# CAKING OF LACTOSE-FREE MILK POWDERS IN STORAGE AND TRANSPORT CONDITIONS

Lappeenranta–Lahti University of Technology LUT

Master's Programme in Chemical Engineering, Master's thesis

2024

Milla Haapa-aho

Examiners: Docent, Rama Layek

Associate Professor, Ritva Tuunila

ABSTRACT

Lappeenranta–Lahti University of Technology LUT

LUT School of Engineering Sciences

Chemical Engineering

Milla Haapa-aho

**Caking of lactose-free milk powders in storage and transport conditions**

Master's thesis

2024

91 pages, 29 figures, 13 tables and 4 appendices

Examiners: Docent Rama Layek and Associate Professor Ritva Tuunila

Keywords: lactose-free milk powder, skim milk powder, whole milk powder, caking, storage and transportation, crystallisation, glass transition temperature

Demand for lactose-free milk powders has increased due to growing awareness of lactose intolerance. These powders, known for their extended shelf-life, are often transported over long distances, exposing them to changing environmental conditions that can lead to undesired physicochemical changes, specifically caking. Theoretical insights highlight the high hygroscopic nature of lactose-free milk powders, with moisture content, temperature, and consolidation identified as key factors influencing caking. Understanding and examining this phenomenon is important for maintaining product quality and customer satisfaction.

This thesis investigates the caking of lactose-free skim milk powder (SMP) and whole milk powder (WMP) under different environmental conditions. Caking was examined for two months, utilizing analytical methods such as wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

Lactose-free SMP and WMP did not experience severe caking under milder transport and storage conditions, although physical changes in particle properties and structure were observed. Minor changes in temperature and moisture content significantly influenced the onset of caking, emphasizing the importance of optimal storage conditions. Carbohydrates were identified as the main cause of hard cake formation. SMP formed harder cakes than WMP due to its higher carbohydrate content and absence of fat. Consolidation stress was also found to induce caking, with significant effects under severe pressure.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

Teknis-luonnontieteellinen

Kemiantekniikka

Milla Haapa-aho

**Laktoosittomien maitojauheiden paakkuuntuminen varastointi- ja kuljetusolosuhteissa**

Kemiantekniikan diplomityö

2024

91 sivua, 29 kuvaa, 13 taulukkoa ja 4 liitettä

Tarkastajat: Dosentti Rama Layek ja Tutkijaopettaja Ritva Tuunila

Avainsanat: Laktoositon maitojauhe, rasvaton maitojauhe, täysmaitojauhe, paakkuuntuminen, varastointi ja kuljetus, kiteytyminen, lasisiirtymälämpötila

Laktoosittomien maitojauheiden kysyntä on kasvanut, sillä ihmiset ovat yhä tietoisempia laktoosi-intoleranssista. Maitojauheilla on pitkä säilyvyysaika, minkä vuoksi ne ovat suosittuja ja niitä kuljetetaan pitkiä matkoja. Tällöin jauheet altistuvat muuttuville ympäristöolosuhteille, mikä voi johtaa ei-toivottuihin fysikaaliskemiallisiin muutoksiin kuten paakkuuntumiseen. Laktoosittomat maitojauheet ovat erittäin hygroskooppisia, ja kosteuspitoisuus, lämpötila sekä paino on tunnistettu keskeisiksi paakkuuntumista aiheuttaviksi tekijöiksi. Paakkuuntumisilmiön ymmärtäminen ja tutkiminen on tärkeää tuotteen laadun sekä asiakastyytyväisyyden säilyttämiseksi.

Tämä tutkielma tutkii laktoosittoman rasvattoman maitojauheen (SMP) ja täysmaitojauheen (WMP) paakkuuntumista eri ympäristöolosuhteissa. Paakkuuntumista tutkittiin kahden kuukauden ajan hyödyntäen analyyttisiä menetelmiä kuten differentiaalinen pyyhkäisykalorimetria (DSC), pyyhkäisyelektronimikroskopia (SEM), Fourier-muunnos infrapunaspektroskopia (FTIR) ja laajakulmaröntgendiffraktio (WAXS).

Laktoositon SMP ja WMP eivät paakkuuntuneet merkittävästi normaaleissa kuljetus- ja varastointiolosuhteissa, vaikka partikkelien ominaisuuksissa havaittiin joitakin fysikaalisia muutoksia. Pienet lämpötilan ja kosteuspitoisuuden muutokset vaikuttivat merkittävästi paakkuuntumiseen. Hiilihydraatit tunnistettiin pääasialliseksi syyksi kovien paakkujen muodostumisessa. Painon todettiin myös aiheuttavan paakkuuntumista, ja mitä voimakkaampi paino, sitä voimakkaampi vaikutus.

ABBREVIATIONS

| | |
|---|---|
| AGEs | Advanced glycation end products |
| $a_w$ | Water activity |
| CCP | Colloidal calcium phosphate |
| CM | Casein micelle |
| DSC | Differential scanning calorimetry |
| Eila | No-lactose |
| FTIR | Fourier Transform Infrared Spectroscopy |
| LHMP | Lactose hydrolysed milk powder |
| MCC | Micellar casein concentrate |
| MFGM | Milk fat globule membrane |
| RH | Relative humidity |
| RSMP | Reconstituted skim milk powder |
| SEM | Scanning electron microscopy |
| SMP | Skim milk powder |
| SMPHL | Skim milk powder with hydrolysed lactose |
| $T_g$ | Glass transition temperature |
| WAXS | Wide-angle X-ray scattering |
| WMP | Whole milk powder |

Table of contents

Abstract

Abbreviations

1 Introduction ..... 6
Theoretical part ..... 8
2 Characteristics of dairy powders ..... 8
2.1 Powder production ..... 8
2.2 Chemical composition ..... 11
2.3 Particle interactions ..... 13
2.4 Flowability ..... 14
2.5 Reconstitution properties of powder ..... 14
2.6 Bulk density ..... 15
3 Caking phenomenon ..... 16
3.1 Mechanisms of caking ..... 16
3.1.1 Liquid and solid bridge formation ..... 16
3.1.2 Glass transition and moisture content ..... 17
3.1.3 Sintering mechanism ..... 20
3.1.4 Lactose crystallisation ..... 21
3.1.5 Protein denaturation and aggregation ..... 22
3.1.6 Mechanical caking ..... 22
3.2 Kinetics of caking ..... 23
4 Storage conditions ..... 26
4.1 Effects of storage conditions ..... 26
4.2 Impacts of caking on dairy powder storage stability ..... 27
4.2.1 Powder properties ..... 27
4.2.2 Chemical reactions ..... 29
4.3 Prevention of caking ..... 30
5 Methods used to study the caking of powders ..... 31
Applied part ..... 35

6 Materials and methods ..... 35
6.1 Eila SMP and WMP ..... 35
6.2 Experimental setup ..... 36
6.3 Sample preparation ..... 38
6.4 Applied methods ..... 39
7 Results and discussion ..... 44
7.1 Particle surface morphology ..... 46
7.2 Powder crystallinity ..... 48
7.3 Analysis of macromolecular changes ..... 50
7.4 Cake strength analysis ..... 54
7.5 Free fat (%) analysis ..... 58
7.6 Wettability analysis ..... 59
7.7 Thermal behaviour of fat and $T_g$ ..... 61
7.8 Particle size analysis ..... 64
7.9 Flowability of Eila SMP and WMP ..... 67
7.10 Summary of findings ..... 69
7.10.1 Factors influencing caking ..... 70
7.10.2 Induction time for caking ..... 72
8 Conclusions and recommendations ..... 73
References ..... 76

Appendices

Appendix I Images of powder caking in Eila SMP and WMP

Appendix II Cake strength (g) of Eila WMP and SMP

Appendix III Main effects screener plots

Appendix IV Free fat (%) of Eila WMP

# 1 Introduction

Dairy industries developed milk powders to extend the shelf life of milk (Dairy World, 2024). Unlike liquid milk, which typically expires within weeks, properly stored whole milk powder can retain its quality for up to a year, whereas skim milk powder for nearly two years (Kim et al., 2008). Milk powders are produced by removing water partially from milk, skim milk, cream or their mixtures, ensuring a final water content of no more than 5 % by weight. (Council Directive 2001/114/EC) Today, milk powders are popular among consumers, and there are a variety of milk powders produced, including lactose-free milk powder. Demand for this lactose-free powder increases due to a rising awareness of lactose intolerance. The long shelf-life of milk powders enables global transportation, during which powders are prone to undergo undesired changes like caking, browning and fat oxidation (Kim et al., 2008). These changes are mostly due to environmental changes such as temperature and humidity increase, or due to consolidation stress and storage time.

In 2022, the European Union contributed approximately 3 million tonnes to global dairy powder production, with Finland accounting for 1.5% of this total. Dairy products, especially dairy powders, are Finland's most exported food product with a total of 47 tonnes of milk powder exported abroad in 2023, mostly to markets in China (32 %), Malaysia (22 %) and Thailand (10 %). (ETL, 2024) Lactose-free milk powders, however, have been noticed to experience severe caking during these long-distance transportations and this caking has been observed to be more pronounced compared to traditional milk powders. Given the critical importance of maintaining powder quality for consumer satisfaction, understanding and mitigating these changes are paramount. This thesis aims to provide a broad understanding of the phenomenon of lactose-free milk powder caking, examining the main environmental factors and milk components causing this issue.

Previous research has primarily focused on traditional milk powders, with limited attention given to lactose-free milk powders. These studies have already identified and addressed various factors contributing to caking; for example, Ryabova et al. (2023) studied that consolidation stress has an impact on caking while Phosanam et al. (2021) studied the effects of storage conditions. These studies highlight moisture content, temperature, consolidation, and time as critical factors contributing to caking. Now that the contributing factors have

been identified, the next step is to determine at which time caking occurs under milder storage conditions and which factors contribute the most to this phenomenon.

This thesis focuses on examining the caking behaviour of lactose-free dairy powders in relation to temperature, moisture, consolidation, and time. Despite the growing demand for lactose-free products, there is a significant knowledge gap regarding the products. There are a limited number of studies specifically addressing how lactose-free milk powders behave in terms of caking and specifically at their normal transport and storage conditions. The aim of this study is to find answers to the following research questions:

1. What is the induction time for severe caking in lactose-free milk powders at their transport and storage conditions?
2. What component: fat, protein, or carbohydrate, is the main cause for the formation of hard lumps?
3. Can consolidation stress induce severe caking?
4. How do minor changes in temperature and moisture content influence the onset of caking?

The literature review will focus on examining the dairy powder characteristics and caking phenomenon in general. Due to limited studies concentrating on lactose-free milk powders, this literature part concentrates more on the characteristics of traditional milk powders. The applied part will concentrate solely on examining powder caking in two lactose-free milk powders (skim milk and whole milk) under varied environmental conditions using diverse analytical techniques. Caking could be studied for 2 months, and the amount of sample contributed to which analysis methods could be used.

In this thesis, the effects of various factors on the caking of lactose-free milk powders were studied, focusing for example on cake strength (g), crystallinity (%), macromolecular changes, and free fat (%). The key findings from this thesis are that even minor changes in the initial moisture and temperature have a significant effect on caking. Still, at milder storage and transportation conditions, no severe caking was observed. It was found that consolidation stress does induce severe caking and it is important to reduce the load weight of these powders. One of the key finding was that carbohydrates were identified as the main cause of hard cake formation which will have a significant importance when thinking about

solutions to this caking problem. In addition, this thesis examined how much the environmental factors contributed to the caking.

# Theoretical part

# 2 Characteristics of dairy powders

Particle properties like size, shape, composition, and density determine the behaviour and structure of particles. One must understand the basic characteristics of dairy powders to understand the changes and behaviour during handling and storage.

## 2.1 Powder production

Food powders are produced from liquid or solid-state materials for example by drying, crystallisation, granulation or mixing. Drying is a fast and mature process where water content is reduced from wet material to obtain dry powders with particle sizes ranging between 10-250 µm (Bhandari, 2024). The moisture is removed by applying hot air to the feed product.

Tamime (2009) states that the most used technique to produce milk powder from milk is spray drying. The core principle of spray-drying is that the liquid milk is fed into a spray-drying chamber where it is atomized into fine droplets through a nozzle. Atomization is a crucial step in this process because it determines particle size. Small droplet sizes make the drying process more efficient, and they impact the quality of the product. Hot air (150-300°C) is simultaneously fed into the drying chamber where it rapidly gets into contact with the droplets. Water starts to evaporate from the milk droplets and the milk solids start to concentrate. After the surface moisture is evaporated, milk solids form a dry solid phase on the surface. The bound water inside the droplet is removed by osmosis. While the moisture evaporates from the droplet surface, a solute concentration gradient forms and causes the suspended materials to diffuse into the droplet. According to Tamime (2009), lactose has the

highest diffusivity, compared to other components, meaning it will migrate inwards the fastest before proteins and fat. Because of this, fat is accumulated on the particle surface which can cause stickiness during the high-temperature drying process. Completely dried droplets descend to the bottom of the chamber, where they are continuously gathered, separated, and cooled.

Powders agglomerate during spray drying and they obtain irregularly porous shape. When the liquid milk is fed and mixed with hot air, semi-dried sticky particles collide with dry particles from a cyclone separator and thus form stable, irregular shaped porous agglomerates that have excellent instant properties. (Cuq et al., 2013) Agglomeration is a unit operation process in which particles combine to form larger agglomerates where the individual particles remain distinguishable (Bhandari, 2024). It is a desired process because it has been observed to improve powder functionalities like reconstitution and flow properties (Murrieta-Pazos et al., 2012). Powder surface can contain large or small vacuoles distributed throughout the particle. Dairy powders have an amorphous structure which means that the molecules are disordered, more open and porous which makes them absorb water easily. (Bhandari, 2024) These properties make amorphous agglomerated powders quickly re-hydratable (Palzer, 2011).

In addition to traditional milk powders, there is a huge market for lactose-free milk powders. People who have lactose intolerance do not produce lactase enzyme (β-galactosidase) which would hydrolyse lactose into the monosaccharides: glucose and galactose. For that reason, they cannot drink or eat lactose-containing substances. (Fialho et al., 2017; Schulz & Rizvi, 2023) Lactose is hydrolysed by using lactase enzyme which splits lactose into glucose and galactose more easily digested in human bodies. Lactose-hydrolysed milk powders (LHMP) are produced similarly except the process undergoes lactose hydrolysis before the spray drying step. Lactose-hydrolysed milk powders contain lactose <0.5%. (US8986768B2, 2015)

Amorphous powders are in a non-equilibrium state meaning they can go through crystallisation under changing conditions. (Bhandari, 2024) Figure 1 presents the scanning electron microscopy (SEM) image of traditional milk powder (left) and LHMP (right). Fialho et al. (2019) compared these powders on a pilot scale using the same drying parameters, and they concluded that LHMP particles agglomerated better compared to traditional milk powder particles. Torres et al. (2017) research supports this finding as they

studied lactose hydrolysed milk powder production on a large scale with different hydrolysis levels and concluded that there was more adhesion between the particles in the drying chamber with low-lactose milk powders. Optimizing the drying process parameters can lead to different outcomes regarding the agglomeration and overall quality of the powders.

