and then using a spray dryer to atomize the milk droplets and produce a powder (Tehrany and Sonneveld, 2009). Drying of the powder can also be done on a fluidized bed. Figure 2.1 presents the concentration and filtration pathways required to obtain various dairy powder products (Schuck, 2002).

During powder manufacturing, metal hoppers, silos, and bins are commonly used to transport and store the powders. In these environments, the powders can inadvertently be exposed to higher relative humidity environments, fluctuating temperatures, and long storage times. In powder processing plants, these conditions may cause lack of flowability, ultimately leading to bigger problems such as clogging of powder in conveying lines and hoppers, stickiness, and powder dust explosions. Poorly designed equipment or changes in the physical properties of powders can lead to a lack of flowability. Physical changes, such as caking, stickiness, and particle-to-particle interactions within the powder can adversely affect flowability. For example, flowability is reduced as powder forms cakes or clumps, causing more friction. Similarly, if the product is moist and at high temperatures, it tends to stick to material surfaces. Common interactions between particles include: the formation of liquid bridges due to increased moisture, surface tension, and intermolecular and electrostatic forces (Juliano and Barbosa-Cánovas, 2010). Interactions will always be prevalent to some extent during

powder processing, but prevalence can change due to factors like particle size and moisture content.

In addition to stickiness, caking, and particle interactions, there are also several common flowability issues specific to storage silos. These core flow issues include: product arching, funnel flow, rat-holing, flooding of product into processing area, and particle size segregation (Figure 2.1), (Crowley et al., 2014; Schulze, 2008).

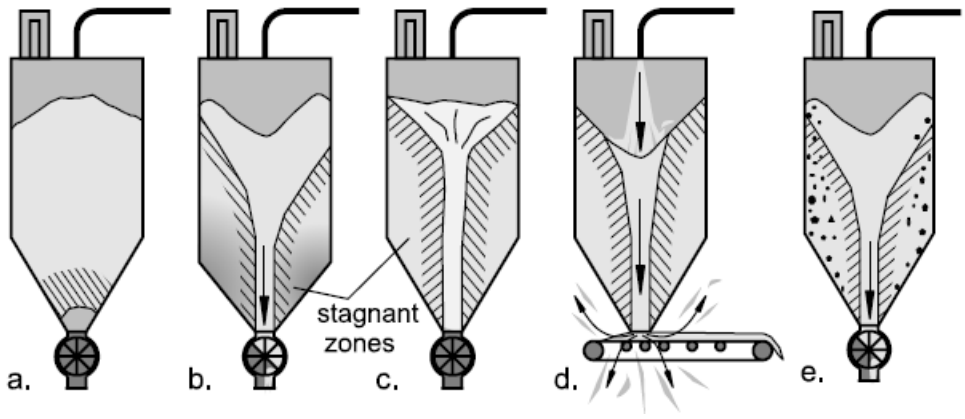

Fig 2.1. Flowability problems during discharge of powder from storage silos; a. arching; b. funnel flow; c. rat-holing, d. flooding; e. segregation. Used with permission and obtained from Powders and Bulk Solids. Behavior, Characterization, Storage and Flow. *Schulze 2008.*

These larger problems occur as a result of caking and particle-to-particle interactions. For example, powder arches will form within the silo when powders with very small particles are consolidated, and particle to particle cohesion forces occur (Figure 2.1a) (Schulze, 2008). Funnel flow phenomena occurs when the powder is unable to flow downwards toward the bottom of the hopper because of excess friction from the powder mass and the silo wall. This reduced flow leads to the build-up of stagnant zones, in which the powder is stuck and will not move down in the hopper, leading to rat-holing. Flooding occurs when too much powder is forced downward toward the hopper and the rate of flowability cannot be controlled. Funnel flow of the powder can also induce segregation of the powder particles, based upon particle size and density differences, and can cause the product to become non-uniform (Schulze, 2008). In product manufacturing and ingredient blending, these problems are not acceptable as they lead to inconsistent product and increased processing times.

2.3: Rheological analysis

The study of powder rheology, or powder's tendency and ability to flow rather than stick to walls and clump together, is critical for multiple reasons. Equipment used for processing, transportation, and the storage of food powders require specific engineering and design to ensure that the product can be made, stored, and used efficiently without loss of quality (Juliano and Barbosa-Cánovas, 2010).

The prevention of common issues like stickiness, caking, and silo flow issues is necessary to ensure efficient processing and a consistent quality product. Knowledge of how powder will behave under specific conditions helps in identifying critical control factors in processing and conveying. Determination of optimal environmental storage conditions to ensure powder flow, non-stickiness and lack of cohesivity, are critical components of powder rheology.

Rheological analysis can be performed on powders using multiple techniques; however, two common methods are the use of shear cell or a flow cell (Figure 2.2a and 2.2b, respectively.) A shear cell specifically measures the amount of force needed for a powder mass in static conditions to begin to flow. This method uses both normal compressive and rotational shear forces simultaneously to initiate a flow (measured as a shear-to-failure point) in the powder mass. This method can mimic the flow conditions exerted due to a gravitational load force during the unloading of a silo, or the force of a hopper blade trying to move powder out of a bin. Shear testing is applicable to relatively more cohesive powders.

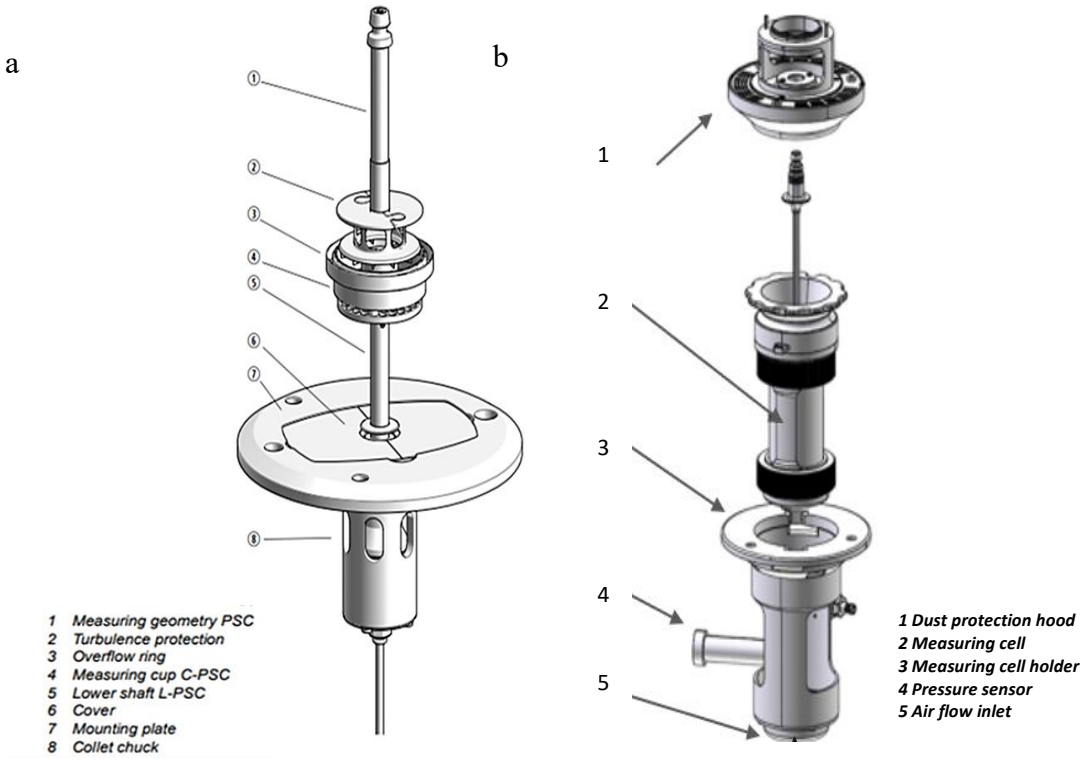

Fig 2.2: Schematic diagram of shear cell (a) and flow cell (b). Used with permission and obtained from Anton Paar Training Materials

On the other hand, flow cell testing can measure the effect of air fluidization on the flow behavior of a powder mass, as well as help determine the cohesive nature of the powders by seeing how much air force/pressure is required to fluidize the powder bed. Both the shear cell and flow cell methods are useful to determine the amount of force required to promote fluidization of powders.

When analyzing the flow properties of a powder using a shear cell, flowability can be defined by to what extent powder flows after subjecting it to a specific load for a specific period of time. From shear testing, we obtain flow function coefficients (*ffc*)

which are directly proportional to how easily the powder will flow. We can measure two different flowability functions, i.e., 1. the instantaneous flow function, which is measured from powder right after consolidation applied with normal force (Schulze, 2008); 2. The time consolidation (temporal) flow function, where the powder is consolidated for a longer amount time (Teunou and Fitzpatrick, 2000). This long-term consolidation action can be completed outside of the rheometer on a weighted platform, or on the rheometer itself. In a typical shear test, powder goes through four steps: conditioning (shear and time history removal), consolidation, pre-shearing, and shearing. Homogeneity of the sample (random particle orientation and air disbursement) as well as removal of consolidation effects, is ensured by the conditioning step. Consolidation and pre-shearing are often completed simultaneously. Compared to the pre-shear step, lower normal stress values are used in the shearing phase in order to ensure failure and incipient flow of the powder under rotational shear (Wang et al., 2016a, 2016b). The instantaneous (incipient) flow function is obtained from a yield locus function. A yield locus is a graphed path obtained by drawing a line through the points (normal stress, shear stress) at which the powder experienced pre-shearing and shearing failure (Figure 2.3) (Crowley et al., 2014; Teunou et al., 1999). The amount of stress imposed on the powder that causes failure (or initiates incipient flow) is called the unconfined yield strength and is typically measured in kilopascals (kPa). Incipient flow is also a term used to describe the instantaneous failure of the powder (Figure 2.3) (Schulze, 2008).

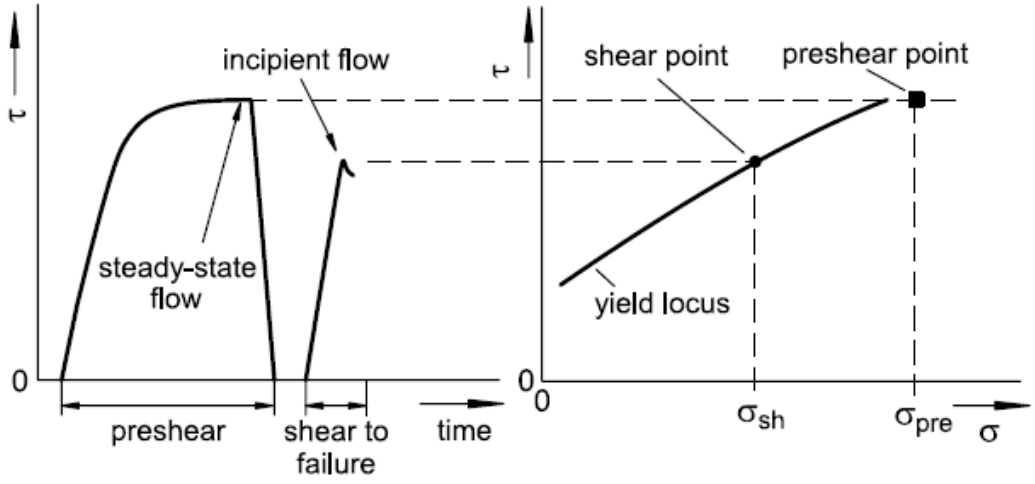

Fig 2.3: Measurement of a point of the yield locus (shear point) by pre-shear and shear to failure. Used with permission and obtained from Powders and Bulk Solids. Behavior, Characterization, Storage and Flow. *Schulze 2008.*

Once at least three yield loci points are established, using different shearing normal stresses, they are used in obtaining a Mohr circle (Figure 2.4), with shear stress on the y-axis and consolidation normal stress on the x-axis. Plotting the yield loci using the Mohr circles allows for the calculation of two values: the unconfined yield strength ($\sigma_{c)}$ and the major principal consolidating stress ($\sigma_{1)}$ (Crowley et al., 2014; Schulze, 2008; Wang et al., 2016a, 2016b).

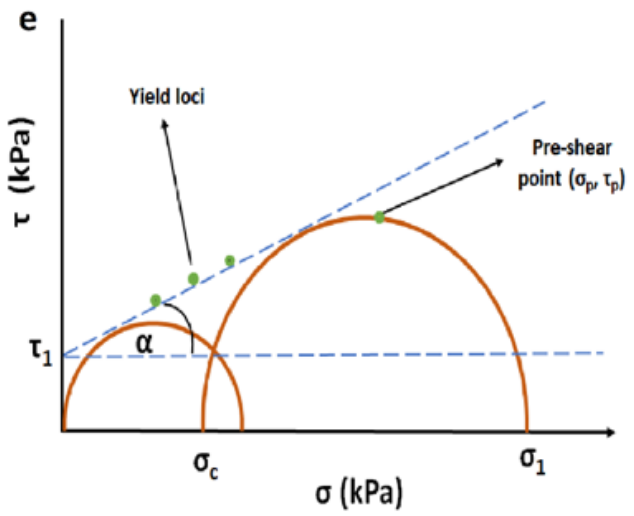

Fig 2.4: Mohr circle representation of the unconfined yield strength (σ_c) and the major principal consolidating stress (σ_1).

Using the Mohr circle analysis, the consolidating stress (σ_1) is determined by drawing a Mohr circle tangent to the established yield locus, and drawing it through the pre-shear point (σ_p, τ_p) which is recorded by the rheometer software during testing. The unconfined yield strength is determined by relationship between the cohesion (intercept of the yield locus function on the y-axis) and the angle of internal friction, as recorded by the rheometer. This relationship can be described in equation 1 (Schulze, 2008; Wang et al., 2016a, 2016b).

$$\tau = \sigma * tan(\alpha) + \tau_1 \quad (1)$$

Where τ = shear stress (kPa), σ = normal stress (kPa), τ_1 = intercept of the linearized yield loci and α = angle of internal friction

The unconfined yield strength and consolidation stresses can be calculated using the following equation 2–4 as described in (Wang et al., 2016a).

$$\sigma_c = \tau_1 * 2 * tan\left[45 + \frac{\alpha}{2}\right] \quad (2)$$

$$\sigma_1 = (1 + sin\,\alpha)\left[\frac{S - \sqrt{S^2 sin^2\alpha - (\tau_p^2 cos^2\alpha)}}{cos^2\alpha}\right] - \frac{\tau_1}{tan\,\alpha} \quad (3)$$

$$S = \sigma_p + \frac{\tau_1}{tan\,\alpha} \quad (4)$$

Where,

S = mathematical constant

φ = angle of internal friction

σ_1 = consolidation principal stress

σ_c = unconfined yield strength

Numerical classification of the powder's flowability can then be obtained by taking the ratio of the major principal consolidating stress (σ_1) to the unconfined yield strength (σ_c), which is known as the flow function coefficient (*ffc*). These *ffc* index values are used to characterized the inferred flowability conditions of the powder (Table 2.1) (Schulze, 2008).

Table 2.1. Cohesive tendency of powders as classified with flow function coefficients (ffc).

ffc Value	***Inferred Flow Condition***
ffc < 1	Non-flowing
1 < ffc < 2	Very cohesive
2 < ffc < 4	Cohesive
4 < ffc < 10	Easy-flowing
ffc > 10	Free-flowing

Flow function testing done by Crowley et al., (2014) on several milk protein concentrate powders with protein content ranging from 40% to 90% established that the major principal consolidating stress used had definite effects on the resulting ffc values. These MPC powders ranged from free-flowing to cohesive, depending on what pre-shear consolidation stress (0.2 – 4.8 kPa) was used. Prior studies also indicate that the flowability rating of powders can be dependent on the amount of major principal stress is used during testing (Chen et al., 2012; Crowley et al., 2014; Teunou et al., 1999).

During shear testing, a phenomenon known as stick-slip may occur. Stick-slip is the tendency of the shearing geometry to jump, or jerk around during shearing of the powder and is manifested in the data as a sawtooth line (Bagga et al., 2012; Schulze, 2008). Previous research indicates that stick-slip occurs due to several different factors, including, increased friction between particle due the shearing action, the shearing speed,

and the relative humidity (Bagga et al., 2012; Cain et al., 2001; Schulze, 2008). Stick-slip is not completely avoidable. Another important factor of shear testing is the rotational speed of the shearing geometry. The optimal speed for producing accurate results is dependent on the intrinsic properties of the powder such as being cohesive versus easy-flowing. If shear speed is not optimized with respect to the powder type, the shearing signal to noise (stick-slip) ratio can decrease and will lead to erroneous data.

2.4: Powder composition and physical properties

Powder flowability characteristics are directly impacted by the powder's composition, moisture content, particle size, and particle morphology (Juliano and Barbosa-Cánovas, 2010). The effects of powder composition on flowability, with specific interest in moisture, fat, protein, and lactose content is particularly important in dairy powder research. The state of lactose (amorphous or crystalline) and the ratio of each will determine in part, how flowable milk powders are (Fitzpatrick et al., 2007). Crystalline lactose is less hygroscopic than the lactose in the amorphous state (Thomas et al., 2004). Therefore, uptake of moisture by amorphous lactose results in a more cohesive and sticky powder that is more prone to caking. The formation of liquid bridges between the powder particles adds cohesive strength to the bulk mass and forms a more caked product (Fitzpatrick et al., 2007). During processing and storage, the product composition, particle size, moisture content and temperature all influence the level of stickiness and stickiness can negatively affect the overall quality of the powder (Caparino et al., 2017) (O'Donoghue et al., 2019). Hygroscopic powders quickly become sticky when manufactured or stored in environments with inadequate humidity and temperature

control. The porous nature of the powders results in quick uptake of moisture and the development of a sticky and caked product (Downton et al., 1982).

The amount of fat present can also have a substantial effect on powder flowability. An increase in cohesiveness and a decrease in flowability was seen when shear testing was completed on powders with increasing fat contents. Skim milk powder with 0.9% fat was significantly less cohesive than whole milk powder containing 26% fat (Fitzpatrick et al., 2007).

2.5: Moisture

Industrial dairy powders have a moisture content range of 2% to 6%, depending on the powder type. Milk permeate powder is commonly around 2%, whole milk powder at 3% and milk protein concentrates and isolates around 5% (ADPI, 2021a; Fitzpatrick et al., 2007). The general nature of water is to act as a solvent and as a result, it also has the ability to modify the inherent properties of powder (Maidannyk et al., 2020). Flowability will be significantly reduced when moisture levels are high as the presence of water allows for capillary interactions and liquid bridging between particles (Figure 2.5) (Crowley et al., 2014). Liquid bridging occurs as water fills the interstitial area between individual particles and connects them (Schulze, 2008). Increased moisture can also affect particles by influencing the strength of Van der Waals forces between the particles and also reducing the friction between particles by acting as a lubricant (Coelho and Harnby, 1978; Lumay et al., 2016; Xu et al., 2007).

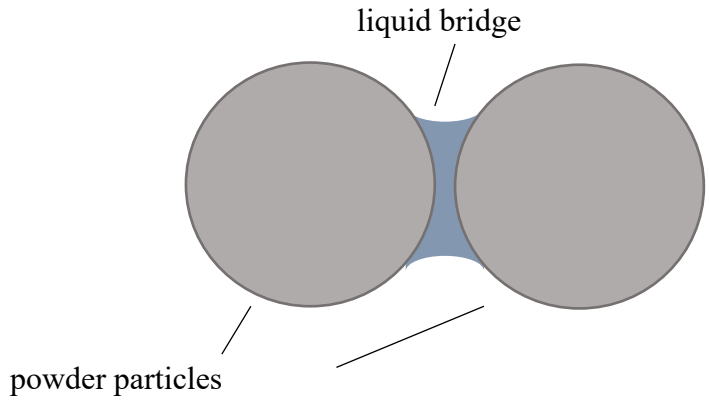

Fig 2.5: Representation of liquid bridging phenomenon between powder particles

To measure the effect of moisture content on powder flowability, saturated salt solutions are frequently used to modify the moisture contents of powders and establish water sorption isotherms. The relative humidity is controlled and sample is added to the environment until it equilibrates to the relative humidity established by the salt solution (Armstrong et al., 2014; Teunou et al., 1999). During the equilibration process, the powder samples are intermittently stirred in order to prevent a crust forming on the surface of the powder and reducing the amount of moisture that can penetrate the sample (Lumay et al., 2016). In food powders, there are observed values of relative humidity, in conjunction with specific temperatures that will act as the critical limit for moisture content, and if the powder exceeds this limit, it will cake and become less flowable (Teunou et al., 1999).

Prior research indicated that an increase in the relative humidity leads to an increase in the moisture content of the high protein powders (whey protein concentrate powder, rennet casein powder and sodium caseinate powder) making these powders more cohesive and less flowable (Fitzpatrick et al., 2007). At ambient temperature, with approximately 11 to 14% moisture content, the powders became very cohesive or caked.

Moisture sorption isotherms on MPC powders demonstrated that lower levels of protein absorbed more water than higher protein levels (Maidannyk et al., 2020). This phenomenon was attributed to the larger amount of lactose present in the low protein (<50%) MPC powder, as compared to the powders with 60 to 80% protein. The higher levels of protein in the MPCs stopped the reaction of the amorphous lactose converting into the crystalline state. It is also important to note that an increase in moisture content largely decreased the glass transition point of all the MPC powders tested in this study, regardless of the amount of protein present (Maidannyk et al., 2020).

For other types of high protein powers, such as rennet casein (RC) powder, sodium caseinate (NaCN) powder and whey protein concentrate (WPC) powder, it was found that the powders easily took on more moisture and became less flowable when they were kept in a high relative humidity environment (76%) (Fitzpatrick et al., 2007). The RC and NaCN powders did not cake, but WPC in particular became caked at 76% RH, and the caking action was attributed to the powder containing a significant amount of amorphous lactose.

2.6: Particle size and morphology

Milk powders that are produced by spray drying generally have a particle size distribution range of 10 to 250 μm (Silva and O'Mahony, 2017). However, powders composed of smaller particles are prone to have decreased flowability (Stavrou et al., 2020). This reduced flowability is a function of increased particle-to-particle interactions and higher bulk density. When the particle is smaller, the surface area becomes greater. As such, the particle-to-particle interactions increase and the additional space to interact creates a more cohesive bulk solid (Fitzpatrick et al., 2007). Changing the general particle size distribution from smaller to larger particles will promote an increase in the flowability of the respective powder because interactive forces between powder particles are reduced when the surface area of the particle is decreased (Fitzpatrick et al., 2004). Less cohesion was observed in whey permeate powder, compared to flour or tea, due in part to the relative size of the particles (Teunou and Fitzpatrick, 2000).

Previous studies with the shear cell suggest that as the protein content of high protein milk powders went up, there was a decrease in particle size for MPC80, MPC85, and MPC90. These powders were classified as cohesive using Jenike's flowability classification standards and the reduction in particle size was correlated to the decrease in flowability in these powders compared to milk powders with lower protein contents (< 75% protein) (Crowley et al., 2014).

The composition of milk powder can influence the powder particle structure on a microscopic level. Thomas et al., (2004) found that high protein milk powders had a non-uniform spherical shape with a greater occurrence of large depressions on the surface of the particles. This phenomena is due to the higher viscosity of the liquid concentrate

before it is spray dried (Thomas et al., 2004). Due to the irregular shape and inconsistent size of the powder particles, free-flow can be hindered by the interlocking of the particles themselves (Thomas et al., 2004).

2.7: Bulk density

Bulk density is a physical characteristic of powders and can be changed depending on the amount of interstitial air and the extent of consolidation. Therefore, bulk density can easily be modified based on storage and packaging conditions and procedures used during analysis. The design of a production process that requires volumetric or gravimetric material analysis heavily relies on bulk density as a key variable (Vasilenko et al., 2013). Bulk density is "process history dependent" meaning that the amount of consolidation and shear history present in the sample will change the overall bulk density. The powder must be handled carefully and consistently in order to obtain accurate data from the bulk density analysis method (Vasilenko et al., 2013). Bulk density can also be affected by particle size, shape and packaging and processing methods. During processing and ingredient blending, bulk density should be consistent to ensure the flow of the powder is uniform and the correct amount of product is added.

2.8 Temperature Effects

Temperature can affect the glass transition temperature (T_g) of a material. If the temperature is greater than the T_g of the powder, physicochemical changes will occur within the amorphous components of the powder and as a result, caking will occur (Carpin et al., 2017). Amorphous lactose will easily take on water, and when the moisture content of the powder increases, the T_g of the powder will decrease, and the powder will

be affected more by temperature changes. Therefore, physicochemical changes related to temperature are also closely related to changes in humidity. Monitoring of the processing environment can prevent these factors from negatively affecting the product.

Temperature affects flowability in relation to the amount of fat and moisture in a product (Fitzpatrick et al., 2007; Rennie et al., 1999). In a study with skim milk powder, whole milk powder, and high fat powder, an increase in temperature resulted in a more cohesive powder for the whole milk and high fat powders. There was only a limited increase in cohesiveness for the skim milk powder. The reduced flowability of the higher fat powders was attributed to the high temperatures melting the milk fat present on the particle surfaces, leading to formation of liquid bridges of melted fat and increased cohesion (Fitzpatrick et al., 2007). Additionally whole milk powder with a moisture content of 2.8% became less flowable at a lower temperature (45°C) compared to whole milk powder with a 1.8% moisture content, that became more cohesive at 55°C (Rennie et al., 1999).

2.9: Time consolidation and storage

If stored incorrectly, milk powders will experience physicochemical and biochemical changes which can reduce flowability (Thomas et al., 2004). Fluctuations in storage temperature can change the flowability of dairy powders. Increased temperature can affect the thermoplastic nature of the powder components, like lactose and fat. Both of these components will melt upon heating and solidify upon cooling, thus, if there are drastic temperature differences during the storage period, the powder is much more likely to cake and increase in cohesiveness (Fitzpatrick et al., 2004). Increases in humidity can

also result in particle caking, particle collapse, and lactose crystallization, thus negatively affecting the powder's ability to flow evenly (Thomas et al., 2004).

Powders are often stored in silos where powder is deposited as a large mass. When bulk solids are subjected to compressive stress over time, they can become more compact and less flowable. This consolidation action can result in caking and is otherwise known as time consolidation. When a powder is consolidated, it undergoes a change in the unconfined yield strength, and becomes a stronger bulk solid that will require more force to induce flow (Schulze, 2008). The extent of time consolidation will vary between product types and other environmental factors.

Whey permeate powder increased in bulk density after consolidation periods of 1,3 and 7 days. This increase in compaction caused the whey permeate powder have a higher unconfined yield strength, requiring more force to induce flow. Similar trends were also observed with flour (Teunou and Fitzpatrick, 2000).

Unconfined yield strength of the powder may also increase over a consolidation period due to more instances of particle surface interactions, increased particle-to-particle friction, the influence of moisture permeation from the air, and subsequent phase changes of components like fat or lactose, resulting in the formation of liquid bridges and increased caking (Fitzpatrick et al., 2007; Teunou and Fitzpatrick, 2000). It can be expected that as the unconfined yield strength increases, the flowability of the powder will be reduced and more external force will be required to transport the powder.

2.10: Scanning electron microscopy

Some powder particles are wrinkled and caved in, while others are smooth. Scanning electron microscopy can be used to analyze the surface morphology of dairy powders (Carpin et al., 2017; de Jesus Silva et al., 2022). Additionally, particle shape and size can be analyzed at a detailed level using this method. The tendency of powders to agglomerate or act more cohesively may also be observed with SEM (de Jesus Silva et al., 2022).

2.11 Microbiological analysis

Control of the water activity (i.e., moisture content) and temperature is a critical factor in the inhibition of microbial growth. Microbial growth cannot occur in milk powders if the water content is approximately 5% and the water activity is low (a_w<0.5). Additionally, microbial load can be reduced by heat treating the milk prior to concentration and spray drying. However, if production or storage parameters are not controlled, there can be post-drying contamination, which can result in microbial growth and spoilage in the product (Tehrany and Sonneveld, 2009). Thermophilic and mesophilic bacteria spores can be found in milk powders and can become problematic during storage, particularly after reconstitution. Prior research has shown that thermophilic spores can be germinated, if the powder is exposed to temperatures greater than 37°C for longer times (Hill and Smythe, 2012). At ambient temperatures (~22°C), thermophilic growth is typically unexpected. When performing microbial analysis for spores, the method often involves a “heat shock” step to activate the viable spores prior to plating the sample. Different incubation temperatures will determine the spores that are able to

germinate, e.g., thermophilic or mesophilic. These standard methods will be incorporated into the analysis of the powder samples.

References

21CFR131.147 [WWW Document], 2022. . –FR - Code Fed. Regul. Title 21. URL https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=131.147 (accessed 4.30.22).

ADPI, 2021a. Concentrated Milk Proteins [WWW Document]. ADPI. URL https://www.adpi.org/dry-milks/concentrated-milk-proteins/ (accessed 4.29.22).

ADPI, 2021b. Nonfat Dry Milk [WWW Document]. ADPI. URL https://www.adpi.org/dry-milks/nonfat-dry-milk/ (accessed 4.30.22).

ADPI, 2021c. Dairy Products Solids [WWW Document]. ADPI. URL https://www.adpi.org/whey/dairy-products-solids/ (accessed 4.29.22).

Agarwal, S., Beausire, R.L.W., Patel, S., Patel, H., 2015. Innovative Uses of Milk Protein Concentrates in Product Development. J. Food Sci. 80, A23–A29. https://doi.org/10.1111/1750-3841.12807

Analytical Methods | GEA Spray Dryers [WWW Document], n.d. . GEA Eng. Better World. URL https://www.gea.com/en/products/dryers-particle-processing/spray-dryers/food-dairy-products/analytical-methods-dry-milk-products.jsp (accessed 9.18.23).

Armstrong, B., Brockbank, K., Clayton, J., 2014. Understand the Effects of Moisture on Powder Behavior. Chem. Eng. Prog. 110, 25–30.

Boiarkina, I., Sang, C., Depree, N., Prince-Pike, A., Yu, W., Wilson, D.I., Young, B.R., 2016. The significance of powder breakdown during conveying within industrial

milk powder plants. Adv. Powder Technol. 27, 2363–2369. https://doi.org/10.1016/j.apt.2016.10.019

Caparino, O.A., Nindo, C.I., Tang, J., Sablani, S.S., 2017. Rheological measurements for characterizing sticky point temperature of selected fruit powders: An experimental investigation. J. Food Eng. 195, 61–72. https://doi.org/10.1016/j.jfoodeng.2016.09.010

Carić, M., Akkerman, J.C., Milanović, S., Kentish, S.E., Tamime, A.Y., 2009. Technology of Evaporators, Membrane Processing and Dryers, in: Dairy Powders and Concentrated Products. John Wiley & Sons, Ltd, pp. 99–148. https://doi.org/10.1002/9781444322729.ch3

Carpin, M., Bertelsen, H., Dalberg, A., Bech, J.K., Risbo, J., Schuck, P., Jeantet, R., 2017. How does particle size influence caking in lactose powder? J. Food Eng. 209, 61–67. https://doi.org/10.1016/j.jfoodeng.2017.04.006

Coelho, M., Harnby, N.J.P.T., 1978. The effect of moisture on the form of water retention in a powder. Powder Technol 20, 209–217.

Crowley, S.V., Gazi, I., Kelly, A.L., Huppertz, T., O'Mahony, J.A., 2014. Influence of protein concentration on the physical characteristics and flow properties of milk protein concentrate powders. J. Food Eng. 135, 31–38. https://doi.org/10.1016/j.jfoodeng.2014.03.005

de Jesus Silva, G., Gonçalves, B.-H.R.F., Conceição, D.G., de Jesus, J.C., Vidigal, M.C.T.R., Simiqueli, A.A., Bonomo, R.C.F., Ferrão, S.P.B., 2022. Microstructural and rheological behavior of buffalo milk chocolates. J. Food Sci. Technol. 59, 572–582. https://doi.org/10.1007/s13197-021-05042-3

Decision, C. on the D. and E. of S.C.S.A.F. to I.G. and I., Technology, B. on C.S. and, Toxicology, B. on E.S. and, Studies, D. on E. and L., Council, N.R., 2014. Physicochemical Properties and Environmental Fate, A Framework to Guide Selection of Chemical Alternatives. National Academies Press (US).

Downton, G.E., Flores-Luna, J.L., King, C.J., 1982. Mechanism of stickiness in hygroscopic, amorphous powders. Ind. Eng. Chem. Fundam. 21, 447–451. https://doi.org/10.1021/i100008a023

Early, R., 2012.–17 - Dairy products and milk-based food ingredients, in: Baines, D., Seal, R. (Eds.), Natural Food Additives, Ingredients and Flavourings, Woodhead Publishing Series in Food Science, Technology and Nutrition. Woodhead Publishing, pp. 417–445. https://doi.org/10.1533/9780857095725.2.417

Emery, E., Oliver, J., Pugsley, T., Sharma, J., Zhou, J., 2009. Flowability of moist pharmaceutical powders. Powder Technol. 189, 409–415. https://doi.org/10.1016/j.powtec.2008.06.017

Fitzpatrick, J.J., Barry, K., Cerqueira, P.S.M., Iqbal, T., O'Neill, J., Roos, Y.H., 2007. Effect of composition and storage conditions on the flowability of dairy powders. Int. Dairy J. 17, 383–392. https://doi.org/10.1016/j.idairyj.2006.04.010

Fitzpatrick, J.J., Iqbal, T., Delaney, C., Twomey, T., Keogh, M.K., 2004. Effect of powder properties and storage conditions on the flowability of milk powders with different fat contents. J. Food Eng. 64, 435–444. https://doi.org/10.1016/j.jfoodeng.2003.11.011

Foster, K.D., Bronlund, J.E., (Tony) Paterson, A.H.J., 2005. The prediction of moisture sorption isotherms for dairy powders. Int. Dairy J. 15, 411–418. https://doi.org/10.1016/j.idairyj.2004.08.003

Fu, X., Huck, D., Makein, L., Armstrong, B., Willen, U., Freeman, T., 2012. Effect of particle shape and size on flow properties of lactose powders. Particuology, Advances in Characterization and Modeling of Particulate Processes 10, 203–208. https://doi.org/10.1016/j.partic.2011.11.003

Greenspan, L., 1977. Humidity Fixed Points of Binary Saturated Aqueous Solutions. J. Res. Natl. Bur. Stand. Sect. Phys. Chem. 81A, 89–96. https://doi.org/10.6028/jres.081A.011

Hare, C., Ghadiri, M., 2013. The influence of aspect ratio and roughness on flowability. AIP Conf. Proc. 1542, 887–890. https://doi.org/10.1063/1.4812074

Havea, P., Baldwin, A.J., Carr, A.J., 2009. Specialised and Novel Powders, in: Dairy Powders and Concentrated Products. John Wiley & Sons, Ltd, pp. 268–293. https://doi.org/10.1002/9781444322729.ch8

Hazlett, R., Schmidmeier, C., O'Mahony, J.A., 2021. Approaches for improving the flowability of high-protein dairy powders post spray drying – A review. Powder Technol. 388, 26–40. https://doi.org/10.1016/j.powtec.2021.03.021

Hill, B.M., Smythe, B.W., 2012. Endospores of Thermophilic Bacteria in Ingredient Milk Powders and Their Significance to the Manufacture of Sterilized Milk Products: An Industrial Perspective. Food Rev. Int. 28, 299–312. https://doi.org/10.1080/87559129.2011.635487

Jana, A., 2017. High Protein Milk Ingredients - A Tool for Value-Addition to Dairy and Food Products. J. Dairy Vet. Amp Anim. Res. 6.

Juliano, P., Barbosa-Cánovas, G.V., 2010. Food powders flowability characterization: theory, methods, and applications. Annu. Rev. Food Sci. Technol. 1, 211–239. https://doi.org/10.1146/annurev.food.102308.124155

Kamath, S., Puri, V.M., Manbeck, H.B., 1994. Flow property measurement using the Jenike cell for wheat flour at various moisture contents and consolidation times. Powder Technol. 81, 293–297. https://doi.org/10.1016/0032-5910(94)02888-5

Lagrange, V., Whitsett, D., Burris, C., 2015. Global Market for Dairy Proteins. J. Food Sci. 80, A16–A22. https://doi.org/10.1111/1750-3841.12801

Lumay, G., Traina, K., Boschini, F., Delaval, V., Rescaglio, A., Cloots, R., Vandewalle, N., 2016. Effect of relative air humidity on the flowability of lactose powders. J. Drug Deliv. Sci. Technol. 35, 207–212. https://doi.org/10.1016/j.jddst.2016.04.007

Maidannyk, V., McSweeney, D.J., Hogan, S.A., Miao, S., Montgomery, S., Auty, M.A.E., McCarthy, N.A., 2020. Water sorption and hydration in spray-dried milk protein powders: Selected physicochemical properties. Food Chem. 304, 125418. https://doi.org/10.1016/j.foodchem.2019.125418

Martin, G.J.O., Williams, R.P.W., Dunstan, D.E., 2010. Effect of manufacture and reconstitution of milk protein concentrate powder on the size and rennet gelation behaviour of casein micelles. Int. Dairy J. 20, 128–131. https://doi.org/10.1016/j.idairyj.2009.08.007

Mistry, V.V., 2002. Manufacture and application of high milk protein powder. Le Lait 82, 515–522. https://doi.org/10.1051/lait:2002028

Murrieta-Pazos, I., Gaiani, C., Galet, L., Cuq, B., Desobry, S., Scher, J., 2011. Comparative study of particle structure evolution during water sorption: Skim and whole milk powders. Colloids Surf. B Biointerfaces 87, 1–10. https://doi.org/10.1016/j.colsurfb.2011.05.001

O'Donoghue, L.T., Haque, M.K., Kennedy, D., Laffir, F.R., Hogan, S.A., O'Mahony, J.A., Murphy, E.G., 2019. Influence of particle size on the physicochemical properties and stickiness of dairy powders. Int. Dairy J. 98, 54–63. https://doi.org/10.1016/j.idairyj.2019.07.002

Palmer, K., Parhi, A., Shetty, A., Sunkesula, V., Sharma, P., 2023. Development of methodology for assessing flowability of milk protein powders using shear failure testing device. J. Food Eng. 348, 111450. https://doi.org/10.1016/j.jfoodeng.2023.111450

Rennie, P.R., Chen, X.D., Hargreaves, C., Mackereth, A.R., 1999. A study of the cohesion of dairy powders. J. Food Eng. 39, 277–284. https://doi.org/10.1016/S0260-8774(98)00158-7

Saifullah, M., Yusof, Y.A., Chin, N.L., Aziz, M.G., 2016. Physicochemical and flow properties of fruit powder and their effect on the dissolution of fast dissolving fruit powder tablets. Powder Technol. 301, 396–404. https://doi.org/10.1016/j.powtec.2016.06.035

Schuck, P., 2002. Spray drying of dairy products: state of the art. Le Lait 82, 375–382. https://doi.org/10.1051/lait:2002017

Schulze, D., 2008. Powders and bulk solids. Behav. Charact. Storage Flow Springer 22.

Sharma, A., Jana, A.H., Chavan, R.S., 2012. Functionality of Milk Powders and Milk-Based Powders for End Use Applications—A Review. Compr. Rev. Food Sci. Food Saf. 11, 518–528. https://doi.org/10.1111/j.1541-4337.2012.00199.x

Sikand, V., Tong, P.S., Roy, S., Rodriguez-Saona, L.E., Murray, B.A., 2011. Solubility of commercial milk protein concentrates and milk protein isolates. J. Dairy Sci. 94, 6194–6202. https://doi.org/10.3168/jds.2011-4477

Silva, J.V.C., O'Mahony, J.A., 2017. Flowability and wetting behaviour of milk protein ingredients as influenced by powder composition, particle size and microstructure. Int. J. Dairy Technol. 70, 277–286. https://doi.org/10.1111/1471-0307.12368

Stavrou, A.G., Hare, C., Hassanpour, A., Wu, C.-Y., 2020. Investigation of powder flowability at low stresses: Influence of particle size and size distribution. Powder Technol. 364, 98–114. https://doi.org/10.1016/j.powtec.2020.01.068

Tehrany, E.A., Sonneveld, K., 2009. Packaging and the Shelf Life of Milk Powders, in: Food Packaging and Shelf Life: A Practical Guide. CRC Press, pp. 127–141.

Teunou, E., Fitzpatrick, J.J., 2000. Effect of storage time and consolidation on food powder flowability. J. Food Eng. 43, 97–101. https://doi.org/10.1016/S0260-8774(99)00137-5

Teunou, E., Fitzpatrick, J.J., Synnott, E.C., 1999. Characterisation of food powder flowability. J. Food Eng. 39, 31–37. https://doi.org/10.1016/S0260-8774(98)00140-X

Thomas, M.E.C., Scher, J., Desobry-Banon, S., Desobry, S., 2004. Milk Powders Ageing: Effect on Physical and Functional Properties. Crit. Rev. Food Sci. Nutr. 44, 297–322. https://doi.org/10.1080/10408690490464041

Vasilenko, A., Koynov, S., Glasser, B.J., Muzzio, F.J., 2013. Role of consolidation state in the measurement of bulk density and cohesion. Powder Technol. 239, 366–373. https://doi.org/10.1016/j.powtec.2013.02.011

Wang, Y., Koynov, S., Glasser, B.J., Muzzio, F.J., 2016a. A method to analyze shear cell data of powders measured under different initial consolidation stresses. Powder Technol. 294, 105–112. https://doi.org/10.1016/j.powtec.2016.02.027

Wang, Y., Snee, R.D., Meng, W., Muzzio, F.J., 2016b. Predicting flow behavior of pharmaceutical blends using shear cell methodology: A quality by design approach. Powder Technol. 294, 22–29. https://doi.org/10.1016/j.powtec.2016.01.019

Xu, Q., Orpe, A.V., Kudrolli, A., 2007. Lubrication effects on the flow of wet granular materials. Phys. Rev. E 76, 031302. https://doi.org/10.1103/PhysRevE.76.031302

CHAPTER 3

DEVELOPMENT OF METHODOLOGY FOR ASSESSING FLOWABILITY OF MILK PROTEIN POWDERS USING SHEAR FAILURE TESTING DEVICE[1]

ABSTRACT

Protein-rich milk powders can be susceptible to caking and clumping during manufacture and storage. A method was developed for objective and reliable assessment of their flowability, i.e., tendency of powders not to stick to the equipment surfaces. Milk protein powder (MPC 80) was subjected to three-point shear failure testing on a powder shear cell attached to a MCR302e rheometer. Flow function coefficients (*ffc*) were obtained after the Mohr circle analysis of pre-shear and shear-to-failure points. Due to their globular shape and significantly larger particle size (50–70 μm), milk protein powders exhibited more stick-slip phenomenon and lack of shear-to-failure points particularly at higher pre-shear (>6 kPa) and shearing normal stresses than the flat-shaped, smaller size (<20 μm) cohesive calcium carbonate powder (*ffc* value 2.1 at 3.0 kPa). Absence of shear-to-failure points in milk protein powders was attributed to instant

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failure of the powder at higher normal stresses due to larger particle size and globular shape, which was avoided by lowering pre-shear (3, 6, and 9 kPa to 1, 3 and 6 kPa) and shearing normal stresses, increasing data capturing interval and optimizing shear speed. Reliable *ffc* values at 3.0 kPa pre-shear normal stress, characterizing MPC 80 powder (4.6 ± 0.4) as easy flowing and MPI 85 as cohesive (3.7 ± 0.5) were obtained successfully using developed protocol.

3.1: Introduction

Protein-rich dairy powders can be an ideal source for fulfilling the nutritional requirements of the population (Khalesi and FitzGerald, 2021; Gaspard et al., 2021; Silva and O'Mahony, 2017). They are easy to package, carry and store, occupy a lesser volume than their whole, refrigerated shelf-stable counterparts, and have a reduced possibility of microbial contamination and growth during transportation and storage (Khalesi and FitzGerald, 2021; Schulze, 2008; Stavrou et al., 2020). Dried dairy products are a viable and safe alternative to fluid milk due to their attributes of nutritional retention, convenience, and broader functionality, all of which significantly enhance their ease of usage and consumer appreciation (Ji et al., 2016). However, powders can be prone to caking and clumping, which reduces flowability and causes hindrances during processing and storage (Boiarkina et al., 2016; Carpin et al., 2017; Foster et al., 2005). Caking can lead to inconsistent blends and poor rehydration characteristics, lowering consumer satisfaction with the final product. Several factors such as relative humidity, temperature, physical state and morphology of lactose and protein, variability in composition, and the

length of the storage period can influence the extent of caking (Carpin et al., 2017; Crowley et al., 2014; Foster et al., 2005).

Studying the rheological properties of food powders, and particularly the flow function coefficient (*ffc*) i.e., objective measurement of cohesion and flow tendencies of food powders, can assist the food industry in predicting powder flowability. Thus, leading to the optimization of the space required for transportation and storage, and enhancing sustainability of powder handling operations. This is beneficial for milk processing plants. Unlike powder products from pharmaceutical or other industries, dairy powders are highly susceptible to environmental conditions such as moisture and temperature, which affect the powder's flowability (Kamath et al., 1994; Stoklosa et al., 2012). This is because dairy powders are composed of multiple components (fat, protein, and lactose), therefore, are more reactive to environmental conditions, as compared with more robust inorganic powders e. g calcium carbonate powder. In addition to environmental conditions, the flow characteristics of dairy powders are also affected by particle size, morphology, surface composition. Unlike homogenous, inorganic powdered products, the reactive nature of dairy powders can result in serious challenges such as caking and clumping, which reduces flowability and can negatively impact the space required for processing, packaging and storage (Foster et al., 2005; Ji et al., 2016; Wang et al., 2016a). Therefore, measurement of the *ffc* of the dairy powders can assist in hopper design, thus making the process more sustainable by optimizing the available resources (Carpin et al., 2017; Crowley et al., 2014; Wang et al., 2016a). Additionally, understanding the flow behavior of specific powders can provide detailed understanding of the variables that are essential for designing and developing the conveyor systems for food powders with

variable compositional parameters (Boiarkina et al., 2016; Crowley et al., 2014; Schulze, 2008).

A shear cell is ideal for analyzing high to moderately cohesive powders. In addition, the general shear cell methodology provides useful insight into the powder's flow behavior under small load/stress conditions such as flowing through hopper or storing in silos. This is especially significant for food products vulnerable to caking and clumping during storage (Schulze, 2008; Wang et al., 2016a). The shear cell method involves three major steps: consolidation, pre-shear, and shear. The pre-shear minimizes the impact of prior history, while the shearing phase subjects the powders to a combined effect of the normal stress consolidation and shear stresses. The response of the powders is recorded through the shear failure diagrams (Bagga et al., 2012; Schulze, 2008; Wang et al., 2016a).

The shear cell technique has been successfully applied in studying the flow behavior of inorganic powders, specifically the pharmaceutical powders (Wang et al., 2016a, 2016b). Calcium carbonate powder has been used previously as a standard or reference for characterizing the powder flowability with a ring shear testing method for round robin testing (Akers, 1990; Parrella et al., 2008). The powder is cohesive and provides consistent results. In addition, CaCO3 powders consist of rigid particles, and do not conform to orientation phenomena during the shearing process, even at higher consolidation stresses, making it a reliable source for comparing the flow curves resulting from shearing of other powders.

However, there are a few studies on the use of shear cell method for determining the flow behavior of milk protein powders (Crowley et al., 2014; Fournaise et al., 2020). None of these studies provided details of the actual testing protocol/methodology (pre-shear and shearing consolidation stresses, shear failure points, rotational speed), nor gave exact details of the Mohr circle analysis. Additionally, there is no literature available in relation to obtaining reliable shear-to-failure points and estimation of flow function coefficient (*ffc*) for relatively less cohesive dairy powders. Prior research has also not included shear-to-failure diagrams that could further explain the shear failure mechanism. Shear cells using the three-point shear failure testing model are typically used for more cohesive powders. However, dairy powders are generally less cohesive due to their larger particle size range of 85–250 μm (Tuohy et al., 1989). As a result, the previously researched methods were not effective in determining an approach to analyze the milk protein powders. The lack of this data makes it challenging for the food industry to take advantage of this excellent method in obtaining a more detailed understanding of powder rheology. Since prior research has predominantly characterized non-food or pharmaceutical cohesive powders (Wang et al., 2016a, 2016b), these methods may, or may not, conform when food powders are subjected to a similar protocol, necessitating a thorough study involving a new method development. Schulze (2008) mentioned that stick-slip, which is one of the predominant phenomena involving powders, primarily depends on the material properties and testing conditions. Hence, it is necessary to develop a methodology capable of gathering a deeper understanding of the flow behavior of food powders using a shear cell. Although air bearing rheometers in conjunction with powder accessories have been used in the past for various powder characterization studies

(Chang et al., 2020; Hartig et al., 2022; Iams et al., 2022; Jange et al., 2020; Mishra et al., 2020, 2022; Ramaraju et al., 2022; Zhao et al., 2021) the shear cell attachment has not yet been explored on dairy powders. Testing food powders in varying temperature and relative humidity will provide useful insights of the flowability behavior, and the shear cell can now be equipped with an attached temperature and relative humidity cabinet. However, the absence of reliable test methods for measuring flowability of dairy powders leads to underutilization of these attachments.

Regardless of powder type, traditional rheology methods available in literature do not provide detailed information about the analysis used for calculating the *ffc* and other flow parameters in a shear cell (Schulze, 2008). The primary hypothesis of this study was that food powders require a highly specific protocol for measuring their flow behavior in a shear cell. Based upon this, the current study focused on developing a methodology to successfully analyze less cohesive food protein powders for flowability using a shear cell. The study experimented with two dairy powders: milk protein concentrate (MPC 80) and milk protein isolate (MPI 85). The powders were subjected to two main test protocols, distinguished by the pre-shear normal stresses (3, 6, and 9 kPa and 1, 3, and 6 kPa). The second phase of testing studied impact of four shear speeds (0.003, 0.005, 0.006, and 0.009 rpm) and two different measurement point durations (0.5 s and 2 s) on the quality and reliability of flowability data. The results obtained from the milk powders were compared with the analysis results from the standard calcium carbonate powder as completed with the default instrument procedures. Furthermore, the morphological properties, and particle sizes of the powders were measured and correlated with the flowability.

3.2: Materials and methods

3.2.1 Milk protein powders

Two commercial milk protein powders: milk protein concentrate (MPC 80) and milk protein isolate (MPI 85), were procured from Idaho Milk Products (Jerome, ID). The powders were placed in an airtight container to prevent moisture exposure during the duration of the study.

3.2.2 Measurement of physicochemical properties

3.2.2.1 Water activity

The water activity of the powders was measured at 22°C using a water activity meter (Aqua Lab PRE, Meter food, Pullman, WA). All the measurements were performed in triplicate.

3.2.2.2 Moisture content

The moisture content was measured in a rapid moisture analyzer (CEM Smart System 5, CEM Corporation Matthews, NC). The measurements were performed in triplicate.

3.2.2.3 Bulk density

The bulk density was measured in terms of the loose and packed bulk densities. For measuring the loose density, a 100 mL graduated plastic cylinder was weighed and tared. Then, the graduated cylinder was manually filled with powder to the 100 mL mark

and the weight was noted. The density was calculated based on the weight of the powder contained in the 100 mL volume. Subsequently, the packed (tapped) density was calculated by tapping the cylinder containing the powder 100 times on the benchtop. After 100 taps, the tapping ceased, and the weight of the powder was measured and change in powder volume noted. The packed density was calculated by dividing weight of the tapped powder by the volume of the powder in the cylinder (Crowley et al., 2014). Both the measurements were performed in duplicate.

3.2.2.4 Particle size analysis

The particle size distribution of the milk powders was measured by laser diffraction using a particle size analyzer (PSA 1190 LD, Anton Paar GmBH, Austria). Each test was performed in triplicate, and the mean particle size by volume was recorded.

3.2.2.5 Sample preparation for shear cell methodology

The shear cell set-up included a sample cup (18.9 mL) and the upper rotating geometry (Fig. 3.1). The sample preparation bench was used to gently load the powder into the sample cup, without excessive packing force or movement. A scraper bar was used to remove the excess powder and create a flat surface of powder across the top of the cup. On average, the cup held 5.75 ± 0.35 g of milk protein powder and 12.6 ± 0.5 g of calcium carbonate powder. The filled sample cup was placed on the rheometer platform and shear tested at room temperature (22°C).

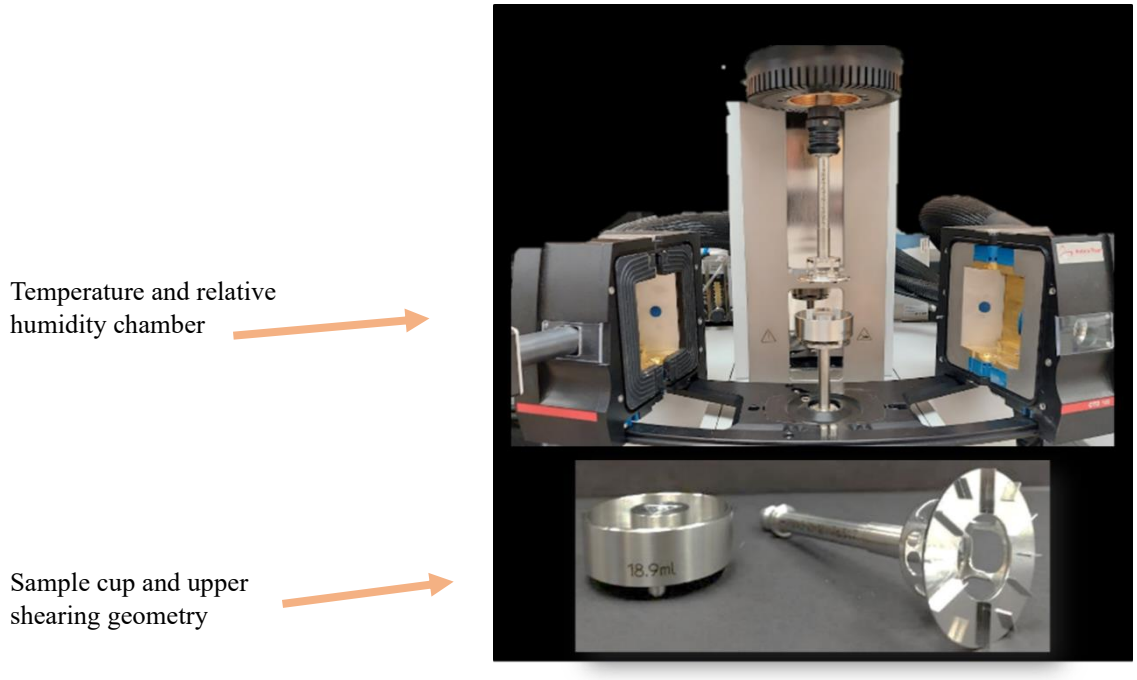


Fig 3.1: Shear cell rheology cell set-up attached to MCR302e rheometer, equipped with temperature and relative humidity chamber.

3.2.2.6 Shear cell measurements

An Anton Paar MCR302e Rheometer (Anton Paar, GmBH, Austria) with shear cell attachments was used for measuring flow properties of milk protein powders. The Rheocompass software (V1.30.1064) was used for analyzing data.

The measurements method consisted of two phases within each major section of the shear test: pre-shearing and shearing (Fig. 3.2). Pre-shearing was done to eliminate history of the powder samples. In this step, the powder sample was pre-sheared at a higher normal stress and subsequently sheared at a much lower normal stresses, yielding

instantaneous powder flow. During the shearing process, the material's response was recorded as the shear stress needed to cause failure in the material upon applying constant normal stress. Prior to analyzing the milk protein samples, a certified reference (BCR-116 calcium carbonate powder) was used as the standard reference for the shear tests. The first round of testing with the BCR-116 calcium carbonate standard was performed with the default template (pre-shear normal stresses: 3, 6, and 9 kPa at 0.005 rpm) available within Rheocompass software. Subsequently, the milk protein powders were also subjected to the same shear testing parameters. The tests were consecutively conducted at three different pre-shear normal stresses, which spanned three action blocks in the software, each consisting of three shearing normal stresses The same powder was used throughout each of these action blocks. Test results were expressed in terms of a ratio of maximum principal stress (σ1) to the unconfined yield strength (σc) of the powder, also known as flow function coefficient (*ffc*). Using the Mohr's circle, the yield loci of the powder were plotted, providing the framework for calculating the flow function coefficient (*ffc*) for the powder samples.

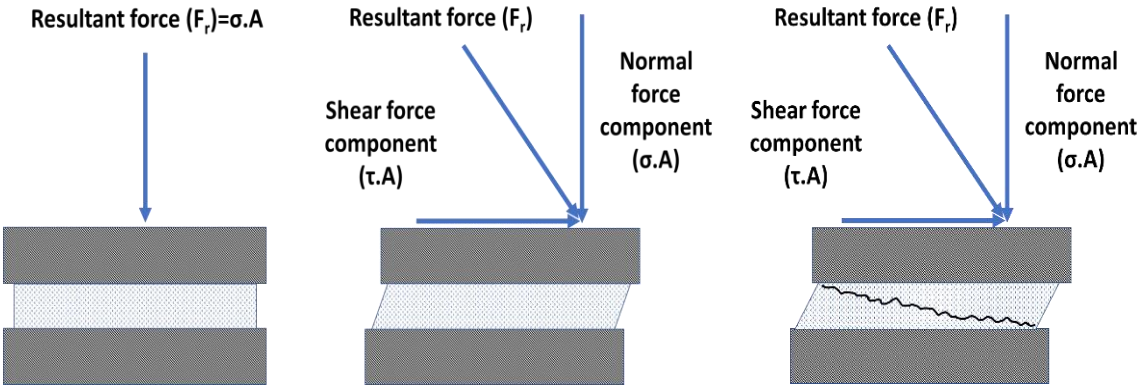


Fig 3.2: Schematic diagram representing force resolution during shear cell testing; a. Bulk solid under rest conditions, b. pre-shear conditions, c. shear-to-failure condition.

3.2.2.7 *Calculation of the flow function coefficient (ffc)*

The Mohr's circle can be used to calculate the flow function coefficient by applying the Mohr-Coulomb model (Figure 3.3). While the pre-shear points (σ_p, τ_p) are gathered by the instrument software during the shear test, the Cohesion (C) is calculated as an intercept (τ_1) crossing y-axis using a linear regression line fitted through the yield loci. The angle of linearized yield locus (α) is the slope of the line connecting the yield loci and is affected in the manner by which the powder particles move past each other when subjected to a combination of the shear and normal stresses (Wang et al., 2016a). The Mohr-Coulomb model can be described in equation 1.

$$\tau = \sigma * tan(\alpha) + \tau_1 \quad (1)$$

Where τ = shear stress (kPa), σ = normal stress (kPa), τ_1 = intercept of the linearized yield loci which is also called Cohesion, S = mathematical constant, and α = angle of linearized yield locus.

The unconfined yield strength and consolidation stresses can be calculated using the following equation 2–4 as described in (Wang et al., 2016a).

$$\sigma_c = \tau_1 * 2 * tan\left[45 + \frac{\alpha}{2}\right] \quad (2)$$

$$\sigma_1 = (1 + sin\,\alpha)\left[\frac{S - \sqrt{S^2 sin^2\alpha - (\tau_p^2 cos^2\alpha)}}{cos^2\alpha}\right] - \frac{\tau_1}{tan\,\alpha} \quad (3)$$

$$S = \sigma_p + \frac{\tau_1}{tan\,\alpha} \quad (4)$$

Where,

σ_1 = principal consolidation stress

σ_c = unconfined yield strength

The flow function coefficient (*ffc*) indicates the extent of flowability which is inversely related to cohesivity of the powders. The *ffc* can be calculated from the values of the maximum principal stress and unconfined yield strength of the powder, as described in equation 5.

$$ffc = \frac{\sigma 1}{\sigma_c} \quad (5)$$

The range of the *ffc* determines whether a powder is cohesive or flowable. As described by Schulze (2008), an *ffc* of less than 1, indicates the powder is non-flowing,

while an *ffc* between 1 and 2, indicates the powder sample is highly cohesive. At the same time, an *ffc* of 2–4, demonstrates cohesiveness in the sample, while an *ffc* in the range of 4–10, demonstrates easy-flowing characteristics. Lastly, an *ffc* greater than 10 is an indicator of high flowability of the sample.

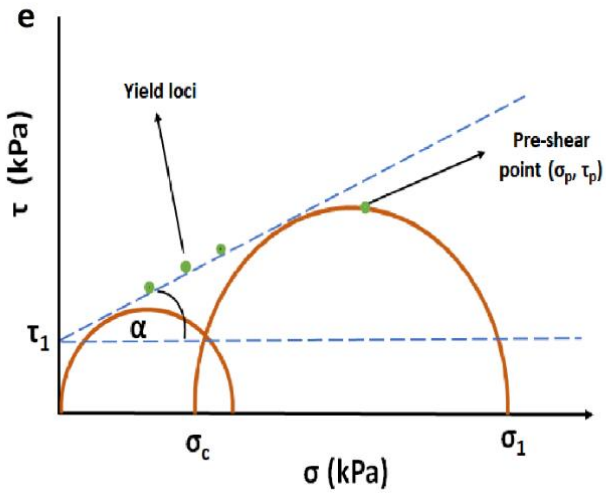


Fig 3.3: Schematic representation of yield locus and pre-shear point. Mohr's circle. Mohr circle analysis can be used to derive cohesion (τ_1), unconfined yield strength (σ_c), and major principal stress (σ_1).

3.2.2.7 Scanning electron microscopy (SEM)

Along with the particle size, the shape of the particles can also have an impact on the flow behavior of the powders (Juliano and Barbosa-C´anovas, 2010). To assess the particle morphology, a scanning electron microscope was used (SEM, FEI Quanta 650 F, Thermo Scientific Quanta, Hillsboro, OR) under high vacuum (accelerating voltage: 15 KV, spot size: 2, detector: ETD). Powder samples were placed on aluminum stubs fixed with carbon tabs, flushed with nitrogen for 10 s and sputter coated with 10 nm of gold and palladium sputter coater (Q 150 V, Quorum technologies, Laughton, East Sussex, UK). All the samples were analyzed in duplicate ($N > 30$).

3.2.2.8 Statistical analysis

The significant differences due to various treatments were analyzed using a one-way ANOVA in OriginPro (2021) for comparing means. The mean values of each parameter were compared for significant differences using Tukey's HSD post Hoc test at a 5% of level of significance.

3.3: Results and discussion

3.3.1: Physicochemical properties

3.3.1.1 Bulk density and water activity

Physicochemical properties of milk protein powders are presented in Table 3.1. Despite of slightly larger particle size ($P < 0.05$), MPC 80 had higher bulk density and particle density than MPI 85 ($P > 0.05$), which can be attributed to the slightly higher moisture content, lactose, and ash content. Purification of proteins during ultrafiltration is achieved by adding water to the retentate through diafiltration steps which washes out lactose and mineral. MPC 80 powder had a higher moisture, water activity, fat, and lactose content than the MPI 85 powder.

3.3.1.2 Particle size

In this study, the particle size of the MPC 80 and the MPI 85 was 77.7 μm and 52.5 μm, respectively. Particle size of both milk protein powders was higher than ($P < 0.05$) the BCR-116 calcium carbonate standard which had a mean particle size of 4.03 μm (Table 3.1; Fig. 3.4). The particle size can have a direct impact on the powder flowability. Prior research has shown that the particle size of milk protein powders is inversely proportional to the specific surface area (*SSA*) for powders with similar protein concentrations (Silva and O'Mahony, 2017). Increased surface area will create more friction between particles. Milk protein concentrate powders with a larger particle size (particle diameter: 160 μm), and higher protein content (70%), had a higher flow index of

8.7, classifying it as free-flowing. We also observed a similar trend with respect to particle size and *ffc* values of CaCO3 standard and milk protein powders (Tables 3.1 and 3.3). Crowley et al. (2014) noted that for milk protein powders composed of 80 and 85% protein, the particle size decreased with an increasing protein content. This aligns with the measurements in our study, where the MPI 85 powders had a smaller particle size (52.5 μm) than the MPC 80 powders (77.7 μm). This lowered their flowability due to a higher particle-particle interaction and greater friction between particles (Crowley et al., 2014).

Table 3.1: Physicochemical properties of the powders.

Powder	Moisture (%)	Fat (%)	Protein (%)	Lactose (%)	Ash (%)	Water Activity (a_w)	Bulk density (g/mL)		Particle density (g/mL)	D 10 (µm)	D 50 (µm)	D 90 (µm)	Mean Size Volume D [4,3] (µm)
							Loose bulk density	Tap Bulk density					
MPC 80	5.50	0.92	81.0	5.38	7.00	0.19 ±0.003[a]	0.31	0.43	0.85	21.1 ±0.4[a]	58.1 ±0.2[a]	139.5±3.7[a]	77.7±0.7[a]
MPI 85	5.04	0.82	86.7	5.12	6.63	0.15 ±0.009[b]	0.29	0.38	0.78	7.85 ±0.3[b]	46.3 ±0.6[b]	96.2±0.6[b]	52.5±0.6[b]

Different lowercase superscripts show significant differences ($P<0.05$) within the column.

3.3.1.3 Particle morphology

There was a distinct difference in the morphological characteristics of the calcium carbonate standard compared to the milk protein powders. The calcium carbonate standard had smaller particles with flatter surfaces having sharp corners and irregular shape. In comparison to calcium carbonate, both MPC 80 and MPI 85 powders had a relatively globular shape (Fig. 3.4 b, c). The MPI 85 had a smaller particle size, with a large number of wrinkled marks on the surface than the MPC 80 powders. Both the milk protein powders had several smaller particles attached to the larger particle. These could be smaller protein structures that may have been formed during the spray-drying process. Prior studies have shown that the milk powders can have both a smooth and spherical surface, as well as grooved, or wrinkled surfaces (de Jesus Silva et al., 2021; Ji et al., 2016; Maidannyk et al., 2020; Silva and O'Mahony, 2017). These grooves could have resulted during the spray-drying process itself (de Jesus Silva et al., 2021).

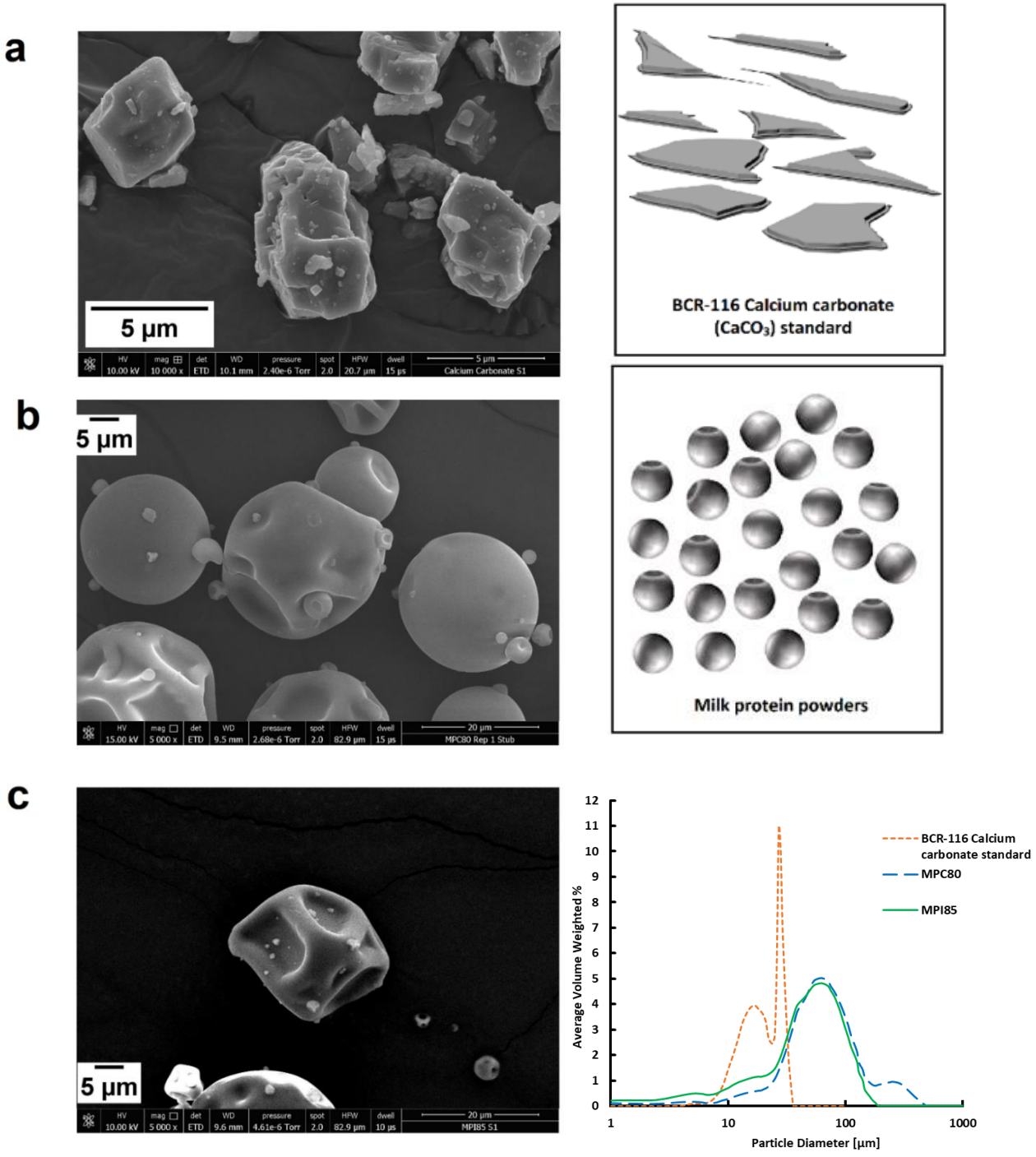


Fig 3.4: Scanning electron micrographs of powders with schematics for particle shape; BCR-116 calcium carbonate standard (a), MPC 80 (b) and MPI 85 (c). Volume weighted particle size distribution of three powders is also depicted.

3.3.2: Shear cell testing with a set of 3, 6 and 9 kPa pre-shear normal stress

3.3.2.1 BCR-116 calcium carbonate standard – 3, 6, and 9 kPa

Shear-to-failure diagrams of the calcium carbonate standard at three pre-shear normal stresses are presented in Fig. 3.5. It is clearly shown in the figure that after achieving critically consolidated state on each pre-shear normal stress (3, 6, 9 kPa), the sample was subjected to much lower shearing normal stress. The BCR-116 calcium carbonate powder showed visible shear-to-fail peaks on each shearing normal stress on each pre-shear consolidation stress at a shear speed of 0.005 rpm. Throughout the test, the-shear-to failure points incrementally increased with the increase in applied normal stress (both pre-shear and shearing) (Table 3.2). The reference powder was classified as cohesive at 3 and 6 kPa, as indicated by the *ffc* values ranging from 2.1 to 3.5 (Schulze, 2008). Cohesive nature of this powder can be attributed to the smaller particle size and irregular shape of the powder particles as described in section 3.3.1.2 and 3.3.1.3. The *ffc* values increased with the applied pre-shear normal and shearing normal stresses during testing (Table 3.2). The presence of shear-to-failure points on stress diagrams was shown as the response of the powder to the applied stresses, measured in terms of a distinct yield point or failure point, at which the powder yields and starts flowing. The occurrence of these discrete yield points is critical for predicting the exact shear stress at which the sample begins to flow, thereby paving way for using the shear cell with less cohesive dairy powders, such as MPC 80 and MPI 85. It is clearly visible that set of 3,6, 9 kPa of pre-shear consolidation stress worked well for calcium carbonate powder, providing with very consistent *ffc* values.

Table 3.2: Flow function coefficients (ffc) of the milk protein powders and calcium carbonate at 3, 6 and 9 kPa pre-shear normal stress intervals, with shear speed of 0.005 rpm.

Powders	Pre-shear normal stress (kPa)	Shearing normal stresses (kPa)	*ffc* values	Coefficient of Variance	Remarks
BCR-116 calcium carbonate standard	3	0.9, 1.65,2.4	2.1±0.1	3.7	Consistent shear failure point and absence of stick-slip phenomenon. Sample classified as cohesive at 3, 6 kPa and easy flowing at 9 kPa.
	6	1.8, 3.3, 4.8	3.5±0.1	3.4	
	9	2.7, 4.95, 7.2	4.9±0.2	4.2	
MPC 80	3	0.9, 1.65, 2.4	6.6	nd	Only one replicate successful, inconsistent *ffc* values, stick-slip phenomenon present
	6	1.8, 3.3, 4.8	10.3	nd	Two replicates possible, inconsistent *ffc* values, stick-slip phenomenon present
	9	2.7, 4.95, 7.2	8.4	nd	Two replicates possible, inconsistent *ffc* values
MPI 85	3	0.9, 1.65, 2.4	8.7	nd	Lack of defined shear-to-failure points, classified as free flowing throughout each interval
	6	1.8, 3.3, 4.8	11.3	nd	Inconsistent *ffc* values
	9	2.7, 4.95, 7.2	10.6	nd	Lack of defined shear-to-failure points

The range of ffc values used in the classification of flowability of powders were as obtained from Schulze (2008). Free flowing ffc > 10; Easy flowing 4 < ffc < 10; Cohesive 2 < ffc < 4; Very cohesive 1 < ffc <2; not flowing ffc < 1. The ffc values are presented as Mean ± SD for Calcium Carbonate. nd= not done

3.3.2.2 MPC 80 and MPI 85

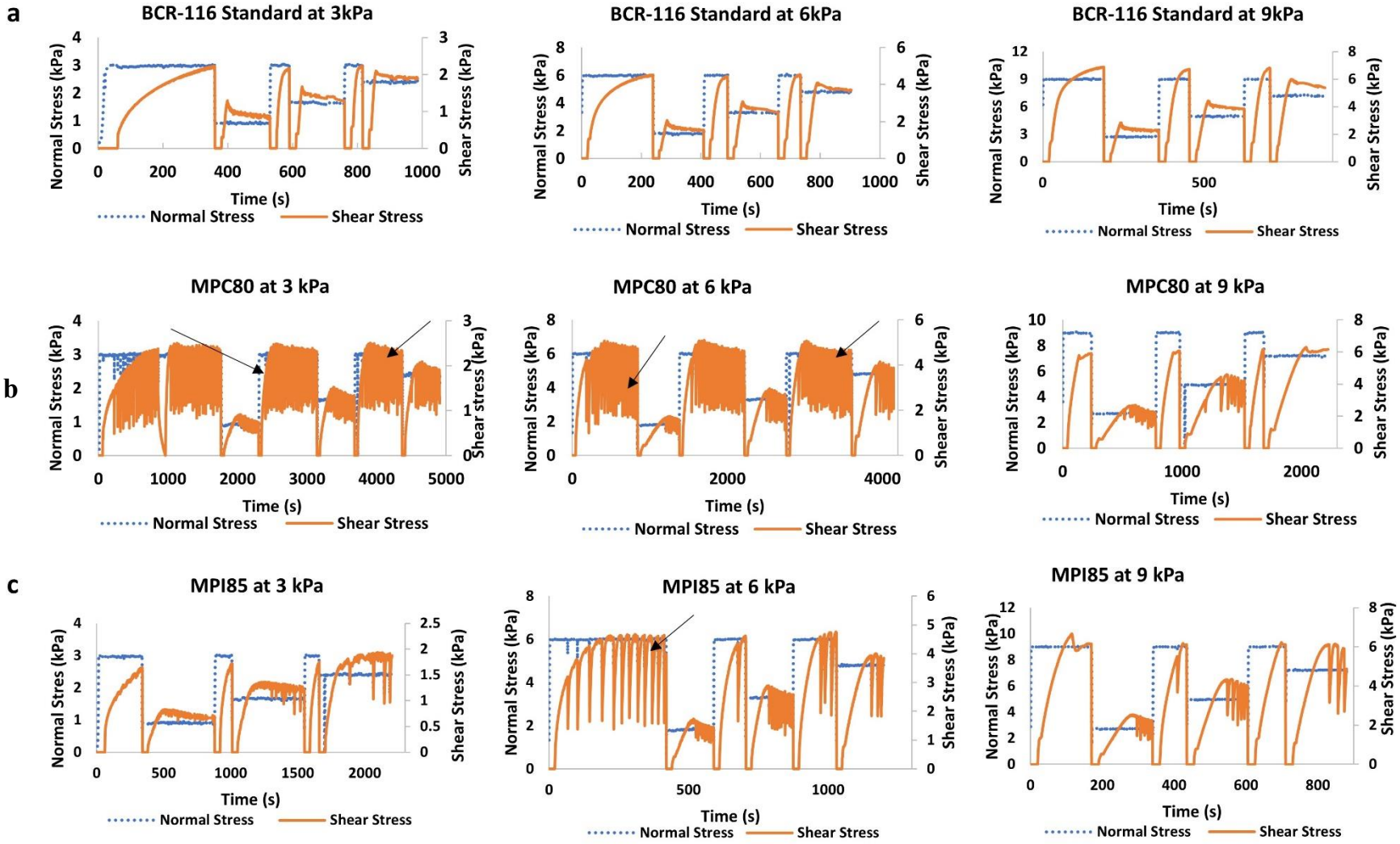
The next step in the shear cell measurements was to subject the milk protein powders (MPC 80 and MPI 85) to similar stress conditions as the standard (pre-shear 3, 6, and 9 kPa at a shear speed of 0.005). Neither of these powders showed a distinctive shear-to-failure peak at any of the applied shearing normal stresses (Table 3.2), in contrast to the standard calcium carbonate (Fig. 3.5). Absence of shear-to-failure point can be attributed to the fact that consolidation stresses in both pre-shear and shearing were so high that they were causing instant flow of the powder particles (Schulze, 2008). This can be attributed to the fact both powders had larger and smoother particles than calcium carbonate, facilitating incipient flow of these powders (Fig. 3.4). Both powders exhibited stick-slip behavior (fluctuating shear stress). Because of these fluctuations, or noises, distinctive shear-to-failure peaks were not present. Interestingly, MPC 80 powders experienced more of these fluctuations than MPI 85, as seen in Fig. 3.5 (b) and (c).

Further, the *ffc* values of both milk protein powders were inconsistent and were obtained only for less than three replicates (Table 3.2). The *ffc* increased with the applied pre-shear normal stresses until 6 kPa, like the phenomenon observed in the case of the calcium carbonate standard. However, the *ffc* value decreased when the powders were subjected to the 9 kPa pre-shear normal stresses. This decrease in *ffc* values can be attributed to the fact that at higher normal stress levels powders tend to flow instantly, and therefore do not show distinctive failure points. Along with the large variations in the shear-to-failure peaks and the occasional absence of such peaks made methods of determining *ffc* values of these powders highly challenging, thus hindering further analysis of the milk protein powders when tested at higher consolidation stresses.

Table 3.3: Flow function coefficients (ffc) of the milk protein powders at 1, 3 and 6 kPa pre-shear normal stress intervals.

Powders	Shear speed (rpm)	*ffc*			Remarks*
		1 kPa	3 kPa	6 kPa	
MPC 80	0.003	3.5 ± 0.5^{a}	12.1 ± 6.1^{c}	6.5 ± 3.8^{d}	Lack of defined shear-to-failure points
	0.005	4.6 ± 0.4^{b}	10.2 ± 4.2^{c}	9.4 ± 2.2^{d}	Inaccurate shear-to-failure points
	0.006	4.6 ± 0.4^{bA}	7.6 ± 1.2^{cB}	20.3 ± 6.2^{dC}	Reduced stick-slip, definitive shear-to-failure points in each interval
	0.009	4.3 ± 0.3^{b}	8.4 ± 1.1^{c}	48.9 ± 60.1^{d}	Inaccurate shear-to-failure points
MPI 85	0.006	3.7 ± 0.5^{A}	6.7 ± 0.8^{B}	9.2 ± 1.1^{C}	Definitive shear-to-failure points in each interval

The range of ffc values used in the classification of flowability of powders were as obtained from Schulze (2008). Free flowing ffc > 10; Easy flowing 4 < ffc < 10; Cohesive 2 < ffc < 4; Very cohesive 1 < ffc <2; not flowing ffc < 1. Shearing normal stress values were varied according to pre-shear normal stress values i.e., 0.2, 0.6, 1.2 kPa; 0.4, 1.2, 2.4; and 0.6, 1.8, 3.6 at 1.0, 3, and 6 kPa of pre-shear normal stresses, respectively. The ffc values are presented as Mean ± SD. Different lowercase superscripts show significant differences (P<0.05) between ffc values obtained using different shear speeds at a corresponding pre-shear normal stress. Uppercase subscripts show significant difference (P<0.05) between MPC 80 and MPI 85 at the shear speed of 0.006 rpm


a
BCR-116 Standard at 3kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress
BCR-116 Standard at 6kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress
BCR-116 Standard at 9kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress
b
MPC80 at 3 kPa
Normal Stress (kPa)
Shear stress (kPa)
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MPI85 at 6 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress
MPI85 at 9 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress

Fig 3.5. The shear failure diagrams of the powders at 3, 6, 9, kPa pre-shear normal stresses with a, b and c representing the BCR-116 calcium carbonate standard, MPC 80 and MPI 85, respectively. All the tests were conducted in triplicate. However, single set of the data presented in this figure to clearly indicate presence of stick slip events. Arrows indicates presence of stick-slip phenomenon in the case of milk protein samples. Absence of shear to failure points can also be seen at 6 and 9 kPa pre-shear normal stresses.