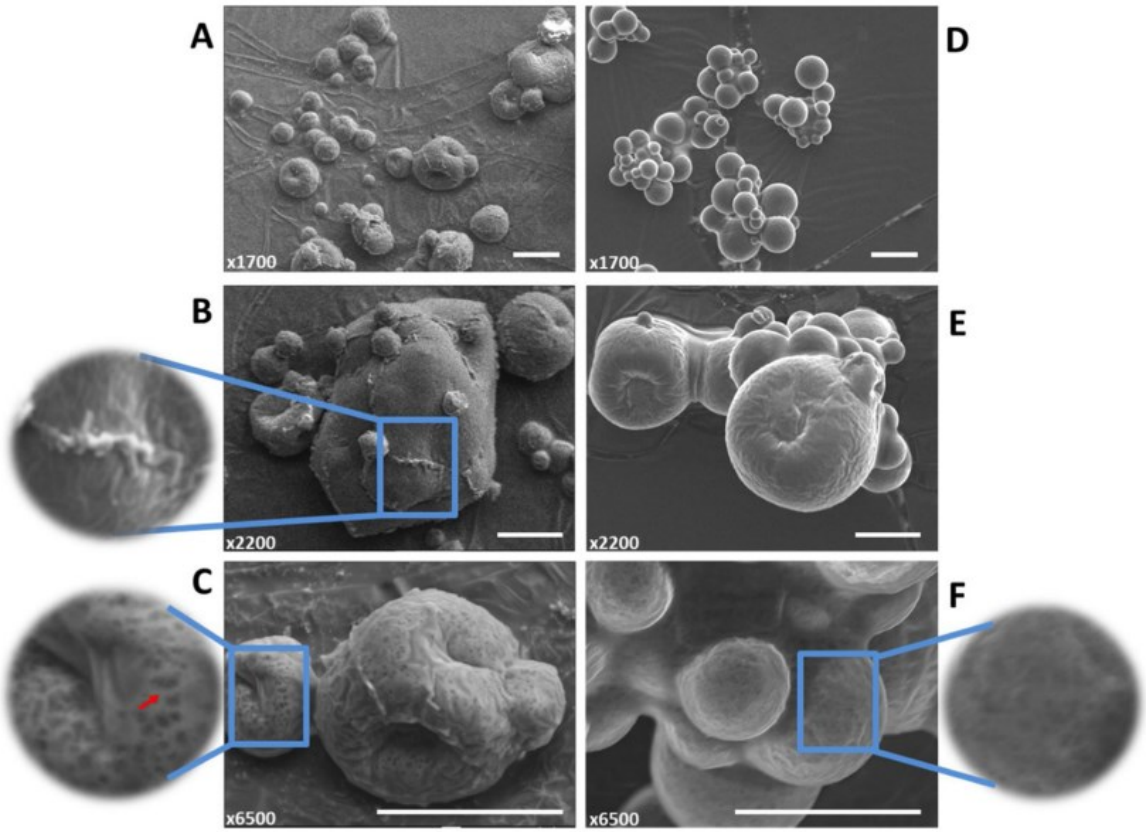


Figure 1. Scanning electron microscopy (SEM) image of traditional milk powder (left) and LHMP (right). Red arrows are vacuoles and white scale bar is 10 µm. (Fialho et al., 2019)

LHMP do not have any vacuoles nor crystals present in the surface. Although lactose is mainly in the amorphous state in milk powders, a small amount of crystal formation can occur at the surface after the drying process. Tamime (2007) suggested is due to high lactose concentration, high lactose hygroscopicity and humidity in the chamber. Schuck et al. (2005) studied that galactose and glucose increase the heat capacity ($\Delta C_p$) of the sample and thus, monosaccharides are more difficult to undergo crystallisation.

## 2.2 Chemical composition

Milk powder consists of carbohydrates, protein, and fat with different proportions depending on the powder type. Milk powders are classified by their fat content. Whole milk powder (WMP) contains fat between 26-42 % of its total weight whereas skim milk powder (SMP) contains less than 1.5 %. (Council Directive 2001/114/EC) When lactose-hydrolysed SMP or WMP is a desired, lactose hydrolysis step is added to the process.

Chemical composition and especially the surface composition of powder determines and affects largely to physical and chemical properties like wettability, stickiness, flowability and size distribution of the powder. Depending on the milk powder, fat covers approximately 26 % of the composition in WMP and 1 % in SMP (Valio, 2024). According to Tamime (2009) and Jeantet et al. (2016), most of the fat present in the powder is in the form of triglyceride (~98 %), and phospholipids which are present in much smaller quantities (~0.6 %). Triglyceride consists of fatty acids with varying chain lengths (C4-C18). Fatty acids define the physical properties of fat such as crystallisation properties and melting point. Fat exists in the form of fat globules, typically with an average diameter of 4 µm (Jeantet et al., 2016). Jeantet et al. (2016) estimated that approximately 90 % of the milk fat globules are in the range of 1-8 µm. Each globule has a membrane enabling fat to disperse into the liquid phase. This membrane complex is called the milk fat globule membrane (MFGM). The inner fat globule consists of neutral lipids such as triglycerides, but the membrane consists of polar lipids and proteins which protect the fat from enzymatic and chemical reactions. The spray-drying process can alter fat composition by disrupting MFGM and thus releasing free fat. Free fat is non-emulsified fat that is formed during spray drying. When the moisture evaporates from the droplets, most of the fat globules are coalesced by the protein and carbohydrate but some of the fat migrates to the surface resulting in free fat.

Protein covers approximately 35 % of the milk powder composition. According to Tamime (2009), the protein existing in milk powders consists of caseins (80 %) and whey proteins (20 %). Caseins consist of four main components that are αs1, αs2, β, and κ in the proportion of 4:1:3.5:1,5. Lysine is an amino acid which is the most essential and reactive one in caseins. McMahon & Brown (1984) studied that 90 % of caseins exist in a colloidal form known as micelle form and 95% of them have a diameter in a range from 80 to 440 nm. They are unstructured open proteins that are stable for heat.

Milk contains small proportions of minerals and vitamins. Potassium, calcium, phosphorus, and sodium are the most abundant ones. Calcium and phosphorus are associated with protein casein micelle which means that their content is dependent on the casein micelle behaviour. If the micelle is ruptured, minerals are removed in the filtration step. (Jeantet et al., 2016) Du et al. (2023) state that the internal structure of casein micelles is stabilizes by the sequestration of calcium between αs- and β-casein and colloidal calcium phosphate (CCP). κ-casein is calcium-sensitive so it will form a "hairy" layer on the micelle surface and thus limit the casein micelle size but also stabilize the structure (Mendoza, 2016; Du et al., 2023). McMahon & Brown (1984) studied that the heat treatment of milk would be the cause of calcium and phosphate depositing onto these "hairs". Du et al. (2023) studied the internal structure of casein micelles (CMs) in reconstituted skim milk powder (RSMP). The study concluded the schematic presentation of the internal structure of casein micelles based on the nanocluster model and it is presented in Figure 2.

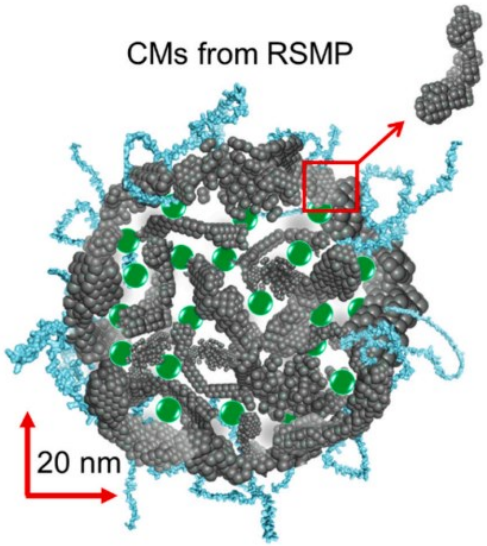


Figure 2. Internal structure of casein micelles (CMs) from RSMP. Green circles illustrate CCP, grey clusters illustrate casein cluster, blue strings illustrate κ-caseins. (Du et al., 2023)

Grey clusters illustrate casein clusters, green circles illustrate colloidal calcium phosphates (CCP), and the blue "hairy" strings illustrate the calcium-sensitive κ-caseins. It has been studied that high-temperature pasteurization at 72°C does not affect the casein micelle

structure but higher temperatures can cause denaturation of β-lactoglobulin. The higher increase in temperature causes dissociation of κ-casein which will change the structure. (Mendoza, 2016)

Carbohydrates cover approximately 41% of powder composition. Skim milk powder contains around 30 % more carbohydrates compared to whole milk powder. (Valio, 2024) Carpin et al. (2016) found in their study that the primary carbohydrate in milk is lactose, a disaccharide made up of D-galactose and D-glucose units linked by a β-1,4-glycosidic bond. Lactose can be in two different forms: α-form and β-form. Dairy powders contain lactose in the amorphous state which consists of a mixture of α-lactose and β-lactose. Amorphous lactose is solid due to high viscosity which only increases during the spray-drying process. Amorphous lactose is highly hydroscopic which creates problems in powders by furthering caking and stickiness. (Jeantet et al., 2016)

In LHMP, the lactose has been hydrolysed into monosaccharides glucose and galactose. According to Roos (1993), these monosaccharides are more hygroscopic compared to lactose because there are higher amount of molecules in the amorphous state. Glucose and galactose have lower molecular weight, leading to increased particle mobility. This causes more problems like caking and browning. Lactose hydrolysis enhances the sweetness of powder because glucose and galactose have a sweetness level of 75% and 60% of sucrose respectively whereas lactose has only 20% of the sweetness of sucrose (Schulz & Rizvi, 2023; Harju et al., 2012). In LHMP, more monosaccharides were detected around protein compared to the traditional milk powder sample. Fialho et al. (2019) studied that LHMP monosaccharide-protein interactions are more favourable than monosaccharides-monosaccharide interactions.

## 2.3 Particle interactions

Cohesive forces give crucial information and aspects to physical properties of the substance. There are many interparticle forces and they can be categorized according to their magnitudes. The forces ranked from strongest to weakest are solid bridges, liquid bridges, van der Waals, electrostatic, and magnetic forces. These forces do not cause caking on their own but different circumstances such as humidity and temperature can lead to caking. (Zafar et al. 2017) Multiple factors determine which forces will form between the particles and

understanding them enables manufacturers to influence what forces will dominate. In dairy powders produced by spray drying, temperature, humidity, particle size, shape and composition play a crucial role when thinking about the forces.

## 2.4 Flowability

Flowability refers to the capacity of a powder to flow smoothly and unrestrictedly without lump or aggregate formation. It can easily be measured by taking the time of a certain volume of powder to flow through a specific opening. Particles flow on the surface of other particles and thus, the particle properties like size, shape, density, and cohesive forces affect the flowability. For example, larger particles with narrow size distribution flow more easily compared to fine particles with a similar size distribution. Dairy powders with spherical shapes and smooth surfaces have high flowability. However, cohesion and adhesion forces affect flowability and an increase within those forces affect negatively to the flowability and lumps and aggregates are more prone to occur. Handling, transportation, and storage of powders is difficult because of cohesion between the particles and adhesion between particle and container surface. (Ermis, 2021; Bhandari, 2024)

## 2.5 Reconstitution properties of powder

Dairy powders as well as most food additives are dissolved before their usage. Reconstitution means the powder takes its initial form as a liquid by absorbing water (Ermis, 2021). Anandharamakrishnan (2017) states that reconstitution means the ability of the power to become wet, sink, disperse and dissolve. The spray-dried powder contains fine particles and thus it is difficult to hydrate. It is very common for powders to form lumps when it's mixed with water but for example, mixing will help the powder to dissolve. Lumps are prone to form because after the first layer of powder dissolves, it forms a thicker layer which resists water. (Anandharamakrishnan, 2017)

Wettability indicates the ability of the powder to absorb water on the surface (Bhandari, 2024; Ermis, 2021). Wettability is highly dependent on the particle size, density, surface area, and surface composition (Tamime, 2009). Wettability is determined by contact angle $\theta$, which is the angle between the powder surface and the water. Thus, powder surface

composition has a huge impact on wettability. Small and fine particles are more cohesive and have tight structures which makes the water absorption more difficult. Water cannot get between those fine particles because the gaps between them are small. (Ermis, 2021)

Sinkability determines the capacity of powder to surpass the water's surface tension and to sink into the water after that. Density and particle size affect the sinkability and higher-density particles tend to sink faster than low-density particles. Dispersibility illustrates the ability of the wetted particle to disperse and dissolve in water. If powder has high dispersibility, it can be identified as instant powder. (Bhandari, 2024) To obtain good dispersibility, there should be no fine particles in the powder (Tamime, 2009). Solubility refers to powder's ability to dissolve in a liquid. Amorphous powders are more soluble compared to crystallised powders because their structure is more easily disrupted. Powders must be soluble in water to maintain the quality of the product. (Bhandari, 2024)

Reconstitution properties are highly affected by physical - and chemical changes in particles. For this reason, it is important to maintain the properties that powder has after its production. Any defective problems such as caking, stickiness or browning affect the solubility and reconstitution properties making the powder unusable.

## 2.6 Bulk density

Bulk density is a measure of the mass of a powder per unit volume (g/mL). It can be used to determine how much powder can be put into a package of a certain volume. It is a critical parameter to characterize and control the storage requirements of bulk materials such as milk powder. Bulk density affects the flowability, storage capacity and handling of the powder. Larger particle size distribution increases bulk density but large particle size does the opposite. SMP has a higher bulk density compared to WMP due to differences in milk fat density and lactose composition. Fat is less dense compared to proteins and lactose. Since SMP contains no fat, it has a higher proportion of these denser components, resulting in a higher bulk density. A more porous structure favours occluded air within the particles which lowers the bulk density. (Tamime, 2009)

# 3 Caking phenomenon

One of the biggest problems with dairy powders is caking. Time consolidation (caking) is a transformation process whereby a free-flowing powder clumps together as a result of particle bridging and undesired agglomeration of sticky particles (Schulnies & Kleinschmidt, 2018; Hartmann & Palzer, 2011; Schulze, 2021). Hartmann & Palzer (2011) stated that powder agglomeration is a desired process when it is used to provide good dispersibility and rehydrate properties to the powder which happens during powder production. Undesired agglomeration happens mostly when powders are handled, stored, or transported and caking and lumping are good examples of this. Caking happens between powder particles mostly because of moisture and temperature changes. Environmental changes initiate physical and chemical changes to particle structure and behaviour. Milk powders have amorphous structures containing water-soluble substances which make them very sensitive to caking.

Next, the different caking mechanisms typical to dairy powders are looked at more in detail. The primary factors that commonly affect the caking phenomenon are temperature and humidity changes and consolidation stress. After the end of the chapter, the focus is on storage conditions and possible ways to prevent caking.

## 3.1 Mechanisms of caking

Moisture and high T and RH are the main factors identified to cause caking. Dairy powders are often transported long distances, during which climate can change drastically. In these circumstances, the caking is caused by humidity and temperature changes as well as by pressure. Several distinct caking mechanisms include for example crystallisation and sintering which are all influenced by factors such as composition, processing conditions and environmental factors. (Phosanam et al., 2021)

### 3.1.1 Liquid and solid bridge formation

The most common mechanism for caking is the formation of liquid and solid bridges. Liquid bridges are formed after mobile liquid gets released from the particle by melting or

dissolution of the surface components (Bhandari, 2024; Tham et al., 2017) Liquid can also be added or absorbed from the air (Zafar et al., 2017). Amorphous carbohydrates as highly hydroscopic components increase the moisture absorption which creates liquid to form between particles.

In addition, the surface of milk powder particles contains fat which melts easily when temperature or humidity increases. Fat usually melts at quite low temperatures which enhances the liquid bridge formation. This can ultimately lead to fat undergoing crystallisation if temperature is lowered which means conversion from liquid bridges to solid bridges. (Tham et al., 2017; Phosanam et al., 2021) Phosanam et al. (2021) also found that significant caking occurred in powders containing fat over 41 % w/w or having surface fat content over 13 % w/w.

Solid bridges form stronger forces between particles which leads to the formation of harder bulk powder cakes. Solid bridges can also be formed by sintering and glass transition mechanisms. (Bhandari, 2024; Tham et al., 2017; Zafar et al., 2017)

### 3.1.2 Glass transition and moisture content

Glass transition describes the conversion of an amorphous solid-state material to a rubbery liquid-like material. Amorphous materials, like lactose, have an individual glass transition temperature $T_g$, which depends on molecular morphology and water content within the material. Above $T_g$, amorphous materials are in a liquid-like rubber state (sticky state) which means the material has greater water mobility. On the other hand, amorphous materials exist in a hard glassy-like state which indicates low water mobility when they are below the $T_g$. Milk powders contain amorphous lactose which exposes them to this phenomenon. When the material is in solid state, it has low surface energy and high viscosity. Thus, the molecule mobility is restricted, and it won't stick to any solid surface. Above $T_g$, in a liquid-rubbery state, the surface energy increases, viscosity decreases, and the molecules can interact with solid surfaces. (Kamyabi et al., 2017; Schuck et al., 2012; Fitzpatrick et al., 2007)

The glass transition of lactose-free SMP is presented in Figure 3. Fitzpatrick et al. (2007) stated that lactose as an amorphous material is very hygroscopic and prone to crystallise above the $T_g$. Powder particles get sticky above the $T_g$ in the so-called sticky point

temperature. For materials with low molecular weight (e.g. lactose), the sticky point is approximately 10-20 °C above the $T_g$. If the temperature increases above the sticky point temperature, the powder becomes sticky, and it leads to higher adhesion and agglomeration between particles. Figure 3 illustrates the importance of maintaining the moisture content at low levels because the moisture content influences the quality of the powder in many ways affecting its properties and product stability during storage.

Water activity ($a_w$) is an indicator of stability, and it determines the $T_g$. With high moisture content, the water activity grows. (Roos et al., 1993) According to Council directive 2001/114/EC, the moisture content of milk powders cannot exceed 5 % w/w. Pisecky (2012) studied that the average $a_w$ in milk powders ranges between 0.2-0.25. For SMP, the maximum water content must be under 4 % w/w and for whole milk powder under 2.5 % w/w. Schuck et al. (2012) have specified that the optimum stability for SMP is at 25 °C. In that case, the $a_w$ is close to 0.2 and the $T_g$ is close to 50 °C. This means that the temperature should rise to 50 °C for the powder to undergo conversion to a rubbery state. Zafar et al. (2017), Phosanam et al. (2021) and Schuck et al. (2012) stated that glass transition can also occur without temperature change or other conditions can change at the same time as temperature changes. Amorphous material absorbs water easily and that lowers the glass transition temperature. In these situations, moisture acts as a plasticiser and the material can convert from a solid state to a liquid state even without the temperature change.

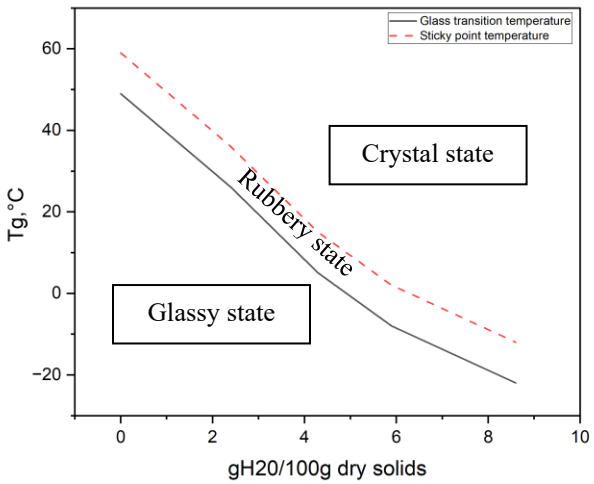


Figure 3. Glass transition of lactose-free SMP (adapted from Jouppila & Roos, 1994)

Roos (1993) estimated that the $T_g$ of anhydrous lactose is at 98°C whereas Fialho et al. (2018) estimate it at 101°C. According to Roos (1993), the $T_g$ of anhydrous monosaccharides glucose and galactose are 31°C and 30°C which are much lower than lactose due to their lower molecular weight. This affects the physicochemical properties of lactose-free milk powders. Figure 4 shows the moisture content and $T_g$ of lactose and skim milk powder with hydrolysed lactose (SMPHL) from two different studies at various water activities at 23 °C (Shrestha et al., 2007) and at 24 °C (Jouppila & Roos, 1994). There is a clear indication that lactose has higher $T_g$ compared to hydrolysed monosaccharides glucose and galactose.

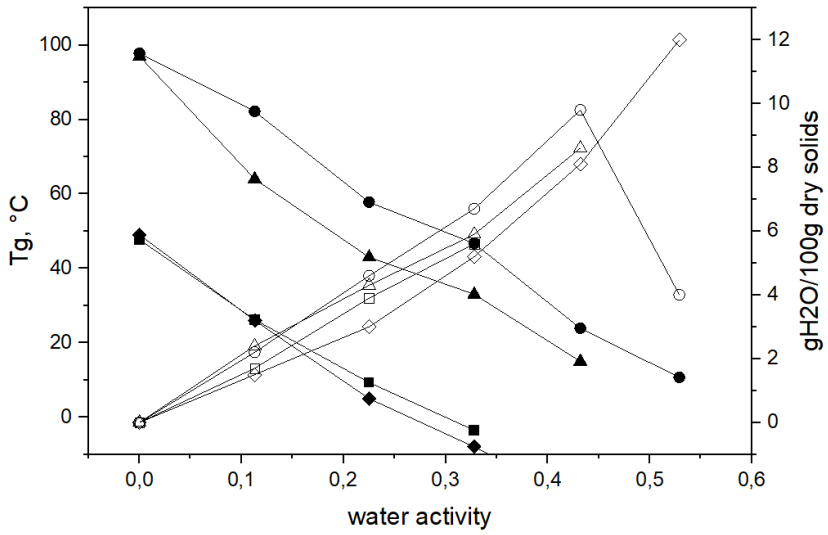


Figure 4. Moisture content and glass transition temperatures of lactose and SMPHL at various water activities: $T_g$ lactose (●) and for SMPHL (■) at 23°C (Shrestha et al., 2007), $T_g$ for lactose (▲) and for SMPHL (♦) at 24°C (Jouppila & Roos, 1994), moisture for lactose (○) and for SMPHL (□) at 23°C (Shrestha et al., 2007) & moisture for lactose (Δ) and for SMPHL (◊) at 24°C (Jouppila & Roos, 1994).

Jouppila & Roos (1994) studied the differences between regular and lactose-free milk powder. Because of the low $T_g$, even slight changes in moisture content can cause more severe caking and stickiness problems compared to lactose-containing milk powders. Hydrolysed lactose doubles the reducing sugar molecules which causes difficulties in

dehydration, and it increases the reactivity resulting in an increase of Maillard reactions which are reactions happening between lactose and α-amino groups. In these reactions, cross-links between these components and polymeric aggregates increase. This decreases the lysine content which causes the colour and flavour changes in powders.

### 3.1.3 Sintering mechanism

Sintering is a caking mechanism where molecules move and form bonds between particles leading to the formation of cake mass due to heat and moisture increase (Hartmann & Palzer, 2011). Hartmann & Palzer also state in their research that sintering is the main mechanism to cause caking in amorphous food powders. The main cause for this is temperature increase above the $T_g$. Temperature increase above $T_g$ decreases viscosity and thus, the molecules can move and flow between the particles. When two particles get in contact, molecules move to the contact point to minimise the free surface area (Zafar et al., 2017; Phosanam et al., 2021). Hartmann and Palzer (2011) illustrate sintering happening in four different phases and the process is presented in Figure 5.

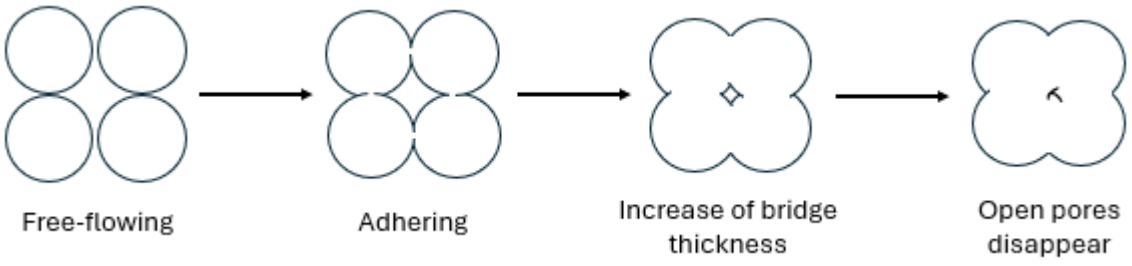


Figure 5. Sintering mechanisms (adapted from Hartmann & Palzer, 2011)

First, the particles are free flowing but due to changing conditions, powder begins to get sticky and the adhesion between particles increases due to surface diffusion. This decreases the flowability of the bulk and the sinter bridge diameter grows making the cake stronger. Initially, the powder structure collapses which leads to open pores disappearing leading to powder shrinkage and increasing its bulk density. After that, a solid particle lump is obtained.

The strength of the cake increases when the temperature increases. (Hartmann & Palzer, 2011; Zafar et al., 2017; Phosanam et al., 2021; Kamyabi et al., 2017)

### 3.1.4 Lactose crystallisation

In lactose crystallisation, the non-ordered glassy-state lactose transforms into an organised crystalline structure due to high RH and temperature. Amorphous lactose in dairy powders makes them highly hygroscopic, meaning they absorb moisture from their environment easily. This increases the mobility of lactose molecules, enabling the transition from an amorphous state to a crystalline state. The crystallisation process is further accelerated at higher temperatures and RH levels because these conditions increase molecular mobility, promoting the crystallisation. (Phosanam et al., 2021). Amorphous lactose is also prone to crystallise if the powder temperature exceeds the $T_g$. In storage conditions moisture absorption lowers the $T_g$ because water acts as a plasticizer which furthers the crystallisation. The changes in the microstructure and surface properties of powder induce caking and affect the flowability and solubility of the powder. (Qi et al., 2024; Fitzpatrick et al., 2007)

Schulnies and Kleinschmidt (2018) found that lactose crystallisation occurred in SMP within 200-600 h when the powder was stored at 24-25°C and 40-54 % relative humidity (RH). On the other hand, Qi et al. (2024) studied that approximately 68 % of the lactose in SMP is crystallised when powder is stored for four months at 25°C and 53 % RH. In comparison, WMP had crystallised lactose approximately 54 % at the same conditions. When the RH was increased to 75 %, both powders crystallised 4 % more but when RH was only 23 %, the powders were crystallised approximately 2-4 %. Qi et al. (2024) also studied that powders stored at 43-58% RH and 25°C and 40-48% RH and 40°C contained the same phase of lactose and crystallinity. The only difference between those powders was that the crystallite size increased while RH was increased. At 58 % RH, crystal size was studied to be around 0,3 µm.

Lactose crystallisation furthers fat migration to the surface. This happens because crystallisation initiates to separation of lactose from other components and breaks the fat globule membrane (Phosanam et al., 2021; Qi et al., 2024). Thus, fat globules migrate towards the surface and according to Phosanam et al. (2021), the surface fat content increases approximately 37 % after 4 months of storage. Lipid surface content increases when relative

humidity increases due to this phenomenon. Qi et al. (2024) stated that during lactose crystallisation, the absorbed water is released further accelerating chemical changes. They examined that protein absorbs the released water, leading to changes in protein structure.

According to Phosanam et al. (2021), lactose crystallisation can lead to other problems regarding powder stability. Temperature changes, moisture absorption or crystallisation can lead to increasing Maillard reactions. It is a huge problem during storage, and even though temperature and RH are the most critical factors affecting it, the occurrence also depends on powder composition. Phosanam et al. (2021) state that in lactose-free milk powders, glucose and galactose exhibit higher reactivity compared to lactose and thus, Maillard reactions occur more often. These reactions can be minimized by controlling RH and using moisture-resistant packaging.

### 3.1.5 Protein denaturation and aggregation

Boland et al. (2014) state that denaturation is a process where the polypeptide chains of protein molecules change to a disordered arrangement due to temperature increase. β-lactoglobulin, which is the main whey protein, undergoes aggregation and denaturation at higher temperatures of 70°C. Especially in lactose-hydrolysed milk powders, the protein can undergo denaturation or aggregation due to interactions between monosaccharides glucose and galactose. Because denaturation occurs at high temperatures, they are unlikely to happen in storage and transportation.

### 3.1.6 Mechanical caking

Mechanical caking of milk powders occurs due to the mechanical pressure that powders experience during storage and transportation. At Ryabova et al. (2023) study, the milk powders were transported and stored in wooden pallets where powder bags were placed three in a layer and stacked up to 10 layers. This transportation method affects the product because the load applied to the bag is different to the bottom layer compared to the top layer. In their study, they examined the effect of storage on the change in $a_w$, particle size distribution, caking, rehydration, and heat stability of SMP and WMP. Powders were stored in different temperatures (-30°C, 6°C & 25°C) and different RH (40% & 80%) for 18 months. Powder

bags were arranged in stacks of five layers, each containing three bags. Samples were analysed every three months, and the experiment was performed in a closed environment. Thus, water content and $a_w$ did not undergo any significant changes during this period. Because there were no changes in the moisture content, the study concluded that the weight load on powder affected lumping and particle size distribution significantly by increasing the particle adhesion and compaction. They also found that an increase in the mass fraction of fat increased the clump's size. This is most certainly due to surface-free fat formation. When powders were stored at below-zero temperatures the load pressure did not affect the powder. On the other hand, load pressure at 25°C had a significant impact on the powder quality. Signs of changes in product quality first appeared after 15 months of storage so this implies that powders could be stored that long without any changes. Nevertheless, this experiment was performed in a closed environment, where the conditions were controlled when in real life this is not always the case. Schulnies & Kleinschmidt's (2018) study supports these findings and they also concluded that higher storage pressures result in faster caking.

According to Carpin et al. (2016), mechanical pressure has an impact on cohesive forces between the particles. For example, van der Waals forces are forces between particles at close distance due to the electrostatic attraction between the nuclei of one molecule and the electrons of another. In spray drying, milk is atomized into fine particles which promotes the van der Waals forces to form. Even though these forces are weak, they get stronger when the distances get shorter between the particles. When powders are packed and stored, the mechanical pressure grows increasing cohesion. As the particles get more closer together, the contact surface gets bigger and van der Waals interactions cause more cohesion and adhesion which will lead to more aggressive aggregation.

## 3.2 Kinetics of caking

There have been studies regarding its affection for caking and the strength of clumps. It has been determined that storage time strengthens cohesive forces and stickiness over time as well as increases the particle size (Phosanam et al., 2021; Schulnies & Kleinschmidt, 2018; Fitzpatrick et al., 2007; Ryabova et al., 2023).

Özkan et al. (2003) examined the caking time as a function of pressure. The gained results are shown in Figure 6. With increasing temperature and pressure, the caking time decreases. For example, when pressure is 20000 Pa, the caking time with temperature at 60°C is approximately 260 min and at 65°C is approximately 60 min. This means that pressure has an impact on caking time, and it should be considered when stacking powders for transportation and storage.