Prior research has shown that when powders are exposed to higher pre-shear or shearing normal stress, they tend to undergo stick-slip friction (Bagga et al., 2012; Blau, 2009; Kamath et al., 1994; Lubert and de Ryck, 2001; Schulze, 2008). Stick-slip happens when the powder particles move past each other in a way that creates intermittent relative friction within the sample or between particle and equipment surface (Bagga et al., 2012; Blau, 2009; Pant et al., 2020; Schulze, 2008). This phenomenon is often explained by alternating slipping and sticking tendency of contact surfaces. Stick-slip is usually observed within the materials with larger particles with less cohesivity, such as sand, ash, and organic materials, including food powder and polymers. Stick-slip phenomenon is also associated with static and kinematic friction (Bagga et al., 2012; Blau, 2009; Schulze, 2008) and can occur between the particles themselves, or on the contact surfaces of the solid materials when handled as a bulk system. Switch over from static (high) to kinematic (lower) friction causes sticking and slipping tendency. The stick-slip events sensed by the rheometer are expressed by jumps or sawtooth patterns seen in the shear stress profile, as the upper geometry moves within the powder (Fig. 3.5). These sawtooth patterns can cause an error in the accurate estimation of the shear-to-failure stress which can cause error in the Mohr's circle analysis. Therefore, in order to ensure reliable measurement of *ffc* values, stick-slip effect needs to be minimized as much as possible.

The mechanical behavior of granular materials such as powders depends on the particle size, arrangement of particles, amount of interstitial air present between particles, porosity, and surface characteristics of the powder particles (Roussel, 2005). Changes in the internal arrangements of the particles or their movement during shearing and/or applying normal stress can influence flow behavior of bulk powders. During sticking,

powder particles are close packed at the interface, exhibiting higher shear strength (Cain et al., 2001). A periodic dilatancy at the bulk level is observed when powder particles slide over each other creating more void space and minimizing frictional force (Powrie, 2017). Roussel (2005) suggested that stick-slip behavior during shearing is a manifestation of formation of columns or chains supporting load, if it collapses there is a drop in the stress. This tendency of stick-slip can decrease with an increase in the particles size, but this is mostly related to contact points and friction between the particles, rather than the size. In our case, we observed the standard calcium carbonate with a mean particle size of 4.03 μm showed a reduced or low stick-slip tendency as compared to the milk protein powders with a higher particle size (Table 3.1). This could be due to smaller size and the shape of calcium carbonate particles compared to the milk protein powders. The scanning electron micrographs of the calcium carbonate presented a flat surface with an irregular shape of the particulates. This morphology may have contributed to its added cohesiveness compared to the spherically shaped milk protein powders (Fig. 3.4). Moreover, $CaCO_3$ particles have weak attractive interactions such as van der Waals forces which contributes to cohesiveness (Schulze, 2008). At the same time, the specific morphology of the calcium carbonate also indicates why these samples worked so well with the default protocol i.e., 3, 6, 9 kPa pre-shear consolidation stresses. However, this template did not work for milk protein powder samples because of their round shape and larger particle size (Table 3.1) causing instant failure or flow of the samples even in the pre-shearing phase. This led to non-reliable shear-to-failure points needed for consistent values of *ffc*. Therefore, the above protocol which worked with the standard did not work well with the milk powder.

Ideally, at each shearing phase, irrespective of the amount of pre-shear normal stress employed (3, 6, and 9 kPa), the powder should exhibit definite shear-to-failure peaks or yield points. At a given pre-shear normal stress, three shear-to-failure peaks constitute the yield loci of the powder sample. At the end of the test, we observed three separate yield points, one from each major pre-shear interval. These three yield points formed the basis for constructing the Mohr's circle and subsequent *ffc* calculations. Inconsistent shear-to-failure point, induced by the frequent stick-slip or due to instant flow, especially with 9 kPa, caused errors in determining these points, preventing the accurate depiction of the associated Mohr's circle. Milk protein powders tend to be more flowable than other powders. When used in the shear cell, they did not experience failure in the shearing phase. This could be due to higher pre-shear normal stresses which may have already initiated the incipient flow even during the pre-shearing stage and contributed towards the stick-slip, causing inconsistencies in the shear-to-failure points at each consolidation point. Teunou et al. (1999) concluded that, pre-shear normal stresses larger than 8 kPa can cause invalidity in the results, and hence must be avoided for food powders.

3.3.2.3 Testing with 1, 3, and 6 kPa pre-shear normal stress and reduced shearing normal stresses

Once it was apparent that the protein powders did not exhibit distinctive shear-to-failure peaks like the calcium carbonate standard at 3, 6, and 9 kPa, our next strategy was to reduce the pre-shear normal stresses to 1, 3, and 6 kPa and shearing normal stresses by almost half values at each of the pre-shear normal stresses (Tables 3.1 and 3.2) and assess their effect on reducing the instant failure of the powder and stick- slip type fluctuations

on the shear-failure curves. Fig. 3.6 presents the shear-to-failure peaks in the MPC 80 samples when subjected to the pre-shear normal stresses of 1, 3, and 6 kPa at lower shearing normal stresses (Table 3.3). The MPC 80 powder showed a lower stick-slip phenomenon at all the pre-shear intervals (1, 3, 6 kPa normal stress). It is clearly evident that lowering the pre-shear and shearing normal stresses significantly reduced stick-slip effect, eliminated instant failure of the bulk powder, making it possible to get accurate and reliable shear-to-failure points. Previously, researchers have also observed a similar pattern with other dairy powders. Using shear cell analysis, Bagga et al. (2012) studied the effects of temperature on the rheological properties of skim milk, whole milk, and cream powders. The authors concluded that the amplitude of these stick-slip patterns can be minimized by lowering the consolidation stresses during pre-shear and shearing phases.

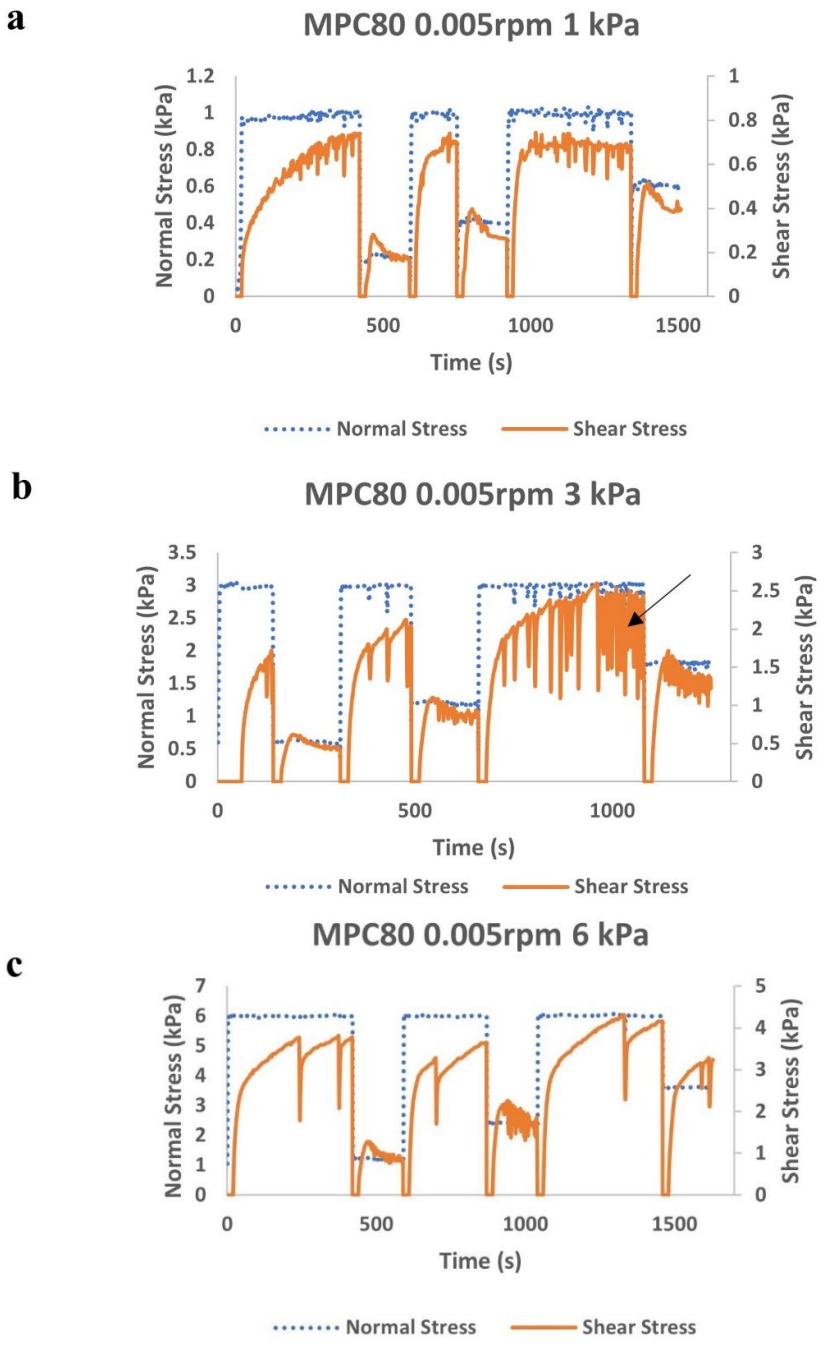


Fig 3.6. Shear failure behavior of MPC 80 powder exposed to 1,3,6 kPa pre-shear normal stresses at 0.005 rpm. All the tests were conducted in triplicate however, data presented here represent one test replicate.

3.3.2.4 Impact of the measurement point duration on shear-failure peaks

Fig. 3.7 presents the shear-failure curves acquired at 0.5 and 2 s data capture intervals. We observed a contrast between the two acquisition intervals (measurement point durations) adopted for collecting the points during the shear test measurements. When data was gathered every 0.5 s, there was an increase of stick-slip phenomena which was significantly reduced with 2 s measurement point duration. At 2 s interval the sawtooth patterns were less prevalent. More frequent data capturing leads to insufficient measurement duration, giving less chance for stress dissipation. Shorter measurement duration does not allow attainment of steady state, leaving transient effects (Sharma et al., 2015). To obtain reliable and accurate shear-to-failure points, it is important to give enough time for stress or strain loading during pre-shearing phase for attaining steady state conditions. This helps with alignment of particles on the surface, forming a cohesive and an elastic bed. During shearing phase, a relative motion between the particles and the contact surface is activated which causes eventual failure (incipient flow) of the material (Schulze, 2008). This is achieved by simultaneously applying normal and shear stresses.

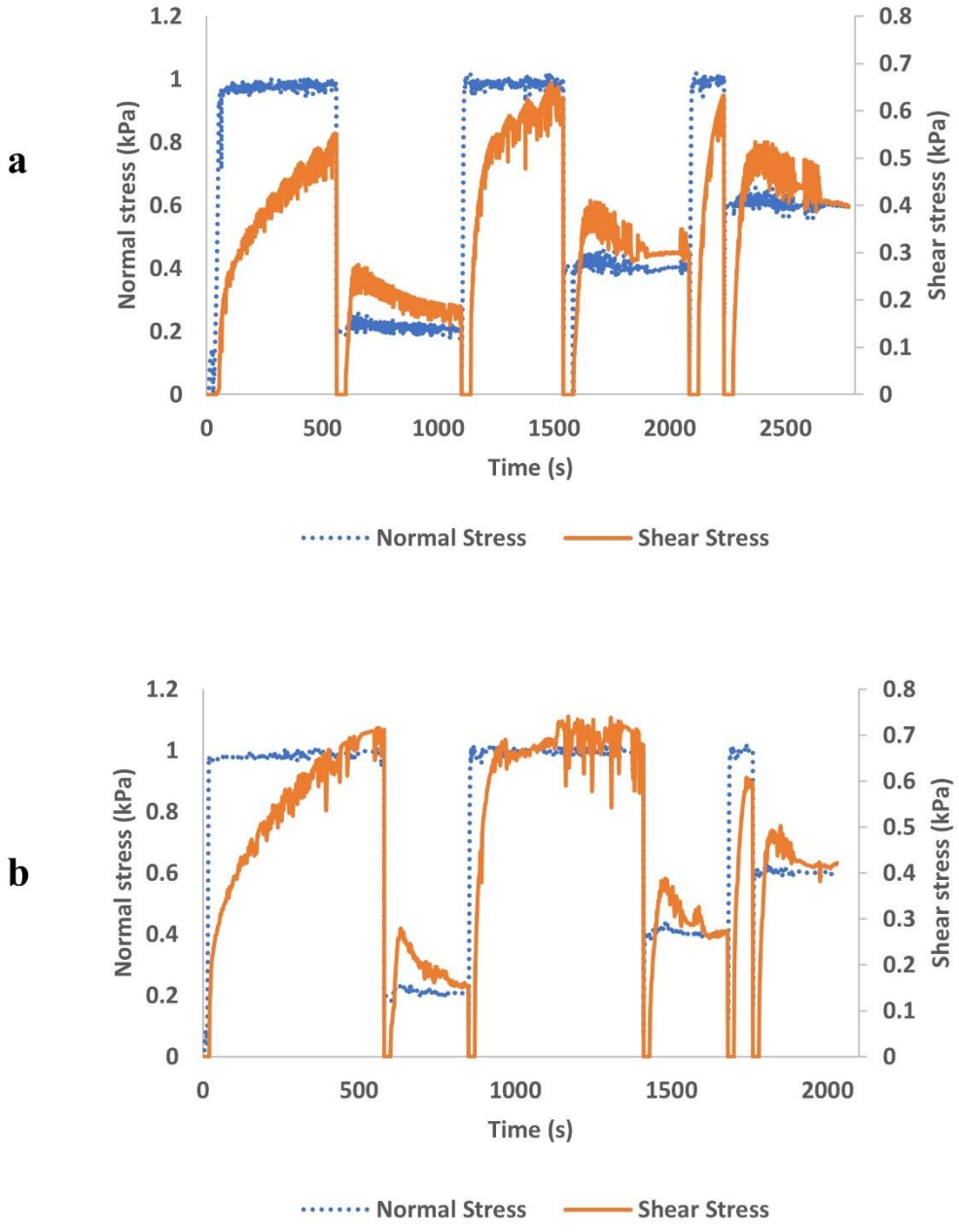


Fig. 3.7. Shear failure in MPC 80 powders at 0.003 rpm and 1 kPa pre-shear normal stresses; a and b represent data acquired at 0.5 and 2 s per interval, respectively. All the tests were conducted in triplicate however, data presented here represent one test replicate.

As explained previously, the milk protein powders were more flowable or less cohesive than the calcium carbonate standard. Therefore, 0.5 s data capturing interval was enough for attaining steady flow for CaCo3 standard but was not for the more flowable milk protein powders. Since the standard was more cohesive than MPC 80, a shorter measurement point duration worked well since the stress curves showed clear shear-to-failure points. However, in the case of MPC 80, the increased flowability may have reduced the time required for the powder particles to attain a steady state and make a compact bed at the interface. As a result, the shear-to-failure peaks for the MPC 80 powders contained a higher number of stick-slip points. However, when the same powders were measured at 2 s interval, we observed a marked improvement in the shear-to-failure peaks (Fig. 3.7). We attribute this to attaining steady state and formation of cohesive bed at interface, ready for the failure in the shearing phase.

3.3.2.5 Effects of the rotation speed

The powders were subjected to a range of shear speeds varying from 0.003 rpm to 0.009 rpm to assess the impact of shear speed. Fig. 3.8 represents the effects of different shear rotation speeds on the powders at 1, 3, and 6 kPa pre-shear normal stresses. The variations in shear speeds resulted in several interesting phenomena. It is clearly evident in Fig. 3.5 that at low pre-shear normal stresses (1 kPa) shear-to-failure points can be observed clearly at all three rotational speeds. However, the powder samples did show clear shear-to-failure points at 0.003 rpm with 3 and 6 kPa pre-shar normal stresses, thus severely depleting the further use of the data (Fig. 3.3). With an increasing shear speed (0.009), the powder samples showed a distinctive shear-to-failure points at all three pre-shear normal stresses (1, 3, 6 kPa). However, at 6 kPa normal stress, anomalies were

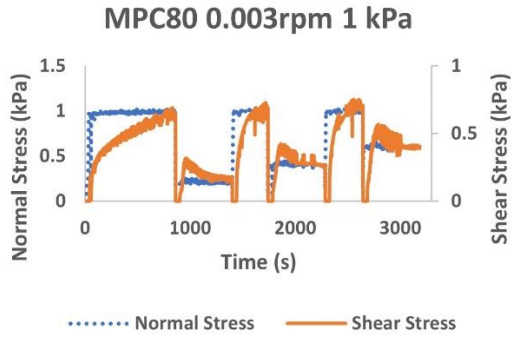
observed in pre-shearing steady state flow conditions. Extreme amounts of stick-slip events occurred in the 3 kPa section when sheared at 0.009 rpm. Frequency of stick-slip behavior depends upon the shear velocity and the nature of interactions within powder particles or between surface of a rigid body (Schulze, 2008). Usually stick-slip behavior is more prevalent where bulk solid moves across the equipment contact surface. Shear stress at steady state decreased with consecutive shearing intervals, indicating concomitant changes in the organization of powder particles. This resulted to inaccurate shear-to-failure points, not suitable for obtaining reliable *ffc* values (Table 3.3). The frequency and amplitude of stick-slip events were reduced with the increasing shear speeds (from 0.003 to 0.006) at 6 kPa pre-shear normal stress (Fig. 3.8). The shear speed of 0.006 rpm gave most consistent and reliable data during pre-shear and shearing of the powder across all the pre-shear normal stresses. Therefore, *ffc* values obtained at 0.006 rpm were most consistent. Depending upon particle characteristics, their arrangement due to consolidation and shearing, extent of void spaces, the stress or strain dissipation in the bulk solids varies. Optimum shear speed ensures arrangement of these structural elements, therefore steady state, and incipient flow.

The shear speed effects and associated results observed in this study were consistent with the prior research where a higher stick-slip was observed at higher shear rates (Bagga et al., 2012; Schulze, 2008). This was due to the inability of the bulk solids to flow at a higher shear speed, thereby increasing the particle-particle interactions. We observed that the flowability of milk protein powders increased with the shear speed at the 1 and 6 kPa pre-shear intervals (Table 3.3). This could be due to the increasing energy

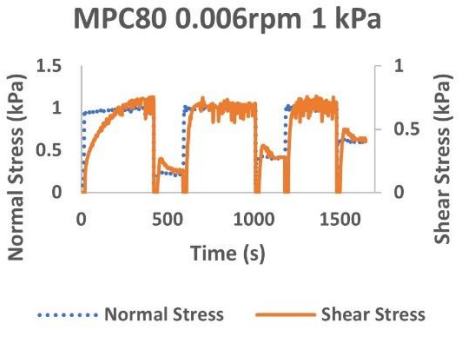
associated with the higher shear speeds, which may have caused the powders to be more flowable (Table 3.3).

To validate the robustness of the revised shear cell test, the most optimum shear cell test conditions (1,3, 6 kPa pre-shear normal stress; 0.006 rpm shear speed and 2 s measurement point duration) were applied on the MPI 85 sample (Fig. 3.9). The powder showed distinctive shear-to-failure peaks at all kPa pre-shear normal stresses, This assisted in the calculation of an accurate *ffc*. The protocol developed in this study can be applied to various dairy powders. More research is needed to understand the impact of other external factors such as moisture and temperature on the flow characteristics of dairy powders with varying composition.

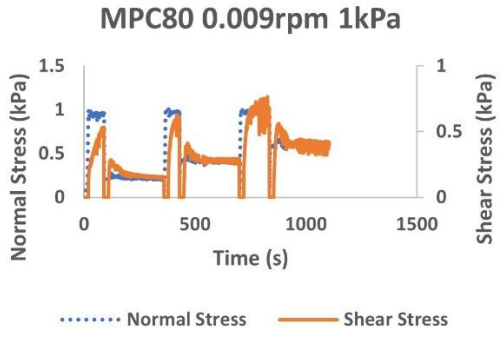
a

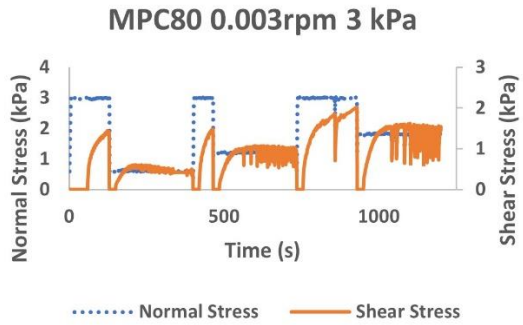

MPC80 0.003rpm 1 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress

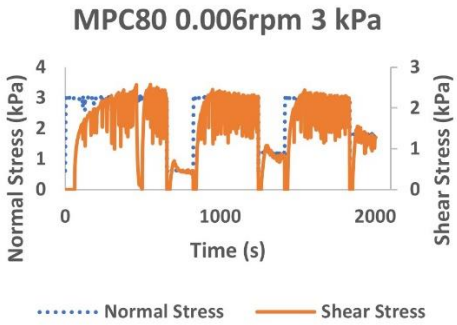
b

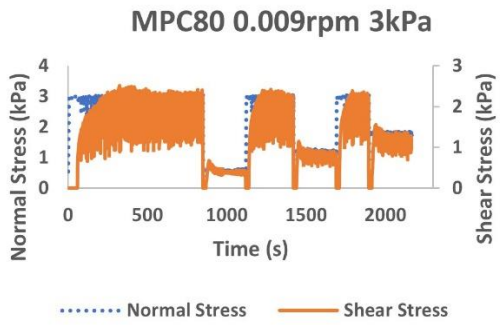

MPC80 0.006rpm 1 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress

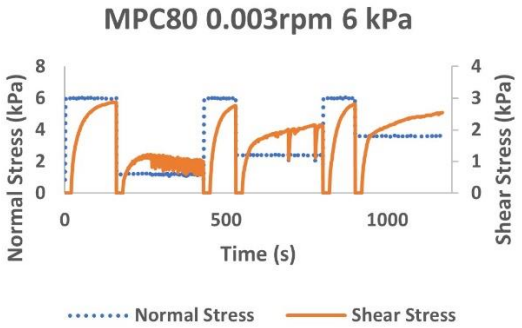
c

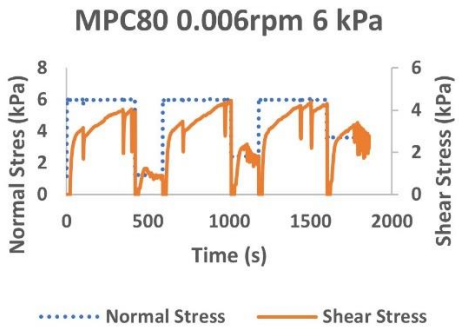

MPC80 0.009rpm 1kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress


MPC80 0.003rpm 3 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress


MPC80 0.006rpm 3 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress


MPC80 0.009rpm 3kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress


MPC80 0.003rpm 6 kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress


MPC80 0.006rpm 6 kPa
Normal Stres (kPa)
Shear Stress (kPa)
Time (s)
Normal Stress
Shear Stress

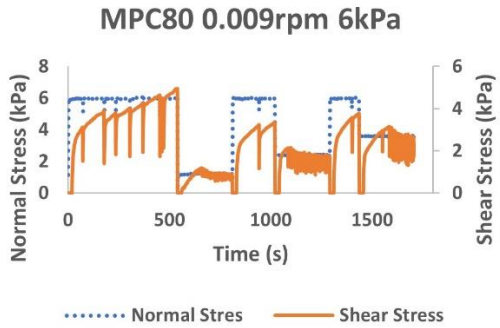
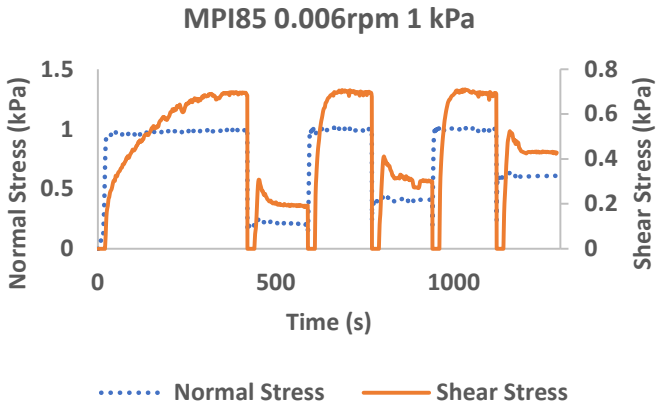
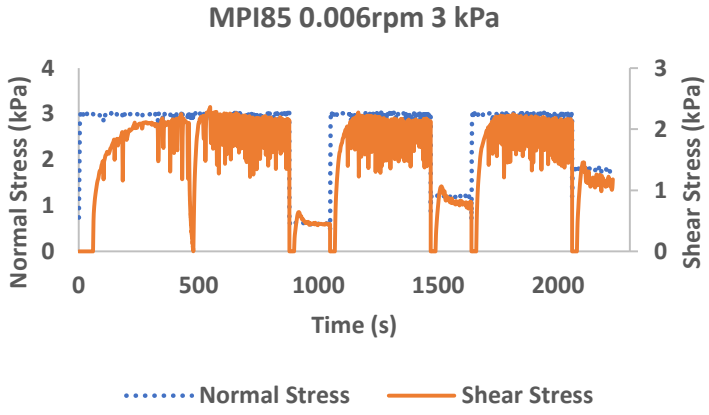

MPC80 0.009rpm 6kPa
Normal Stress (kPa)
Shear Stress (kPa)
Time (s)
Normal Stres
Shear Stress

Fig 3.8. Effect of shear speed on flow behavior of MPC 80 powder at 1, 3 and 6 kPa pre-shear normal stresses; a, b and c represent the shear speeds 0.003, 0.006 and 0.009 rpm, respectively. All the tests were conducted in triplicate however, data presented here represent one test replicate.

a



b



c

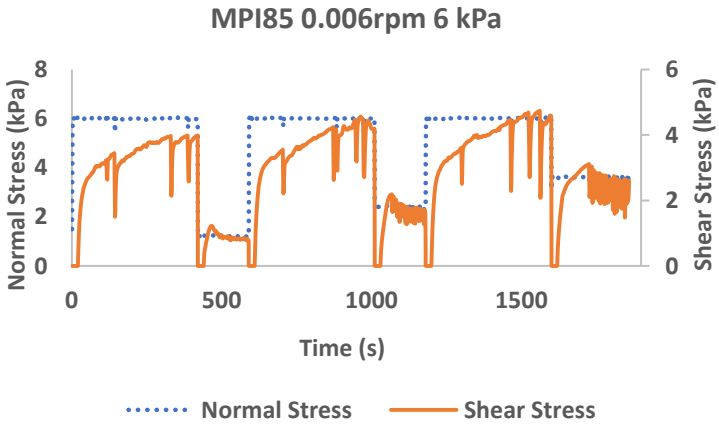


Fig 3.9: Shear failure behavior of MPI 85 powders at 1, 3 and 6 kPa pre-shear normal stresses and 0.006 rpm. All the tests were conducted in triplicate however, data presented here represent one replicate.

3.4 Conclusion

The development of a shear cell method specifically for milk powders was critical to achieve *ffc* values that allowed for accurate assessment of the flow behavior. The milk protein powders behaved very differently compared to the inorganic calcium carbonate which is widely used as a standard for shear cell methodology. Factors such as powder density, particle size, and morphology contributed to shear behavior of the powders and influenced the specific test parameters required for each powder type. Lowering the pre-shear normal stresses from 3, 6, and 9 kPa to 1, 3, and 6 kPa and reducing shearing normal stresses minimized the stick-slip events in the MPC 80 and MPI 85 powders. A shear speed of 0.006 rpm worked best with both milk powders and provided consistent shear peaks from which an accurate *ffc* values could be obtained. Particle size and SEM measurements provided detailed information that was applicable in developing a greater understanding of the differences in the flow behaviors between sample types. There were substantial differences between the protein rich dairy powders and the calcium carbonate powder used in this study in relation to particle size and morphology. This work clearly demonstrates the nature of organic vs inorganic powder samples when shear tested and reveals the need for a methodology that is effective and can be utilized to characterize milk protein powders.

3.4.1 Acknowledgements

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References

Akers, R.J., 1990. The Certification of a Limestone Powder for Jenike Shear Testing CRM-116. Loughborough Univ. of Technology, UK. BCR/163/90, Community Bureau of reference.

Bagga, P., Brisson, G., Baldwin, A., Davies, C.E., 2012. Stick-slip behavior of dairy powders: temperature effects. Powder Technol. 223, 46–51. https://doi.org/10.1016/j.powtec.2011.05.015.

Blau, P.J., 2009. Friction Science and Technology: from Concepts to Applications, seconded. CRC Press, Boca Raton, FL.

Boiarkina, I., Sang, C., Depree, N., Prince-Pike, A., Yu, W., Wilson, D.I., Young, B.R., 2016. The significance of powder breakdown during conveying within industrial milk powder plants. Adv. Powder Technol. 27, 2363–2369. https://doi.org/10.1016/j.apt.2016.10.019.

Cain, R.G., Page, N.W., Biggs, S., 2001. Microscopic and macroscopic aspects of stick-slip motion in granular shear. Phys. Rev. E 64, 016413. https://doi.org/10.1103/PhysRevE.64.016413.

Carpin, M., Bertelsen, H., Dalberg, A., Bech, J.K., Risbo, J., Schuck, P., Jeantet, R., 2017. How does particle size influence caking in lactose powder? J. Food Eng. 209, 61–67. https://doi.org/10.1016/j.jfoodeng.2017.04.006.

Chang, S.-Y., Li, S.W., Kowsari, K., Shetty, A., Sorrells, L., Sen, K., Nagapudi, K., Chaudhuri, B., Ma, A.W.K., 2020. Binder-jet 3D printing of indomethacin-laden pharmaceutical dosage forms. J. Pharmaceut. Sci. 109, 3054–3063. https://doi.org/10.1016/j.xphs.2020.06.027.

Crowley, S.V., Gazi, I., Kelly, A.L., Huppertz, T., O'Mahony, J.A., 2014. Influence of protein concentration on the physical characteristics and flow properties of milk protein concentrate powders. J. Food Eng. 135, 31–38. https://doi.org/10.1016/j.jfoodeng.2014.03.005.

de Jesus Silva, G., Gonçalves, B.-H.R.F., Conceiç˜ao, D.G., de Jesus, J.C., Vidigal, M.C.T. R., Simiqueli, A.A., Bonomo, R.C.F., Ferr˜ao, S.P.B., 2021. Microstructural and rheological behavior of buffalo milk chocolates. J. Food Sci. Technol. https://doi.org/10.1007/s13197-021-05042-3.

Foster, K.D., Bronlund, J.E., Paterson, A.H.J., Tony), 2005. The contribution of milk fat towards the caking of dairy powders. Int. Dairy J. 15, 85–91. https://doi.org/10.1016/j.idairyj.2004.05.005.

Fournaise, T., Burgain, J., Perroud, C., Scher, J., Gaiani, C., Petit, J., 2020. Impact of formulation on reconstitution and flowability of spray-dried milk powders. Powder Technol. 372, 107–116. https://doi.org/10.1016/j.powtec.2020.05.085.

Gaspard, S.J., Sharma, P., Fitzgerald, C., Tobin, J.T., O'Mahony, J.A., Kelly, A.L., Brodkorb, A., 2021. Influence of chaperone-like activity of caseinomacropeptide

on the gelation behaviour of whey proteins at pH 6.4 and 7.2. Food Hydrocolloids 112, 106249. https://doi.org/10.1016/j.foodhyd.2020.106249.

Hartig, J., Shetty, A., Conklin, D.R., Weimer, A.W., 2022. Aeration and cohesive effects on flowability in a vibrating powder conveyor. Powder Technol. 408, 117724 https://doi.org/10.1016/j.powtec.2022.117724.

Iams, A.D., Gao, M.Z., Shetty, A., Palmer, T.A., 2022. Influence of particle size on powder rheology and effects on mass flow during directed energy deposition additive manufacturing. Powder Technol. 396, 316–326. https://doi.org/10.1016/j.powtec.2021.10.059.

Jange, C.G., Taku, P., Peng, S., Dixon, M.P., Shetty, A., Ambrose, R.P.K., 2020. Cohesivity assessment of semi-crystalline and crystalline powders using a Warren Springs cohesion tester. Powder Technol. 371, 96–105. https://doi.org/10.1016/j.powtec.2020.05.077.

Ji, J., Fitzpatrick, J., Cronin, K., Maguire, P., Zhang, H., Miao, S., 2016. Rehydration behaviours of high protein dairy powders: the influence of agglomeration on wettability, dispersibility and solubility. Food Hydrocolloids 58, 194–203. https://doi.org/10.1016/j.foodhyd.2016.02.030.

Juliano, P., Barbosa-C´anovas, G.V., 2010. Food powders flowability characterization: theory, methods, and applications. Annu. Rev. Food Sci. Technol. 1, 211–239. https://doi.org/10.1146/annurev.food.102308.124155.

Kamath, S., Puri, V.M., Manbeck, H.B., 1994. Flow property measurement using the Jenike cell for wheat flour at various moisture contents and consolidation times. Powder Technol. 81, 293–297. https://doi.org/10.1016/0032-5910(94)02888-5.

Khalesi, M., FitzGerald, R.J., 2021. Investigation of the flowability, thermal stability and emulsification properties of two milk protein concentrates having different levels of native whey proteins. Food Res. Int. 147, 110576 https://doi.org/10.1016/j.foodres.2021.110576.

Lubert, M., de Ryck, A., 2001. Slip events and dilatancy in a sheared fine noncohesive powder. Phys. Rev. 63, 021502 https://doi.org/10.1103/PhysRevE.63.021502.

Maidannyk, V., McSweeney, D.J., Hogan, S.A., Miao, S., Montgomery, S., Auty, M.A.E., McCarthy, N.A., 2020. Water sorption and hydration in spray-dried milk protein powders: selected physicochemical properties. Food Chem. 304, 125418 https://doi.org/10.1016/j.foodchem.2019.125418.

Mishra, I., Liu, P., Shetty, A., Hrenya, C.M., 2020. On the use of a powder rheometer to probe defluidization of cohesive particles. Chem. Eng. Sci. 214, 115422 https://doi.org/10.1016/j.ces.2019.115422.

Mishra, I., Molnar, M.J., Hwang, M.Y., Shetty, A., Hrenya, C.M., 2022. Experimental validation of the extraction of a particle-particle cohesion model (square-force) from simple bulk measurements (defluidization in a rheometer). Chem. Eng. Sci. 259, 117782 https://doi.org/10.1016/j.ces.2022.117782.

Pant, A., Ramana, G.V., Datta, M., 2020. Stick-slip behavior of dry fly ash. Part. Sci. Technol. 38, 605–616. https://doi.org/10.1080/02726351.2019.1571543.

Parrella, L., Barletta, D., Boerefijn, R., Poletto, M., 2008. Comparison between a uniaxial compaction tester and a shear tester for the characterization of powder flowability. KONA 26, 178–189. https://doi.org/10.14356/kona.2008016.

Powrie, W., 2017. Soil Mechanics: Concepts and Applications, third ed., third ed. CRC Press, London. https://doi.org/10.1201/9781315275284.

Ramaraju, H., Landry, A.M., Sashidharan, S., Shetty, A., Crotts, S.J., Maher, K.O., Goudy, S.L., Hollister, S.J., 2022. Clinical grade manufacture of 3D printed patient specific biodegradable devices for pediatric airway support. Biomaterials 289, 121702. https://doi.org/10.1016/j.biomaterials.2022.121702.

Roussel, L.E., 2005. Experimental investigation of stick-slip behavior in granular materials. Louisiana State University, Master's Theses. 4145. https://digitalcommons.lsu.edu/gradschool_theses/4145.

Schulze, D., 2008. Powders and Bulk Solids: Behavior, Characterization, Storage and Flow. Springer, Berlin ; New York.

Sharma, P., Dessev, T.T., Munro, P.A., Wiles, P.G., Gillies, G., Golding, M., James, B., Janssen, P., 2015. Measurement techniques for steady shear viscosity of Mozzarellatype cheeses at high shear rates and high temperature. Int. Dairy J. 47, 102–108. https://doi.org/10.1016/j.idairyj.2015.03.005.

Silva, J.V.C., O'Mahony, J.A., 2017. Flowability and wetting behaviour of milk protein ingredients as influenced by powder composition, particle size and microstructure. Int. J. Dairy Technol. 70, 277–286. https://doi.org/10.1111/1471-0307.12368.

Stavrou, A.G., Hare, C., Hassanpour, A., Wu, C.-Y., 2020. Investigation of powder flowability at low stresses: influence of particle size and size distribution. Powder Technol. 364, 98–114. https://doi.org/10.1016/j.powtec.2020.01.068.

Stoklosa, A.M., Lipasek, R.A., Taylor, L.S., Mauer, L.J., 2012. Effects of storage conditions, formulation, and particle size on moisture sorption and flowability of powders: a study of deliquescent ingredient blends. Food Res. Int. 49, 783–791. https://doi.org/10.1016/j.foodres.2012.09.034.

Teunou, E., Fitzpatrick, J.J., Synnott, E.C., 1999. Characterisation of food powder flowability. J. Food Eng. 7.

Tuohy, J.J., 1989. Some physical properties of milk powders. Ir. J. Food Sci. Technol. 13, 141–152.

Wang, Y., Koynov, S., Glasser, B.J., Muzzio, F.J., 2016a. A method to analyze shear cell data of powders measured under different initial consolidation stresses. Powder Technol. 294, 105–112. https://doi.org/10.1016/j.powtec.2016.02.027.

Wang, Y., Snee, R.D., Meng, W., Muzzio, F.J., 2016b. Predicting flow behavior of pharmaceutical blends using shear cell methodology: a quality by design

approach. Powder Technol. 294, 22–29. https://doi.org/10.1016/j.powtec.2016.01.019.

Zhao, Y., Phalswal, P., Shetty, A., Ambrose, R.P.K., 2021. Effects of Powder Vibration and Time Consolidation on Soft and Hard Wheat Flour Properties. KONA Powder and Particle Journal advpub, 2021007. https://doi.org/10.14356/kona.2021007.

CHAPTER 4

EFFECT OF MOISTURE CONTENT, TEMPERATURE, AND PARTICLE SIZE ON FLOWABILITY OF PROTEIN-RICH AND LACTOSE-RICH DAIRY POWDERS

ABSTRACT

In this study, we investigated the critical environmental limits (temperature and relative humidity) in processing conditions which could have impact on powder flow properties of protein-rich powders (MPC 80, MPI 85 low lactose, MPI 90) and lactose-rich dairy powder (MPP). Impact of compositional and physical characteristics, including particle size, moisture content and temperature, on powder flowability were also investigated.

Moisture content and particle size can play a significant role on controlling flowability of dairy powders. Increased moisture content (from 5 to 9%) in the powders resulted in a higher level of cohesion (0.13 to 0.21) and reduced flowability (*ffc* = ~4.5 to *ffc* = ~3) for each of the samples. MPP was most noticeably affected because the higher moisture content decreased flowability to the point where it could be accurately measured using the *ffc* flowability index (*ffc* = ~8.6 to *ffc* = ~ 2.1), as opposed to the natural non-equilibrated powder that was naturally flowable and difficult to measure using the *ffc*

index. Three testing methods (shear cell test, Warren Springs Cohesion, and wall friction) were utilized to determine the impact of particle size. The impact of particle size was most noticeable with the smallest size particles (< 50 μm) and the largest particles (> 250 μm), both of which had decreased flowability due to increased particle-particle interactions and increased friction between particles, respectively. Flowability was typically the highest for particles in the range of 50-150 μm. As expected, shear testing and Warren springs Cohesion produced similar, but inverse results to classify the flow characteristics of the powder samples. However, data gathered from the wall friction test did not seem to be truly representative of the powder samples due to high variation in the wall friction angle values. SEM analysis was used to further analyze the morphological details of MPC 80 power exposed to ~54% moisture and for MPI 90 segregated particle size samples. Visual analysis revealed that increased moisture content promoted formation of larger particle aggregates. Visual inspection of the particle size samples showed that particle size increased due to aggregates forming from individual particles. Overall, temperature had no limiting or promoting effect on the flow characteristics of the protein-rich powders (MPC 80, MPI 85 low lactose, MPI 90) and lactose-rich dairy powder (MPP) samples. These results can be used to further optimize the processing and storage procedures of these products.

4.1: Introduction

Milk protein concentrates (MPCs) and isolates (MPIs) are highly functional and nutritional dairy powder products that are used worldwide. By changing their composition, they can be modified based on the desired nutritional components or functional properties. These dairy powders can be used in numerous applications, including, cheese making, dry soup mixes, nutritional drinks, and baby formula (Early, 2012; Sharma et al., 2012). Additionally, their functional properties such as emulsification, water binding, gelling and solubility are very desirable for the food manufacturing industry (Sharma et al., 2012; Silva and O'Mahony, 2017). Milk permeate powder (MPP) is composed primarily of lactose and is the byproduct of MPC and MPI powder products. MPP can also be used in a wide variety of food applications including: sugar replacements, bakery ingredients, sports drinks and confectionary items (O'Donoghue and Murphy, 2023).

Milk protein concentrates and isolates come in a range of compositions based on the percentage of milk protein present in the milk (Agarwal et al., 2015). Milk protein concentrate powders have a minimum concentration of 42% and a maximum of 85% protein on a dry matter basis. Milk protein isolates contain at least 90% protein on a dry matter basis (Agarwal et al., 2015). MPP contains a minimum of 75% lactose and approximately 3% protein (ADPI, 2021c).

In a global food industry, transporting and storing large amounts of liquid dairy ingredients is not energy efficient or sustainable process. Most liquid dairy products require refrigeration and have a relatively short shelf life (Sharma et al., 2012). Thus, the

conversion of liquid to powder is necessary to retain product quality during storage and increase sustainability in transport and energy usage.

Milk protein concentrate powders are made with skim milk, using ultrafiltration and diafiltration to concentrate the retentate (Martin et al., 2010). The byproduct of this process is the milk permeate. To produce milk protein concentrate, vacuum evaporation is utilized to remove as much water as possible before spray drying or roller drying the retentate (Carić et al., 2009; Early, 2012; Sikand et al., 2011). After drying, the powder product is collected and transported pneumatically through pipes, using cyclones and fluidized beds respectively (Carić et al., 2009; Hazlett et al., 2021). The final destination can be a storage silo or bin, a mixing hopper, or a food package (Hazlett et al., 2021). To produce the permeate product, the permeate is concentrated further and then crystallized in crystallization holding tanks. Once this process is done, the same spray drying and post drying processes used for MPCs and MPIs is applied to the permeate powder (O'Donoghue and Murphy, 2023).

Environmental conditions during transport and storage stages must be strictly controlled in order to preserve the quality and integrity of the product. This also ensures that the flowability of the powders is maintained to prevent issues with clumping, consolidation, and caking during transportation and storage (Havea et al., 2009; Juliano and Barbosa-Cánovas, 2010; Schulze, 2008). The environmental factors that will affect the flow properties of powders include: temperature changes, moisture differences between the powder and the surrounding air, length of storage, and the amount of gravitational load present on the powder mass itself. Additionally, the physical characteristics of the powder itself that influence the flow characteristics include: particle

size and shape, moisture content, and percent composition of fat, protein and lactose (Hazlett et al., 2021; Juliano and Barbosa-Cánovas, 2010). Higher level of water activity/moisture content, not only has potential to increase microbial growth but also to make powders more cohesive by formation of liquid bridges, causing the powder mass to clump, cake, and become sticky (Schulze, 2008). Amorphous lactose may also change conformation to crystalline state when exposed to moisture (Juliano and Barbosa-Cánovas, 2010; Rennie et al., 1999). Nonenzymatic browning can also occur if milk powders have high moisture contents and held at higher temperature (Sharma et al., 2012). If fat is present within the powder, temperature may affect the powder by changing the state of the fat from a solid to a liquid, and create a liquid fat bridge between the particles, leading to reduced flowability (Rennie et al., 1999). Heat may also increase molecular mobility within the particles, leading to particle degradation.

The objective of this research was to identify critical limits of the external environmental factors found in processing conditions and determine their effect on the flow properties of the powders. Analysis of the compositional and physical characteristics found in these powders was also completed to see the potential correlation with particle size, moisture content, and temperature, in relation to the flowability of protein rich and lactose rich powder.

4.2: Materials and methods

4.2.1 Milk powders

Four commercial milk powder samples: milk protein concentrate 80 (MPC 80), milk protein isolate 85 low lactose (MPI 85 low lactose), milk protein isolate 90 (MPI 90) and milk permeate powder (MPP) were obtained in 55 lb. pound bags from Idaho Milk Products (Jerome, ID). Two distinct manufacturing lots were received for each powder type and designated as Lot A and Lot B. After receival, each of the powder lots were distributed into smaller, hard plastic, airtight containers for each of the studies. Storage in airtight containers prevented moisture transfer during the study.

4.2.2 Sieving process

A single-speed, mechanical Sieve Shaker, Model RX-86 (Cole-Parmer, Vernon Hills, IL), with VWR U.S.A Standard Testing Sieves was utilized to separate the powder samples into four different particle size ranges (μm). The size ranges consisted of <50, 50-100, 100-150,150-250 and >250 μm. Segregated samples were stored in airtight storage containers.

4.2.3 Moisture content equilibration

To analyze the effect of moisture content on the powder, moisture levels within the range of 5% - 9% were tested as 5% being the industry target, and 8% is the typical industry maximum. Different relative humidity environments were established using saturated salt solutions. Four saturated salt solutions, Lithium Chloride, Magnesium

Chloride, Potassium Carbonate and Magnesium Nitrate were made with DI water and held in desiccators (Table 6) (Greenspan, 1977; Murrieta-Pazos et al., 2011). Five gram powder samples (MPP, MPC 80, MPI 85 low lactose, and MPI 90) were then equilibrated in duplicate in the closed desiccator system for approximately one to two weeks (Foster et al., 2005). Water activity was checked periodically to ensure equilibration and samples were stirred with a clean, dry metal spatula to ensure all powder particles were exposed to the environment. If the powder did not reach the desired water activity (the salt's water activity) prior to analysis, it was then equilibrated in the relative humidity chamber attached to the powder rheometer at the respective humidity at 25°C until the correct water activity was attained.

Salt	a_w at 20°C	RH (%) at 20°C
Lithium Chloride *LiCl*	0.113	11.31
Magnesium Chloride $MgCl_2$	0.335	33.07
Potassium Carbonate K_2CO_3	0.431	43.16
Magnesium Nitrate $Mg(NO_3)_2$	0.544	54.38

Table 4.1: Chemical salts used for moisture content equilibration and their respective water activity and relative humidity at room temperature (20°C).

4.2.4 Temperature equilibration

Powder samples (MPP, MPC 80, MPI 85 low lactose, and MPI 90 were tested at 4 different temperatures (22°C, 30°C, 50°C, 70°C). These temperature points were chosen to represent a typical room temperature and the common temperature range of 30°C - 70°C, that is found in industrial spray drying operations (Rennie et al., 1999). Temperature equilibration was conducted by placing the powder into the rheometer sample cup and heating it up to the desired temperature with dry air and oven conduction in the temperature oven chamber attached to the powder rheometer for approximately 60 to 90 minutes, or until the correct temperature was attained. Samples were tested in triplicate at each temperature point.

4.2.5 Water activity meter

The water activity of the powder samples was measured at 22°C using a water activity meter (Aqua Lab PRE, Meter food, Pullman, WA). All measurements were completed in triplicate.

4.2.6 Moisture content

The moisture content was measured in a rapid moisture analyzer (CEM Smart System 5, CEM Corporation Matthews, NC). The powder was analyzed with a drying time of five minutes and a maximum temperature of 130°C. Approximately 2 grams of powder was used in each test. The measurements were performed in triplicate.

4.2.7 Rheological analysis

An Anton Paar MCR302e Rheometer (Anton Paar GmBH, Graz, Austria) was used to perform both the shear cell and flow cell tests. The Rheocompass software (V1.30.1227) was used to analyze the data.

Samples modified for moisture, temperature, and particle size were all analyzed using the shear cell method found in (Palmer et al., 2023) (Chapter 3). Shear cell rheology on each samples was conducted in triplicate.

Segregated samples in different particle size ranges were also analyzed using the flow cell for the Warren Springs Cohesion test and the Wall friction test. All the samples were tested in triplicate.

To prepare the sample for the Warren Springs Cohesion test, an empty, graduated cylinder was weighed and tared. The powder sample was then placed in the cylinder until it reached approximately 80-90 mL. The cylinder was tapped 50 times to ensure a consistent amount of powder was present without any large air pockets, and the resulting amount of tapped powder was measured at approximately 70 mL. The weight of the sample was taken and recorded. The sample was then poured into the glass flow cell tube (140 mL volume capacity) (Figure 4.1a) and the tube was placed inside the rheometer and firmly locked into place by twisting it in a clockwise motion. The upper geometry for the first portion of the test was a flat, air-permeable compression disc (Identification # ST36-8V-10/PFC 71194) and the upper geometry for the second part of the test was the Warren Springs piece (Identification # D-PFC-7/185) (Figure 4.1b). See figure 2.2 in Chapter 2 for a representation of the full flow cell set up.

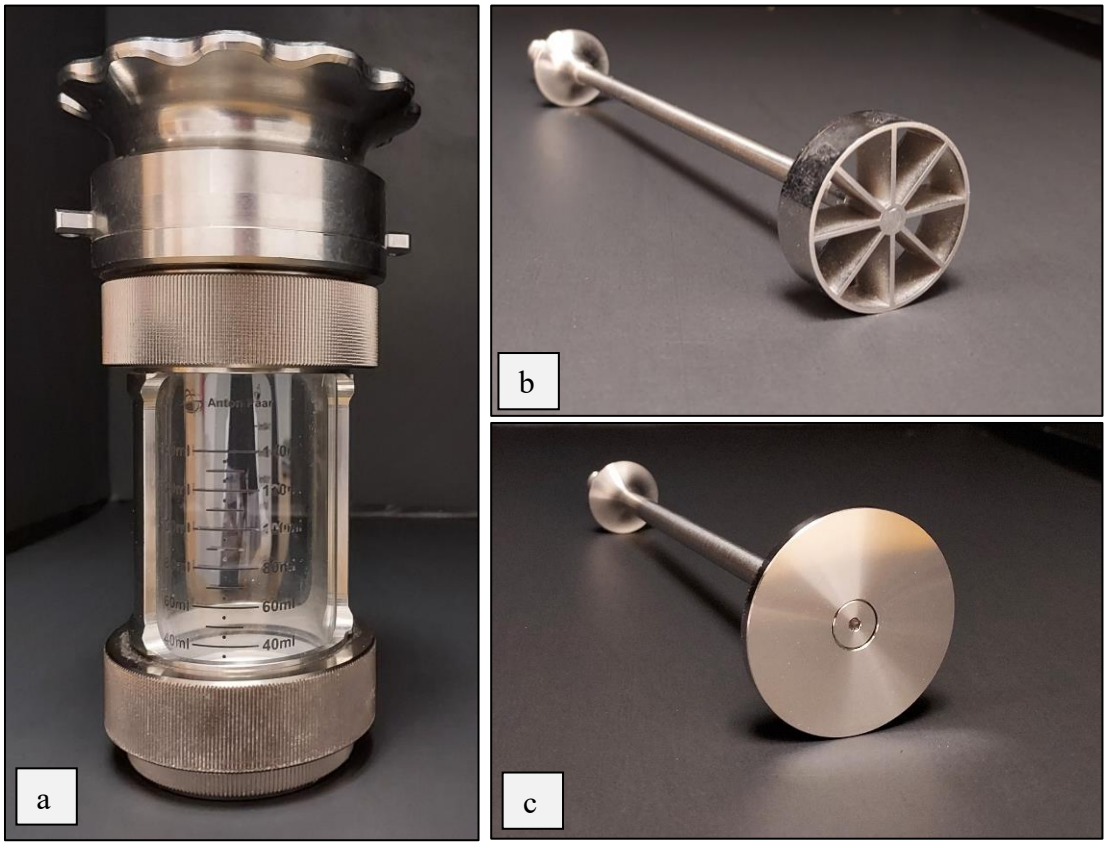


Figure 4.1: Components of the flow cell for the Warren Springs and Wall friction tests. (a) – glass flow cell container. (b) – Warren Springs geometry piece. (c) – Wall friction compression piece.

The measurement portion included a powder preparation step (compression) and a shearing step. The Warren Springs Cohesion test has three different normal forces (3, 6, 9 kPa) that are applied during the compression steps of the test. Shearing occurs when the second geometry is put into the machine and the powder is analyzed for the maximum shear stress that is needed to induce failure in the consolidated material. The maximum

shear stress point is labeled as Cohesion and can be calculated using the following Warren Spring equation as described in (Schulze, 2008). Where τ = shear stress (kPa), σ = normal stress (kPa), σ_τ = tensile strength, τ_c = Cohesion and n = exponent with values between 1 and 2 that characterizes the flowability.

$$\left(\frac{\tau}{\tau_c}\right)^n = \frac{\sigma}{\sigma_\tau} + 1$$

The Wall Friction test has the exact same preparation as described for the Warren Springs Cohesion test, except only one geometry is used and the powder is manually consolidated before starting the test. The upper geometry is a flat, stainless-steel disc (Figure 4.1c). This disc is gently put into the glass flow cell (Figure 4.1a) and the powder is consolidated until the top of the powder bed is smooth and not releasing any more entrapped air. In this test, the Wall Friction Angle is established by the stainless steel disc shearing the top of the powder bed and establishing a locus by which the wall friction angle is calculated with the ratio of wall shear stress to wall normal stress (Figure 4.2) (Schulze, 2008).

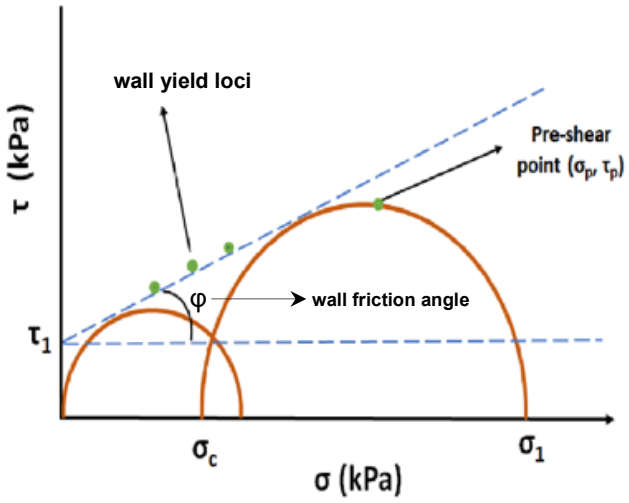


Figure 4.2: Determination of the wall friction angle (φ) as the ratio of shear stress (τ) and the normal stress (σ).

4.2.8 Bulk density, particle density, and volume of occluded air

Samples were analyzed using the bulk density method described in Palmer et al., (2023) (Chapter 3). Each sample was analyzed in triplicate.

Particle density and volume of occluded air were determined by weighing out 25 g of powder into a graduated cylinder. 50 mL of petroleum ether was added to the cylinder and the powder was vibrated until the petroleum ether was throughout the entire cylinder. 10 mL of petroleum ether was used to rinse off the powder remaining on the sides of the cylinder. The total volume of the powder and petroleum ether was read and recorded. These values were input into an equation as given in ("Analytical Methods | GEA Spray

Dryers," n.d.) and the output was given as particle density and the determination of volume of occluded air.

4.2.9 Particle size analysis

Laser diffraction was used to analyze the particle size distribution of the milk powders in a particle size analyzer (PSA 1190 LD, Anton Paar GmBH, Graz, Austria). Each sample was analyzed in triplicate and the volume weighted mean particle size (d_{43}) was recorded.

4.2.10 SEM analysis

To determine differences in particle size morphology, powder samples were imaged under high vacuum conditions (accelerating voltage: 15 KV, spot size: 2, detector: ETD) using a scanning electron microscope (SEM, FEI Quanta 650 F, Thermo Scientific Quanta, Hillsboro, OR). Powder samples were placed on aluminum stubs secured with carbon tape, flushed with nitrogen for 10 s and sputter-coated with 10 nm of gold and palladium layer, using a Q 150 V sputter coater (Q 150 V, Quorum technologies, Laughton, East Sussex, UK). Samples were analyzed in single replicates for particle size and effect of moisture.

4.2.11 Statistical analysis

The significant differences due to various treatments were analyzed using a one sample t-test to determine physicochemical differences between powder lots, and a one-way ANOVA in OriginPro (2021) for comparing means of the different treatments. The

mean values of each parameter were compared for significant differences using Tukey's HSD post Hoc test at a 5% of level of significance.

4.3: Results and discussion

4.3.1 Physicochemical properties

4.3.1.1 Composition, water activity, bulk density, and particle size

The physico-chemical properties of the powders are presented in Table 4.2. Each powder type has two distinctive lots, designated by the general labels of "Lot A" and "Lot B." Data will be shown from select lots within the text. Data from the other lot can be found in the appendix. With higher protein content in the protein rich powders (MPC 80, MPI 85 low lactose, and MPI 90) ash and lactose content were less, owing to the removal of these components in the permeate by ultrafiltration (Martin et al., 2010; Mistry and Hassan, 1991). MPP contained the lowest amount of protein in comparison with other protein rich powders, however it contained nearly 90% lactose.

Table 4.2: Physicochemical properties of the powder samples.

Powders	Moisture (%)	Fat (%)	Protein (%)	Lactose (%)	Ash (%)	Water Activity (a_w)	Bulk density (g/mL)		Particle density (g/mL)	Voa	Mean Size Volume D [4,3] (µm)
							Loose bulk density	Tap Bulk density			
MPC 80 Lot A	5.30	1.00	83.72	2.89	7.00	$0.160\pm3.3x10^{-4Aa}$	$0.295\pm3.2x10^{-3Aa}$	$0.390\pm2.6x10^{-3Aac}$	$0.759\pm0.11x10^{-3a}$	70.33 ± 2.28^{a}	$73.3\pm6.0x10^{-1Aac}$
MPC 80 Lot B	5.43	0.96	81.09	5.55	6.97	$0.163\pm10x10^{-4Ba}$	$0.319\pm4.2x10^{-3Bb}$	$0.420\pm2.7x10^{-3Bb}$			$72.2\pm2.4x10^{-1Aa}$
MPI 85 low lactose Lot A	5.56	0.96	81.69	1.95	6.70	$0.151\pm12x10^{-4Cb}$	$0.313\pm.49x10^{-3Cab}$	$0.407\pm2.6x10^{-3Cab}$	$0.905\pm8.6x10^{-3b}$	50.21 ± 1.29^{b}	$53.5\pm2.1x10^{-1Bb}$
MPI 85 low lactose Lot B	5.50	1.00	82.23	1.86	6.72	$0.163\pm15x10^{-4Da}$	$0.318\pm1.1x10^{-3Db}$	$0.417\pm2.6x10^{-3Cb}$			$54.8\pm2.8x10^{-1Cb}$
MPI 90 Lot A	5.67	1.01	85.24	1.43	6.65	$0.176\pm0.0x10^{-4Ec}$	$0.297\pm2.9x10^{-3Eab}$	$0.392\pm3.0x10^{-3Dac}$	$0.825\pm7.2x10^{-3ab}$	58.41 ± 1.31^{c}	$79.0\pm14x10^{-1Dc}$
MPI 90 Lot B	5.43	0.98	85.75	1.16	6.68	$0.152\pm8.8x10^{-4Fb}$	$0.297\pm2.9x10^{-3Ea}$	$0.386\pm3.3x10^{-3Dc}$			$57.4\pm0.2x10^{-1Eb}$
MPP Lot A	1.59	0.08	3.40	86.97	8.02	$0.147\pm20x10^{-4Gb}$	$0.764\pm6.2x10e^{-3Fc}$	$0.913\pm5.0x10^{-3Ed}$	$1.604\pm0.27x10^{-3c}$	58.49 ± 1.26^{c}	$98.4\pm6.2x10^{-1Fd}$
MPP Lot B	1.53	0.08	3.70	86.53	8.16	$0.174\pm5.8x10^{-4Hc}$	$0.764\pm5.7x10^{-3Fc}$	$0.878\pm6.6x10^{-3Fe}$			$110.9\pm31x10^{-1Fe}$

Different uppercase subscripts show significant differences (P<0.05) between lots of the same powder type. Different lowercase superscripts show significant differences (P<0.05) within the column.

As shown in table 4.2, the inherent moisture content of MPP powders (~1.5%) was lower than the protein rich powders (~5.0%), on the other hand, water activity values for all of these powders were in the range of 0.15-0.17. Bulk density of MPP powder (0.91 g/mL) was significantly higher ($P < 0.05$) than MPC 80, MPI 85 low lactose and MPI 90 (~0.40) owing to a higher proportion of heavier lactose content as indicated by the particle density (1.604).

Particle size of the four types of powders ranged from 53 to 110 μm. Particle size between lots was significantly different for MPI 85 low lactose and for MPI 90. This is attributed to natural variation found in processing and random sampling. The powder with the greatest mean size volume, (D,[4,3] ~100 μm) was MPP, and showed significant difference ($P < 0.05$) between protein powder types (50-73 μm) (Table 4.2).

4.3.2 Effect of equilibrated moisture content

4.3.2.1 SEM analysis of RH modified powder

During the powder preparation and analysis process, it was observed that there was a difference between natural, non-equilibrated powder samples and powder equilibrated with $Mg(NO_3)_2$ (a_w, 0.574) (Figure 4.3). Upon examination, the modified powder looked fluffier and when placed in the sample preparation cup prior to testing, the powder stuck together in small clumps more easily. From these observations, it was considered valuable to analyze the particle interactions in a more detailed way. SEM was utilized to study the morphological differences of an MPC 80 powder sample that had been equilibrated at ~54% relative humidity. Powder was imaged at 250x and 500x to see

the general morphology and shapes of the particles and to see if there were any additional aggregates present due to the increase in moisture content as compared to natural powder.

SEM analysis presented visual data that confirmed a difference in the modified powder's structure and morphology (a) as compared to the unmodified powder sample (b). The unmodified powder had more un-clumped, free standing spherical particles, whereas the powder equilibrated at ~54% RH had visibly more particles stuck together and more large, irregularly shaped particles (Figure 4.3).

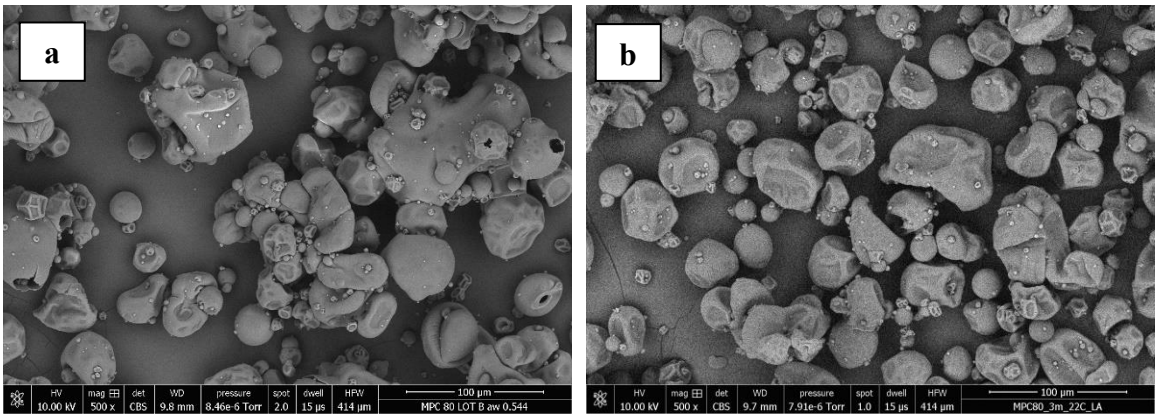


Figure 4.3: A SEM image comparison between different MPC 80 powder samples (natural vs increased moisture). Powders were imaged at 500x to see the general morphology and shapes of the particles. (a) – powder equilibrated at 54% RH. (b) – powder in the original, non-moisture equilibrated state.

4.3.2.2 Effect of moisture content on the flow function coefficient and cohesion

In this study, four powders (MPI 80, MPI 85 low lactose, MPI 90, MPP) were analyzed to study the effect of moisture content on the flowability or cohesiveness of the powder samples. According to the method available in the literature (Sharma et al., 2009), the powders were equilibrated in saturated salt modified environments and then equilibrated to their final moisture content by keeping them in the relative humidity chamber. The resultant moisture content and water activity of each powder was then used in correlation with the shear test *ffc* values and the cohesion values (τ_c).

The flow function coefficient (*ffc*) comes from an index that describes the level of powder flowability (Palmer et al., 2023). Due to the less cohesive nature of milk protein powders, *ffc* and cohesion τ_c in kPa, were reported at 1 kPa consolidation (normal stress). Each powder was tested for *ffc* using shear cell at 1, 3, 6, kPa pre-shear normal stresses as described by Palmer et al., 2023, however only data from 1 kPa will be discussed in this chapter (because of consistency of data) unless an incredibly distinct result was seen in the data from the 3 or 6 kPa portions of the shear test.

MPP

MPP contains over 85% lactose (Table 4.2) most of which is in the crystalline forms according to common industry manufacturing practices. Despite the fact the crystalline lactose content in the MPP was higher, *ffc* values decreased from 8 to 2 with increase in the water activity content, indicating reduction in flowability with increasing moisture content. Similar trends were reported in the literature (Lumay et al., 2016). The shear testing completed on the natural and equilibrated samples at higher pre-shear normal stress was inconclusive, as the *ffc* values were highly variable and unreproducible.

The unreproducible nature of the test is due to the strong flow tendency of MPP (higher *ffc* values >4). This error occurred in testing due to the MPP being highly flowable and the shear cell being unable to correctly detect the interactions within the powder bed due to incipient flow (Palmer et al., 2023).

The *ffc* trends observed in figure 4.4 indicate that increasing the moisture content within the powder slightly decreased flowability. Significant differences were found between the various RH equilibrated samples, but cannot be reasonably trusted due to the large amount of error in the resultant *ffc* values. A comparison between both lots at 1 kPa indicated that there was no significant difference between the *ffc* values of powders at different relative humidities ($P>0.05$). Rapid moisture analysis was used for all the other powder samples in the study. However, the MPP samples required a more sophisticated method to obtain the total and free moisture in the sample, and reliable equipment for this test was not available. Thus, the moisture content vs *ffc* value correlation could not be presented.

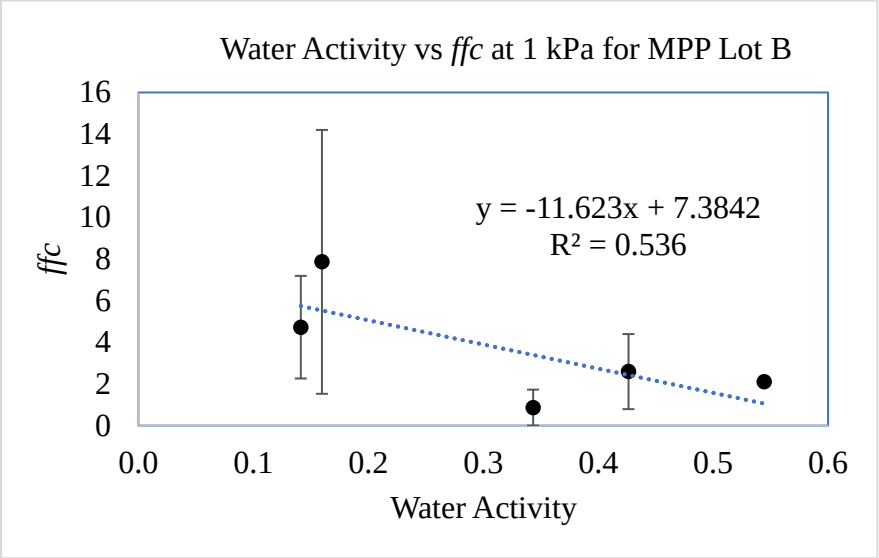


Figure 4.4: Water activity vs average ffc *values of different equilibrated MPP powders (Lot B). Obtained at 1 kPa*

Cohesion (τ_c) values were more consistent for MPP powder (Figure 4.5). With cohesion, the general trends were more readily visible. As moisture content increased, the cohesivity of the samples increased. Nevertheless, these changes in flowability were not significant enough to retain significant difference (P>0.05).

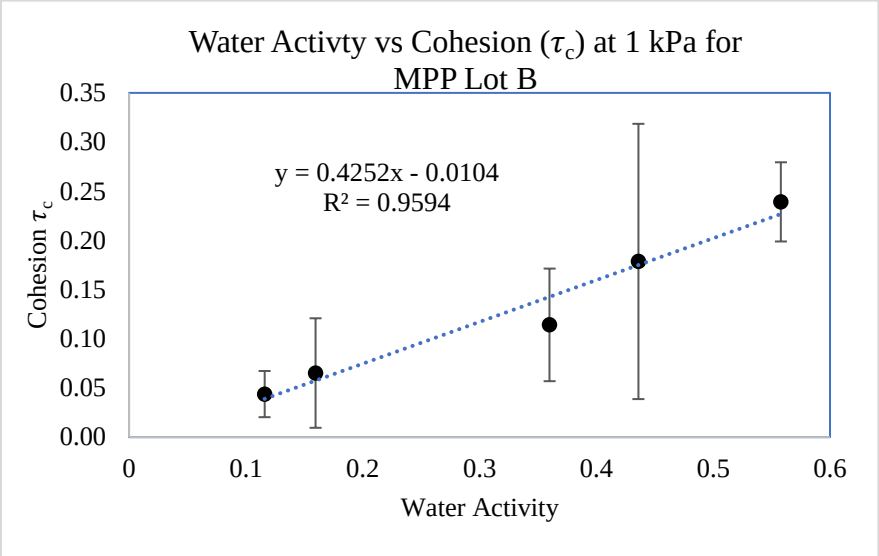


Figure 4.5: Water activity vs average cohesion τ_c values of different equilibrated MPP powders (Lot B). Obtained at 1 kPa

MPC 80

The *ffc* and cohesion values of the MPC 80 samples for both Lot A and B equilibrated at different RH are presented in Table 4.3. Due to batch to batch variations, flowability for Lot A and B had differences. A decreasing trend was observed for *ffc* value of Lot A in figure 4.6b. This declining trend demonstrates that flowability decreased as moisture content was increased. Overall flowability as impacted by moisture content (%) was different between Lot A and Lot B. Lot A was less flowable overall compared to Lot B (Table 4.3).

Table 4.3: Impact of relative humidity on the flowability of MPC 80.

Samples with various moisture contents	RH %	Moisture Content %	*ffc*	Cohesion τ_c
MPC 80 lot A	11	4.79	3.24 ± 0.1^{c}	0.1975 ± 0.013^{abc}
MPC 80 lot B	11	4.83	6.21 ± 0.1^{bc}	0.1909 ± 0.013^{abc}
MPC 80 lot A Natural Powder	16	4.93	3.25 ± 0.3^{c}	0.1504 ± 0.014^{bc}
MPC 80 lot B Natural Powder	16	5.09	10.8 ± 1.2^{a}	0.1261 ± 0.009^{c}
MPC 80 lot A	33	6.68	2.86 ± 0.1^{c}	0.2295 ± 0.022^{ab}
MPC 80 lot B	33	6.49	5.96 ± 0.5^{bc}	0.2264 ± 0.004^{ab}
MPC 80 lot A	43	8.07	2.87 ± 0.2^{c}	0.2382 ± 0.018^{ab}
MPC 80 lot B	43	7.91	8.01 ± 2.1^{ab}	0.2117 ± 0.016^{abc}
MPC 80 lot A	54	9.33	2.68 ± 0.2^{c}	0.2626 ± 0.026^{a}
MPC 80 lot B	54	8.98	7.55 ± 0.1^{ab}	0.2121 ± 0.033^{abc}

Lowercase superscripts show significant differences (P<0.05) between values within the column.

Moisture content plotted against cohesion τ_c, indicated that cohesion, followed an opposite trend as *ffc,* and cohesion increases incrementally in response increasing moisture content (Figure 4.6). *ffc* value correlated very well with moisture content (R^2 =0.91), however the *ffc* values were not significantly different (P >0.05). The cohesion values between samples did retain significant difference in flowability between samples

($P<0.05$). *ffc* value decreased more rapidly than the increase in cohesion with increasing moisture content from 4 to 9% indicating *ffc* value being more responsive to change in moisture content. With increasing moisture content, a decrease in flowability is associated with moisture acting as plasticizing material between two powder particles and also causing hydration/solvation of polar groups present in the protein molecules (Sharma et al., 2009).

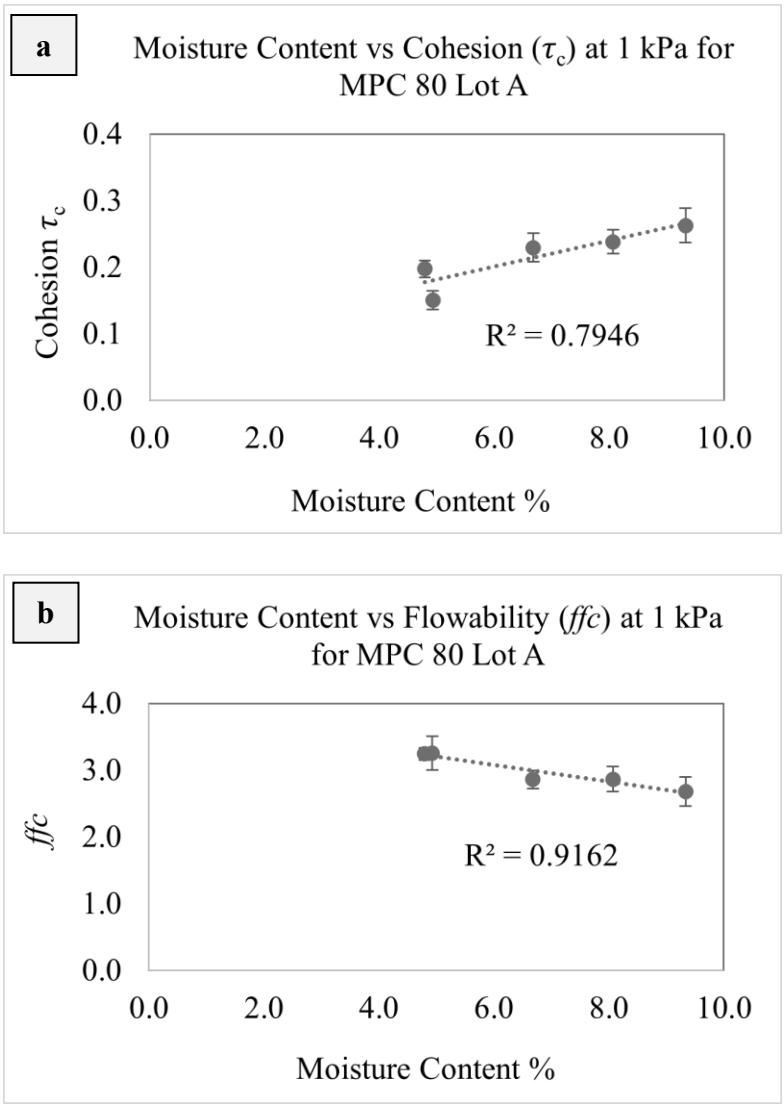


Figure 4.6: Comparison of MPC 80 Lot A flowability as impacted by moisture content. (a) – level of flowability measured by τ_c. (b) – level of flowability measured by ffc.

MPI 85 low lactose

The *ffc* values of MPI low lactose powder revealed that the natural, unmodified powders were significantly different at 1 kPa than all other equilibrated samples ($P<0.05$) (Figure 4.7). For this powder too, cohesion increases with increased moisture content indicating powder particles becoming more cohesive upon moisture sorption, may be due to quenching of polar groups present in the structures. Excluding the natural powders from both lot A and B, all other powders indicated cohesive behavior ($2<ffc<4$). However, due to only having slight changes in the recorded flowability, significant differences were not observed between the equilibrated powders themselves. Overall, flowability of the MPI 85 low lactose powder decreased significantly from the natural powder state ($P<0.05$). This trend was observed with analysis of both *ffc* and cohesion. The less flowable behavior of MPI 85 low lactose equilibrated with lithium chloride (11% RH) in comparison to the natural powder (16% RH) sample (Figure 4.8) may be due to moisture desorption opening new reactive sites in the interior and surface of the powder particle (Sharma et al., 2009).

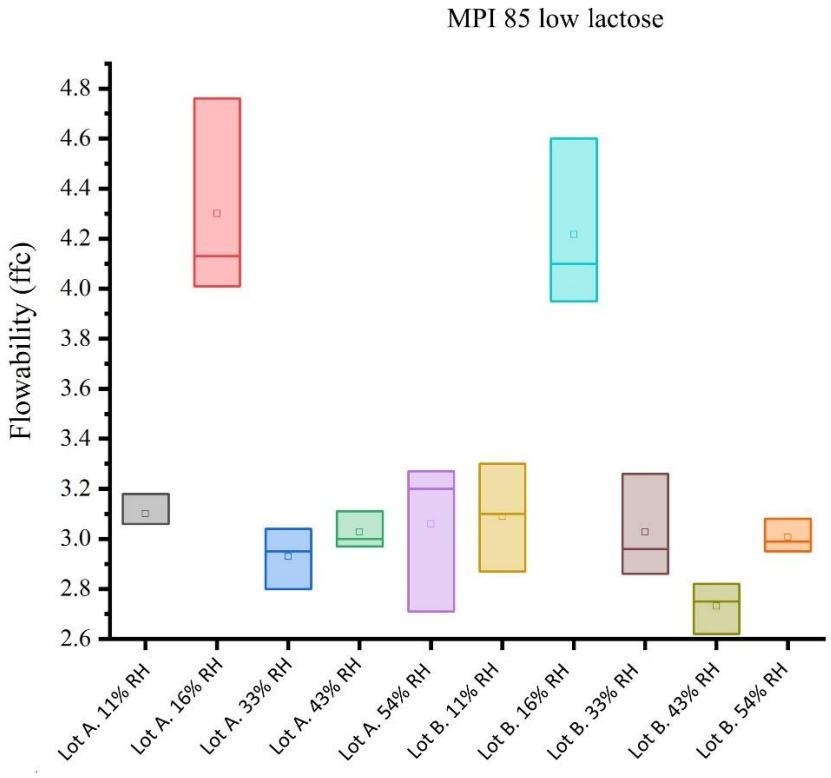


Figure 4.7: Boxplot depicting the significant difference of the natural, non-equilibrated (RH=16%) MPI 85 low lactose powders in comparison to the other moisture equilibrated MPI 85 low lactose powders. Error shown as standard error.

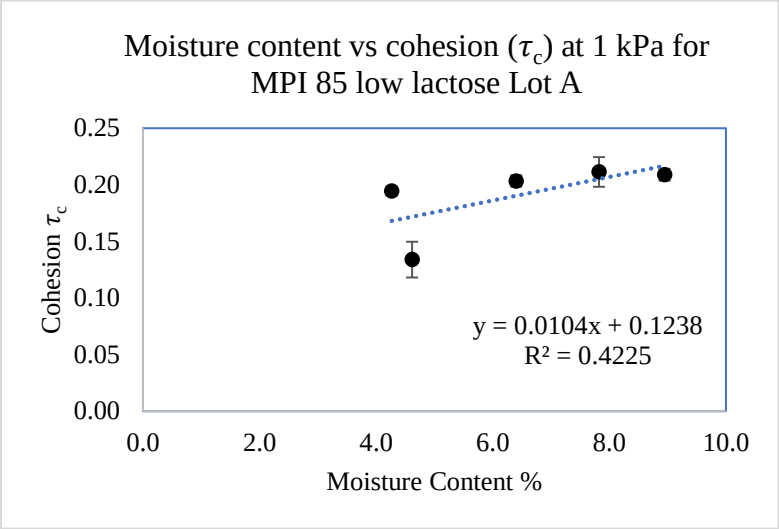


Figure 4.8: Moisture content vs cohesion (τ_c) for MPI 85 low lactose Lot A. The outlier value represents the natural unmodified powder. All other data points show a gradual upwards trend in relative cohesivity as the moisture content is modified (P > 0.05).

MPI 90

MPI 90 powder followed a similar trend as seen in the MPI 85 low lactose powder (Figure 4.9). Flowability has a decreasing trend at 1 kPa with respect to an increase in the moisture content. The mean values for *ffc* and cohesion as impacted by moisture content were found to be statistically significant (P<0.05). There was a significant difference in cohesion and *ffc* for the Lot A Natural Powder sample and the Lot B sample equilibrated at 43% RH. However, these differences were quite minor, as can be seen in Table 4.4. Additionally, the differences between samples in Lot B were significant, as the natural powder sample was significantly different from the sample

equilibrated at 43% RH (P<0.05). All powder samples demonstrated similar flow behavior, acting as a "cohesive" bulk mass (2 < *ffc* < 4) with the exception of the natural, non-equilibrated powder samples retaining an "easy-flowing" behavior (4 < *ffc* < 10) (Table 4.4).

Table 4.4: Impact of relative humidity on the flowability of MPI 90.

Samples with various moisture contents	RH %	Moisture Content %	*ffc*	Cohesion τ_c
MPI 90 lot A	11	4.67	3.52±0.2^{ab}	0.1635±0.018^{ab}
MPI 90 lot B	11	4.90	3.37±0.3^{ab}	0.1874±0.024 ^{ab}
MPI 90 lot A Natural Powder	16	5.53	4.59±0.2^{a}	0.1154±0.005^{b}
MPI 90 lot B Natural Powder	16	5.30	4.46±0.6^{ab}	0.1217±0.019 ^{ab}
MPI 90 lot A	33	6.75	3.52±0.3^{ab}	0.1563±0.019^{ab}
MPI 90 lot B	33	6.86	3.34±0.1^{ab}	0.1807±0.005 ^{ab}
MPI 90 lot A	43	8.10	3.51±0.1^{ab}	0.1817±0.005^{ab}
MPI 90 lot B	43	8.20	3.16±0.0^{b}	0.1912±0.010^{a}
MPI 90 lot A	54	9.21	3.77±0.3^{ab}	0.1444±0.016 ^{ab}
MPI 90 lot B	54	9.38	3.44±0.0^{ab}	0.1667±0.003^{ab}

Lowercase superscripts show significant differences (P<0.05) between values within the column.