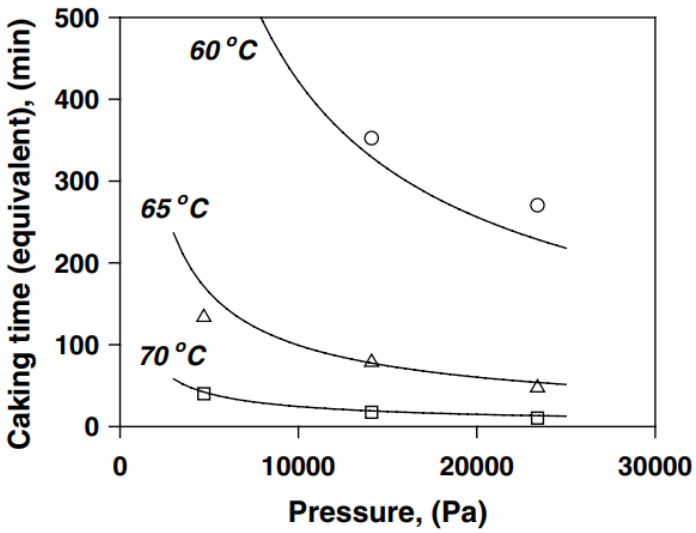


Figure 6. Caking time as a function of pressure (Özkan et al., 2003) Examined caking time is presented with solid lines and predicted caking times symbols.

Fitzpatrick et al. (2007) studied the effect of temperature, RH and exposure duration on the cake strength and the results are presented in Figure 7. At 25°C and RH at 76 %, the cake strength was near 0 N in the range of exposure time of 0-6 hours. When the exposure time increased over 12 hours, the cake strength increased to 2 N. Cake strength increased from 1 N to 3.5 N when temperature was increased from 10°C to 40°C at RH 76 %. It is notable that higher temperatures result in more severe cake strength. It is obvious that regarding the temperature and RH, the cake strength increases as the time of exposure increases. Based on this knowledge, it can be said that caking is time dependent.

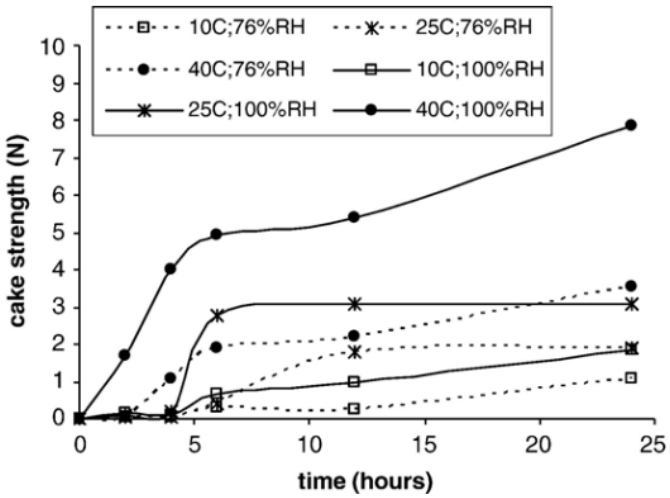


Figure 7. Effect of temperature, RH, and exposure duration on the cake strength of SMP (Fitzpatrick et al., 2007).

Ryabova et al. (2023) studied the effects of storage conditions on particle size distribution in in different temperatures (-30°C, 6°C & 25°C) and different load pressures for 18 months. The results for WMP (a) and SMP (b) are presented in Figure 8.

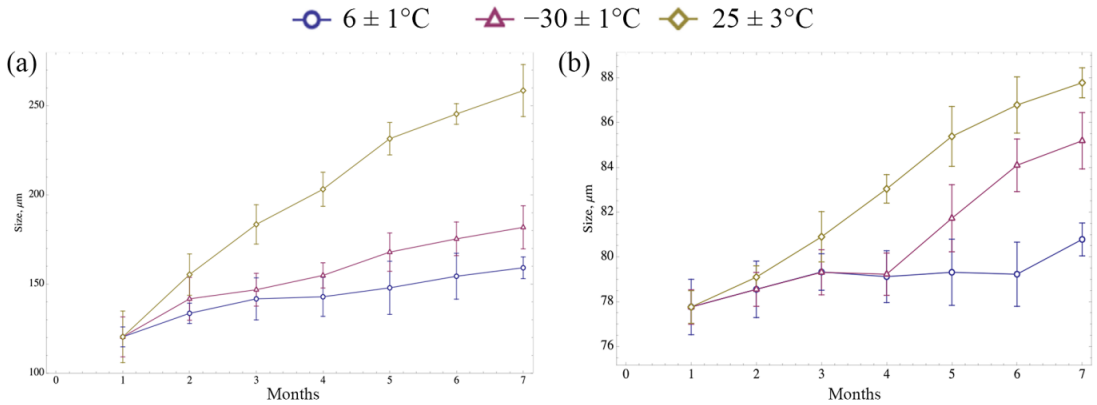


Figure 8. Effect of storage temperature on the average particle size in (a) WMP and (b) SMP (Ryabova et al., 2023).

Samples stored at 25°C had significant changes in the particle size distribution regardless of the load pressure in both powders. In other temperatures (-30°C and 6°C), only the bottom-

layer powders showed changes in the particle size distribution. Temperature and load together have an impact on the size distribution during storage. The longer the particles are stored, the wider the particle size distribution is indicating that the particles undergo physical changes.

# 4 Storage conditions

Storage conditions have a significant impact on the quality and caking of dairy powders. Proper powder packaging is crucial for powders to ensure their quality and consumer demands. Dairy powders can be stored for more than two years, and they will inevitably undergo negative physical and chemical changes due to environmental changes. For this reason, the packaging and storage conditions are important to maintain constant. With the right kind of packaging and monitoring, these changes can be prevented. The most important factors to consider are moisture prevention and temperature stabilisation during storage.

## 4.1 Effects of storage conditions

The impact of temperature and RH on quality has been studied a lot. Semeniuc et al. (2008) studied that when WMP with a fat content of 26% was stored at 15°C and 25°C for 6 months, there were no changes in the moisture content. The moisture content doubled, after a year of storage. Masum et al. (2019) studied the moisture content of infant milk formula for 6 months in desiccators placed in incubators at temperatures ranging between 22-40°C and RH ranging between 11-54%. They detected that the moisture content increased enormously when RH was 54%. When stored at room temperature (22°C) and RH at 54%, moisture content increased substantially and then gradually. After 2 months of storage, moisture content decreased due to crystallisation and caking. Phosanam et al. (2020) studied the effects of T and storage RH on cake strength in spray-dried milk powders (SMP and WMP) which were packed in aluminium foil bags. They observed the caking strength at 25°C, 35°C and 45°C and with relative humidities of 11%, 44% and 85%. They detected that no caking occurred at any temperature when RH was 11%. When temperature was at 25°C caking occurred only when RH was at 85% but with temperatures at 35°C and 45°C, severe caking

occurred when RH was 35% and 45%. Higher RH increases the caking process and cake strength. Temperature increases from 25°C to 35°C resulted in more severe caking which indicates that even small changes in conditions can have a significant effect on caking. These studies indicate that storage conditions have an important role to play regarding caking.

## 4.2 Impacts of caking on dairy powder storage stability

In storage conditions, powder may undergo multiple changes. Powder stability determines the ability of powder to maintain its physical, chemical, and microbiological properties over time under specific storage conditions. Figure 9 presents the factors that have an impact on powder stability. Factors can be split into different categories based on the impact that they have on powders. Stability can be affected by chemical reactions or changes in powder characteristics. These factors can also cause chain reactions and it is common that different factors affect the powder stability at the same time.

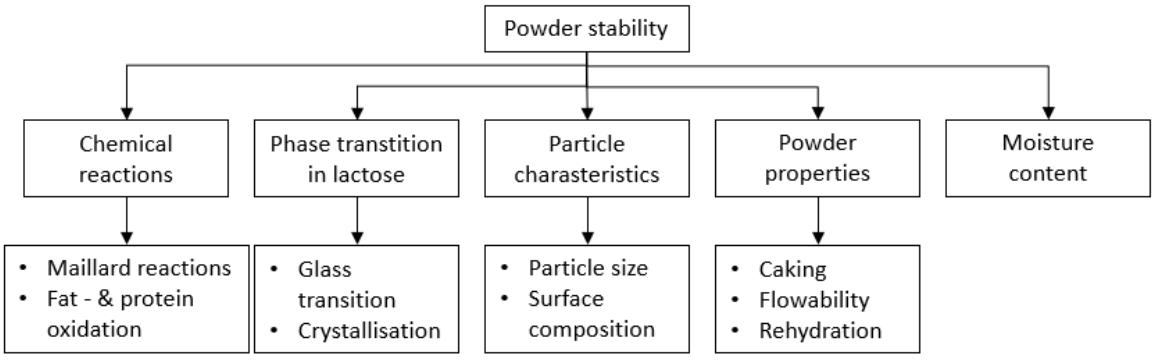


Figure 9. Factors that affect powder stability. (Adapted from Phosanam et al., 2021)

### 4.2.1 Powder properties

Phosanam et al. (2021) stated that increased cohesion and caking are due to moisture increase during storage. Moisture absorption leads to liquid bridge formation and ultimately to caking. Kim et al. (2008) state that flowability is a surface-related property which means that it is hugely affected by the powder surface composition. An increase in temperature also

affects the flowability negatively due to fat melting which leads to liquid bridging and stickiness. Phosanam et al. (2021) state that whole milk powders have higher fat content making them more likely to face flowability problems due to higher cohesiveness during temperature increases. This happens because most fats start to melt at 10-30 °C. Their study also claims that SMP face more stickiness than WMP when exposed to high RH. This is due to the higher hygroscopicity of lactose and the high hydrophobicity of milk fat.

Kim et al. (2008) state that the particle surface is hydrophobic due to the surface fat in the particle which increases the contact angle between the surface and water which weakens the wettability. According to Phosanam et al. (2021), high lipid and protein content on the surface reduces the wettability but high lactose content increases it. To support these claims, Tamime's (2009) study that SMP has high wettability because it mainly consists of lactose and protein which both absorb water easily. On the contrary, WMP has a higher fat content, which weakens the wettability. High-fat content does not mean that the powder cannot be wetted. Fat consists of triglyceride and phospholipids. Phospholipids, for example, lecithin, are known for being both lipophilic and hydrophilic which means that they can absorb water.

Caking causes powder structure damage which will affect powder solubility. For instant powders, solubility is an important factor regarding quality. Changes that happen in particle surfaces have a huge impact on rehydration properties. Lactose crystallisation and fat migration towards the surface decrease the wettability and dispersibility and ultimately affect solubility. Ryabova et al. (2023) state that milk powders are soluble when the insolubility index is less than 1 mL (99%) and that solubility highly depends on the nature and structure of proteins (Felfoul et al., 2021). Lactose crystallisation can start protein denaturation which means that protein structure gets damaged. In the process of spray-drying, lactose displaces water molecules that are bound to hydrated proteins. When lactose crystallises, these bonds are broken, and the protein structure is damaged. Whey proteins, which account for 20 % of protein composition, are less soluble when denaturised. Denatured proteins are more likely to interact with each other and thus form bigger aggregates which will lead to poor solubility. (Thomas et al., 2004)

Mechanical stress is also found to cause caking and changes in molecular structure which affects solubility. Pressure modifies the structure of β-lactoglobulin which is the main whey protein in bovine milk. This causes denaturation and it reduces the solubility. (Boland et al., 2014)

### 4.2.2 Chemical reactions

Maillard reactions pose a challenge for milk powders, mainly because of their high levels of lysine-rich proteins and reducing sugars. Figure 10 illustrates the Maillard reaction pathway in dairy powders which is a complex series of chemical reactions. The carbonyl group of reducing sugars reacts with the free amino group of the protein (lysine) to form a compound called lactosyl-lysine or Schiff's base. This compound is chemically unstable and undergoes further rearrangements, called Amadori rearrangements, resulting in the formation of a more stable intermediate called the Amadori product. These intermediates can break down into reactive compounds which can further form advanced glycation end products (AGEs). AGEs contribute to browning and reduce the nutritional value of the powder. Additionally, these reactive intermediates can polymerize to form melanoidins, which are brown-pigmented compounds. High temperatures, low moisture content and long storage time accelerate these reactions, making them a concern for milk powders. (Phosanam et al., 2021)

Naranjo et al. (2013) stated that lactose hydrolysed milk powders contain more reducing sugars (glucose and galactose) compared to lactose-containing ones, and thus the nonenzymatic browning is more commonly seen in hydrolysed powders. Glucose and galactose exhibit a higher reactivity with lysine compared to lactose.

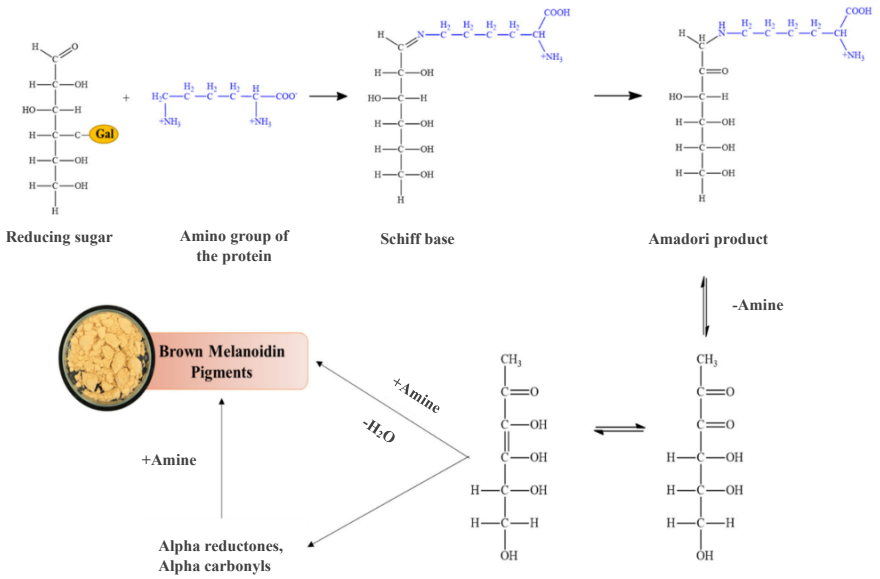


Figure 10. Maillard reaction pathway in milk powders (Phosanam et al., 2021)

Phosanam et al. (2021) studied the differences in browning between β-casein (casein protein) and β-lactoglobulin (whey protein). Maillard reaction occurred more in the case of β-lactoglobulin possibly due to β-casein hydrophobicity. This observation shows that Maillard reactions also depend on powder composition in addition to temperature and RH impact. These reactions weaken powder stability and quality, and they can be prevented with controlled circumstances.

Lipid oxidation is a severe problem especially in high fat-containing powders during storage. It has a negative impact on quality and consumer satisfaction. Air contains oxygen which easily reacts with fat at temperatures higher than 30°C. Phosanam et al. (2021) stated in their study that the free fat that migrates towards the surface due to fat globule membrane disruption, which happens due to crystallisation, is more prone to oxidation. This oxidation can produce hydroperoxides which ultimately lead to the production of off-flavours to the powders. The oxidation rate is dependent on temperature, it being faster in high temperatures. According to Tamime (2009), low moisture content accelerates oxidation rates because it causes particle disintegration, thereby increasing the exposed surface area of fat. For this reason, it is important to lower the oxygen content in the package and the storage conditions to ensure that lipid oxidation does not occur.