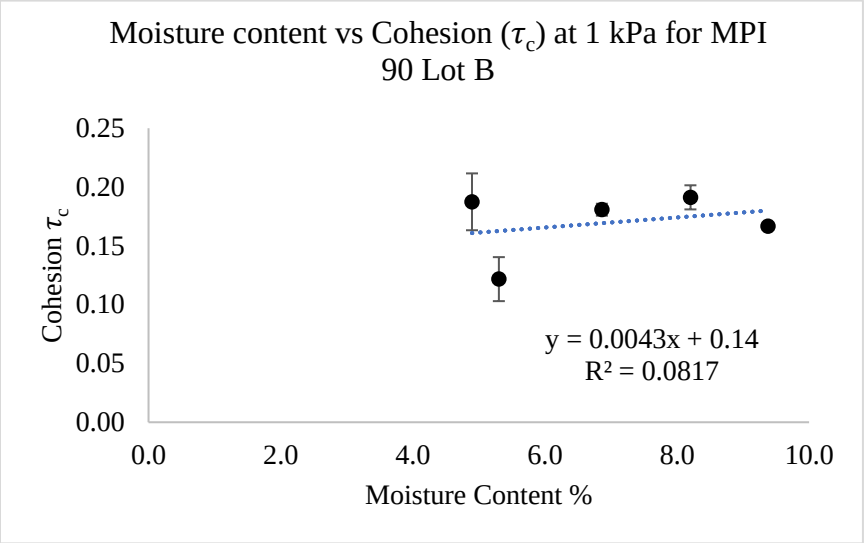


Figure 4.9: Moisture content vs cohesion (τ_c) for MPI 90 Lot B. The outlier value represents the natural unmodified powder. All other data points show a gradual upwards trend in relative cohesivity as the moisture content is modified.

It is important to note that moisture in the powders is a necessary component which can play significant role in controlling powder flow. With increasing levels of external relative humidity, and thus the associated increase in moisture content in the powder, flowability for of the powders was hypothesized to decrease (Emery et al., 2009; Kamath et al., 1994). Armstrong (2014), noted that moisture present in the powder can reduce potential electrostatic charge between particles and can have a lubricating or plasticizing effect. When powder was exposed to ~11% RH (LiCl) this reduced the amount of moisture within the powder sample. This phenomenon may explain why the powders equilibrated and tested at a relative humidity of ~11% RH (LiCl), had a lower *ffc* compared to that of the natural powder ~16% RH. Increase in moisture from ~16% to

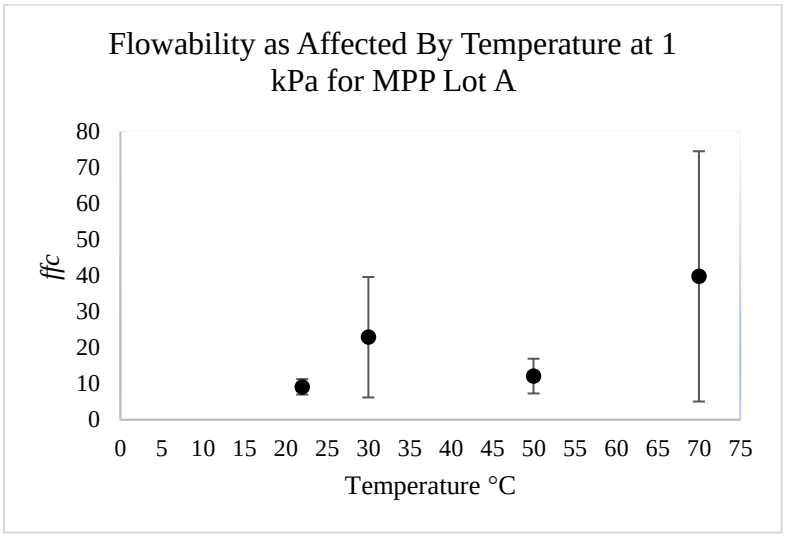
~54% allowed for significant increases in cohesion within the powder samples. This increase in cohesion was likely due to the formation of liquid bridges as well as the potential caking effect between particles (Armstrong et al., 2014)

4.3.3 Effect of testing temperature

In this study, four different temperatures (22, 30, 50, and 70°C) were used to study impact on the flowability of the high protein and high lactose dairy powders. Each powder sample was held at the designated temperature during shear testing and *ffc* flowability index values were determined.

4.3.3.2 MPP, MPC 80, MPI 85 low lactose, and MPI 90

MPP samples had no significant difference between temperature treatments and lot A and B, indicating the material was less temperature sensitive (Figure 4.10). However, the lack of impact from this environmental modification is consistent with previous research conducted on lactose in skim milk powders by Rennie (1999). Furthermore, the *ffc* index values for this sample were once again highly variable and irreplicable attributing to incipient flow, therefore lack of reliable shear-to-failure points (Palmer et al., 2023; Chapter 3).



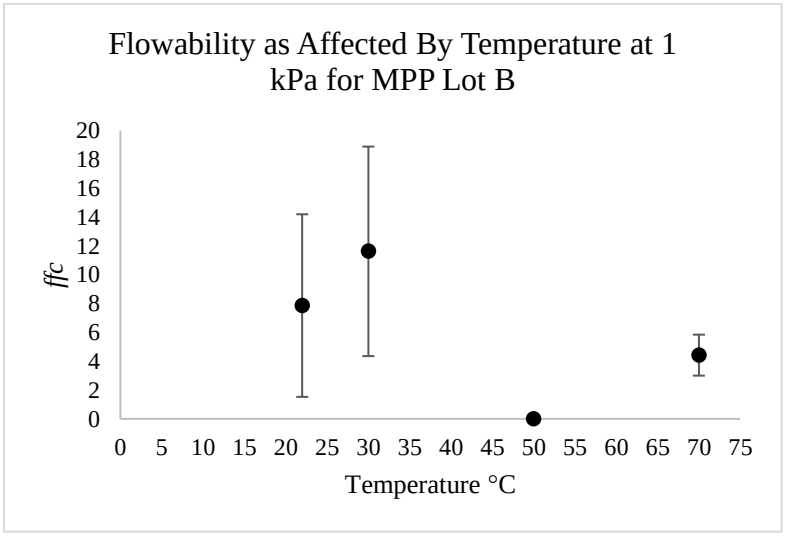


Figure 4.10: ffc vs temperature for MPP Lot A and Lot B.

Within each MPC 80 lot, there was no statistically significant difference between the samples tested at different temperatures. However, the *ffc* value decreased with increasing temperature, indicating slight increase in the cohesivity. Interestingly, lot A

and B had some differences in terms of *ffc* values which could be attributed to compositional differences in lactose content and protein % due to normal batch to batch variations (Table 4.5). MPC 80 samples from lot A were all classified as “cohesive” according to the *ffc* index and samples from lot B were all classified as “easy-flowing” (Table 2.1.)

Table 4.5: Differences in flowability for MPC 80 due to temperature.

Sample Name and temperature	*ffc*
MPC 80 lot A 22°C	3.25 ± 0.3^{c}
MPC 80 lot A 30°C	3.41 ± 0.1^{bc}
MPC 80 lot A 50°C	3.45 ± 0.0^{bc}
MPC 80 lot A 70°C	3.51 ± 0.0^{bc}
MPC 80 lot B 22°C	4.49 ± 0.2^{a}
MPC 80 lot B 30°C	$4.45\pm0.0.1^{a}$
MPC 80 lot B 50°C	4.46 ± 0.0^{a}
MPC 80 lot B 70°C	4.00 ± 0.1^{ab}

Lowercase superscripts show significant differences ($P<0.05$) between values within the column.

Statistical analysis of both MPI 85 low lactose and MPI 90 revealed that there was no statistical difference ($P>0.05$) within or between lots from the powder samples shear

tested at different temperatures. Regardless of the treatment, both powder types were classified as "easy-flowing" ($4 > ffc < 10$) (Figure 4.11). Thus, temperature alone did not create a significant effect on flowability.

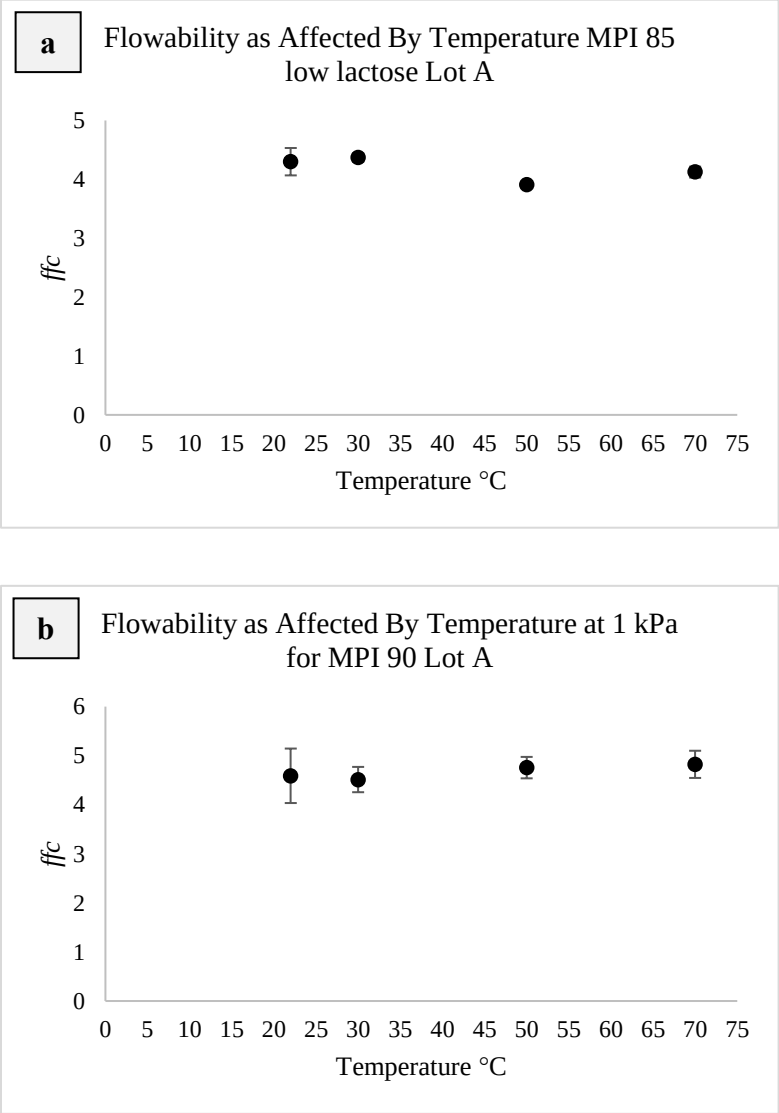


Figure 4.11: ffc vs temperature for MPI 85 low lactose Lot A (a) and MPI 90 Lot A (b).

The lack of significant difference between samples in each powder may indicate that the natural state of the powder and the associated moisture content was not enough to cause temperature induced changes. Additionally, each of these powders contained ≤ 1.0% fat. Previous work (Fitzpatrick et al., 2007, 2004; Rennie et al., 1999), shows that when greater amounts of fat are present within a powder, that increases in temperature can cause the fat to melt and form liquid bridges between the particles. This liquid bridging phenomena can decrease flowability within the powder bed. However, the high protein powders and the high lactose powder used in this study all contained low amounts of fat. Therefore, temperature may have had a lesser effect on the flowability of the samples.

In terms of other compositional factors, the low level of lactose may have also prevented temperature from having a significant effect. High milk protein powders do not contain significant amounts of lactose. So, the potential effect of amorphous lactose in the protein-rich powder samples changing state due to temperature and thus increasing cohesion may have been limited as well.

4.3.4 Effect of particle size

4.3.4.1 SEM analysis of different powder particle sizes

Throughout the particle segregation process, the general size and morphological differences between the different particle sizes were determined using SEM technique. It was determined that SEM would be useful to further characterize both the MPI 90 (a

protein-rich powder) and MPP (a lactose-rich powder) to see the general morphology and shapes of the particles and to identify any distinct differences in particle characteristics as the particles increased in size (Figure 4.12, 4.13). Each of the particle size ranges: <50 µm, 50-100 µm, 150-250 µm, 100-150 µm and >250 µm were analyzed using SEM.

The morphological differences of the particle could potentially be used to explain the differences in the flowability of powder. Morphology changes for both powder samples (MPI 90 and MPP) were clearly evident as particle size increased from <50 to >150 µm. MPI 90 particles became more aggregated as the particle size increased. Individual protein particles were only seen in the <50 µm category. The greatest particle size category, 150-250 µm, had some individual particles, but these were very small compared to the large aggregates of powder present. Additionally, as particle size increased, the protein powder particles became less spherical in morphology and more irregular in size and shape. For the MPP sample, increased magnification allowed observations for particle characteristics to be seen in greater detail. The visualization of the lactose crystals for particle size < 50 µm, showed that while there were larger particles (approximately ~50 µm) present in the sample, a substantial portion of the particles were very fine and much smaller than 50 µm. This differed from the < 50 MPI 90 sample, because it had a visibly less amount of powder fines. As MPP particle size increased, the particles became larger overall but retained the general morphology and shape throughout the different samples. Overall changes in flowability for both powder samples may be related to the differences in particle size of the powder samples.

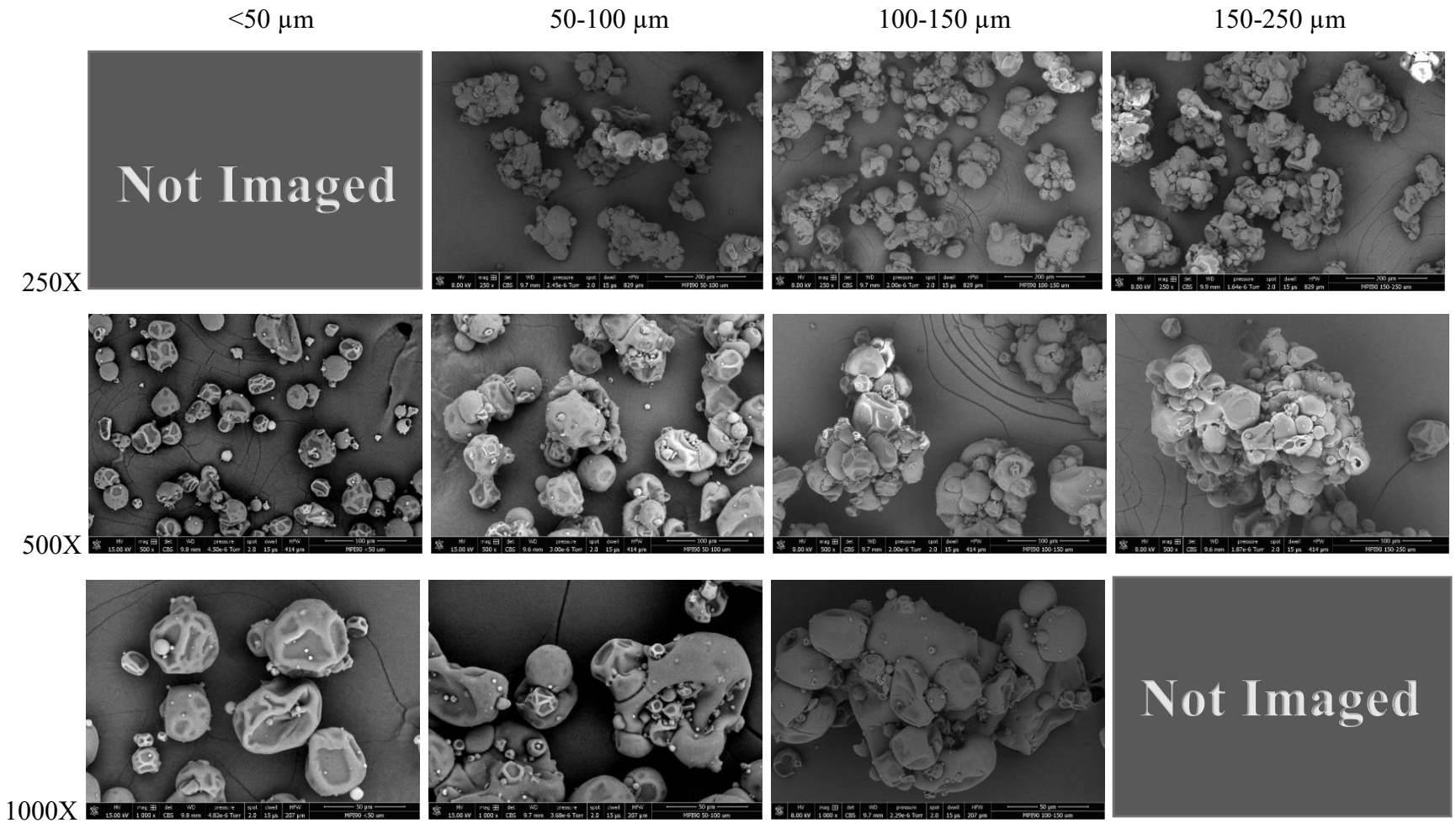


Figure 4.12: A SEM image comparison between different MPI 90 powder particles segregated by size. Images were not taken at 250X for <50 µm or at 1000X for 150-250 µm due to morphological characteristics being unrepresentative.

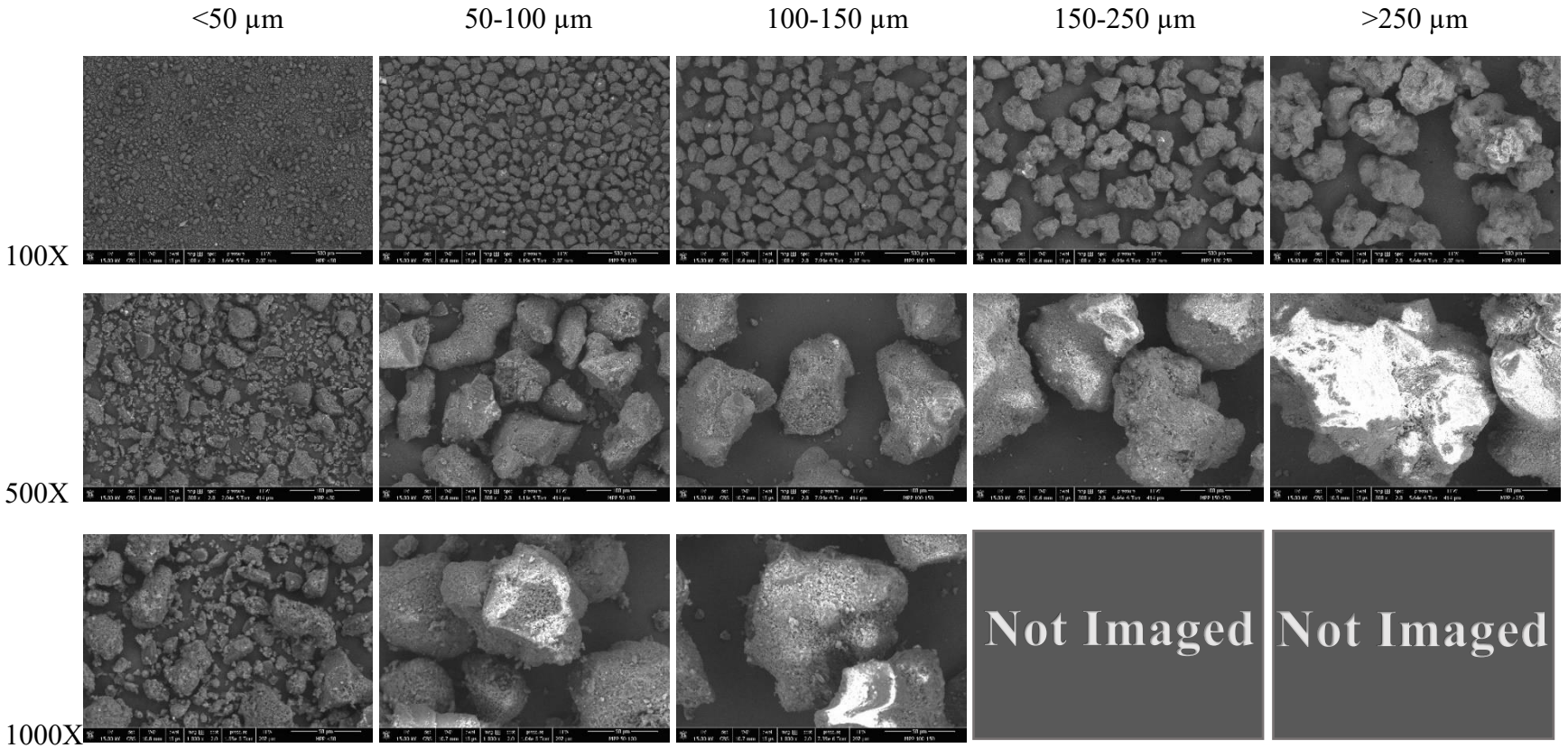
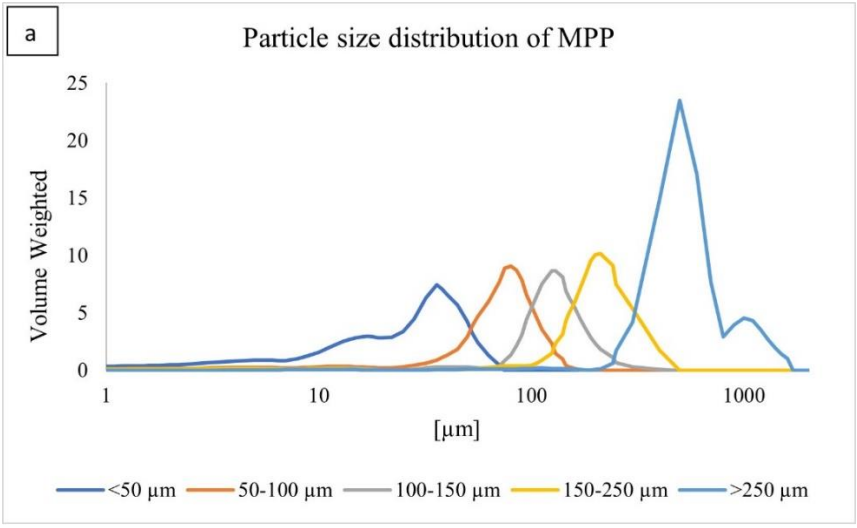


Figure 4.13: A SEM image comparison between different MPP powder particles segregated by size. Images were not taken at 1000X for particles: 150-250 µm and >250 µm due to significant electron charging within the particles preventing a representative image.

4.3.4.2 Effect of particle size-segregated powders on flow behavior and powder characteristics

Each of the powders were segregated into four particle size groups, with the exception of MPP, which contained an additional size range of particles. Physical properties of different size groups are presented in Table 4.6. Tapped bulk density of the all four powders decreased with increasing particle size. It should be noted that the segregation of the samples was not ideal for some powders (Figure 4.11). This issue has been seen before by Rennie (1999). Achieving the exact size range was not possible due to the powder particles sticking together, even with multiple rounds of sieving. Another reason for not having a narrow particle size range is related to the aspect ratio of the particles (Hare and Ghadiri, 2013).



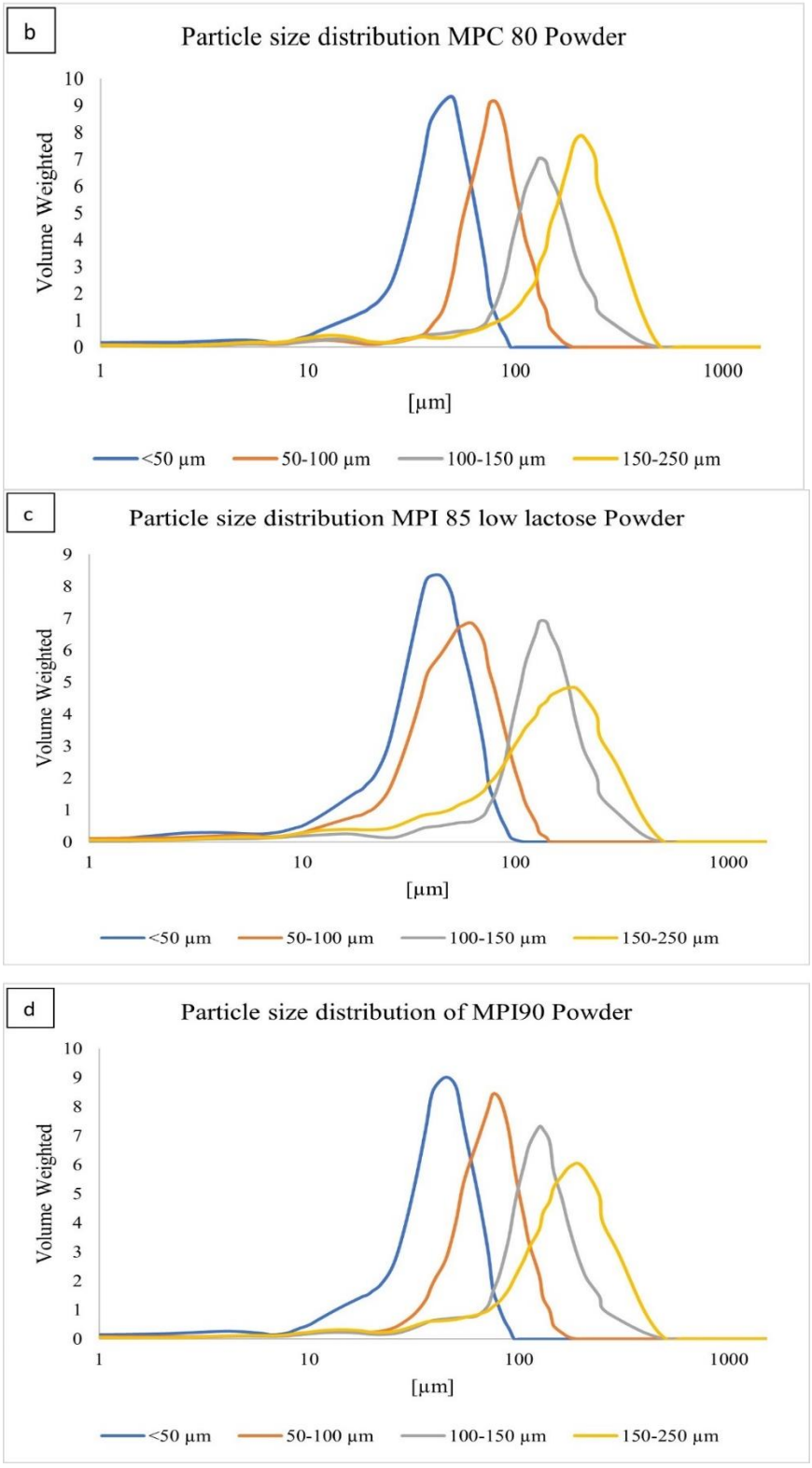


Figure 4.14: Particle size distributions for MPP (a), MPC 80 (b), MPI 85 low lactose (c) and MPI 90 (d).

Table 4.6: Physical properties of segregated particle size samples.

Powders	Segregated Size Range (µm)	Bulk density (g/mL)		Mean Size Volume D [4,3] (µm)
		Loose bulk density	Tap bulk density	
MPP	<50	$0.548\pm7.0\times10^{-3a}$	$0.740\pm3.9\times10^{-3a}$	25.82 ± 0.10^{a}
	50-100	$0.693\pm1.6\times10^{-3b}$	$0.806\pm4.3\times10^{-3b}$	69.87 ± 0.49^{b}
	100-150	$0.714\pm1.4\times10^{-3d}$	$0.773\pm3.3\times10^{-3c}$	124.9 ± 0.77^{c}
	150-250	$0.684\pm3.5\times10^{-3b}$	$0.736\pm2.3\times10^{-3a}$	206.9 ± 1.4^{d}
	>250	$0.604\pm5.9\times10^{-3c}$	$0.653\pm5.6\times10^{-3d}$	581.2±2.2e
MPC 80	<50	$0.267\pm1.6\times10^{-3a}$	$0.367\pm7.4\times10^{-3a}$	40.36 ± 0.21^{a}
	50-100	$0.286\pm1.2\times10^{-3b}$	$0.392\pm4.7\times10^{-3b}$	75.78 ± 0.15^{b}
	100-150	$0.269\pm1.1\times10^{-3a}$	$0.350\pm2.8\times10^{-3a}$	131.72 ± 0.26^{c}
	150-250	$0.236\pm1.9\times10^{-3c}$	$0.309\pm.74\times10^{-3c}$	184.99 ± 0.32^{d}
MPI 85 low lactose	<50	$0.228\pm1.4\times10^{-3a}$	$0.388\pm1.9\times10^{-3a}$	37.44 ± 0.16^{a}
	50-100	$0.291\pm3.8\times10^{-3a}$	$0.398\pm4.7\times10^{-3a}$	51.64 ± 0.25^{b}
	100-150	$0.247\pm3.3\times10^{-3b}$	$0.335\pm1.0\times10^{-3b}$	132.66 ± 1.06^{c}
	150-250	$0.235\pm.77\times10^{-3b}$	$0.327\pm3.5\times10^{-3b}$	145.34 ± 1.06^{d}
MPI 90	<50	$0.270\pm.41\times10^{-3a}$	$0.347\pm2.9\times10^{-3a}$	39.34 ± 0.90^{a}
	50-100	$0.295\pm.41\times10^{-3b}$	$0.387\pm5.3\times10^{-3b}$	70.01 ± 0.11^{b}
	100-150	$0.264\pm.35\times10^{-3c}$	$0.344\pm1.5\times10^{-3a}$	124.7 ± 1.63^{c}
	150-250	$0.248\pm.94\times10^{-3d}$	$0.320\pm5.2\times10^{-3c}$	162.0 ± 0.76^{d}

Lowercase superscripts show significant differences ($P<0.05$) between values within the columns.

Shear cell testing was employed for these samples to determine the flowability (*ffc*) of each distinct particle size. Flow cell testing was also employed to demonstrate the usability of the Warren Springs Cohesion test. Since Warren Springs Cohesion testing also uses shear stress as its designated method of determining flowability, only one powder type was analyzed using this specific test. The Wall Friction flow cell test was

completed for all segregated particle size samples. This test demonstrated the amount of potential friction that specific particle sizes would possibly create in a storage silo setting. In this test, the greater the wall friction angle value, the greater amount of cohesion or friction present in the sample.

4.3.4.3 Shear cell analysis

MPP

Most interestingly, the various particle size samples for MPP were significantly different on the population level for flowability ($P < 0.05$) (Table 4.2). In a segregated state, MPP behaved more similarly to the other protein powder samples. Attaining reproducible *ffc* index values was much easier for these samples because the powder was in its segregated state and as a result, easier to achieve defined shear-to-failure points (Figure 4.15).

Improved quality of the data could be due to the increase in particle to particle interactions between particles of the same size. The < 50 μm particle size was classified as "easy-flowing," but was much more cohesive than the larger particle sizes due to the fine nature of the powder particles reducing the interstitial spaces. The middle sizes were classified as "free-flowing," with the 150-250 and < 250 μm particle sizes being classified as "cohesive" and "easy-flowing," respectively. This decrease in flowability as the particle sizes became bigger may be due to the large irregular shapes of the lactose crystals. In the SEM analysis (Figure 4.13), one can observe the large crystals and then the additional presence of powder fines. Cohesivity (*ffc < 10)* may have increased due to potential increases in particle friction by the settling of fines between the larger particles

as well as the lack of space and increased friction occurring between the large particles themselves.

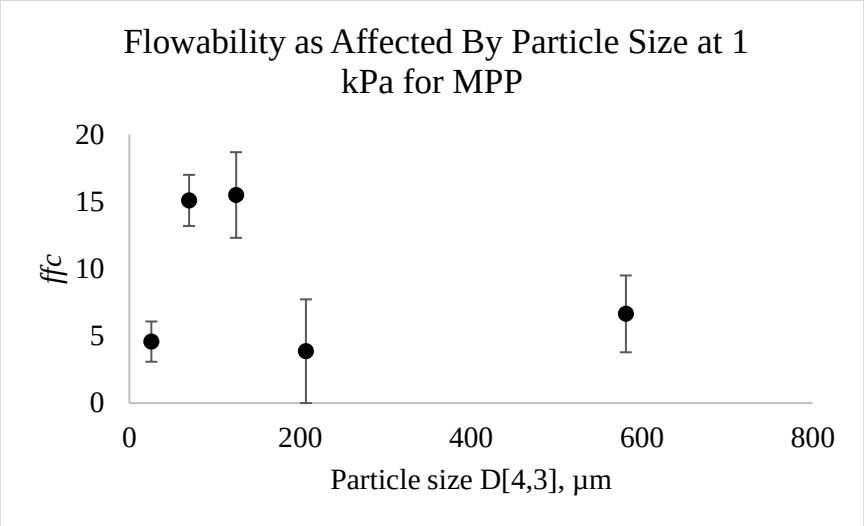


Figure 4.15: Changes in flowability (ffc) as related to MPP particle size.

MPC 80

At 1 kPa, flowability for MPC 80 particles was classified as "cohesive" (2 > *ffc* < 4*)* for particles in the size range of <50 µm, 50-100 µm and 150-250 µm. The particle size range of 100-150 µm was classified as "easy-flowing" (4 > *ffc* < 10*)*. However, there was no statistical difference in flowability between the different particle sizes (P > 0.05) (Figure 4.16a).

Smaller particles often have a more cohesive nature. This is due to the increased particle to particle interactions as well as the increase in surface area in the powder bed. Thus, these powders are less prone to flow and will create a more cohesive mass (Stavrou et al., 2020). This was evident during shear testing as the <50 µm particle size group

created a very cohesive wall around the shear tester, that unlike other samples, did not break during testing. This wall was so cohesive that it withstood the movements of the shear tester and clearly demonstrated the powders' cohesive ability (Figure 4.16b).

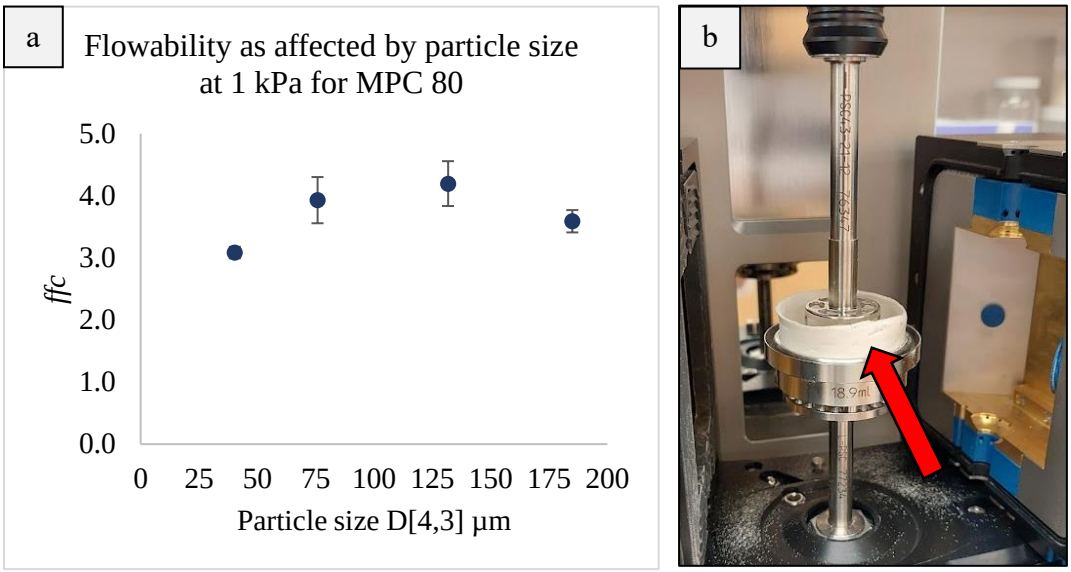


Figure 4.16: a – Flowability (ffc) distribution in relation to D[4,3] particle size (µm) of the segregated MPC 80 powder samples. b – Formation of a cohesive powder wall (indicated by red arrow) during shear testing for the MPC 80 <50 µm sample.

MPI 85 low lactose

Flowability trends were not as readily evident for this powder type (Figure 4.17). In fact, the sample group of 50-100 µm was more variable in nature compared to the

other particle size samples. Analysis showed that at 1 kPa, the 50-100 µm particle size group data resulted in an outlier. However, regardless of the visual outlier, there was no significant difference between the powder samples. Flowability was recorded as "cohesive" for the smallest particle size and as "free flowing" for the remaining sizes.

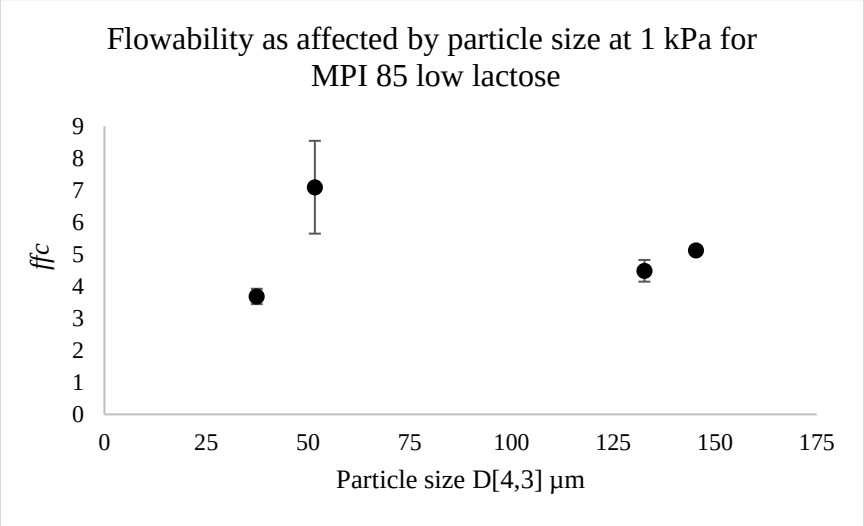


Figure 4.17: Changes in flowability (ffc) as related to MPI 85 low lactose particle size.

MPI 90

Flowability analysis at 1 kPa showed a trend similar to what was observed in MPC 80 particle sizes (Figure 4.18). This similarity would seem reasonable due to the powders having similar compositions, as well as particle size ranges. Particle size < 50 and 150-250 µm had an index classification of "cohesive" and particle sizes 50-100 and

100-150 µm were classified as “easy-flowing.” There were no statistical differences between particle sizes in terms of overall *ffc* index analysis.

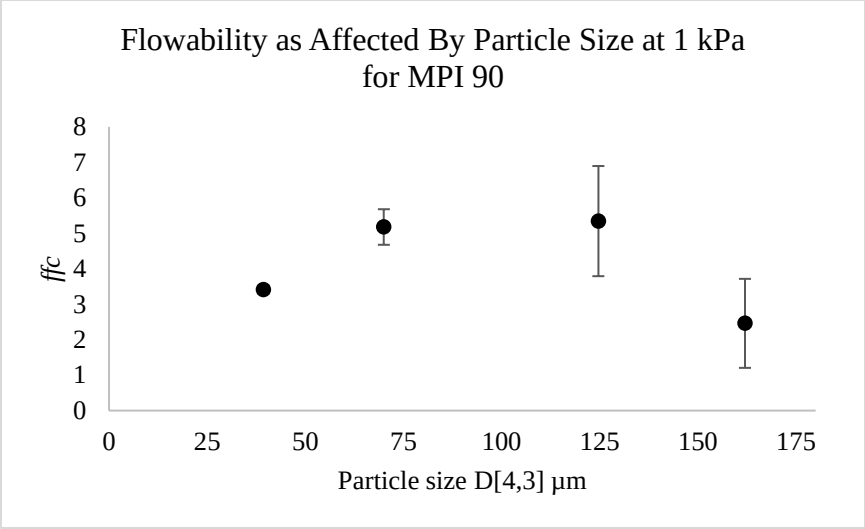


Figure 4.18: Changes in flowability (ffc) as related to MPI 90 particle size.

4.3.4.4 Flow cell analysis

Warren Springs

MPI 90

The Warren Springs Cohesion test was performed on the MPI 90 segregated particle size samples. Cohesion values indicated how much shear stress was required to activate flow within the powder bed. The higher the value, the more shear stress was

required. At 3 kPa, the lowest normal force setting for this test, there was a significant difference between the largest particle size (150-250 μm) and the other particle sizes (Figure 4.16). Out of all of the samples, particle size 150-250 μm required the greatest amount of shear stress on average to induce movement within the powder bed. Larger particles tend to flow more easily (Silva and O'Mahony, 2017), however, due to the narrow distribution of particle sizes within this particular sample (150-250 μm), as opposed to a non-segregated sample, cohesion may have increased due to the larger particles all being of similar morphology and general size. Potential friction due to large particles rubbing together or the interlocking of the randomly shaped aggregates (Figure 4.13) may have led to an increase in overall cohesion (Fu et al., 2012; Hare and Ghadiri, 2013; Stavrou et al., 2020). Similar to the inverse trend observed between cohesion and *ffc* in the moisture content testing, there was an inverse relationship between Warren Springs Cohesion and the shear cell *ffc* value (Figure 4.19). This trend further confirms the relationship between the flowability and cohesion can be correlated.