## 4.3 Prevention of caking

Caking can be prevented or minimised in different ways that have already been discussed earlier. Moisture, temperature, and pressure affect caking the most so monitoring and controlling storage conditions are the most important measures to do. In addition, there are a few other options for preventing caking like monitoring and altering drying conditions and particle size during production. During spray-drying the atomizing nozzle determines the particle size. Finer particles have been found to cause more caking and stickiness so decreasing the amount of fine particle content in the powder, reduces caking. (Zafar et al. 2017)

Anti-caking agents are often used in food systems to reduce caking and stickiness. They are used to help maintain a consistent flow or to enhance powder flow rate. There are a variety of additives in the market, and they have different mechanisms to overcome the caking. Most additives obtain a porous structure which makes them absorb large amounts of water before

the host powder absorbs it. Some additives increase $T_g$ and hence increase the stability of the powder. Another reduction method is to use anticaking agents on the particle surface where they create a moisture-protective barrier without transitioning into the amorphous phase. (Ermis, 2021) The usage of anti-caking agents is restricted and limited by the world health organization. Commonly used anticaking agents include for example silica, calcium carbonate, calcium silicate, and magnesium carbonate. Additives can be added 10 000 mg/kg singly or in combination with powder. (CODEX STAN 207-1999)

Powders should be stored and packed in a moisture-free atmosphere so powders would not absorb water. Karaman et al. (2015) stated that gas- and moisture-resistant packaging in a cool and dry environment would be optimal packaging and storage conditions. Most used packaging materials for milk powders are a combination of kraft paper and polyethylene lining, metal cans, laminated polymeric packages and composite cans. Powders contained in metal cans or composite cans cannot undergo changes due to moisture change, light, or oxygen change because they are enclosed from the environment. Thus, powders that have a long shelf life are often contained in cans.

WMP's maximum shelf life is approximately 6 months due to fat oxidation (Anandharamakrishnan, 2017). It is usually packed in cans or drums. Other packaging materials can lead to changes in product properties depending on the packaging material's water vapour permeability. Phosanam et al. (2021) stated that moisture absorption can be minimised by monitoring and controlling RH and using packaging materials with high moisture barriers.

# 5 Methods used to study the caking of powders

This chapter introduces a few key analysis methods commonly used in previous studies on caking. For example, differential scanning calorimetry (DSC) is frequently used to determine the $T_g$ of powders, while scanning electron microscopy (SEM) is widely used to examine the surface morphology and structure.

**Glass transition temperature analysis**

Jouppila & Roos (1994) among other researchers studied the milk powder $T_g$ and instant crystallisation temperatures for lactose with DSC. It is a thermal analytical technique used to measure physical changes as a function of temperature. DSC allows measurements in a wide temperature range (-90-550°C) and it provides qualitative and quantitative information on the thermal properties (Leyva-Porras et al., 2019). It is commonly used to study phase transitions in powders which include for example crystallisation, melting, and glass transition. Jouppila & Roos (1994) were able to determine the $T_g$ for anhydrous lactose (97 °C) with this method and they also found that the instant crystallisation temperature ($T_{cr}$) of pure lactose was lower than that of lactose in milk powder. Tham et al. (2016) used DSC to study the surface free-fat melting temperature in infant formula. They detected that a higher concentration of unsaturated or short-chain fatty acids resulted in lower melting points compared to a higher concentration of long-chain saturated fatty acids.

**Powder structure and morphology analysis**

Electron microscopes can be used to study the morphology and structure of food powder surfaces. Scanning electron microscope (SEM) analysis is an often used method to study the morphology of powders like particle shape, size and surface characteristics. (Bhandari, 2024) Yazdanpanah & Langrish (2012) used SEM analysis to detect the morphology changes of milk powder after storage. SEM analysis provided clear images of the particle surfaces, revealing the presence of lactose crystals. Agglomerates and bridge formations as well as insoluble particles and pores can also be detected with SEM analysis.

Kim et al. (2009) alongside Yazdanpanah & Langrish (2012) used an X-ray diffractometer (XRD) to study the crystalline compounds in milk powders. Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to characterise the molecular composition and structure of materials. Yazdanpanah & Langrish (2012) also used FTIR to study the surface crystallinity. FTIR analysis indicated that after 30 weeks of storage, powder surface crystallinity increased significantly resulting in higher peaks in the spectrum compared to fresh milk powder. FTIR has also been used to study changes in protein secondary structures. They found out that the secondary structure of protein undergoes changes after long storage.

**Wettability determination**

Wettability is an important factor that indicates how well the powder surface absorbs water. A tensiometer is an instrument that measures the contact angle (θ) between powder and water where the wettability can be determined. Ermis (2021) explains that powders are usually compacted into tablets, after which a deionised water droplet is dropped onto the powder surface. The tensiometer captures a series of images depicting the deformation of the droplet over time, allowing the contact angle to be determined. Ji et al. (2016) studied how agglomeration affects the wetting properties of high-protein powders with tensiometers. θ above 90° means that the liquid does not wet the solid but when the θ is below 90°, the liquid wets the solid well. In addition, θ indicates powder surface content because highly hydrophobic components like protein increase the θ.

**Flowability measurement**

A powder rheometer can be used to determine powder behaviour under dynamic conditions. It is mainly used to study powder flowability. Rheometer can be used with a wide range of environmental conditions. (Zafar et al., 2017) Brockbank et al. (2015) used a rheometer to measure the flow energy of powder samples before and after caking to quantify the resistance to flow. A rheometer can also be used to quantify the size and strength of a strong cap or crust that is formed on the top of a powder sample. Crusting is extent of moisture migration on powders to form a hard layer on the surface. The rheometer detects this moisture-induced phenomenon as peaks in the force and torque measurements.

**Accelerated caking methods**

Caking usually occurs after powders have been stored for longer periods. When caking is examined on a laboratory scale, accelerated methods are used to promote caking in a shorter timeframe. Environmental parameters like temperature and relative humidity affect caking the most so these parameters can be adjusted higher so that powder undergoes changes faster. Higher temperatures increase molecular mobility resulting in accelerated caking whereas higher humidity promotes moisture absorption which results in liquid bridge formation and ultimately caking.

For example, Calvert et al. (2013) have developed an accelerated caking method, where a powder sample is put into a chamber where the caking can be studied under varying conditions of temperature, relative humidity, and consolidation stress. Temperature can be

set up to 50℃, relative humidity up to 95% and consolidation stress up to 50 kPa. Many other researchers have been studying caking in accelerated conditions. For example, Novaes et al. (2018) studied the stability of omega-3 enriched milk powders in different packages with accelerated conditions where powders were exposed to temperatures of 34℃ and 43℃ and relative humidities of 83%. Lactose crystallisation, lipid oxidation and moisture absorption were observed even after 3 weeks of storage. In these tests, it is important to remember that when powders are exposed to elevated conditions, powder may undergo changes that would not happen in real-life situations and thus the results might be misleading.

# Applied part

# 6 Materials and methods

In the experimental part of the thesis, the focus is on investigating the phenomenon of caking over time for lactose-free skim milk powder (SMP) and whole milk powder (WMP). These hydrolysed SMP and WMP samples are examined at different storage conditions to understand how different conditions affect the caking and quality of these products and how could caking be prevented. This chapter describes the used materials and applied methods used in this thesis to study the caking.

## 6.1 Eila SMP and WMP

The lactose-free milk powders for the experimental part were provided by Valio (Seinäjoki, Finland). Powders were stored in sealed 25 kg bags until use. Two different powders were provided: Eila Pro WMP and Eila Pro SMP and the powder compositions and initial moisture contents (%) are shown in Table 1 (Valio, 2024a; Valio, 2024b). Eila means “no-lactose”, so the experimented powders were lactose-hydrolysed, which means that the carbohydrates present were in the form of glucose and galactose.

Table 1. Chemical composition of Valio Eila milk powders

| **Powders** | **Fat, %** | **Protein, %** | **Carbohydrate, %** |
|---|---|---|---|
| Valio Eila Pro WMP | 26 | 32 | 32 |
| Valio Eila Pro SMP | 0.9 | 47 | 41.2 |

SMP has low fat content, so there are more proteins and carbohydrates present in the powder. Fat being hydrophobic, SMP absorbs more water compared to WMP which thus has lower moisture content. In the beginning, the fresh powders moisture of the non-fat dry matter was approximately 66 % higher in WMP compared to SMP with the initial moisture content.

When the powders were moistened to gain higher water activity ($a_w$), the non-fat dry matter moisture content difference between these powders was only approximately 5 %. The higher moisture content in the non-fat dry matter has an effect on the physical and chemical changes.

## 6.2 Experimental setup

The literature review implies that storage conditions such as temperature, moisture, RH, and consolidation stress were the main causes of caking. Thus, caking was studied with different moisture contents and temperatures and under specified consolidation stress. Figure 11 illustrates the experimental setup that both hydrolysed WMP and SMP were studied.

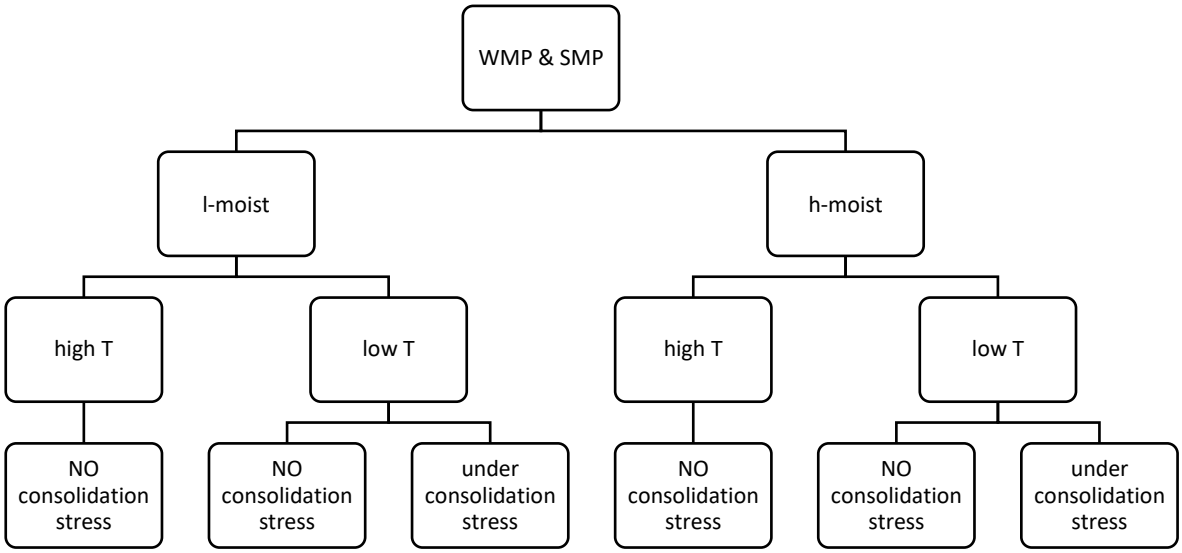


Figure 11. Experimental circumstances for Eila WMP and SMP

Two different moisture contents were selected to get quality results under varying conditions. These were selected based on initial information about $a_w$ and $T_g$. The first, and lower, moisture content selected was the initial moisture content that the powders were stabilised to during production. The maximum acceptable moisture content is < 5% and the initial moisture contents of these powders were low. For obtaining broader results, caking

was wanted to study in a circumstance where the powders would be produced and stabilised to a higher moisture content so higher moisture content powders were also studied.

Both low and high moisture content WMP and SMP samples were studied at two different temperatures referred as low T and high T. These temperatures were selected based on the analysis of $a_w$ and the calculation of $T_g$ at different moisture contents as Figure 12 presents. Both the fresh powder samples and moistened powder samples were below their $T_g$ at both low and high T. Some of the moistened powder samples were close to their $T_g$ at the higher temperature after a few weeks of storage. This gave information on how the powders behave near the glass transition circumstances. In addition, these temperatures had a sufficient temperature gap between them in which case this caking test gave broader results. The room temperature conditions were easy to implement in a storage room and the high T environment was created in an aging oven.

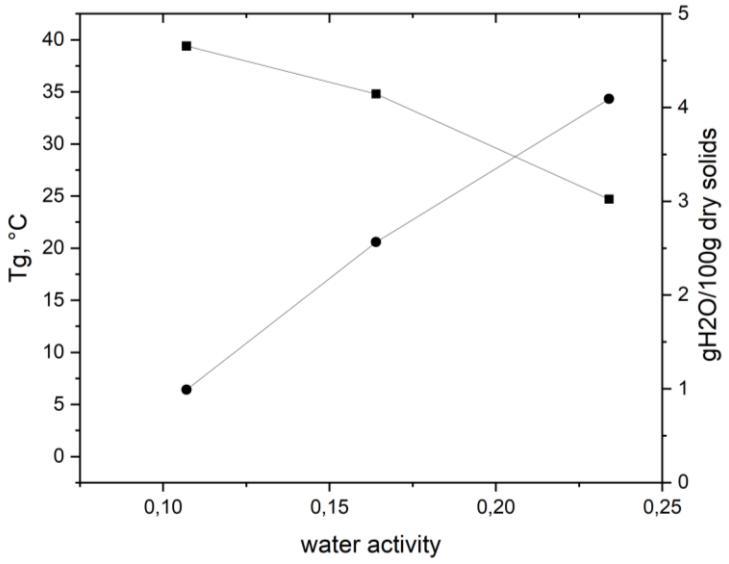


Figure 12. $a_w$, $T_g$ (■), and moisture content (●) for Eila SMP

Furthermore, consolidation stress had been identified as a significant contributing factor to caking and cake strength and thus it was also included in the experimental framework. Consolidation stress was only studied at the low temperature because the experimental design was difficult to execute in an ageing oven. The magnitude of consolidation stress was calculated based on given real-life storage and transportation conditions. In this study, the

maximum load to the powders at the bottom layer is estimated to be 1000 kg. This weight is evenly distributed to the whole area of the pallet, which is known to be 800 x 1200 mm. Based on this information, the consolidation stress was calculated to correspond to a smaller area where the powder samples were placed. The needed force to correspond to the weight was 40 kg.

## 6.3 Sample preparation

When the 25 kg powder sacks were opened for the first time, approximately 3L of both SMP and WMP were packed in plastic bags and foil bags and then frozen to prevent caking. When powders were stored under minus temperatures, there would be no alterations in their properties and thus, the powders could be classified as "fresh" even after long periods of storage.

For both SMP and WMP, 10 g powder samples were weighted into resealable airtight bags made of low-density polyethylene (LD-PE) which were furthermore sealed into foil bags to ensure a controlled, environment-free circumstance from external moisture interference. Then, these samples were moved into the environments in which the studies took place. For the higher temperature, an oven was used to create the environmental circumstances and the room temperature experiment was implemented in a storage room.

To obtain the higher moisture content samples, the lactose-free SMP and WMP powders were incubated and stabilised using a moisture sorption analyser (Vsorp, ProUmid, Germany) at 25 °C with 15 % RH for one week. After this step, these samples were weighted into 10 g bags the same way as the fresh powder samples and then placed into the experimental environments.

Eila Pro SMP and WMP powders were also analysed in accelerated conditions to obtain fully caked samples. Eila Pro SMP and WMP samples were stored in open petri dishes to obtain significantly caked powders. Another SMP and WMP samples were stored in the same plastic bags as the 2-month period samples but without the foil bag for obtaining caked and lumped powders without drastic moisture change. These powders were stored in climatic chambers with a temperature of 35 °C and relative humidity of 70 %. From now on, the experimented samples are referred to as indicated in Table 2 which also presents the $T_g$ for

these studied samples. The powders were stored over a period of two months to facilitate the study of the caking. During this period, the samples were examined biweekly for physical changes.

Table 2. Eila SMP and WMP sample reference names

| Sample name | Referred in the thesis as: | $T_g$, °C |
|---|---|---|
| SMP with a lower moisture content | SMP (l-moist) | 39.4 |
| WMP with a lower moisture content | WMP (l-moist) | 39.4 |
| SMP with a higher moisture content | SMP (h-moist) | 34.8 |
| WMP with a higher moisture content | WMP (h-moist) | 34.8 |
| SMP at accelerated test (dish) | SMP (acc. dish) | 30.1 |
| WMP at accelerated test (dish) | WMP (acc. dish) | 30.1 |
| SMP at accelerated test (bag) | SMP (acc. bag) | 24.7 |
| WMP at accelerated test (bag) | WMP (acc. bag) | 24.7 |

## 6.4 Applied methods

Powder samples were analysed with different methods during the two-month period. Next, the basic principles and sample preparations are described more in detail.