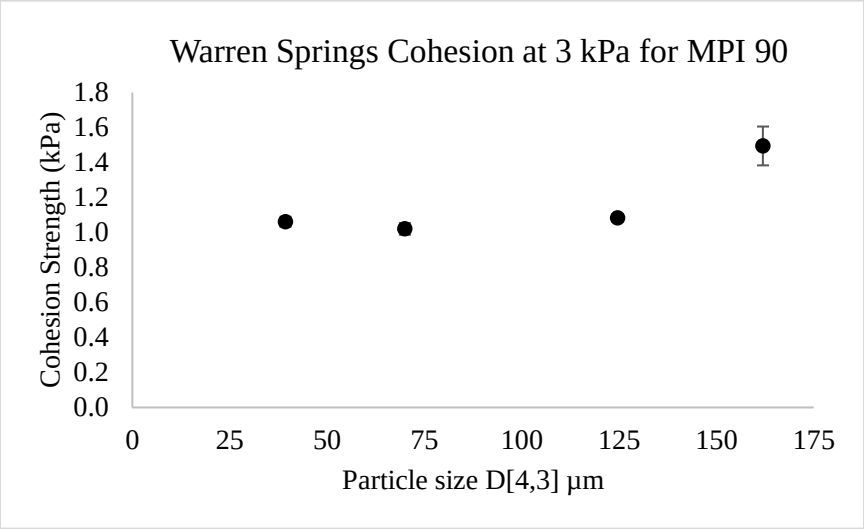


Figure 4.19: Changes in Warren Springs Cohesion strength as related to MPI 90 particle size.

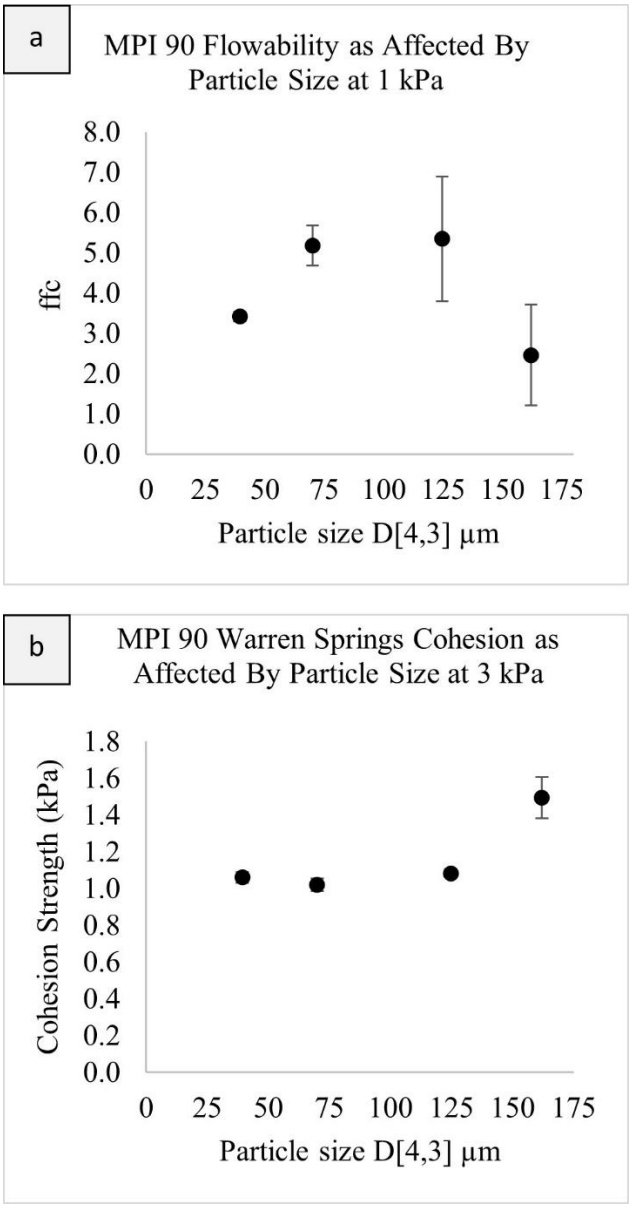


Figure 4.20: Comparison of the inverse correlation between ffc (a) and Warren Springs Cohesion (b) for different MPI 90 particle sizes.

Wall Friction

Powders are typically held in bulk amounts in powder silos or hoppers that are made of stainless steel. The interactive particle nature of these powders has already been discussed regarding the interactions within the powder itself. However, powder particles and powder mass as a whole can interact with the walls of the bins or silos that it is held in. This interaction manifests as friction and can greatly inhibit powder from flowing consistently (Iqbal and Fitzpatrick, 2006). Wall friction, in fact, is a critical factor in the configuration of how the powder will discharge from when released from storage (Fitzpatrick et al., 2007).

In this test, the segregated particles from each powder type were analyzed to determine the average amount of wall friction that each particle size range would impart. This data could be used later on for designing hoppers or silos, or in a processing setting to potentially produce powders that achieve a particle size range that promotes flowability or avoid a specific particle size range that could cause flowability issues during transport. In this test, greater values of the wall friction angle (also called the deflection angle (φ)), signify that more friction is occurring in the sample and wall, therefore lower flowability (Schulze, 2008). The amount of friction measured will be relative to the sample type.

MPP

There were no linear trends for friction in this specific sample (Figure 4.21). Interestingly, samples <50 µm, 100-150 µm and >250 µm all had, on average, the same level of friction within the sample, approximately $\varphi = 13.8°$. On the other hand, samples

50-100 µm and 150-250 µm had on average, the same level of friction as well, with φ = 2.8°. These respective groups were statistically different from one another.

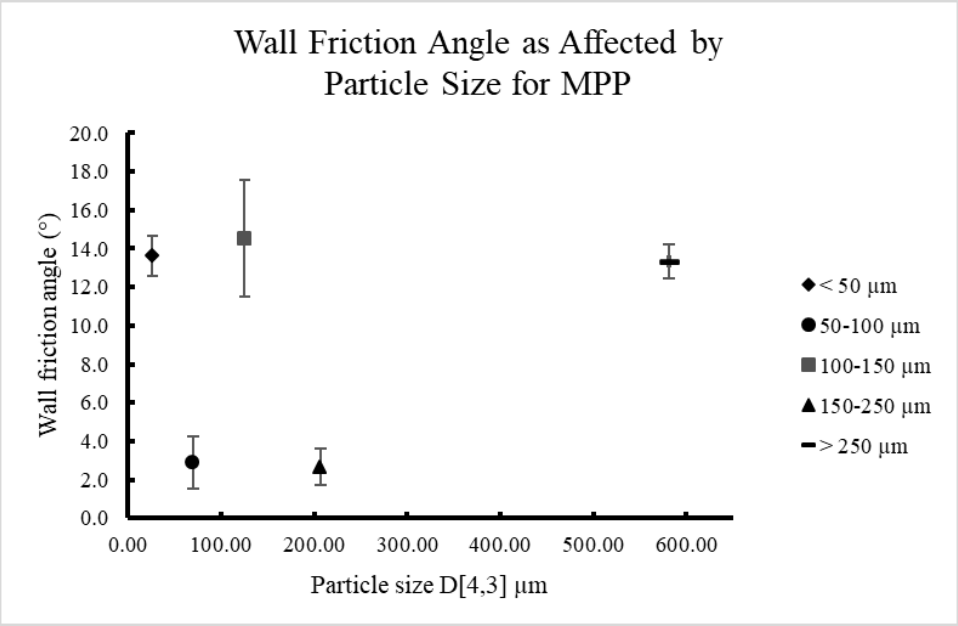


Figure 4.21: Wall friction angle as affected by particle size for MPP powder.

MPC 80

This sample showed very low values of wall friction angle overall compared to the values seen in MPP samples (Figure 4.21). Relative to the MPC 80 sample, particle size <50 µm had the largest average angle of friction at φ = 1.53° (Figure 4.22). This indicates that comparatively, the <50 µm sample had some particle characteristics (fine particles,

overall cohesive nature) that induced more friction than the other particle sizes. Sample 50-100 µm had the lowest wall friction angle at $\varphi = 0.46°$. This implies that this sample's interactions with the steel rheometer plate were very limited and that this sample will flow easily. Overall, the overall wall friction between the different samples were not statistically different.

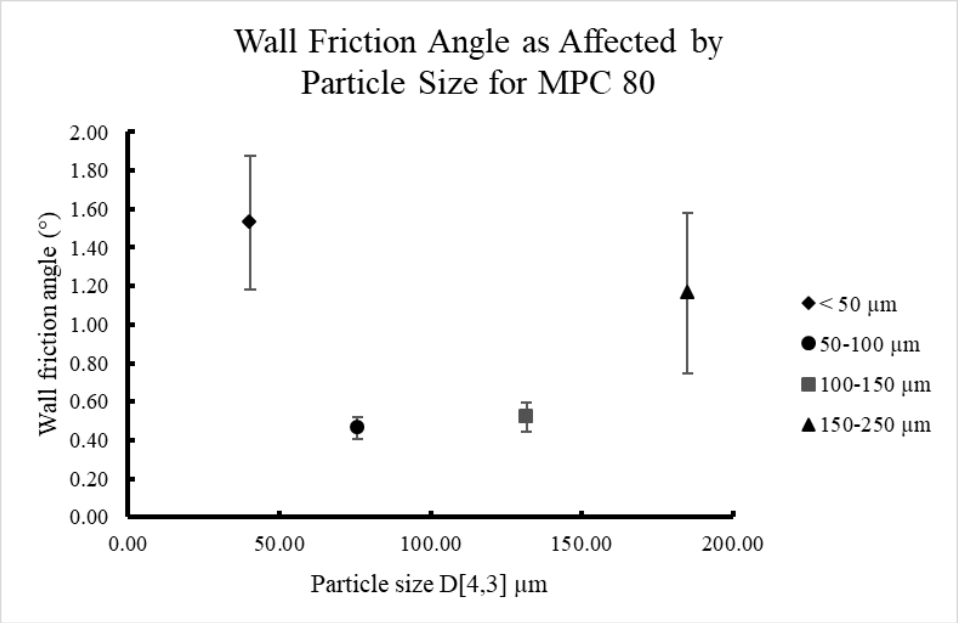


Figure 4.22: *Wall friction angle as affected by particle size for MPC 80 powder.*

MPI85 low lactose

No trend was visible for the MPI 85 low lactose powder and generally speaking, the wall friction angles were relatively low for each of the particle size ranges, (Figure 4.23) suggesting that the powder would flow well from a stainless steel hopper or bin. The particle size < 50 µm had an average wall friction angle of $\varphi = 0.59°$, compared to the particle size 100-150 µm that had a wall friction angle of $\varphi = 7.90°$.

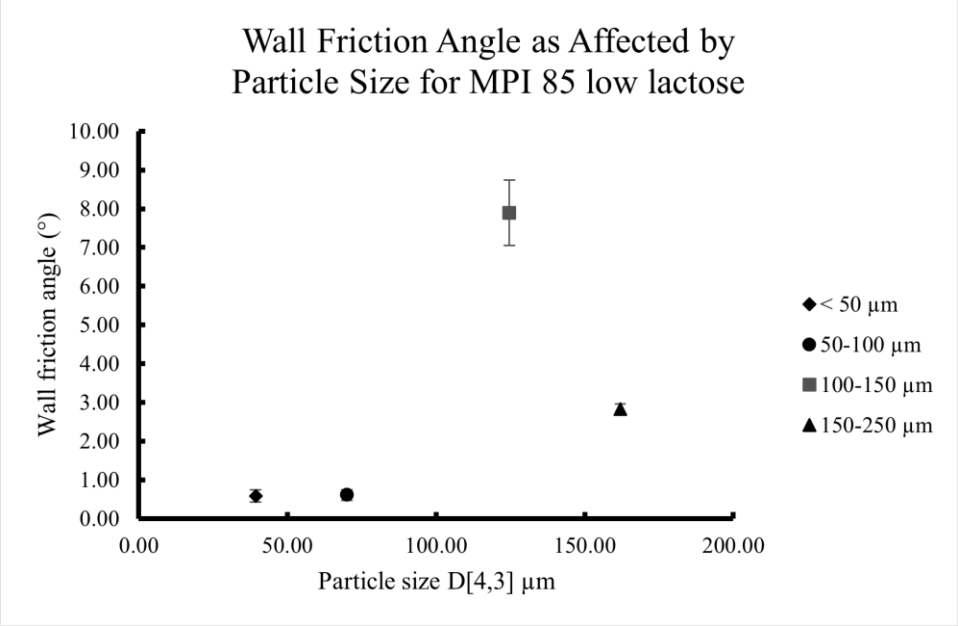


Figure 4.23: Wall friction angle as affected by particle size for MPI 85 low lactose powder.

MPI 90

This sample group was the only one to have a somewhat visible trend based on increasing particle size (Figure 4.24). However, the associated wall friction angle for each group was not consistent with flowability data. In general, smaller particles are more cohesive than larger particles. Smaller particles also have more surface area that is available for interaction. The <50 µm sample had a wall friction angle of $\varphi = 6.3°$, but the 150-250 µm sample had a wall friction angle of $\varphi = 14.0°$. This difference in friction may indicate that larger particle sizes may prove problematic when trying to empty a hopper efficiently.

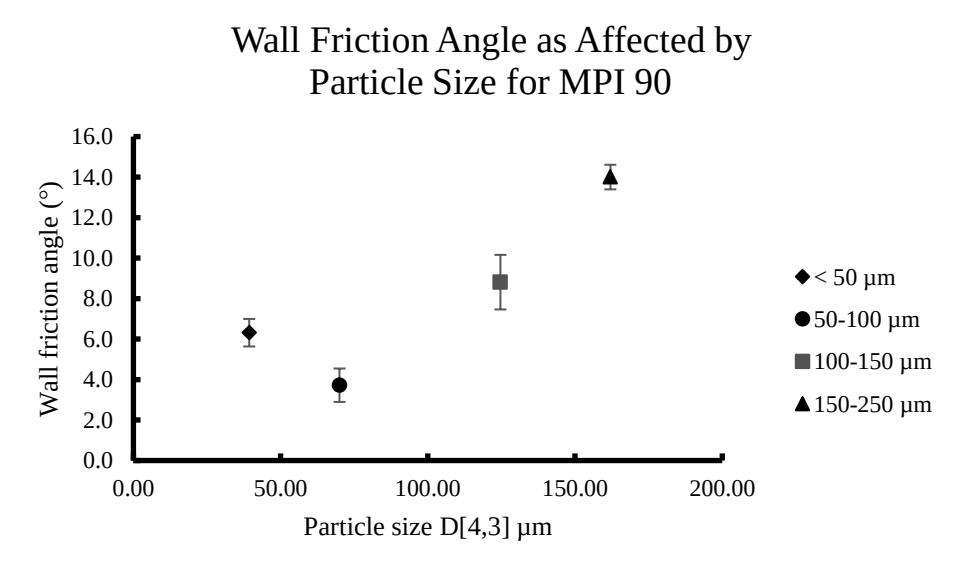


Figure 4.24: Wall friction angle as affected by particle size for MPI 90 powder.

4.4: Conclusion

Overall, flowability decreased in the high protein and high lactose powders when moisture content levels were elevated. Flowability drastically decreased for MPP when moisture content was at ~9% and the high protein powders also had reduced flowability at this specific moisture content.

Differences in powder flowability were not observed when the samples were shear tested at different temperatures. This treatment had little to no significant effect. In the future, research could be completed to see the effect of temperature on these powder samples in conjunction with elevated moisture contents to see if those conditions will impact flowability.

Particle size differences had a significant effect on overall flowability as smaller particles within all of the powder types typically retained higher levels of cohesion. Interestingly, the largest particle size groups (150-250 and >250 μm) also tended to decrease in flowability. There were no contradictions between flow cell and shear cell data when analyzing the effect of particle size, thus further proving that particle size does indeed affect the overall flow nature of a powder. However, wall friction data was not indicative of any trend in relation to particle size and the associated wall friction because after testing, there were no similar trends with the respective particle sizes between any of the protein powders. More research will be needed to ensure this particular test is optimized for high protein and high lactose dairy powders.

In conclusion, the treatments that had the largest effect on enhancing or reducing flowability were the moisture and particle size segregation treatments. Temperature did

not significantly impact overall flowability of the samples. With this in mind, future research would be useful in researching the impact of particle size in conjunction with various moisture contents to determine what combination would optimize overall flowability in a powder processing setting.

4.5: References

ADPI, 2021c. Dairy Products Solids [WWW Document]. ADPI. URL https://www.adpi.org/whey/dairy-products-solids/ (accessed 4.29.22).

Agarwal, S., Beausire, R.L.W., Patel, S., Patel, H., 2015. Innovative Uses of Milk Protein Concentrates in Product Development. J. Food Sci. 80, A23–A29. https://doi.org/10.1111/1750-3841.12807

Analytical Methods | GEA Spray Dryers [WWW Document], n.d. . GEA Eng. Better World. URL https://www.gea.com/en/products/dryers-particle-processing/spray-dryers/food-dairy-products/analytical-methods-dry-milk-products.jsp (accessed 9.18.23).

Armstrong, B., Brockbank, K., Clayton, J., 2014. Understand the Effects of Moisture on Powder Behavior. Chem. Eng. Prog. 110, 25–30.

Carić, M., Akkerman, J.C., Milanović, S., Kentish, S.E., Tamime, A.Y., 2009. Technology of Evaporators, Membrane Processing and Dryers, in: Dairy Powders and Concentrated Products. John Wiley & Sons, Ltd, pp. 99–148. https://doi.org/10.1002/9781444322729.ch3

Early, R., 2012. 17 - Dairy products and milk-based food ingredients, in: Baines, D., Seal, R. (Eds.), Natural Food Additives, Ingredients and Flavourings, Woodhead Publishing Series in Food Science, Technology and Nutrition. Woodhead Publishing, pp. 417–445. https://doi.org/10.1533/9780857095725.2.417

Emery, E., Oliver, J., Pugsley, T., Sharma, J., Zhou, J., 2009. Flowability of moist pharmaceutical powders. Powder Technol. 189, 409–415. https://doi.org/10.1016/j.powtec.2008.06.017

Fitzpatrick, J.J., Barry, K., Cerqueira, P.S.M., Iqbal, T., O'Neill, J., Roos, Y.H., 2007. Effect of composition and storage conditions on the flowability of dairy powders. Int. Dairy J. 17, 383–392. https://doi.org/10.1016/j.idairyj.2006.04.010

Fitzpatrick, J.J., Iqbal, T., Delaney, C., Twomey, T., Keogh, M.K., 2004. Effect of powder properties and storage conditions on the flowability of milk powders with different fat contents. J. Food Eng. 64, 435–444. https://doi.org/10.1016/j.jfoodeng.2003.11.011

Foster, K.D., Bronlund, J.E., (Tony) Paterson, A.H.J., 2005. The prediction of moisture sorption isotherms for dairy powders. Int. Dairy J. 15, 411–418. https://doi.org/10.1016/j.idairyj.2004.08.003

Fu, X., Huck, D., Makein, L., Armstrong, B., Willen, U., Freeman, T., 2012. Effect of particle shape and size on flow properties of lactose powders. Particuology, Advances in Characterization and Modeling of Particulate Processes 10, 203–208. https://doi.org/10.1016/j.partic.2011.11.003

Greenspan, L., 1977. Humidity Fixed Points of Binary Saturated Aqueous Solutions. J. Res. Natl. Bur. Stand. Sect. Phys. Chem. 81A, 89–96. https://doi.org/10.6028/jres.081A.011

Hare, C., Ghadiri, M., 2013. The influence of aspect ratio and roughness on flowability. AIP Conf. Proc. 1542, 887–890. https://doi.org/10.1063/1.4812074

Havea, P., Baldwin, A.J., Carr, A.J., 2009. Specialised and Novel Powders, in: Dairy Powders and Concentrated Products. John Wiley & Sons, Ltd, pp. 268–293. https://doi.org/10.1002/9781444322729.ch8

Hazlett, R., Schmidmeier, C., O'Mahony, J.A., 2021. Approaches for improving the flowability of high-protein dairy powders post spray drying – A review. Powder Technol. 388, 26–40. https://doi.org/10.1016/j.powtec.2021.03.021

Iqbal, T., Fitzpatrick, J.J., 2006. Effect of storage conditions on the wall friction characteristics of three food powders. J. Food Eng. 72, 273–280. https://doi.org/10.1016/j.jfoodeng.2004.12.007

Juliano, P., Barbosa-Cánovas, G.V., 2010. Food powders flowability characterization: theory, methods, and applications. Annu. Rev. Food Sci. Technol. 1, 211–239. https://doi.org/10.1146/annurev.food.102308.124155

Kamath, S., Puri, V.M., Manbeck, H.B., 1994. Flow property measurement using the Jenike cell for wheat flour at various moisture contents and consolidation times. Powder Technol. 81, 293–297. https://doi.org/10.1016/0032-5910(94)02888-5

Lumay, G., Traina, K., Boschini, F., Delaval, V., Rescaglio, A., Cloots, R., Vandewalle, N., 2016. Effect of relative air humidity on the flowability of lactose powders. J. Drug Deliv. Sci. Technol. 35, 207–212. https://doi.org/10.1016/j.jddst.2016.04.007

Martin, G.J.O., Williams, R.P.W., Dunstan, D.E., 2010. Effect of manufacture and reconstitution of milk protein concentrate powder on the size and rennet gelation behaviour of casein micelles. Int. Dairy J. 20, 128–131. https://doi.org/10.1016/j.idairyj.2009.08.007

Mistry, V.V., Hassan, H.N., 1991. Delactosed, High Milk Protein Powder. 1. Manufacture and Composition1. J. Dairy Sci. 74, 1163–1169. https://doi.org/10.3168/jds.S0022-0302(91)78269-6

Murrieta-Pazos, I., Gaiani, C., Galet, L., Cuq, B., Desobry, S., Scher, J., 2011. Comparative study of particle structure evolution during water sorption: Skim and whole milk powders. Colloids Surf. B Biointerfaces 87, 1–10. https://doi.org/10.1016/j.colsurfb.2011.05.001

O'Donoghue, L.T., Murphy, E.G., 2023. Nondairy food applications of whey and milk permeates: Direct and indirect uses. Compr. Rev. Food Sci. Food Saf. 22, 2652–2677. https://doi.org/10.1111/1541-4337.13157

Palmer, K., Parhi, A., Shetty, A., Sunkesula, V., Sharma, P., 2023. Development of methodology for assessing flowability of milk protein powders using shear failure testing device. J. Food Eng. 348, 111450. https://doi.org/10.1016/j.jfoodeng.2023.111450

Rennie, P.R., Chen, X.D., Hargreaves, C., Mackereth, A.R., 1999. A study of the cohesion of dairy powders. J. Food Eng. 39, 277–284. https://doi.org/10.1016/S0260-8774(98)00158-7

Schulze, D., 2008. Powders and bulk solids. Behav. Charact. Storage Flow Springer 22.

Sharma, A., Jana, A.H., Chavan, R.S., 2012. Functionality of Milk Powders and Milk-Based Powders for End Use Applications—A Review. Compr. Rev. Food Sci. Food Saf. 11, 518–528. https://doi.org/10.1111/j.1541-4337.2012.00199.x

Sharma, P., Singh, R. R. B., Singh, A. K., Patel, A. A., & Patil, G. R. (2009). Sorption isotherms and thermodynamics of water sorption of ready-to-use Basundi mix. *LWT-Food Science and Technology*, *42*(1), 441-445.

Sikand, V., Tong, P.S., Roy, S., Rodriguez-Saona, L.E., Murray, B.A., 2011. Solubility of commercial milk protein concentrates and milk protein isolates. J. Dairy Sci. 94, 6194–6202. https://doi.org/10.3168/jds.2011-4477

Silva, J.V.C., O'Mahony, J.A., 2017. Flowability and wetting behaviour of milk protein ingredients as influenced by powder composition, particle size and microstructure. Int. J. Dairy Technol. 70, 277–286. https://doi.org/10.1111/1471-0307.12368

Stavrou, A.G., Hare, C., Hassanpour, A., Wu, C.-Y., 2020. Investigation of powder flowability at low stresses: Influence of particle size and size distribution. Powder Technol. 364, 98–114. https://doi.org/10.1016/j.powtec.2020.01.068

CHAPTER 5

EFFECT OF STORAGE TIME AND TEMPERATURE ON FLOWABILITY OF MILK PROTEIN AND MILK PERMEATE POWDERS

ABSTRACT

Flowability is an extremely critical characteristic for any powder. If a powder becomes less flowable over time, the quality of the powder is typically decreased and the overall ease of processing is decreased as well. In this study, the effect of storage time (0-12 months) and temperature (22°C, 35°C and 42°C) was studied to see what the impact would be on the flow characteristics of protein rich and lactose rich powders.

Throughout storage, milk permeate powder (MPP) was very stable in terms of flowability and physicochemical changes like browning. Milk protein concentrate 80 (MPC 80) and milk protein isolate 90 (MPI 90) samples also retained the "easy-flowing" ($4 < ffc < 10$) flow characteristic over time, regardless of temperature variation (22°C, 35°C and 42°C). Milk protein isolate 85 low lactose (MPI 85 low lactose) remained relatively stable in terms of flowability, but had the most sensitivity to Maillard browning. Storage temperatures of 22°C resulted in the lowest impact on the physicochemical properties, with storage temperatures of 35 and 42°C impacting the each of the powder samples the most. Microbial analysis confirmed that the powders were

high quality and well within the industry limits for microbial load. The overall takeaway from this study is that these powder types are very resilient to temperature and storage conditions when correlated to flowability. Additionally, this study points to the need to control and reduce the storage temperatures to inhibit physicochemical changes to the greatest extent.

5.1: Introduction

Dairy powders are an extremely valuable product throughout the world. They are nutrient dense, highly functional ingredients, and have a long storage life (Agarwal et al., 2015). Dairy powders currently have a global market impact of over $32 billion ("Milk Powder Market Size, Share, Report and Trends 2023-2028," n.d.). Thus, with the incredibly high market demand, dairy powders must be made and stored in a sustainable and efficient manner.

Ideally, high quality dairy powders should experience little to no physicochemical or flowability changes during storage if the storage conditions are highly controlled and optimized. However, achievement of this proves difficult, and some of the common issues that can occur during storage include: Maillard browning, caking and clumping, time consolidation, fat oxidation, and changes in the state of lactose (Mistry and Pulgar, 1996; Phosanam et al., 2021; Stoklosa et al., 2012). While all dairy powder types have the potential to experience some of these issues, it is in fact, the composition of a powder

that is closely related to, and may predict its overall stability during storage (Hogan et al., 2010). Additionally, external temperature or moisture changes, the length of storage, increased gravitational load, exposure to oxygen or a combination of these things can impact powder during storage (Stoklosa et al., 2012). If the final product is modified by these factors during storage, most commonly there will be a reduction in powder quality and overall flowability as well, which is significantly detrimental during processing (Fournaise et al., 2020; Stoklosa et al., 2012; Thomas et al., 2004). Powder must be able to properly flow during processing. If a silo cannot be efficiently emptied as a result of particle bridging or funnel flow action from powder caked to the sides of the equipment, the processing system has to be slowed down or halted to resolve the issue (Schulze, 2008; Thomas et al., 2004).

Identifying the limits by which protein rich and lactose rich powders are susceptible to degradation and reduced flowability is a necessary action. Other researchers have looked into the effects of storage temperature in relation to solubility and chemical changes within high protein powders, and found that solubility tends to decrease when powders are stored at higher temperatures for longer amounts of time (Anema et al., 2006; Le et al., 2011). However, these studies did not look into the effects of time and temperature in relation to flow characteristics. The prior studies in this thesis analyzed the individual factors of increased moisture, increased temperature, and differentiation in particle size in relation to flowability and powder stability. The objective of this study was to analyze the effect of storage time in conjunction with storage temperature to ascertain the resultant effects on the flow characteristics and the physicochemical properties of the protein rich and lactose rich powders.

5.2: Materials and Methods

5.2.1 Milk powders

Four commercial milk powder samples: milk protein concentrate 80 (MPC 80), milk protein isolate 85 low lactose (MPI 85 low lactose), milk protein isolate 90 (MPI 90) and milk permeate powder (MPP) were obtained in 55 lb. pound bags from Idaho Milk Products (Jerome, ID). Two distinct manufacturing lots were received for each powder type and designated as Lot A and Lot B. After receival, each of the powder lots were distributed into individual, hard plastic, airtight containers for each of the storage time points and associated temperatures. Storage in airtight containers prevented moisture transfer during the study.

5.2.2 Storage and temperature equilibration

Powder samples were stored in airtight screw-cap containers at 3 different temperatures (22°C, 35°C, 42°C) for a total of 12 months. Sampling points occurred at 0, 1, 2, 3, 6, and 12 months. Each timepoint had its own sample so the powder samples from future timepoints would not be disturbed.

5.2.3 Rheological analysis

An Anton Paar MCR302e Rheometer (Anton Paar, GmBH, Austria) was used to perform the shear cell tests. The Rheocompass software (V1.30.1227) was used to analyze the data. The samples were all analyzed using the shear cell method found in (Palmer et al., 2023). Samples were analyzed in triplicate.

5.2.4 Bulk density

Samples were analyzed using the Bulk Density method as described in (Palmer et al., 2023). Samples were analyzed in triplicate.

5.2.5 Color analysis

Color analysis was completed using the LAB color space method, using the Colorimeter Konica Minolta CR-400 (Konica Minolta Sensing Inc. Osaka, Japan.) The parameters used were a D65 illuminant, 2^{o} observer angle, and an 8mm aperture port. To analyze the sample, the sample was placed into a clear glass petri dish and the lens was put flat on the bottom of the dish and the measurement was taken. Three individual samples were analyzed, with three measurements per sample.

5.2.6 Microbiological analysis

Microbiological analysis was completed on each powder type using a standard plate count method, and an anerobic and aerobic spore count for both mesophilic and thermophilic spores using a modified procedure based on a method from Murphy (2021). To prepare the sample, 11 g of powder combined with 99 mL of buffer peptone water and stomached for approximately 90 seconds. Serial dilutions were made out to the 5^{th} dilution factor. For the spore plates, a portion of the original diluted powder sample was boiled for 15 minutes and then put directly on ice until cold. Then that portion was put through serial dilutions to be plated. Standard methods agar was used for all plates and spread plating was done for each of the dilution factors 1 through 5. Anerobic conditions were created by placing the inoculated petri dishes in a sealed container containing oxygen absorbing packets. Incubation settings for the standard plate count and both

anerobic and aerobic mesophilic spore count was 35°C for 48 hours. Anerobic and aerobic thermophilic plates were incubated at 55°C for 72 hours. Initial analysis was completed upon receival of powders.

5.2.7 SEM analysis

To determine differences in particle size morphology, particles were analyzed under high vacuum conditions (accelerating voltage: 15 KV, spot size: 2, detector: ETD) using a scanning electron microscope (SEM, FEI Quanta 650 F, Thermo Scientific Quanta, Hillsboro, OR). Powder samples were placed on aluminum stubs secured with carbon tape, flushed with nitrogen for 10 s and sputter-coated with 10 nm of gold and palladium, using a Q 150 V sputter coater (Q 150 V, Quorum technologies, Laughton, East Sussex, UK). Samples were analyzed in single replicates for each powder, for the effect of storage at 22°C and 42°C, for the 3, 6, and 12 month timepoints ($N > 30$).

5.2.8 Statistical analysis

The significant differences and potential interactions due to various treatments were analyzed using a two way ANOVA in OriginPro (2021). The mean values of each parameter were compared for significant differences using Tukey's HSD post Hoc test at a 5% of level of significance.

5.3: Results and Discussion

5.3.1 Physicochemical properties

5.3.1.1 Composition, water activity, bulk density, and particle size

The physico-chemical properties of the powders at the beginning of the storage study are listed in Section 4.3.1.1 and in Table 4.2. The powder samples for this particular study were from the same bulk sample used in the previous experiments.

After 12 months of storage, measurements for loose bulk density and tap bulk density were taken to see if there was any change due to storage time or temperature. The hypothesis was that the bulk density of the powders may change due to the long period of consolidation, because bulk density is reliant on the preceding processing or storage history, and increasing consolidation stress may change the bulk density (Schulze, 2008; Vasilenko et al., 2013). However, regardless of temperature treatment, the 12 month samples either had statistically similar or lower bulk density measurements for each of the four powder types, compared to samples from month 0 (Table 5.1). This reverse in expected bulk density could be attributed to the fact that these powder samples were not overly consolidated while in storage. Since the powders were individually packaged in hard plastic containers, the only consolidation action on these samples was the weight of the powder itself and gravitational force. Thus, there was no extreme consolidation of the powder particles that would reduce the final bulk density.

Table 5.1: Comparison of bulk density values for powders at different time and temperature points.

Powders	**0 Months** Bulk density (g/mL) Loose bulk density	Temperature	**12 Months** Bulk density (g/mL) Loose bulk density
MPC 80	$0.295\pm3.2x10^{-3a}$	22°C	$0.266\pm3.2x10^{-3b}$
		35°C	$0.275\pm1.7x10^{-3b}$
		42°C	$0.266\pm1.2x10^{-3b}$
MPI 85 low lactose	$0.313\pm.49x10^{-3a}$	22°C	$0.303\pm3.3x10^{-3b}$
		35°C	$0.308\pm.88x10^{-3ab}$
		42°C	$0.305\pm.33x10^{-3ab}$
MPI 90	$0.297\pm2.9x10^{-3a}$	22°C	$0.290\pm1.7x10^{-3b}$
		35°C	$0.294\pm.33x10^{-3ab}$
		42°C	$0.297\pm.66x10^{-3ab}$
MPP	$0.764\pm6.2x10e^{-3ab}$	22°C	$0.765\pm2.7x10^{-3a}$
		35°C	$0.747\pm4.2x10^{-3b}$
		42°C	$0.754\pm.58x10^{-3ab}$

Different lowercase superscripts show significant differences ($P<0.05$) within the row.

5.3.2 Effect of storage time and temperature on flowability

5.3.2.1 MPP

MPP is naturally a very flowable powder. Additionally, it has a wide range of particle sizes present within the powder mass. As a result, the flowability patterns tend to

be very random and have high variation in *ffc*, even at low loads of 1 kPa. Some measurements for Lot B had samples that were so flowable, that an *ffc* value could not be obtained nor measured because a yield locus could not be established as discussed in chapter 3. This inconsistency in flowability is demonstrated in Figure 5.1. This powder was classified as "easy flowing" or "free flowing" for the entire duration of the 12 month study, regardless of time or temperature treatment.

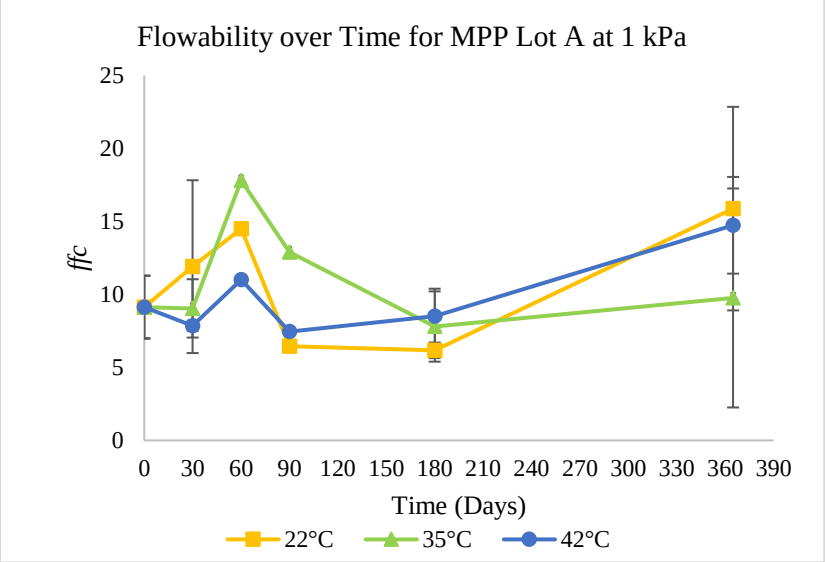


Figure 5.1: Flowability over time for MPP Lot A at 1 kPa.

5.3.2.2 MPC 80

The MPC 80 samples did not have a significant change in flowability due to temperature or storage. At 1 kPa, this sample had relatively the same flowability, regardless of treatment. In figure 5.2a, a slight increase in flowability can be noted for Lot A powder samples held at 22 and 42°C. Powder held at 35°C retained similar flowability for the duration of the study ($P<0.05$).

The sample designated as Lot B also had similar flowability results. The baseline *ffc* value at month 0 was higher than the *ffc* value for Lot A, but throughout storage, flowability did not decrease or increase significantly (Figure 5.2b). However, while this was not a significant change ($P>0.05$) in this lot, samples held at 35°C gradually became less flowable over time compared to powder held at 22°C.

Overall, there was little to no change in flowability for MPC 80 after 12 months of storage at three different temperatures. Over time and regardless of change in temperature, this powder retained its fundamental flowability characteristics. These results were desirable. This powder was classified as “cohesive” for Lot A and “easy-flowing” for Lot B. The difference in baseline flowability between lots could be due to the slight variations in sample composition. These powders neither decreased or increased in flowability significantly. This lack of impact from storage time and temperature demonstrates that this powder type is stable in terms of flow characteristics.

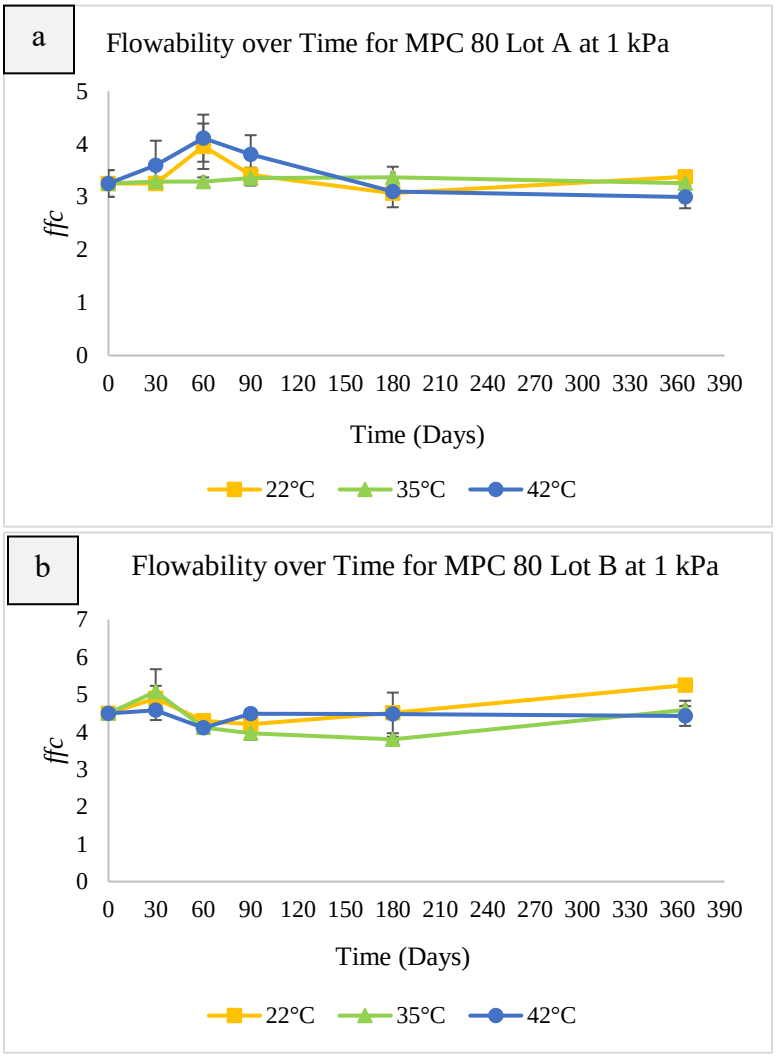


Figure 5.2: Flowability over time for MPC 80 at 1 kPa. a – Lot A. b – Lot B.

5.3.2.3 MPI 85 low lactose

MPI 85 low lactose powder had similar flow characteristics regardless of the lot. Each of the powders were initially classified as “easy flowing” at month 0, “cohesive” at month 6, and by month 12, flowability had returned to the “easy flowing” state. This

pattern was similar for both powder lots. The greatest variation in flowability occurred at month 3, where flowability increased slightly for all 3 samples. This may be due to changes within the powder itself, or it may be due to human error, as there were multiple people conducting the experiment at this time. Additionally, powder stored at 42°C on average was recorded as the most flowable, followed by the 22°C samples next and then the 35°C samples being the least flowable, relative to the other samples (Figure 5.3). Statistically, there was no significant difference between samples stored at different temperatures. There was also no significant interaction between temperature and storage time in relation to the flowability of the powder samples ($P > 0.05$). Once again, this lack of drastic change in flowability is preferable to powder that becomes unstable or less flowable over time.

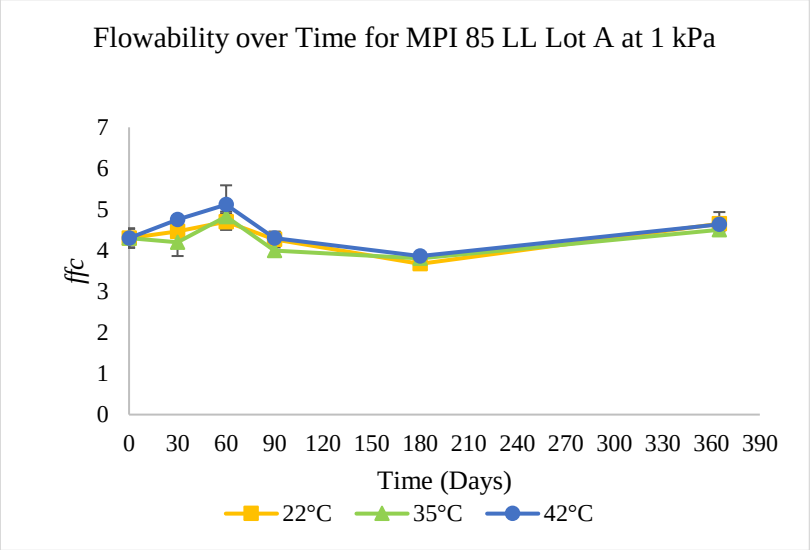


Figure 5.3: Flowability over time for MPI 85 low lactose Lot A at 1 kPa.

5.3.2.4 MPI 90

The MPI 90 samples did not have a significant change in flowability due to temperature or storage (Figure 5.4). Over the 12 month period, there was no significant impact in flowability due to temperature and in regards to storage time, only month 1 and month 6 were significantly different in flowability classification. Samples from month 1 were classified as "easy flowing," while samples month 6 were classified as "cohesive." The baseline flowability for this powder type was "easy-flowing." This powder remained "easy flowing" throughout all time points, unlike the 6 month MPC 80 and MPI 85 low lactose samples that were recorded as "cohesive" before returning back to "easy flowing" at the end of the storage study.

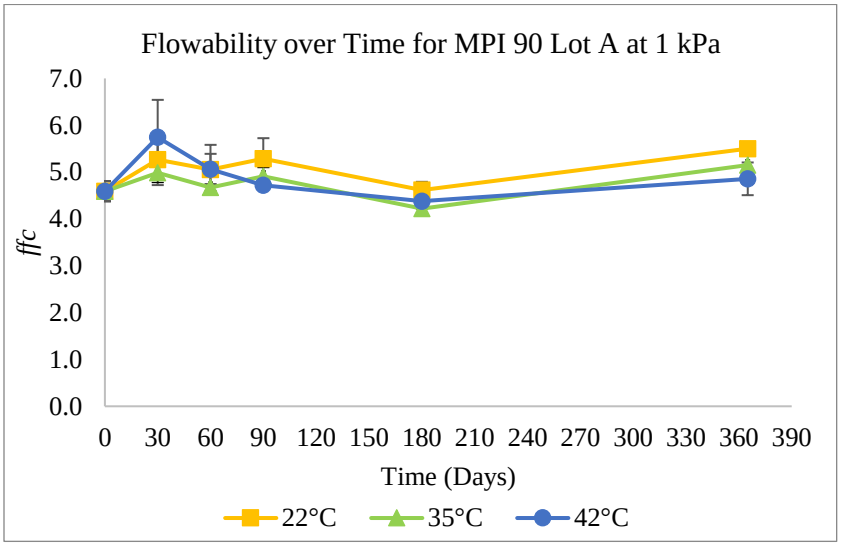


Figure 5.4: Flowability over time for MPI 90 Lot A at 1 kPa.

5.3.3 SEM analysis of different powder particle sizes

The samples were analyzed using SEM to determine if there were any changes in particle morphology and other physical characteristics due to the temperature and time variables. Examination of each of the respective powder samples showed no obvious changes to the powder particles over time. Temperature also did not seem to have a highly significant effect at the particle level. Figures 5.5 - 5.8 below showcase the similarities in particle nature between samples stored at 22 and 42°C for 3, 6 and 12 months. Each of the powders were imaged at 500X magnification in order to retain an overall image of the sample as well as be able to identify potential physical characteristics. Variation in the contrast and brightness of the images is due to sample differences and different exposure settings on the scanning electron microscope.

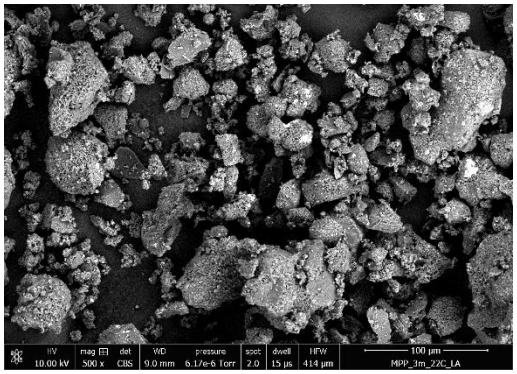
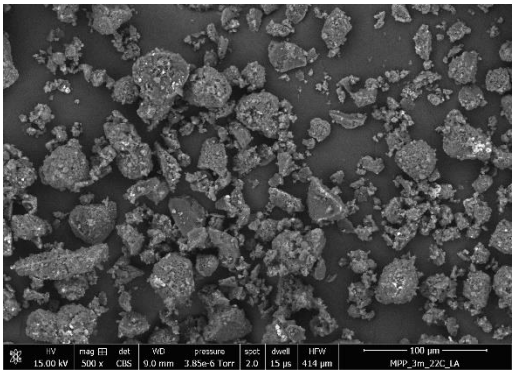
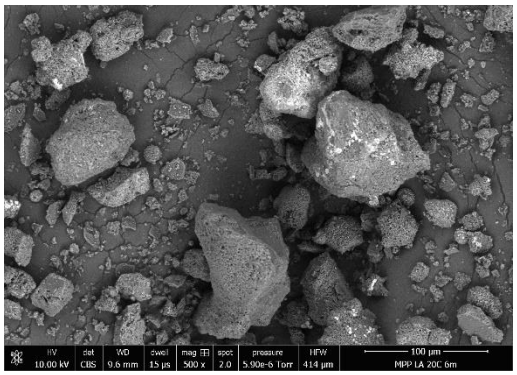
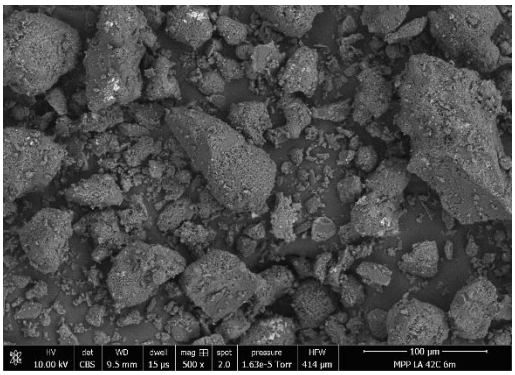
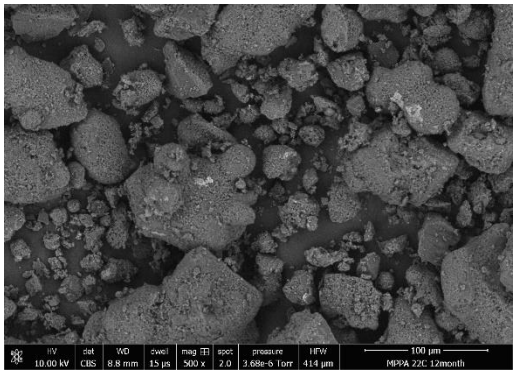
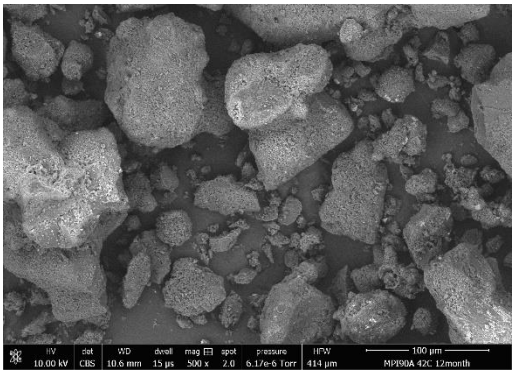
	22°C	42°C
3 M		
6 M		
12 M		

Figure 5.5: A SEM image comparison between different MPP samples as affected by different storage times and temperatures.

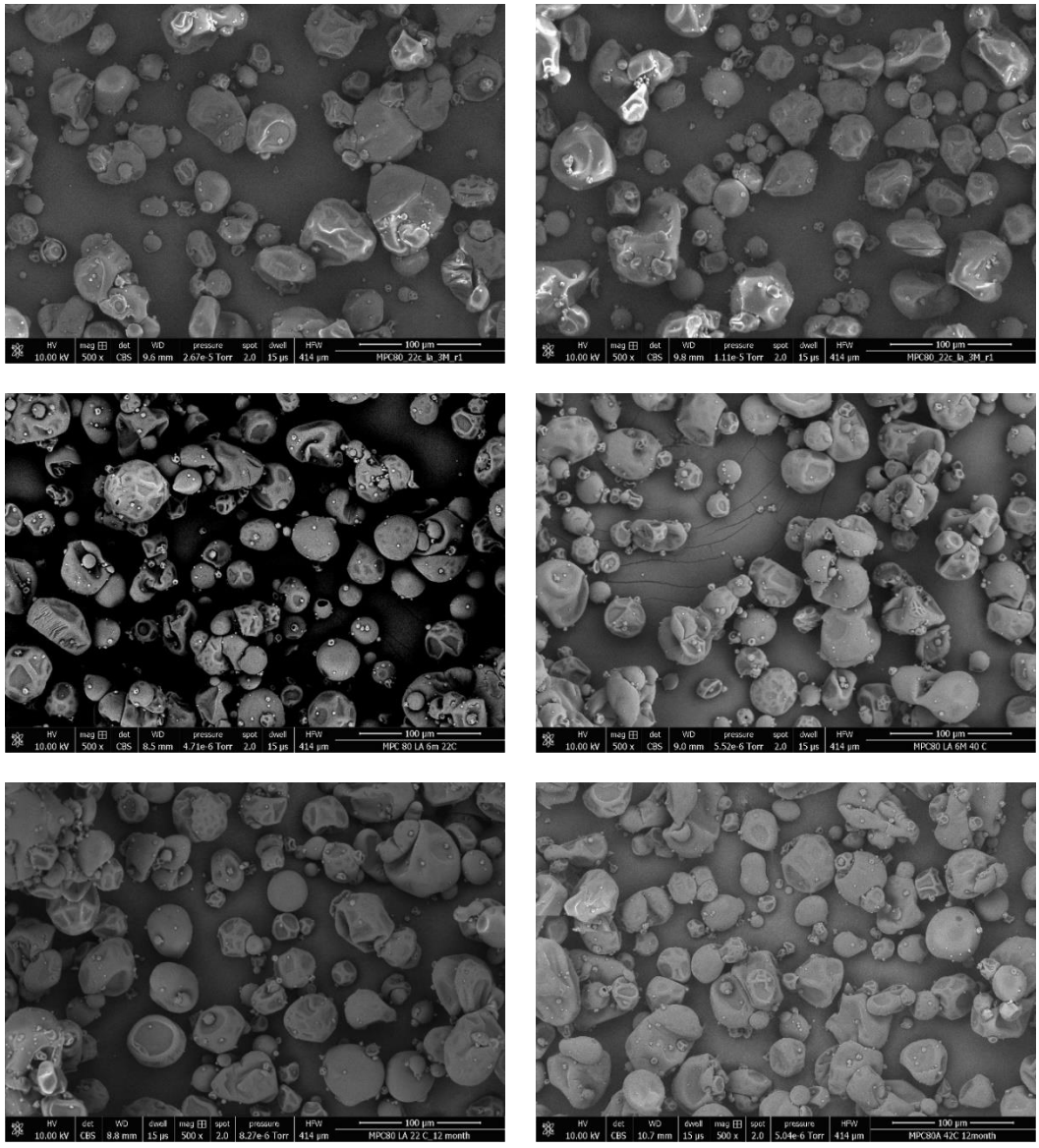


Figure 5.6: A SEM image comparison between different MPC 80 samples as affected by different storage times and temperatures.

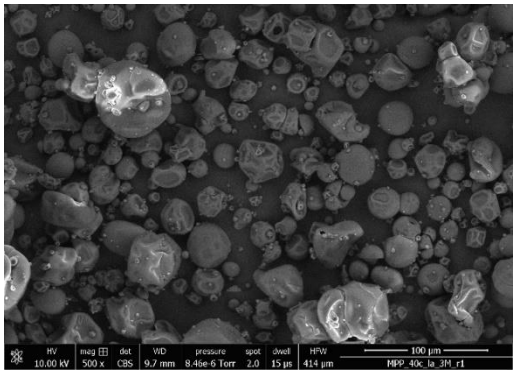
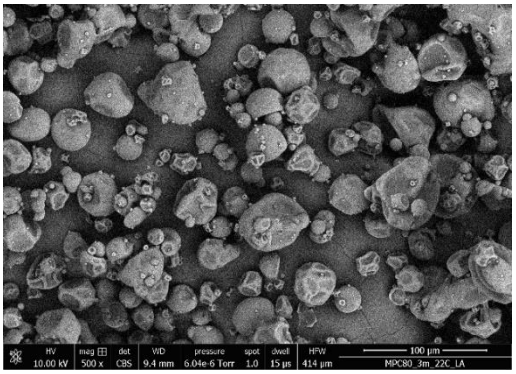
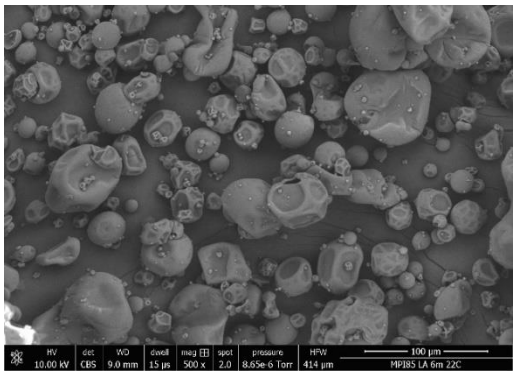
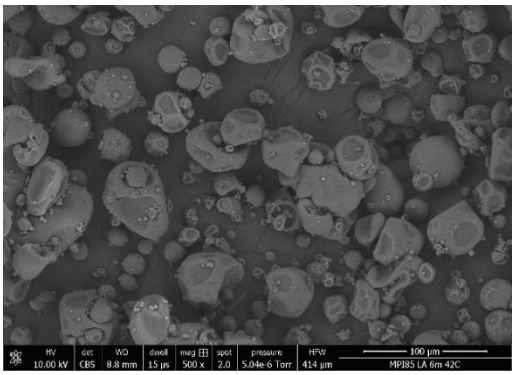
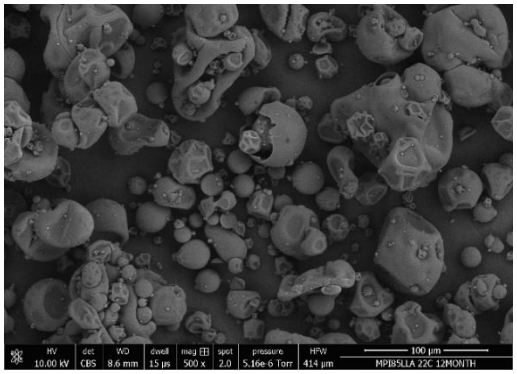
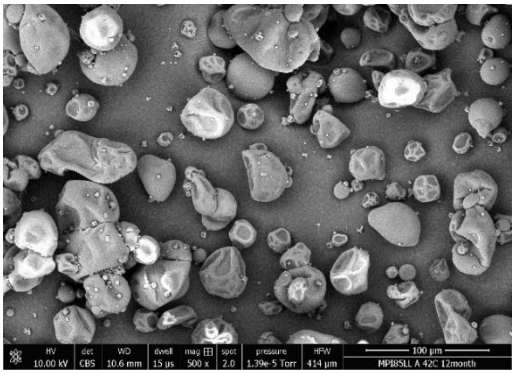
	22°C	42°C
3 M		
6 M		
12 M		

Figure 5.7: A SEM image comparison between different MPI 85 low lactose samples as affected by different storage times and temperatures.

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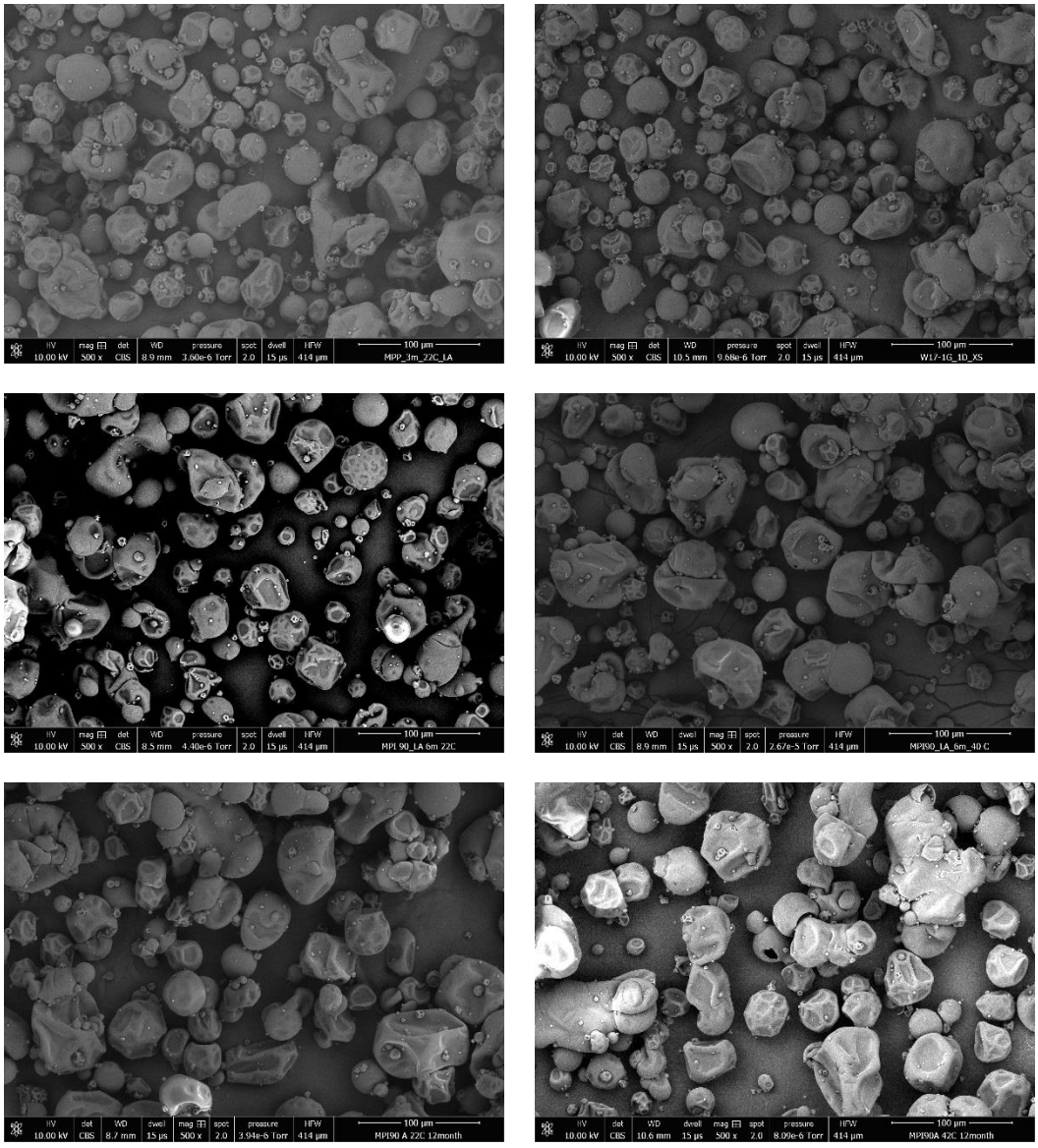


Figure 5.8: A SEM image comparison between different MPI 90 samples as affected by different storage times and temperatures.

5.3.4 Effect of storage time and temperature on physicochemical characteristics

5.3.4.1 Color analysis

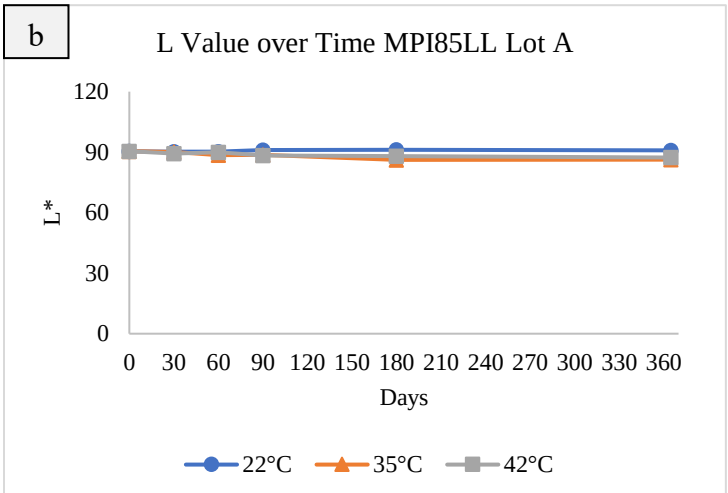
Analysis of the color change of the samples throughout storage was completed using the LAB color space method. Using a colorimeter, the powder samples were analyzed for the overall lightness of the sample (L*), the red/green value of the sample (a*) and the blue/yellow value (b*). The closer the L* values are to 100, the lighter the sample is, and the higher level of white values are present. As the value decreases from 100, the darker the sample is becoming. A positive “a*” value shifts the color towards red and a positive “b*” value shifts the color toward yellow.

The sample with the highest degree of color change in all aspects was MPI 85 low lactose. This color change occurred due to the Maillard browning within the sample. The MPI 85 low lactose sample was particularly susceptible to this phenomena because of the higher levels of glucose and galactose in the powder, which have been found to react at a quicker rate with the available protein than non-hydrolyzed lactose (Naranjo et al., 2013). To make a low lactose powder, the lactase enzyme is added to the retentate and the lactose is hydrolyzed (Schulz and Rizvi, 2023). Once the powder is spray dried, the powder has minimal amounts of lactose and then the residual reducing sugars of glucose and galactose. These reducing sugars are prone to browning over time and with higher levels of heat. Thus, powder samples held at 35 and 42°C changed in color significantly more than the samples held at 22 °C according to each of the LAB measurement values ($P<0.05$). Additionally, there was a significant interaction between storage time and temperature in relation to the L*, a* and b* color change in MPI 85 low lactose, meaning

that both factors impacted the degradation of the powder sample (P<0.05). Figure 5.9a shows the variation in color for the 42°C sample at 1, 3, 6, and 12 months (samples shown from left to right). At 1 month, the color was whiter and had a lighter tint overall. At 12 months, the powder was darker and more yellowish-brown in color. These findings area confirmed in Figure 5.9b, c, and d, where each show the meaningful changes in the respective LAB values (P<0.05) .

a

b



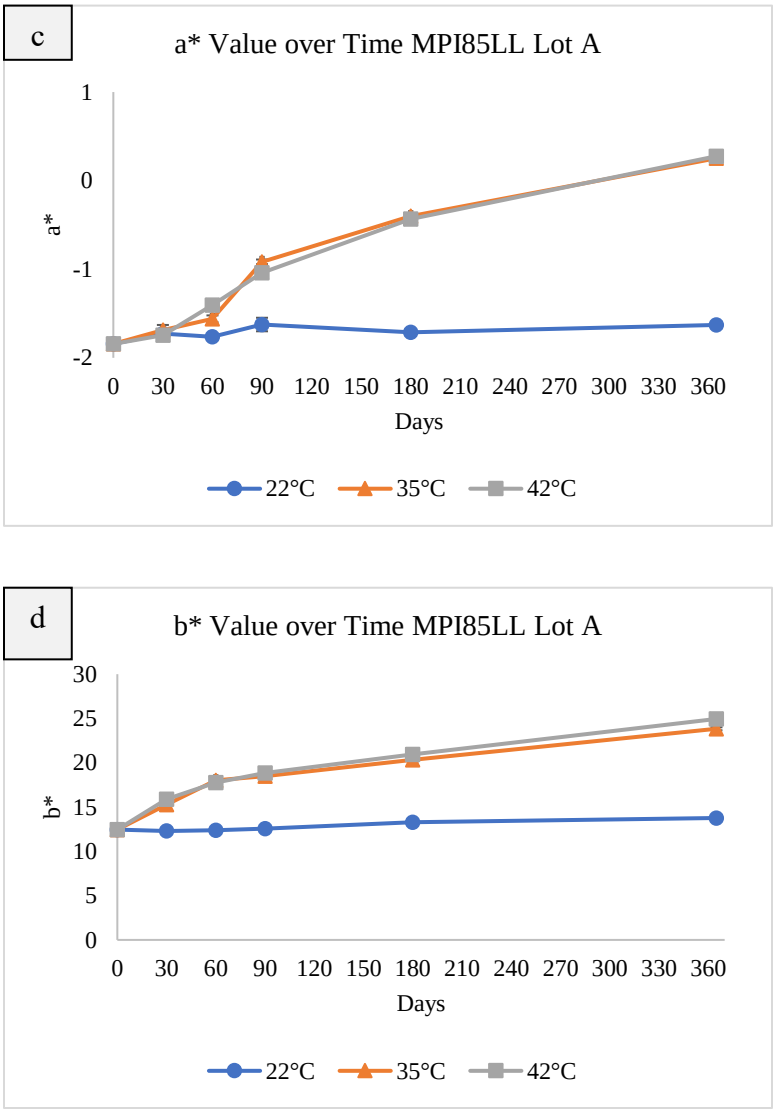
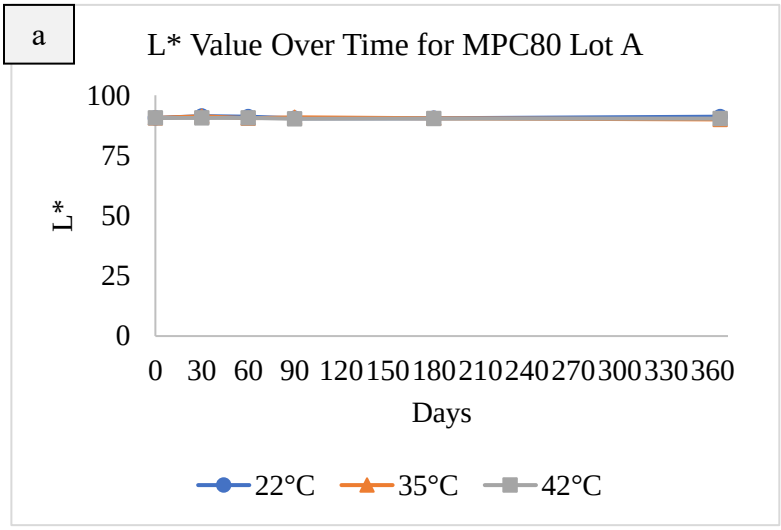


Figure 5.9: (a) Image of MPI 85 low lactose powder held at 42°C for 4 different timepoints. (b) A decreasing trend in the L values in relation to time and temperature. (c) An increasing trend in the a* values in relation to time and temperature. (d) An increasing trend in the b* values in relation to time and temperature.*

MPC 80 and MPI 90 had very similar baseline measurements for color, and as a result, similar color degradation patterns over the duration of 12 months. For the MPC 80 samples, there was a statistically significant difference in overall browning from month 1 to month 12, and in respect to temperature, the samples held at 22°C were significantly different lighter in color compared to samples held at 42°C ($P<0.05$). However, regardless of statistical significance for the L* values, the overall lightness difference from a visual standpoint was very minor (Figure 5.10a). Yellowing, however, was readily evident between samples held at 22°C and those held at 35 and 42°C (Figure 5.10b).

Even though both MPC 80 and MPI 90 experienced browning and became more yellow over time and at temperatures 35 and 42°C, from visual observation and as seen in the data, these powder samples were not yellowed to the extent seen in the majority of the MPI 85 low lactose samples. This is expected because there is no hydrolyzed lactose present in these samples.



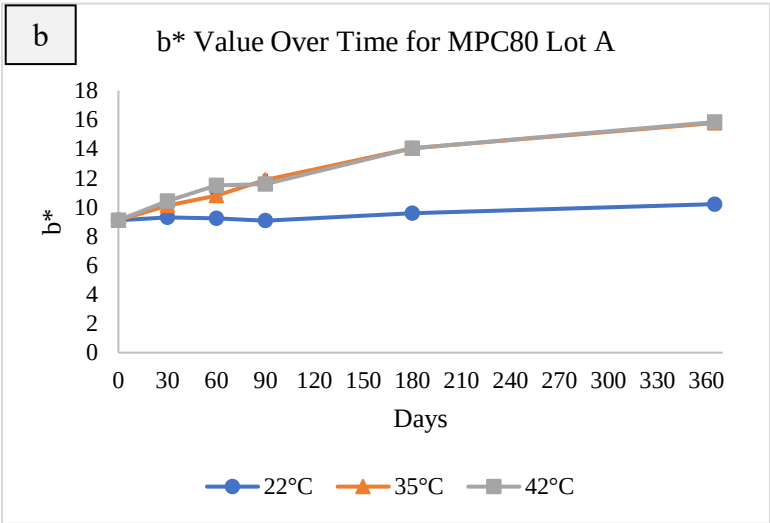


Figure 5.10: (a) A fairly stable trend for the L values in relation to time and temperature for MPC 80. (b) An increasing trend in the b* values in relation to time and temperature for MPC 80.*

One of the biggest compositional differences in MPP is that it is mostly lactose, compared to the other samples that had very high levels of protein and very little lactose. Additionally, the moisture content of MPP is much less than a high protein milk powder. Over the 12 month period, the MPP samples remained the relatively same lightness and yellowness color, with a slight darkening of the sample held at 35°C and 42°C temperatures compared to the sample held at 22°C ($P>0.05$). Interestingly, for this particular sample, the highest degree of color shift occurred with the red/green value (a*), as the powder began shift from green to red values (-a). So over time, and with exposure

to the higher temperatures of 35 and 42°C , the powder must have experienced Maillard browning because there is a significant darkening of the sample ($P<0.05$). Interestingly, the samples held at 35°C had slightly more browning action than those held at 42°C, as seen in the slight increase in a* value ($P<0.05$) (Figure 5.11). While this browning phenomena was mostly imperceptible to the eye, there was a decrease in the natural yellowish green hue of the lactose-rich, MPP powder. This is particularly telling of the compositional impact because when compared to MPC 80 and MPI 90, the biggest shifts for these powders occurred for the b* and L* values, with very minor shifts in the a* values overall.

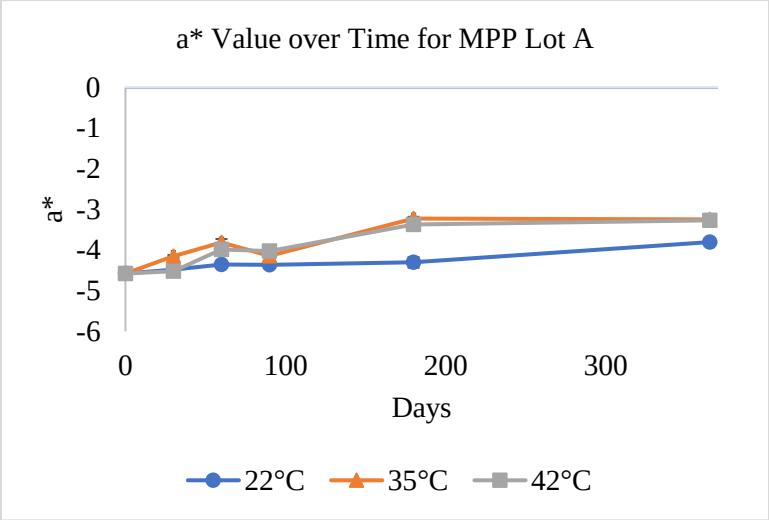
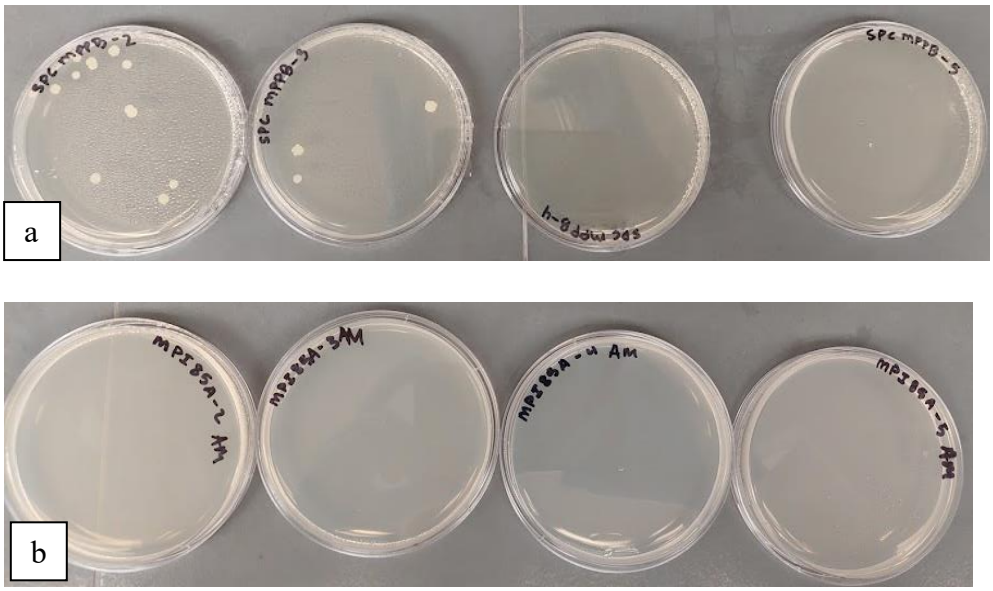


Figure 5.11: An increasing trend in the a values in relation to time and temperature for MPP.*

5.3.4.2 Microbiological analysis

Microbiological testing was completed for the powders upon receival at month 0. Six different analyses were performed as described in section 5.2.6. It was determined prior to testing, that if CFU/g counts were high, relative to the maximum limit defined by industry, then microbiological analysis would continue over time at 6 months and 12 months. However, the analysis did not reveal high microbiological counts for the specific powders, therefore microbiological testing was concluded for each respective powder type at 1 month. Results indicated that at a dilution factor of 3, the CFU/g was less than 10000 for each of the different analyses for the various powder samples (Figure 5.12).



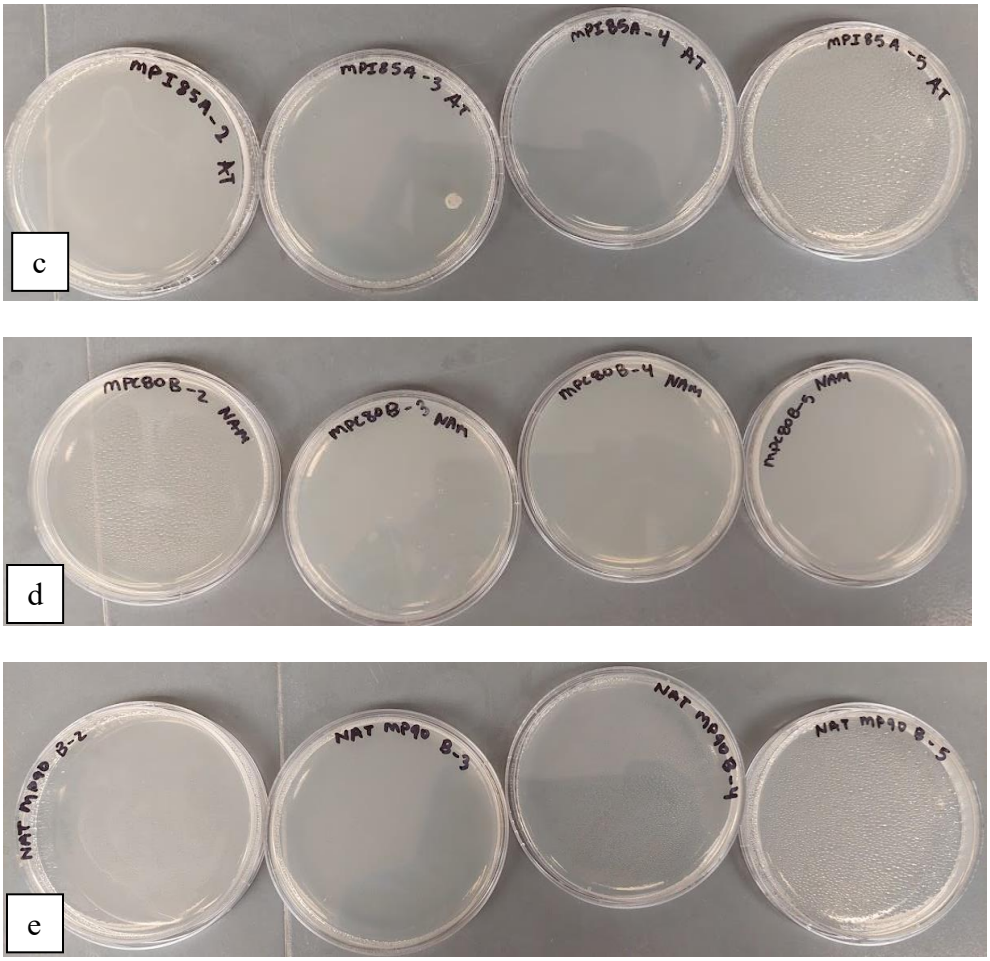


Figure 5.12: Selected images of microbial results from respective test methods. (a) Standard plate count for MPP Lot B. (b) Aerobic mesophilic spore count for MPI 85 low lactose Lot A. (c) Aerobic thermophilic spore count for MPI 85 low lactose Lot A. (d) Anaerobic mesophilic spore count for MPC 80 Lot B. (e) Anaerobic thermophilic spore count for MPI 90 lot B.

5.4 Conclusion

This study revealed the effects of storage time and temperature on the flowability of protein rich and lactose rich powders. The findings showed that MPC 80 and MPI 90 powders maintained stable flowability over the 12 month period, regardless of the temperature they were stored at. These powders were also fairly stable in retention of physicochemical properties. This overall stability highlights the reliability of these powder types for various applications. MPI 85 low lactose power was found to be susceptible to higher levels of Maillard browning. However, the flow characteristics of this powder were fairly stable, because even though there was some *ffc* variation throughout storage, overall, the powder retained its “easy-flowing” features. The microbial analysis revealed low counts, thus confirming that the product was high quality and not prone to microbial degradation when stored appropriately. In conclusion, this study demonstrated that these protein rich and lactose rich powders have the ability to retain the desired flowability, even when held in various storage conditions. The most problematic temperatures were 35 and 42°C because at this temperature, high levels of browning were induced. However, when the powder was held at 22°C, the samples were less reactive as a whole.

5.5 References

Agarwal, S., Beausire, R.L.W., Patel, S., Patel, H., 2015. Innovative Uses of Milk Protein Concentrates in Product Development. J. Food Sci. 80, A23–A29. https://doi.org/10.1111/1750-3841.12807

Anema, S.G., Pinder, D.N., Hunter, R.J., Hemar, Y., 2006. Effects of storage temperature on the solubility of milk protein concentrate (MPC85). Food Hydrocoll., 7th International Hydrocolloids Conference 20, 386–393. https://doi.org/10.1016/j.foodhyd.2005.03.015

Fournaise, T., Burgain, J., Perroud, C., Scher, J., Gaiani, C., Petit, J., 2020. Impact of formulation on reconstitution and flowability of spray-dried milk powders. Powder Technol. 372, 107–116. https://doi.org/10.1016/j.powtec.2020.05.085

Hogan, S.A., Famelart, M.H., O'Callaghan, D.J., Schuck, P., 2010. A novel technique for determining glass–rubber transition in dairy powders. J. Food Eng. 99, 76–82. https://doi.org/10.1016/j.jfoodeng.2010.01.040

Le, T.T., Bhandari, B., Deeth, H.C., 2011. Chemical and Physical Changes in Milk Protein Concentrate (MPC80) Powder during Storage. J. Agric. Food Chem. 59, 5465–5473. https://doi.org/10.1021/jf2003464

Milk Powder Market Size, Share, Report and Trends 2023-2028 [WWW Document], n.d. URL https://www.imarcgroup.com/milk-powder-processing-plant (accessed 10.4.23).