**Contact angle measurement**

Contact angle measurements examine the contact angle between water and powder, and they indicate the wettability and hydrophobicity of the examined powder. The contact angle (θ) of the milk powder was measured with an optic tensiometer (Theta Flex OneAttension, Biolin Scientific, Finland) with the sessile drop method. Tensiometer comprises a camera, a drop dispenser, a sample stage, and a light source. The tensiometer was connected to a measuring program in the computer where the analysis results were obtained. 2 g of powder was pressed with a 2.0 N force for 10 seconds to form the tablet by tablet presser (Vaneox 40t, Fluxana GmbH & Co.KG, Germany). The tablet was then placed in the tensiometer sample stage which was then altered in a way that the tablet surface would show in the measurement programme. A drop of distilled water (5 µl) was dropped to the powder surface and the image of the drop was recorded. The contact angle was determined immediately after

the droplet was placed on the surface. This provides the initial wettability of the surface before significant absorption occurs, and the average contact angle was defined by using the Young-Laplace analysing mode.

**Flowability measurements**

Powder flowability was measured with a Modular Compact Rheometer (MCR) 302e with a powder shear cell and CTD 180 attached to it (Anton Paar, Austria). The Rheocompass software (V1.30.1064) was used for analysing the data. First, the sample powder was gently sieved into a sample cup and then a scraper bar was utilized to clear away excess powder to achieve a flat surface. The sample cup held approximately 2.6 ± 0.20 g of SMP and 1.9 ± 0.20 g of WMP. Then the sample cup was placed on the rheometer and the shear test was measured with the shear cell method which consists of pre-shearing and shearing.

The measurement process included one pre shear point and three shear points at normal stresses of 0.4, 0.8, and 1.2 kPa. The sample was first subjected to a maximum pre shear normal stress of 2 kPa to consolidate it. After that the sample was sheared at different forces until it reached the failure point at where the shear stress increased until the bed sheared or failed and, at that point, the maximum shear stress was recorded. These results were then plotted automatically on a Mohr-Coulomb diagram to determine the flowability properties of the powders.

**Measurement of $T_g$ and thermal behaviour of fat**

The $T_g$ and thermal behaviour of fat can be performed with differential scanning calorimetry (DSC) and the measurements were done with a DSC3+ instrument (Mettler Toledo™ AG, Schwerzenbach, Switzerland) equipped with a cooling system. Eight to fifteen milligrams of powder sample were weighted into a 40 µl aluminium sample pan (Mettler Toledo, Switzerland) and sealed using a sealing press (Mettler Toledo, Switzerland). Then the sample was analysed with DSC where the heat flow was recorded during heating or cooling the sample at a rate of 10 °C/min. In the first heating, the temperature range was 20 °C to 96 °C, in cooling 96 °C to -40 °C and in the second heating -40 °C to 96 °C. From DSC thermograms, phase transition appeared as peaks and step changes in heat flow, which could be detected and further analysed to determine the $T_g$ and thermal behaviour of fat.

**Water activity**

The water activity was measured at 22 °C using a Novasina LabSwift -$a_w$ moisture analyser (Switzerland). All the samples were measured only once because of the limited amount of sample.

**Cake strength**

Özkan et al. (2003) studied that pressure had an impact on caking time and Ryabova et al. (2023) studied that consolidation had an impact on caking. The powder cake hardness was analysed with a texture analyser (TA.XTplus Stable Micro, Surrey, UK). A 45° conical probe penetrated the sample to a depth of 3 mm at 1 mm $s^{-1}$ speed and withdrew at the same speed. When the conical probe first contacted the sample surface, the texture analyser detected the point (trigger force). After this point was detected, the conical probe continued to penetrate the sample until it reached the maximum penetration depth. The applied force was then reported as the cake strength into a computer software and the measurements were made three times for every sample. For these cake strength measurements, Eila WMP and SMP samples were prepared into sealed petri dishes with the same moisture contents as in the 2-month caking test and then these dishes were stored at low and high temperatures The cake strength was also studied for WMP (l-moist) under consolidation using a consolidation kit (Figure 13).

Figure 13. Consolidation kit to analyse cake strength under consolidation

The powder was added to the sample holder and then on top of that was put 10 kPa weights to represent the real-life consolidation pressure that the lower layer powder bags have. The kit was stored in a laboratory room with a temperature in the range of 20-25 °C. Even though the weights covered the whole powder surface, this analysis kit was not sealed from the environment. Possible moisture absorption is possible, so these results were good to compare with the accelerated dish samples where the moisture absorption was significant.

**Analysis of macromolecular changes**

Molecular changes in powder components were measured by Fourier transform infrared (FTIR) spectroscopy using Nicolet$^{TM}$ iS50 FTIR Spectrometer (Thermo Scientific$^{TM}$) controlled by OMNIC 8.2.387. IR spectroscopy was utilized to recognise substances and their molecular structures and, in this study, the changes between samples at different time periods were examined. Saji et al. (2024), among other researchers, stated that IR spectroscopy uses infrared light to identify functional groups in molecules by analysing the absorption of radiation. An infrared beam passed through the sample and reflected it to the detector. Absorption by the sample provided data for an ATR spectrum, which could be compared to a spectral library to identify the sample's components.

The FTIR spectra were collected at a resolution of 4 cm-1 with 32 scans over a range of wavenumbers from 4000-400 $cm^{-1}$. The equipment featured purpose-built accessories and integrated software like attenuated total reflectance (ATR). Before measuring the sample, a background spectrum was collected without the sample in place. After that a small portion of the powder sample was placed into the sample holder and the spectrum was collected to the software where they were analysed further.

**Powder particle size and emulsion particle size**

The particle size distribution was determined using laser diffraction (Mastersizer 2000, Malvern Instruments, Malvern, UK) in an isopropanol medium. The instrument consists of an optical module that includes a laser and detection unit which are connected to a computer unit which displays the results. The refractive index of the solid phase was 1.458, while that of the liquid phase was 1.390. The solution was stirred before dispersing the sample into the dispersion medium where it circulated between the optical and dispersion unit. The sample was added to the point that the obscuration value was above 5 %. Each emulsion was measured 3 times and between every measurement the equipment was eluted with

isopropanol medium. The average particle size value of all sample measurements is presented in the results.

Mastersizer 3000 fitted with a Hydro LV dispersion unit (Malvern Instruments, Malvern, UK), was used to measure the particle size and fat emulsification in the powder samples. Mastersizer 3000 also used laser diffraction to measure the size distribution of particles in the sample. Boiled distilled water was used as the dispersant in this analysis to minimise the air bubbles possibly affecting the measurements. Before dispersing the sample into the dispersant, the milk powder was reconstituted beforehand by mixing 3.125 g of WMP or 2 g of SMP with 25 mL of 50 ℃ water at least for 2 hours before measurements to get the sample to liquid form and to dissolve other components besides fat. Then the sample was added to the dispersant so that the obscuration value was around 5 %. Each sample underwent four measurements per analysis, with replicates performed to ensure data quality. The reported results represent the average of these measurements.

**Powder morphology**

Some of the Eila Pro SMP and WMP samples were also imaged with scanning electron microscopy (SEM) to determine the powder surface morphologies. The milk powder samples were put into a carbon double-sided adhesive tape and then it was coated with a 10 nm gold layer (conductive material). The images were obtained using scanning electron microscopy (Zeiss Sigma VP, USA).

**Powder crystallinity**

The crystallinity was analysed by using an X-ray diffractometer (D8 Advance, Bruker, USA) which was connected to a measurement software (diffract.suite). The X-ray diffractometer operated at an anode current of 40 mA and a voltage of 40 kV. Powder samples were ground into smaller particles and then diluted with ethanol onto a silicon wafer. After the sample dried, it was exposed to CuKα radiation at diffraction angles (2θ) ranging from 10° to 40° (with a step size, of 0.02° and a duration of 0.5 s per step). As the measurement angle is between 5-80°, the measurement is called wide-angle X-ray scattering (WAXS). Monosaccharide crystallisation progress was detected with increasing intensities of peaks in the WAXS pattern. The crystallised monosaccharide peaks from the analysed samples were identified and the peak locations on the WAXS pattern were compared to a databank of materials.

**Free fat accumulation**

Some fat may be liberated from the fat droplets during powder processing and ageing, and this fat is called free fat. Free fat tends to migrate on the powder particle surface, and it is extractable with non-polar solvents. In this study, the free fat accumulation during powder caking was monitored. In the procedure, 0.50 (±0.01) g of powder was suspended in 5 mL of petroleum ether in a kimax-tube. The suspension was mixed thoroughly by vortexing and then shaken for 10 min in a shaker at 350 rpm after which it was centrifuged at 3000 rpm for 15 min. The supernatant, containing the free fat, was carefully poured into a clean pre-weighed kimax-tube. The solvent was evaporated to dryness at 30 °C under a nitrogen stream. After cooling down, the tube containing the free fat was weighed and the free fat was calculated as a percentage of the powder weight.

**Statistical analysis**

Statistical analysis was performed using Minitab statistical software (Minitab LLC, USA). The main effect screener was used to examine differences between level means for one or more factors. From the results, the effect value is the difference between the highest and lowest averages and a higher value means greater effect. A 2-sample t test was used to determine whether the population means of two different groups differ significantly from one another. The result of this analysis yields a P-value, and if the P-value is below the selected significance level (<0.05), it indicates a significant difference between the two groups. Analysis of variance (ANOVA) assesses whether the means of two or more populations are statistically equal. With this, one can determine if there are differences between specific means. (Minitab, 2024)

# 7 Results and discussion

The water activity was measured biweekly for all the samples. Maintaining a constant $a_w$ during the 2-month caking test was crucial to ensure that the moisture content did not vary. The $a_w$ stability allows for an accurate determination of the $T_g$ and a reliable analysis of how the initial moisture content and temperature influence the caking behaviour. If the moisture content varies, it would indicate that the samples are interacting with the surrounding

environment, compromising the reliability of the test results. $A_w$ remained stable during this 2-month period in all samples.

Overall, during this 2-month period, there were clear indications of caking in both Eila SMP and Eila WMP. Caking was already visible with eyes in three different samples which are presented in Figure 14. Both SMP (h-moist) and WMP (h-moist) samples that were stored under consolidation stress at low T, and WMP (h-moist) samples stored at high T, experienced caking visible with eyes. There were already visible lumps in consolidated SMP (h-moist) after 2 weeks of storage and in consolidated WMP (h-moist) after 6 weeks of storage. WMP (h-moist) at high T also had lumping visible after 6 weeks of storage. Those lumps were hard but still breakable when using a spatula. It is obvious that some physical and chemical changes have happened for these powders under these conditions. Consolidation stress together with higher moisture content created circumstances where adhesion between the particles and thus aggregation and caking increased. These three samples were the only ones where caking was already visible to the eyes. In other SMP samples, there was no visible caking and they remained easy flowing (Figure 1 of Appendix I) but in WMP samples it was obvious that the powders got more cohesive over time (Figure 2 of Appendix I).

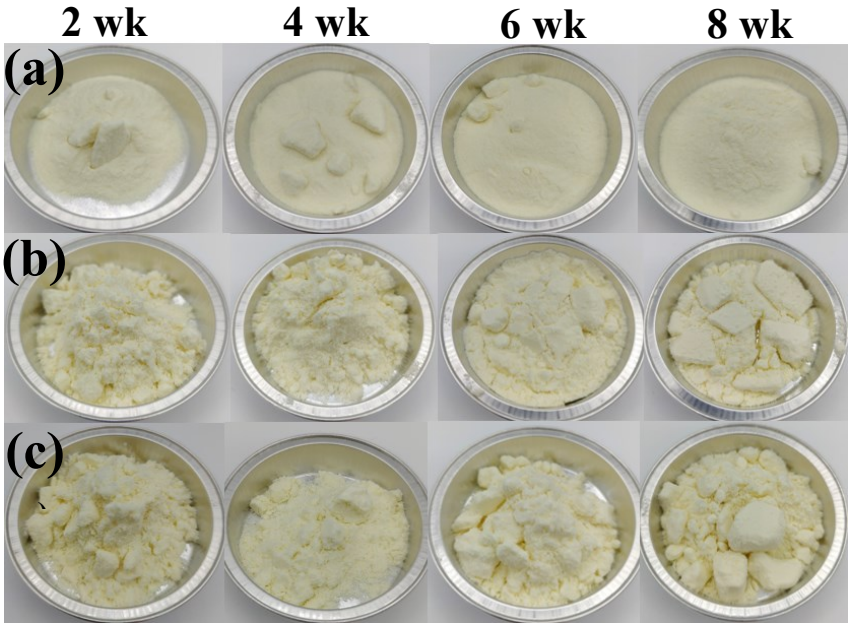


Figure 14. Powder caking in Eila (a) SMP (h-moist) under consolidation at low T (b) WMP (h-moist) under consolidation at low T, (c) WMP (h-moist) at high T. (wk=week)

Although there were no visible lumps in most of the samples, there were clear indications that the samples still experienced physical changes. Both Eila SMP and WMP samples got more cohesive over time and stickiness was detectable when the powders were processed for analysis. None of the powders experienced colour or odour changes during the storage period except the powder samples studied at accelerated conditions. Accelerated test SMP and WMP powders are presented in Figure 15.

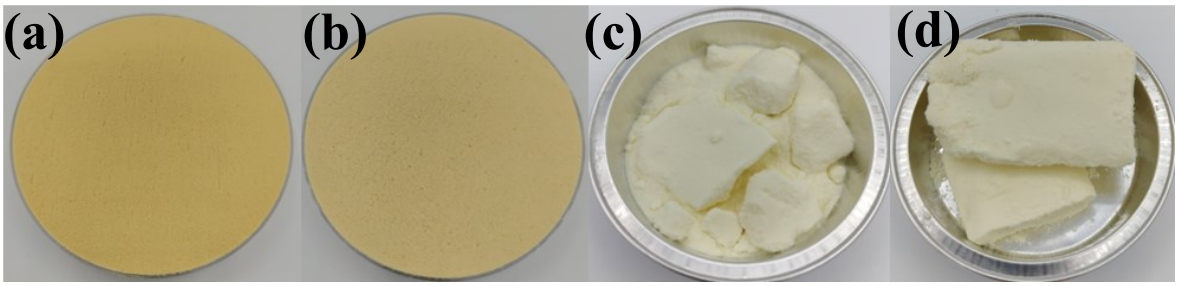


Figure 15. Powder caking in accelerated conditions for Eila (a) SMP (acc. dish), (b) WMP (acc. dish), (c) SMP (acc. bag) & (d) WMP (acc. bag) at 35 °C, 70 RH.

SMP (acc. dish) and WMP (acc. dish) samples experienced significant changes as the powders were thoroughly sticky and caked at the end of the week. Powders which were not sealed from the environment absorbed moisture and the physical changes were evident as the colour changed enormously due to the Maillard reactions. SMP (acc. bag) and WMP (acc. bag) powders experienced caking but no Maillard reactions occurred on those powders presumably because not enough moisture was absorbed.