Mistry, V.V., Pulgar, J.B., 1996. Physical and storage properties of high milk protein powder. Int. Dairy J. 6, 195–203. https://doi.org/10.1016/0958-6946(95)00002-X

Murphy, S.I., Kent, D., Skeens, J., Wiedmann, M., Martin, N.H., 2021. A standard set of testing methods reliably enumerates spores across commercial milk powders. J. Dairy Sci. 104, 2615–2631. https://doi.org/10.3168/jds.2020-19313

Naranjo, G.B., Pereyra Gonzales, A.S., Leiva, G.E., Malec, L.S., 2013. The kinetics of Maillard reaction in lactose-hydrolysed milk powder and related systems containing carbohydrate mixtures. Food Chem. 141, 3790–3795. https://doi.org/10.1016/j.foodchem.2013.06.093

Phosanam, A., Chandrapala, J., Zisu, B., Adhikari, B., 2021. Storage stability of powdered dairy ingredients: a review. Dry. Technol. 39, 1529–1553. https://doi.org/10.1080/07373937.2021.1910955

Schulz, P., Rizvi, S.S.H., 2023. Hydrolysis of Lactose in Milk: Current Status and Future Products. Food Rev. Int. 39, 2875–2894. https://doi.org/10.1080/87559129.2021.1983590

Schulze, D., 2008. Powders and bulk solids. Behav. Charact. Storage Flow Springer 22.

Stoklosa, A.M., Lipasek, R.A., Taylor, L.S., Mauer, L.J., 2012. Effects of storage conditions, formulation, and particle size on moisture sorption and flowability of powders: A study of deliquescent ingredient blends. Food Res. Int. 49, 783–791. https://doi.org/10.1016/j.foodres.2012.09.034

Thomas, M.E.C., Scher, J., Desobry-Banon, S., Desobry, S., 2004. Milk Powders Ageing: Effect on Physical and Functional Properties. Crit. Rev. Food Sci. Nutr. 44, 297–322. https://doi.org/10.1080/10408690490464041

Vasilenko, A., Koynov, S., Glasser, B.J., Muzzio, F.J., 2013. Role of consolidation state in the measurement of bulk density and cohesion. Powder Technol. 239, 366–373. https://doi.org/10.1016/j.powtec.2013.02.011

CHAPTER 6

CONCLUSION

This comprehensive study presents the flow characteristics, the physical and chemical stability, and the functional characteristics of three protein rich and one lactose rich powder. Initial examination of the powders using the MCR302e Rheometer was not successful. This led to the creation of a specific shearing methodology, specifically for protein rich milk powders. It was discovered that stick-slip occurrences could be prevented and minimized when pre-shear and shear normal stresses were reduced and the shear speed was optimized.

In-depth analysis of the critical factors that affect flowability demonstrated that moisture content and particle size play the largest role in diminishing or increasing flowability for these powders. Moisture content at 9% induced caking and increased cohesion within the powder samples. When analyzing the flowability of segregated particle size samples, the smallest particles and the largest particles typically had greater cohesion and were less prone to flow. In general, temperature variation did induce a significant effect on the flowability of the powders in general temperature testing, nor in the temperature testing associated with the storage study.

Overall, flowability did not change drastically for any of the powder samples throughout the 12 month storage study. Nevertheless, the physiochemical property of color was altered due to temperature and storage time. MPI 85 low lactose powder

samples were the most volatile of the powder types and had the most browning. Powders held at 22°C were less reactive and had less color change compared to the powder stored at 35 and 42°C.

While milk protein concentrates, milk protein isolates, and milk permeate powder may have different compositions and physical characteristics, these powders are fairly stable, regardless of the external variables. Future research may benefit from focusing on the optimization of flowability when combining the variables of particle size and moisture content. This combined with previous and current data has the potential to further enhance the dairy industry's understanding of protein rich and lactose rich powder processing.

APPENDICES

APPENDIX A: Supplementary Figures for Chapters 4 and 5

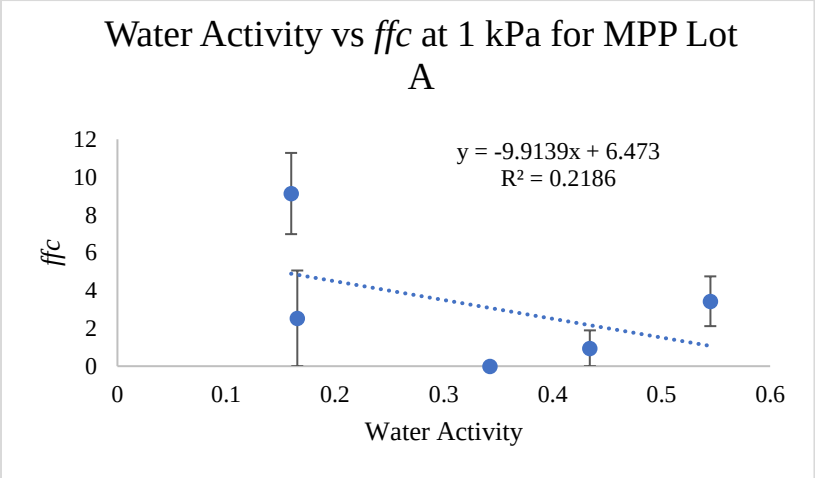


Figure A-1: Water activity vs average ffc values of different equilibrated MPP powders (Lot A). Obtained at 1 kPa

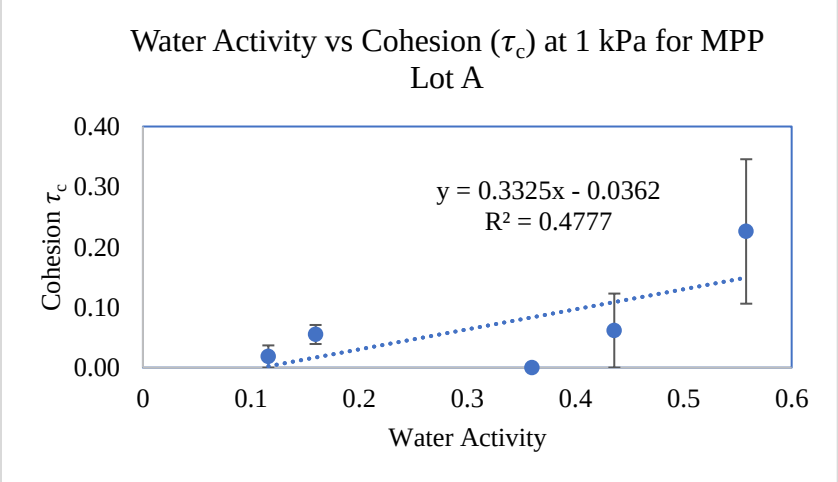
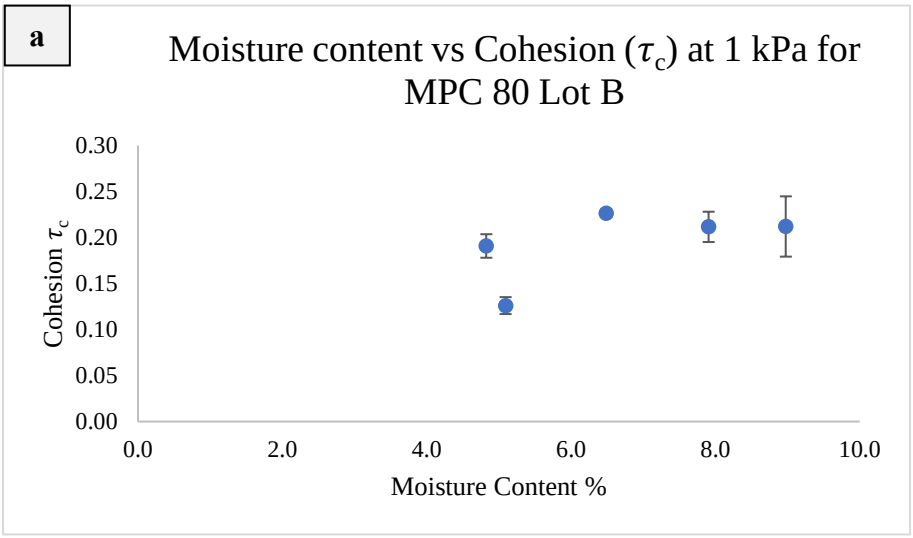


Figure A-2: Water activity vs average cohesion τc values of different equilibrated MPP powders (Lot A). Obtained at 1 kPa



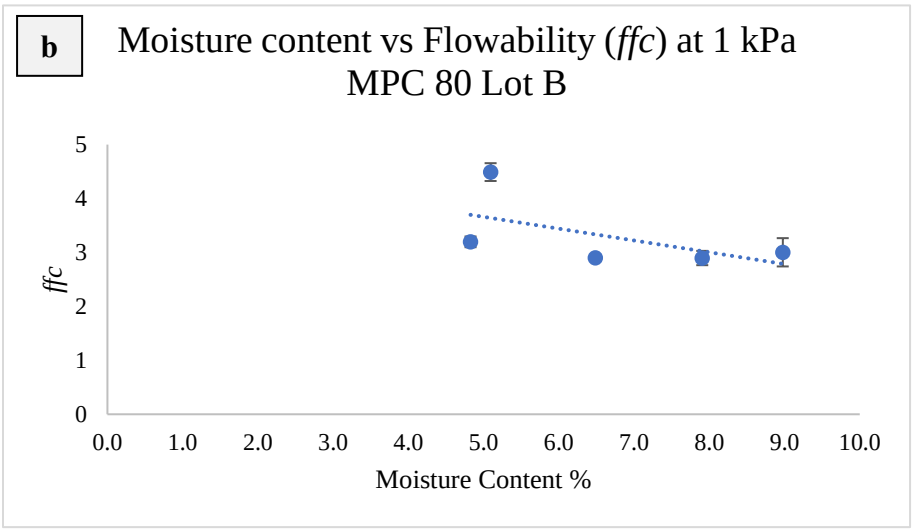


Figure A-3: Comparison of MPC 80 Lot B flowability as impacted by moisture content.

(a) – level of flowability measured by τ_c. (b) – level of flowability measured by ffc.

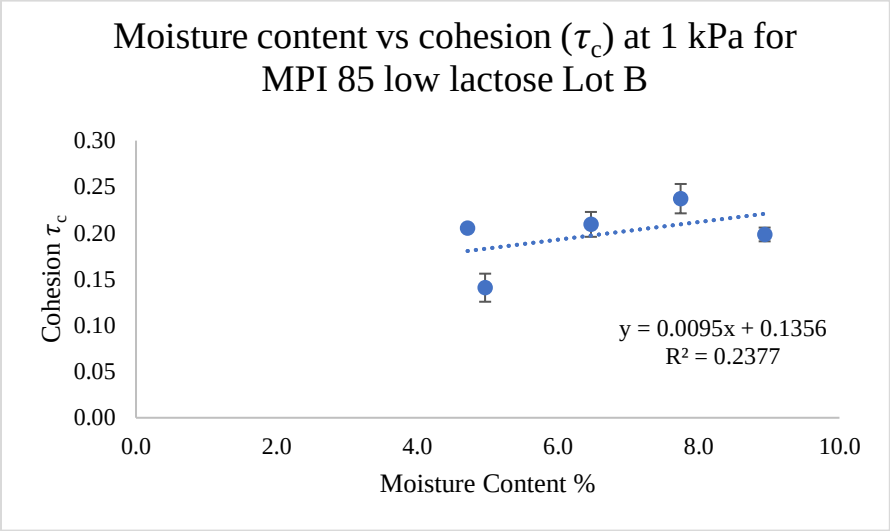


Figure A-4: Moisture content vs cohesion (τ_c) for MPI 85 low lactose Lot B.

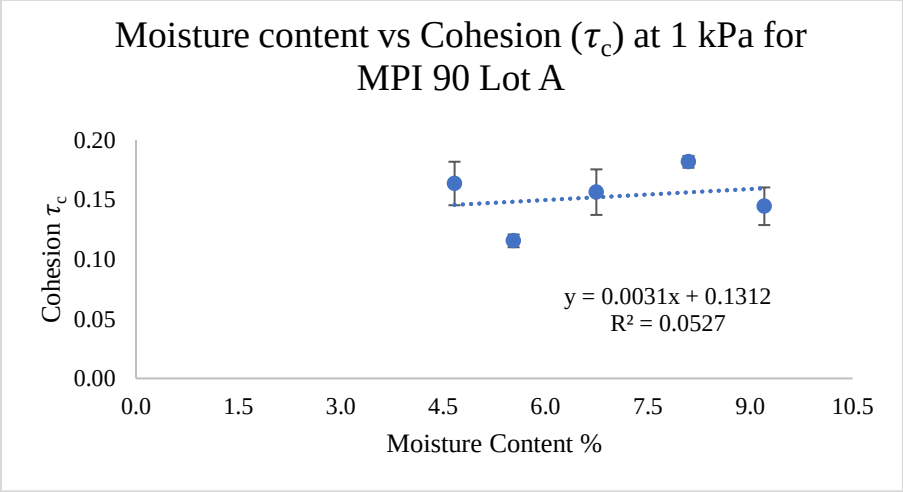


Figure A-5: Moisture content vs cohesion (τ_c) for MPI 90 Lot A.

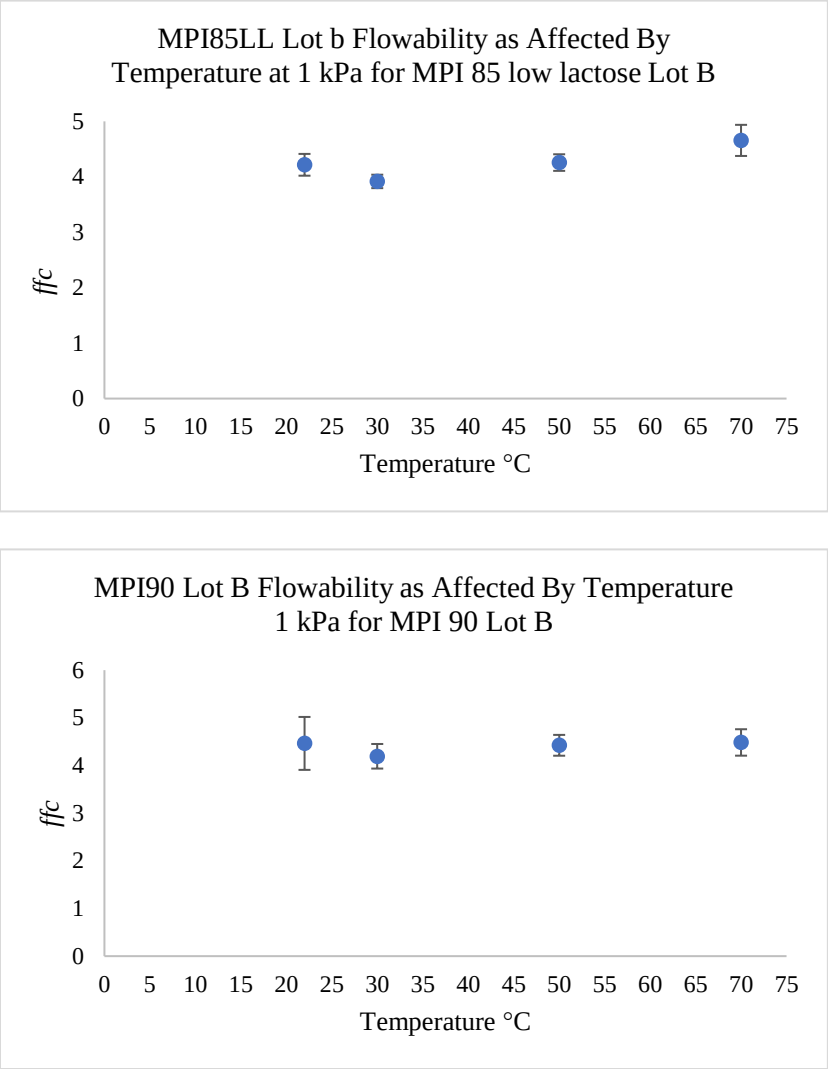


Figure A-6: *ffc* vs temperature for MPI 85 low lactose Lot B (a) and MPI 90 Lot B (b).

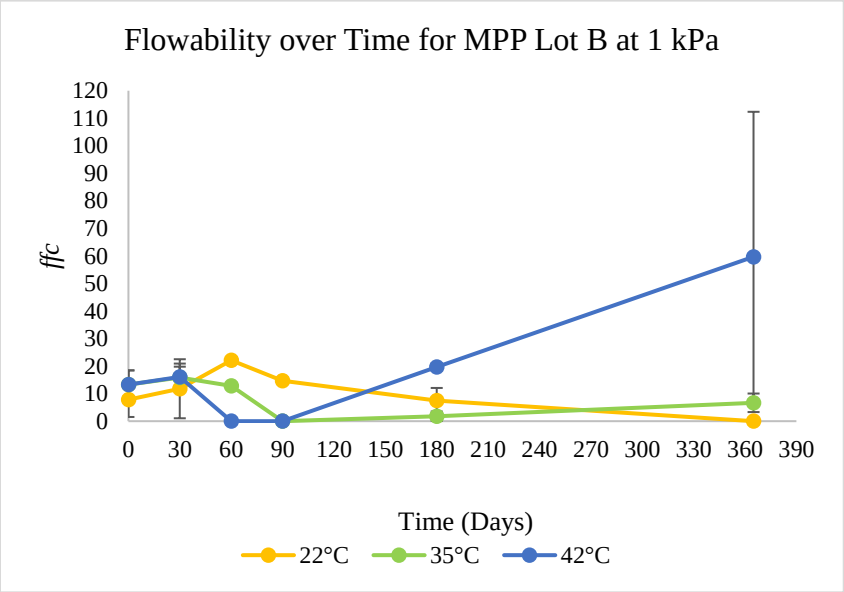


Figure A-7: Flowability over time for MPP Lot B at 1 kPa.

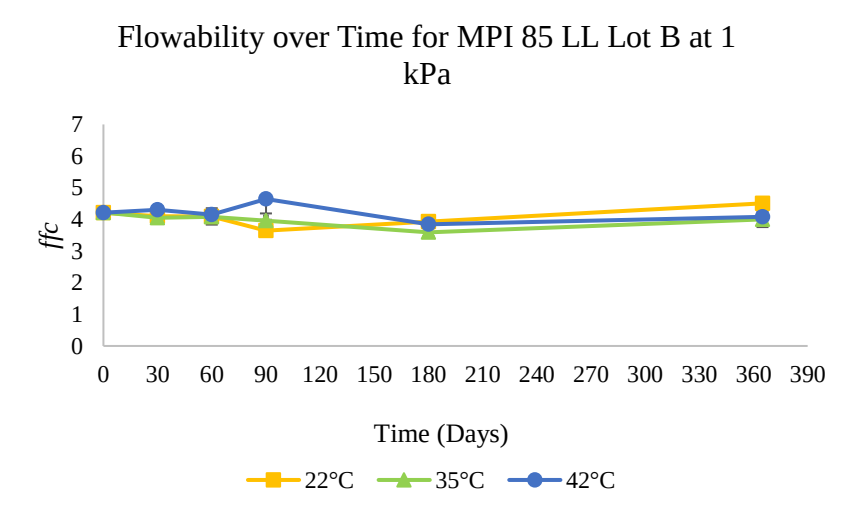


Figure A-8: Flowability over time for MPI 85 low lactose Lot B at 1 kPa.

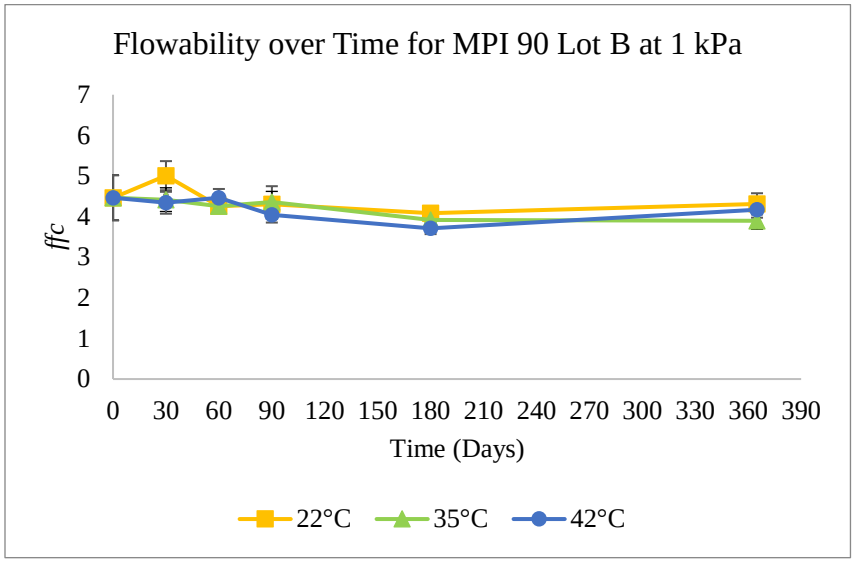


Figure A-9: Flowability over time for MPI 90 Lot B at 1 kPa.

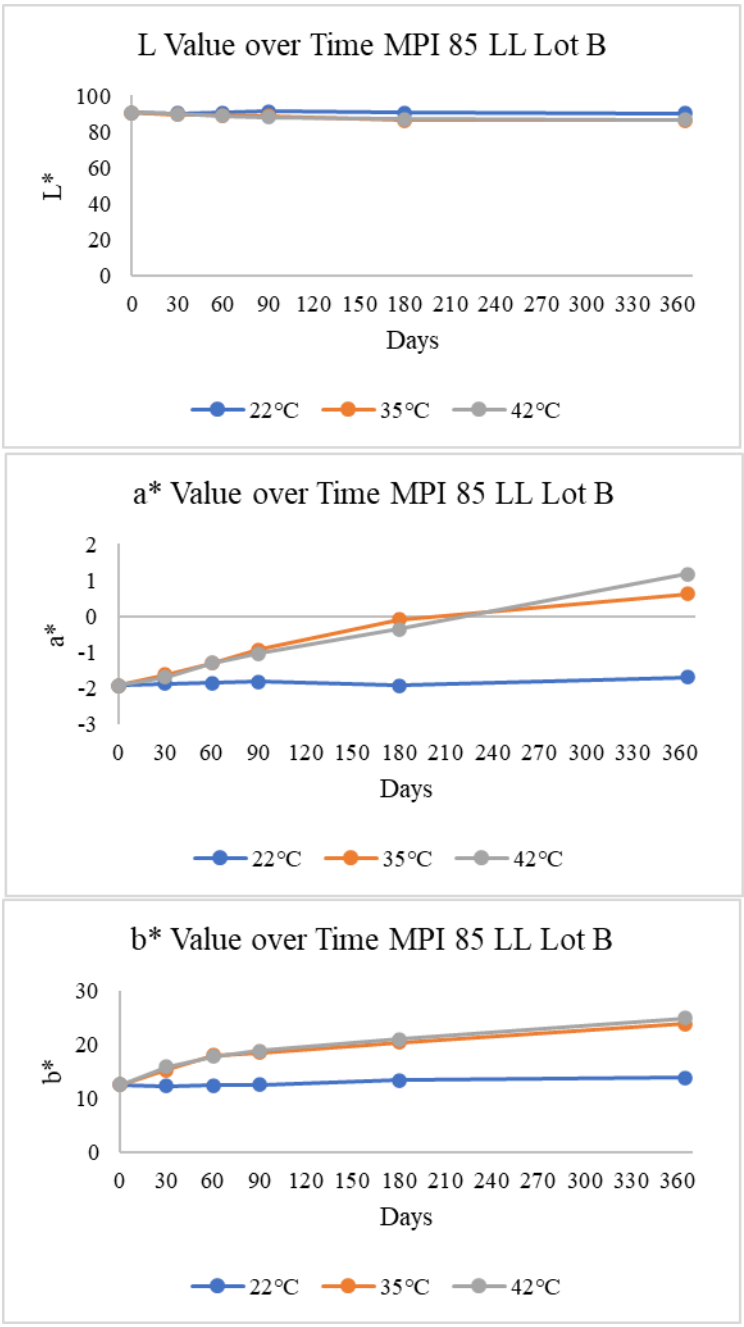


Figure A-10: LAB Color Analysis for MPI 85 low lactose Lot B

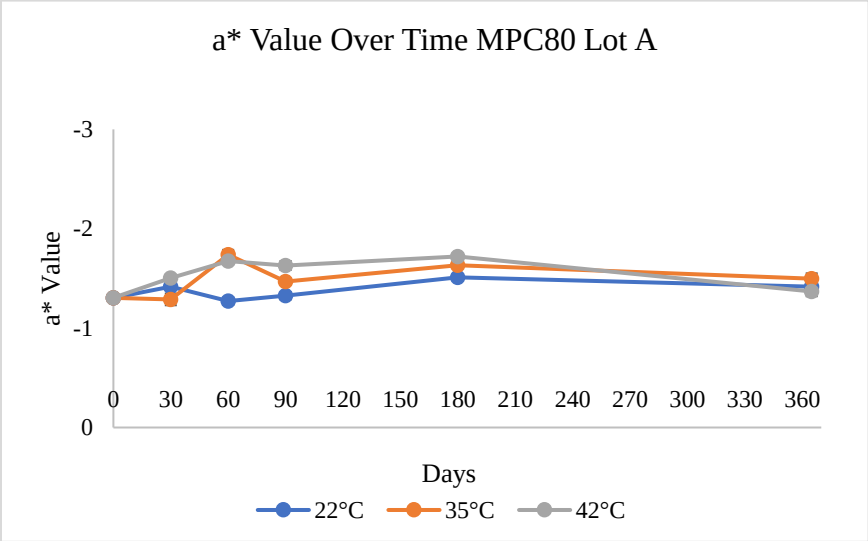


Figure A-11: a* color analysis values for MPC 80 Lot A over time

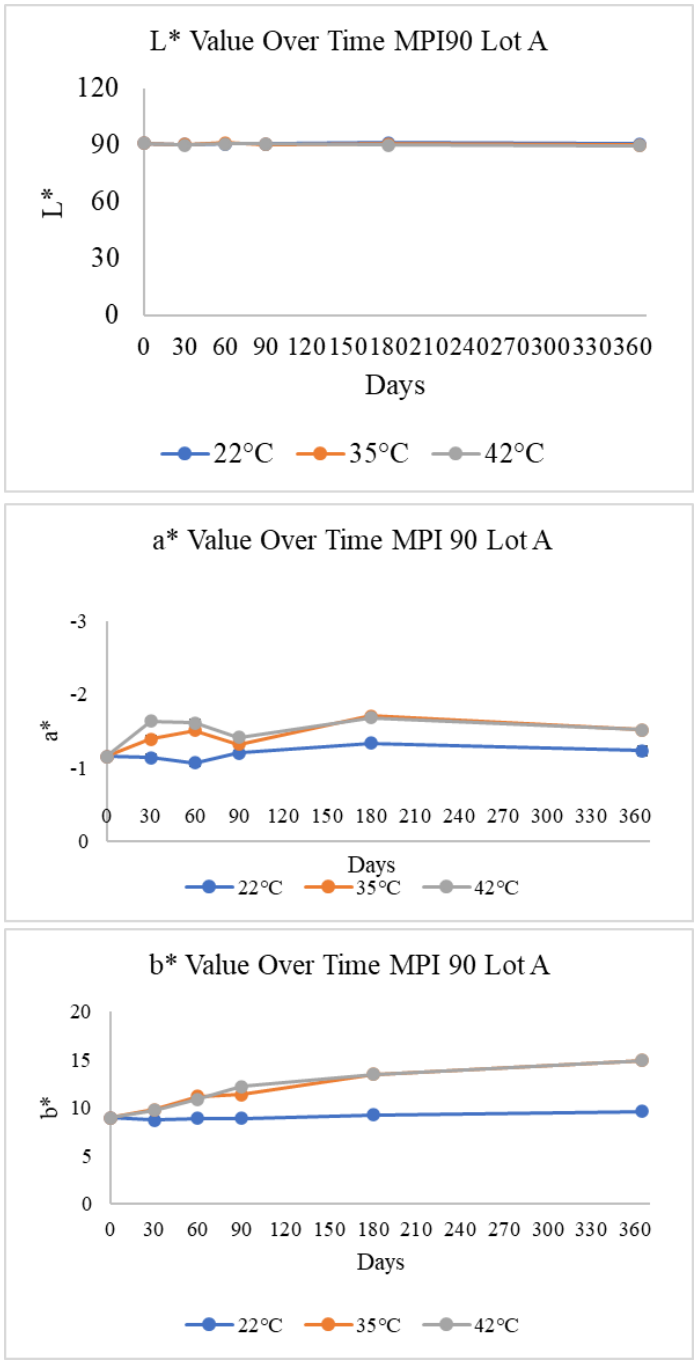


Figure A-12: LAB color analysis values for MPI 90 Lot A

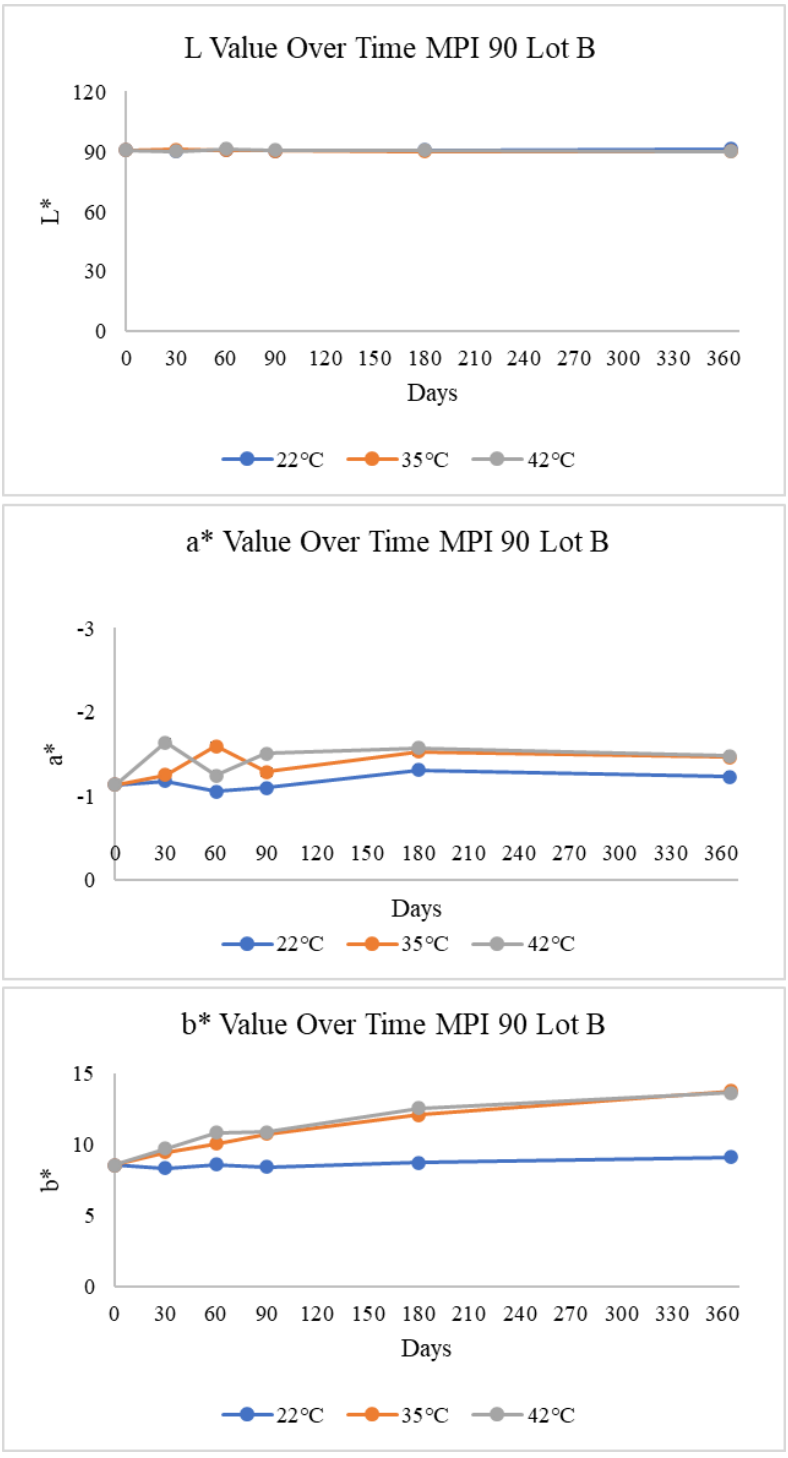


Figure A-13: LAB color analysis values for MPI 90 Lot B

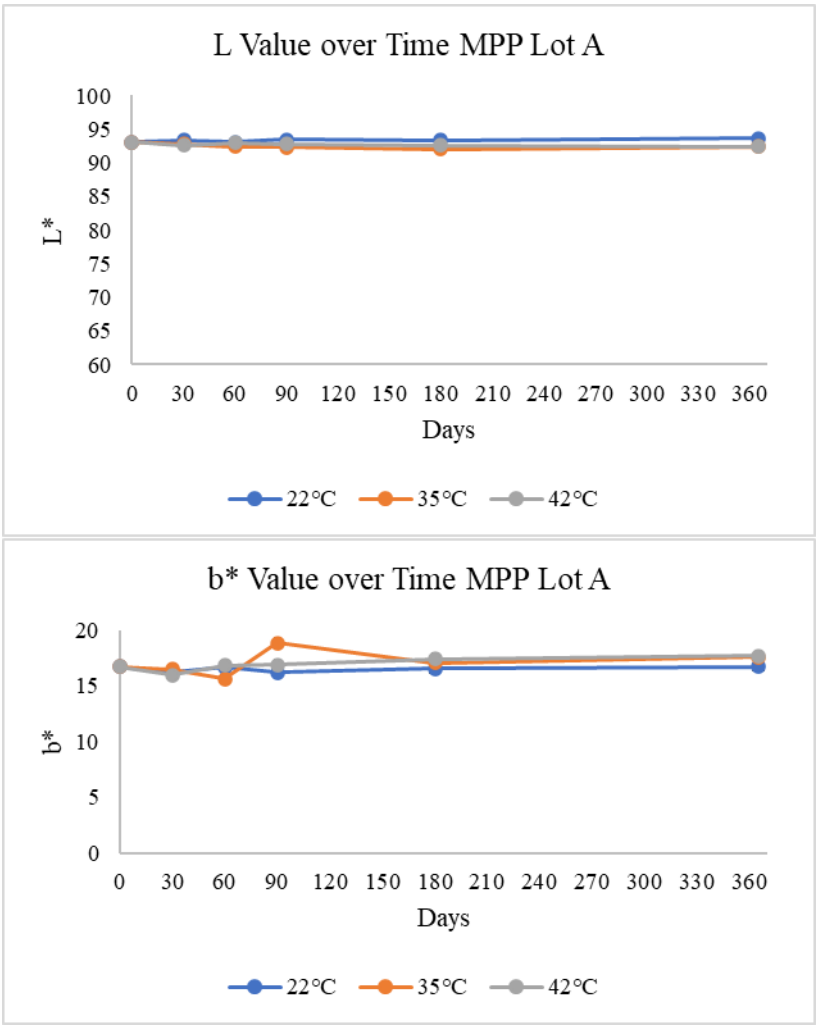


Figure A-14: L* and b* color analysis values for MPP Lot A over time.

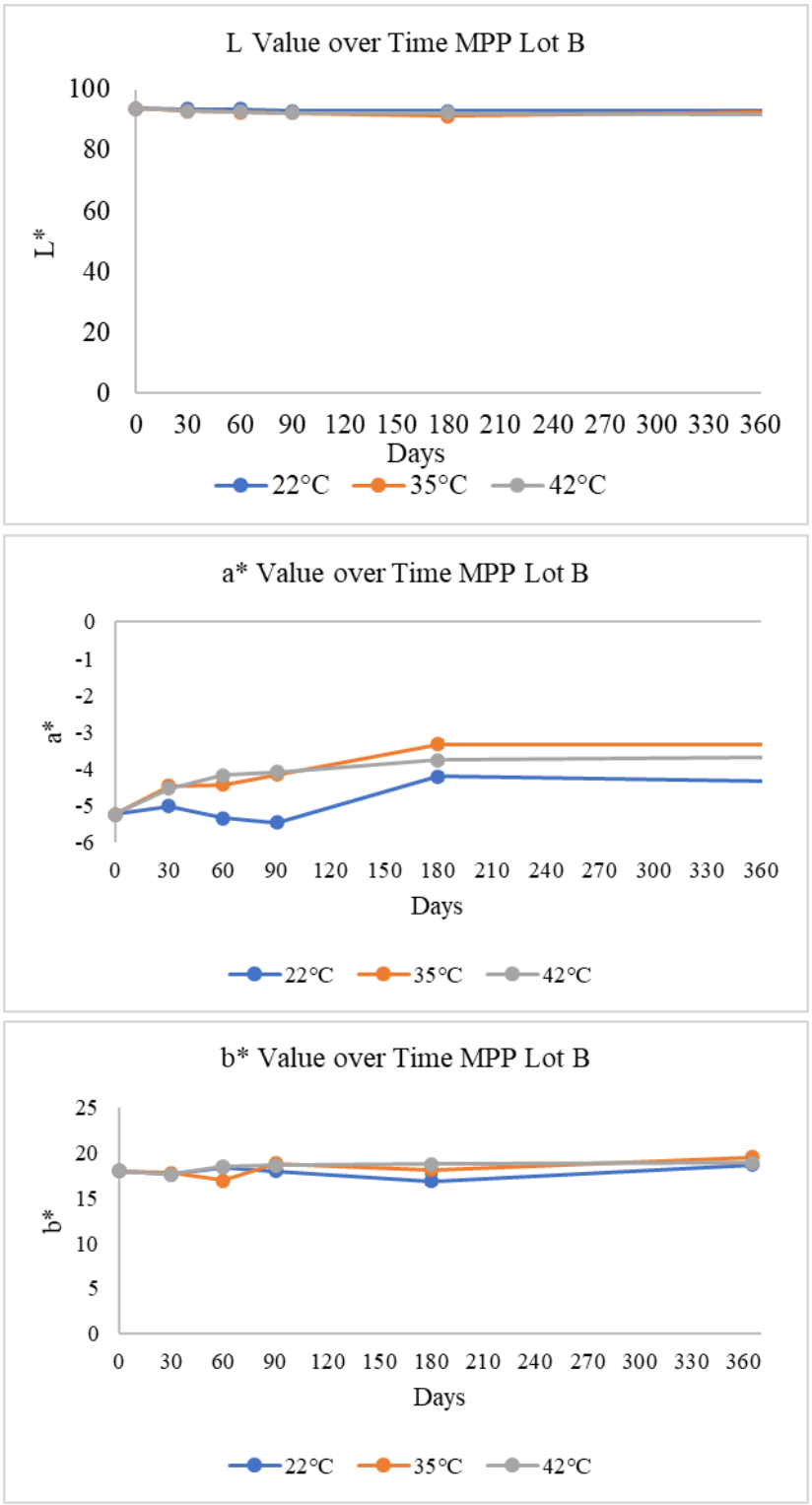


Figure A-15: LAB color analysis values for MPP Lot B

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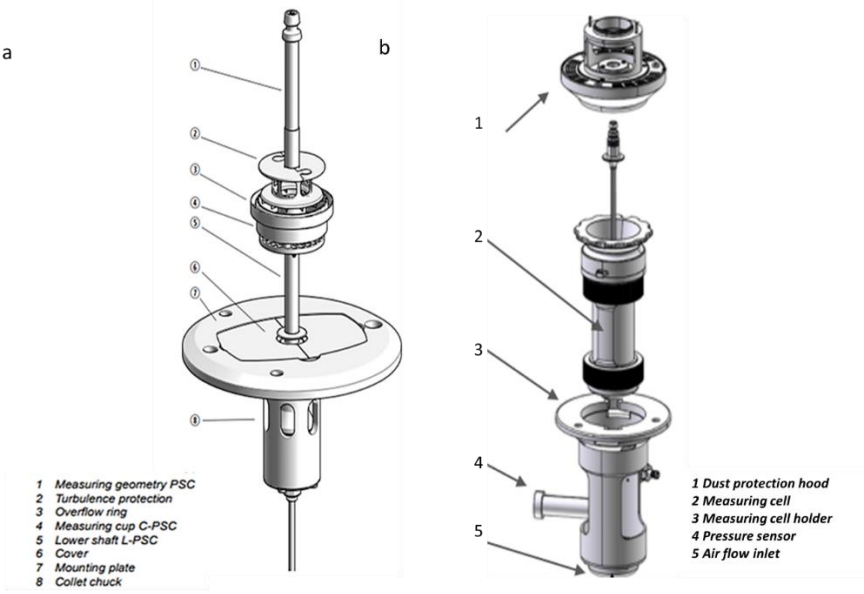

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