## 7.1 Particle surface morphology

SEM-analysis was performed to determine the particle surface morphology and structural changes during caking. Three different lactose-free WMP powders were analysed and there were significant differences between them. WMP (l-moist) fresh powder showed low aggregation (Figure 16 (a)), compared to other WMP samples. Fresh WMP (l-moist) had a clear spherical particle structure, and the particles were individual. Agglomeration was noticed, but in this case, it was desired due to the spray drying process. There were more

aggregated particles, when fresh powder was compared to WMP (acc. dish) (Figure 16 (b)). The particles also appeared as irregular large clusters rather than as individuals. It is also noticeable, that smaller particles were attached to bigger particles and that they were fused and melted together due to moisture absorption and high temperature (white arrow in the figure). When particles melted together, there were no distinct particle boundaries. Figure 16 (c) presents the particle structure of lactose-free WMP (l-moist) from under consolidation, and it showed similar aggregation to WMP (acc. dish). A distinguishing difference between these two samples was that consolidated WMP (l-moist) did not show any signs of melting or fusion between particles. Consolidation stress increased particle cohesion and adhesion, but it did not lead to particle fusion, so particle boundaries were still distinct. Based on these results, consolidation stress alone does not lead to caked particles but together with moisture and temperature increase, it might have severe consequences.

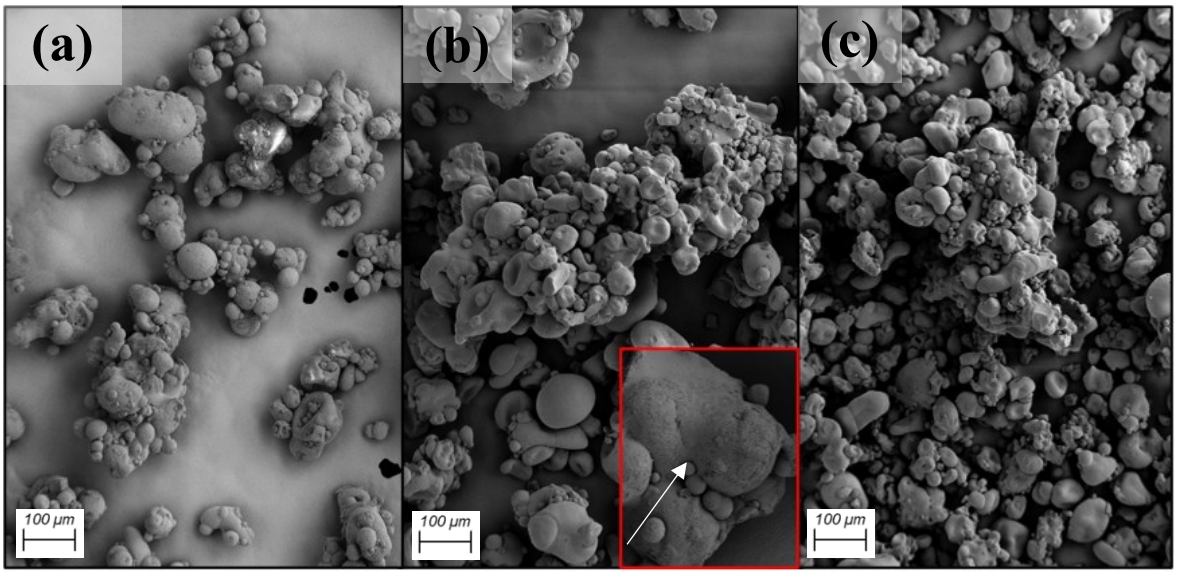


Figure 16. SEM-images of Eila (a) WMP (l-moist) fresh, (b) WMP (acc. bag) & (c) WMP (l-moist) under consolidation at low T. White arrow shows the fusion in close.

SEM-analysis was also conducted on two lactose-free SMP samples. SMP (l-moist) fresh powder had more irregular particles (Figure 17 (a)) compared to fresh WMP (l-moist) due to the absence of fat. The absence of fat also decreased the adhesion between the particles, as fat acts as a binder, and thus the fresh SMP (l-moist) was less agglomerated than the fresh

WMP (l-moist). SMP (acc. dish) showed similar behaviour as WMP (acc. dish) as particles were aggregated and formed irregular shaped clusters (Figure 17 (b)). It is also noticeable that particles had melted and fused together due to moisture absorption and temperature increase.

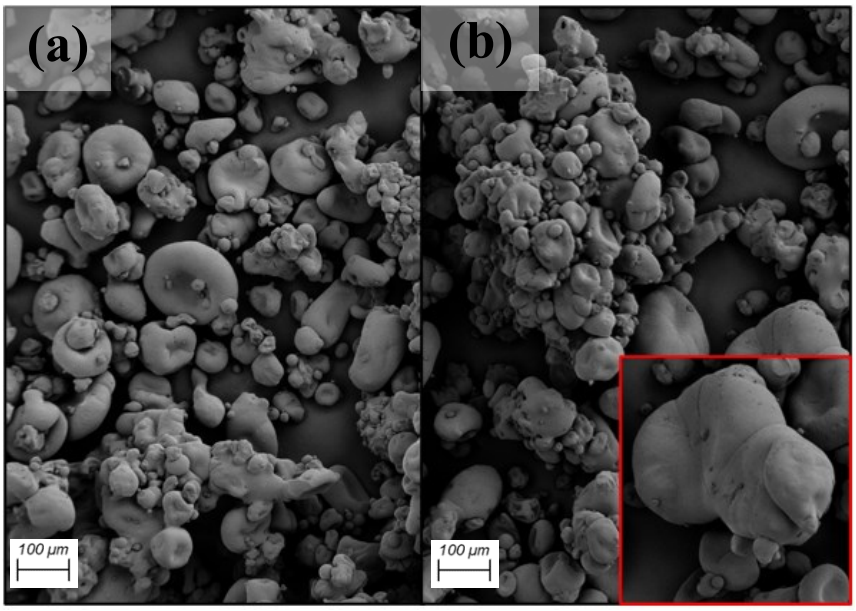


Figure 17. SEM-images of Eila (a) SMP (l-moist) fresh, (b) SMP (acc. bag)

## 7.2 Powder crystallinity

Milk powder crystallinity was analysed using WAXS to determine, which component and how severely it caused crystallisation. Carbohydrate was identified to be the component which crystallised as the location and peak intensities in the obtained WAXS patterns were the same when compared to crystallised carbohydrate data which was obtained from a library database. Figure 18 presents the WAXS result pattern for WMP (acc. dish). The main crystallisation peaks characteristic for carbohydrate are at 18.7°, 19.6°, and 21.9°. A similar WAXS pattern appeared in SMP (acc. dish) and these two samples were the only ones where the crystallisation was very clear. In WMP (acc. dish) the crystallinity was 18.7 % and in SMP (acc. dish) 22.6 %. SMP had higher crystallinity due to its higher carbohydrate content. SMP was also able to absorb more water itself compared to WMP because it did not contain

fat which is hydrophobic. All in all, SMP had more carbohydrates to absorb more water and thus it crystallised more.

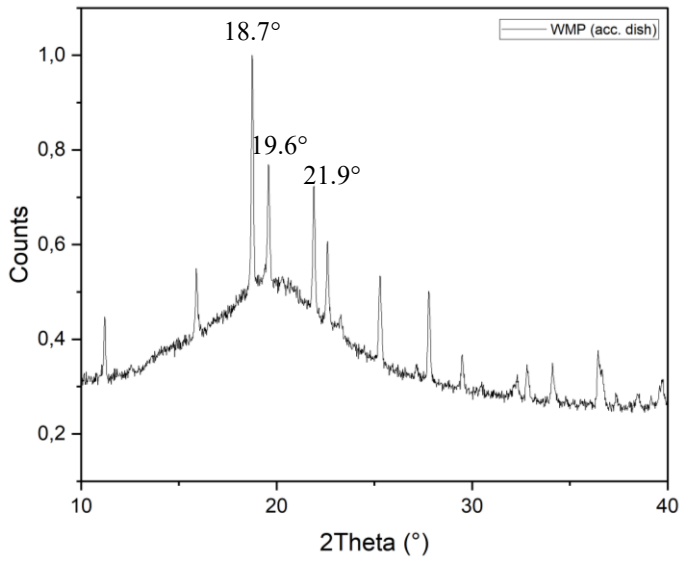


Figure 18. WAXS pattern for WMP (acc. dish)

The crystallinity (%) for all WMP and SMP samples are presented in Table 3. Even fresh WMP and SMP samples had carbohydrates in their crystalline form. Fresh WMP had 2.3 % and fresh SMP 3.1 %. All SMP samples had higher crystallinity at every condition compared to WMP due to their higher carbohydrate content. The crystallisation rate was significant only in the WMP (acc. dish) and SMP (acc. dish) because that was the only sample that experienced severe caking. The key finding from these results was that under all conditions, the crystallinity increased when compared to the fresh powders.

Table 3. Crystallinity (%) of WMP & SMP samples analysed with WAXS

| Sample | Crystallinity % | Sample | Crystallinity % |
|---|---|---|---|
| WMP (acc. dish) | 18.7 | SMP (acc. dish) | 22.6 |
| WMP (h-moist), high T | 5.4 | SMP (h-moist), consolidation+ low T | 6.6 |
| WMP (l-moist), high T | 5.2 | SMP (l-moist), high T | 6.6 |
| WMP (h-moist), low T | 5.2 | SMP (h-moist), high T | 5.9 |
| WMP (l-moist), consolidation+ low T | 5.1 | SMP (l-moist), consolidation+ low T | 5.7 |
| WMP (h-moist), consolidation+ low T | 5.0 | SMP (h-moist), low T | 5.6 |
| WMP (l-moist), low T | 4.3 | SMP (l-moist), low T | 4.7 |
| WMP (l-moist), fresh | 2.3 | SMP (l-moist), fresh | 3.1 |

Using the main effect screener, temperature and initial moisture exhibited the same amount of effect on crystallinity in WMP samples and consolidation had almost 50 % less effect on it (Figure 2 of Appendix III). Temperature, initial moisture, and consolidation all affected the crystallinity in SMP samples (Figure 1 of Appendix III).

## 7.3 Analysis of macromolecular changes

Fourier-transform infrared spectroscopy (FTIR) was used to study the molecular changes in the milk powder components during this 2-month caking test. Figure 19 presents the characteristic wavenumbers for different functional groups. The hypothesis was that there would be noticeable changes happening in the characteristic wavenumbers area for carbohydrates because crystallisation had been observed during storing. The changes were expected to be small except in the accelerated test samples.

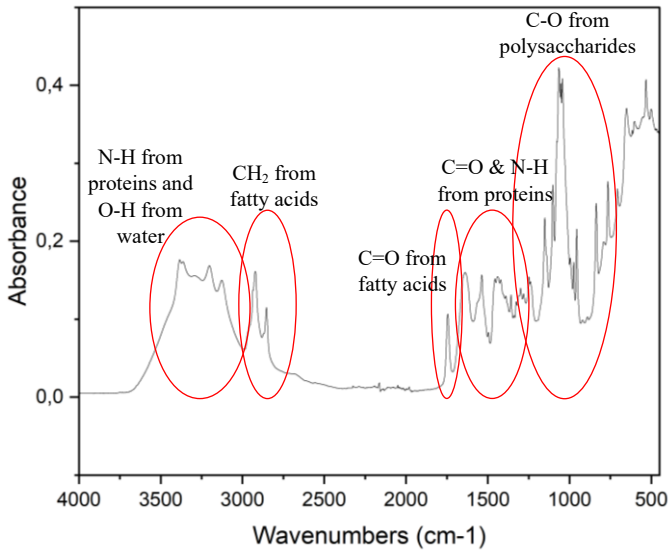


Figure 19. Characteristic wavenumbers for different functional groups

Figure 20 (a) presents results for both fresh WMP (l-moist) and WMP (acc. dish) and Figure 20 (b) for fresh SMP (l-moist) and SMP (acc. dish). The difference between the fresh and severely caked powders was significant, as it was obvious that high intensity peaks were formed in the carbohydrate wavenumbers area. Also, WAXS analysis studies identified carbohydrate crystallisation. When these accelerated test result spectrums were compared to the raw carbohydrate spectrum from the database, it was clear that the formed peaks aligned with carbohydrate's specific peak wavenumbers. Thus, carbohydrate crystallisation could be detected as shifts in peak positions, changes in peak intensities, or appearances/disappearances of specific peaks that indicated structural changes associated with crystallisation.

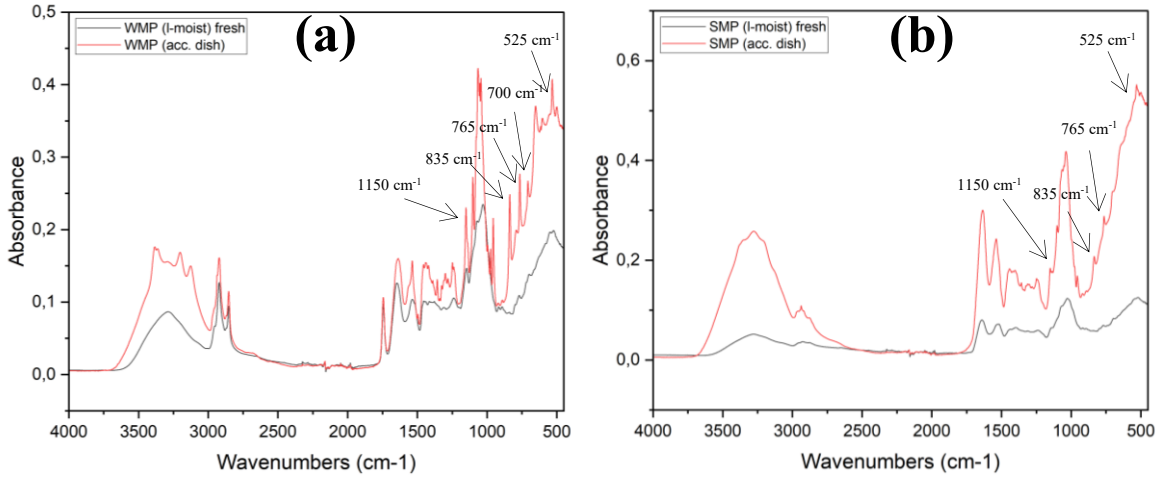


Figure 20. FTIR spectrums for Eila (a) WMP (l-moist) fresh & WMP (acc. dish) and for (b) SMP (l-moist) fresh & SMP (acc.dish)

When comparing WMP and SMP spectrums in general, SMP did not have any fat present (wavenumbers 2800-3000 $cm^{-1}$ and 1750 $cm^{-1}$), as assumed. It is evident that WMP (acc. dish) and SMP (acc. dish) both absorbed water (wavenumbers 3200-3600 $cm^{-1}$) during the accelerated caking test. SMP absorbed more due to its higher hygroscopic component content. This led to the crystallisation of carbohydrate and to increase of Maillard reactions indicated by an increase in peaks at wavenumbers range characteristic to carbohydrates and proteins. Even though SMP (acc. dish) absorbed more water, WMP (acc. dish) had more intense crystallisation peaks in the spectrum. These results indicated that SMP needs to absorb more water before it starts the crystallisation.

FTIR analysis indicated that WMP (acc. dish) would have more crystallinity whereas WAXS analysis contradicted with this finding. WAXS analysis is found to be more reliable for crystallinity studies because it provides precise quantitative information about the crystallinity. Nonetheless, FTIR is a reliable method to detect these different molecular changes in a qualitative manner.

To analyse the 2-month period caking test results for all WMP and SMP samples, 5 main carbohydrate peak wavenumbers were selected for further analysis: 525 $cm^{-1}$, 700 $cm^{-1}$, 765 $cm^{-1}$, 835 $cm^{-1}$ and 1150 $cm^{-1}$. The peak absorbance (A) values were summed from all these wavenumbers for each sample (Table 4) and then the results were compared between

different conditions. The differences were quite small between the samples, but it was noticeable that samples with higher moisture content had higher peak intensities compared to lower moisture content samples. The main effect screener determined that moisture content had the biggest impact on both WMP and SMP samples. Effect plots are presented more in detail in Figure 3 and 4 of Appendix III. In WMP samples, moisture content had approximately 4 times greater impact compared to time and 11 times greater impact compared to temperature. In SMP samples, it had approximately 9 times and 14 times greater impact compared to time and temperature respectively. Samples with the letters "a" or "x" experienced caking.

Table 4. Peak absorbance (A) for all Eila WMP & SMP samples during 2-month caking test. Sample with the same letter are not statistically different (WMP and SMP done separately) (one-way ANOVA) followed by Tukey's test ($p < 0.05$). (wk=week)

| **Sample** | **Peak absorbance (A)** | | | |
|---|---|---|---|---|
| | **2 wk** | **4 wk** | **6 wk** | **8 wk** |
| WMP (l-moist) low T | $0.713^{bcdef}$ | $0.676^{bcdef}$ | $0.687^{bcdef}$ | $0.680^{bcdef}$ |
| WMP (l-moist) high T | $0.715^{bcdef}$ | $0.680^{bcdef}$ | $0.689^{bcdef}$ | $0.616^{f}$ |
| WMP (h-moist) low T | $0.760^{abcd}$ | $0.751^{abcde}$ | $0.781^{ab}$ | $0.725^{bcde}$ |
| WMP (h-moist) high T | $0.748^{abcde}$ | $0.733^{bcde}$ | $0.768^{abc}$ | $0.751^{abcde}$ |
| WMP (l-moist) consolidation + low T | $0.658^{def}$ | $0.643^{ef}$ | $0.649^{ef}$ | $0.668^{cdef}$ |
| WMP (h-moist) consolidation + low T | $0.777^{abc}$ | $0.746^{abcde}$ | $0.763^{abcd}$ | $0.848^{a}$ |
| WMP (acc. dish) | - | - | - | $1.315^{x}$ |
| WMP (acc. bag) | - | - | - | $0.854^{a}$ |
| SMP (l-moist) low T | $0.420^{cdefgh}$ | $0.348^{hij}$ | $0.381^{efghij}$ | $0.313^{j}$ |
| SMP (l-moist) high T | $0.420^{cdefg}$ | $0.355^{ghij}$ | $0.423^{cdefg}$ | $0.343^{ij}$ |
| SMP (h-moist) low T | $0.462^{bcd}$ | $0.460^{bcd}$ | $0.468^{bc}$ | $0.445^{bcde}$ |
| SMP (h-moist) high T | $0.430^{cdef}$ | $0.513^{b}$ | $0.465^{bcd}$ | $0.469^{bc}$ |
| SMP (l-moist) consolidation + low T | $0.395^{defghi}$ | $0.370^{fghij}$ | $0.343^{ij}$ | $0.419^{cdefgh}$ |
| SMP (h-moist) consolidation + low T | $0.506^{b}$ | $0.510^{b}$ | $0.511^{b}$ | $0.616^{a}$ |
| SMP (acc. dish) | - | - | - | $1.538^{x}$ |
| SMP (acc. bag) | - | - | - | $0.614^{a}$ |

It's important to note that there was minimal variation between 2-week and 8-week peak absorbance intensities. In most samples, the 8-week peak intensity was lower than the 2-

week peak intensity. FTIR analysis is highly sensitive, and even minor analytical errors can significantly affect the results in cases where changes are very subtle. Only the WMP (acc. dish) and SMP (acc. dish) samples exhibited clear crystallisation and it could be seen from the peak absorbance values.

## 7.4 Cake strength analysis

The cake strength also known as cake hardness was analysed using a texture analyser which gave the cake strength results as a gram force (g) (Table 1 of Appendix II). Fresh powders should have 0 g cake strength which indicates that the powder is easy flowing. The hypothesis was that the cake strength increases over time and that higher temperatures and higher moisture contents would create harder cakes (Hartmann & Palzer, 2011).

Cake strength for all WMP samples from the 2-month caking test is presented in Figure 21 and for all SMP samples in Figure 22. It is evident that higher temperatures created harder cakes in WMP samples. Using a main effect screener, the factors that had the greatest influence on cake strength were determined and the effect plots are presented in detail in Figurer 5 and 6 of Appendix III. Initial moisture had minimal impact on cake strength in all WMP samples, whereas time and temperature had the most significant influences. After 8 weeks, WMP (l-moist) at high T created harder cakes than WMP (h-moist) at high T. This might be due to that WMP (l-moist) has a denser and more compact structure which enables harder cakes. Specifically, time had approximately 18 % greater impact compared to temperature, indicating that cake strength is time dependent. The maximum cake strength that WMP (l-moist) at high T was 158 g which is very high when 0 g is desired. WMP samples had greater variation between the samples compared to SMP.

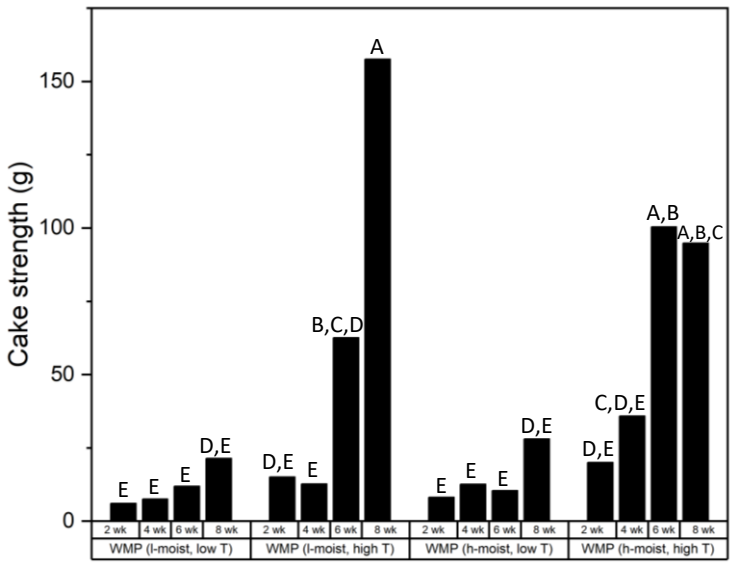


Figure 21. Cake strength (g) for Eila WMP samples taken every 2-weeks (wk=week). Sample with the same letter are not statistically different (one-way ANOVA followed by Tukey's test, $p < 0.05$).

SMP (l-moist) at high T was the only SMP sample which had a significant difference from other SMP samples having a cake strength of 44 g. The median cake strength in all SMP samples was 4.8 g so one sample had quite a big difference from the rest of them. There are a few possibilities that could explain this phenomenon. It is possible that the SMP (l-moist) at high T reached its point, where the physical and chemical alterations started to happen. It can also be that the sample wasn't sealed correctly from the environment and thus it was able to absorb water and form harder cakes. For SMP, time was also the most influential factor on cake strength with twice the effect of temperature and three times that of moisture content.

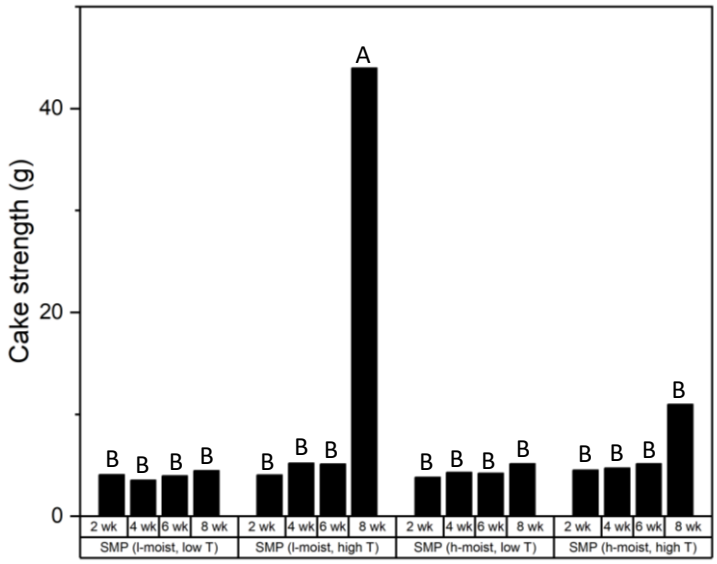


Figure 22. Cake strength (g) for Eila SMP samples taken every 2-weeks (wk=week). Sample with the same letter are not statistically different (one-way ANOVA followed by Tukey's test, $p < 0.05$).

When WMP and SMP samples were compared, it was evident that WMP created harder cakes. These results together with FTIR analysis indicate that SMP needs to absorb more moisture before it starts to form cakes. WMP consist of 98 % of triglycerides which have a melting range varying between -40 to +40 °C (Kim et al., 2005). Because of this, fat melting causes particle adhesion and aggregation which will lead to harder cakes.

When WMP and SMP samples were analysed with accelerated conditions, the results were reversed (Figure 23). Before analysing the hardness in these samples, the powder was added to a petri dish and then the surface was smoothened down. After that, the samples were placed in a low T and high T environments and every 2 weeks the cake strength was analysed. Now SMP (acc. dish) formed significantly harder cakes compared to WMP (acc. dish). When SMP (acc. dish) was able to absorb moisture in the open petri dish (for 1 week), it resulted in higher cake strength due to its higher carbohydrate and protein content. Moisture content had more effect on cake strength in SMP compared to WMP although it was still minimal in both. Higher carbohydrate and protein content enables more bonding between particles and thus SMP forms harder cakes. In these accelerated conditions, protein was also prone to undergo Maillard reactions (see chapter 4.2.2) which increases cake strength as protein and carbohydrate cross-links are formed. These molecular bindings lead

to denser and more stiff particle structures. As SMP has higher protein and carbohydrate content, this can cause stronger cakes.

Although WMP (acc. dish) also created harder cakes than the highest result from the 2-month caking test (158 g), the increase in hardness was not as substantial as between the SMP (acc. dish) and the highest cake strength observed in SMP's 2-month caking test. This indicated that SMP creates harder cakes, but it takes more time and moisture absorption than in WMP.

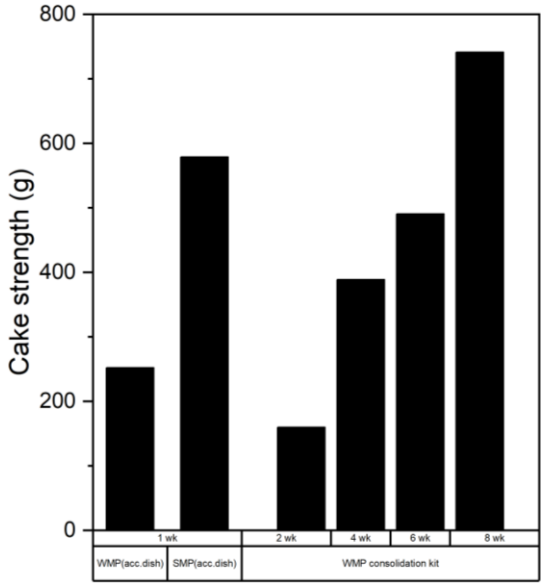


Figure 23. Cake strength for Eila WMP (acc. dish), SMP (acc. dish) & WMP (consolidation kit) (wk=week)

Then the cake strength was measured biweekly for WMP (consolidation kit), and the obtained results are presented in Figure 23. This consolidation kit experiment was only made for WMP because there was only one kit available. Based on these results, consolidation had a very significant impact on cake strength as it resulted in higher strength compared to WMP (acc. dish) after 4 weeks of storage and after 8 weeks of storage, it resulted in higher cake strength than SMP (acc. dish). SMP stored in the consolidation kit would form even higher cakes than WMP (consolidation kit) as it has higher carbohydrates and protein content, but this requires further studies.

## 7.5 Free fat (%) analysis

Free fat analysis in WMP is essential for assessing the quality and stability of the product. Free fat refers to the fat that is not encapsulated within the protein of the powder particles and is instead present on the surface. High levels of free fat can lead to issues such as caking, and poor rehydration properties and thus it can shorten the shelf life. Various previous studies, for example, Kim et al. (2008), have reported that fat-containing powders could release fat onto the powder surface during storage.

Figure 24 presents the free fat (%) of WMP samples at different conditions at different times. The initial free fat content in WMP samples was 0.95 % and the highest free fat content after 8 weeks was 1.2 % in WMP (l-moist) low T The difference between 0-week and 8-week samples was not severe as the free fat content only increased maximum of 0.25 %. There was still an indication of free fat formation already in 8 weeks also in the recommended storage conditions.

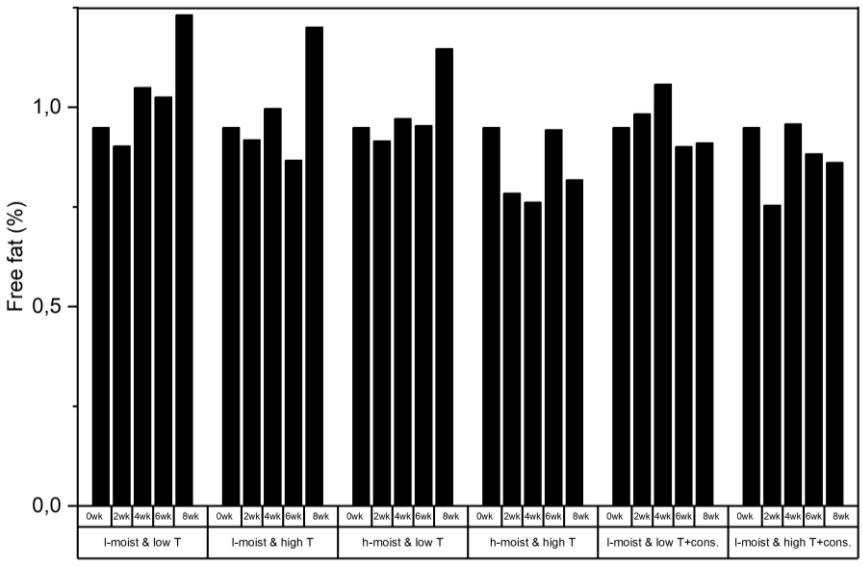


Figure 24. Free fat (%) results for Eila WMP samples taken every 2-weeks (wk=week)

In the WMP (acc. dish) the free fat content was 1.6 % which is the highest value of WMP samples. This is plausible result as free fat migrates towards the surface due to fat globule membrane disruption, which happens due to crystallisation. WMP (consolidation kit) had a

free fat (%) of 1.7 % which is significantly higher compared to other WMP samples. Based on WAXS data, WMP (consolidation kit) crystallinity was only 5.5 % which indicates that consolidation increases the free fat formation. Consolidation damages the fat globules or due to it fat migrates to the surface leading to higher free fat content. The detailed results of free fat (%) in WMP samples are presented in Table 1 of Appendix IV.

## 7.6 Wettability analysis

The contact angle was measured using a tensiometer where a water droplet was pipetted onto the powder surface and the contact angle was measured at the point where the droplet's surface met the solid surface (Figure 25). As stated earlier, a contact angle above 90° indicates low wettability (hydrophobic surface) (Ji et al., 2016). The hypothesis was that the contact angle would increase during this 2-month period study and that WMP samples would have a higher contact angle compared to SMP due to hydrophobic fat.

Figure 25 (a) presents the image of a water droplet on the surface of fresh WMP (l-moist) powder and Figure 25 (b) presents the same for fresh SMP (l-moist). Fresh WMP had a contact angle near 90° which means that it has low wettability qualities whereas fresh SMP has much higher wettability as the contact angle was lower. Fat globules are present near the surface, in WMP, where they act as barriers that reduce the interactions between water molecules and powder molecules.

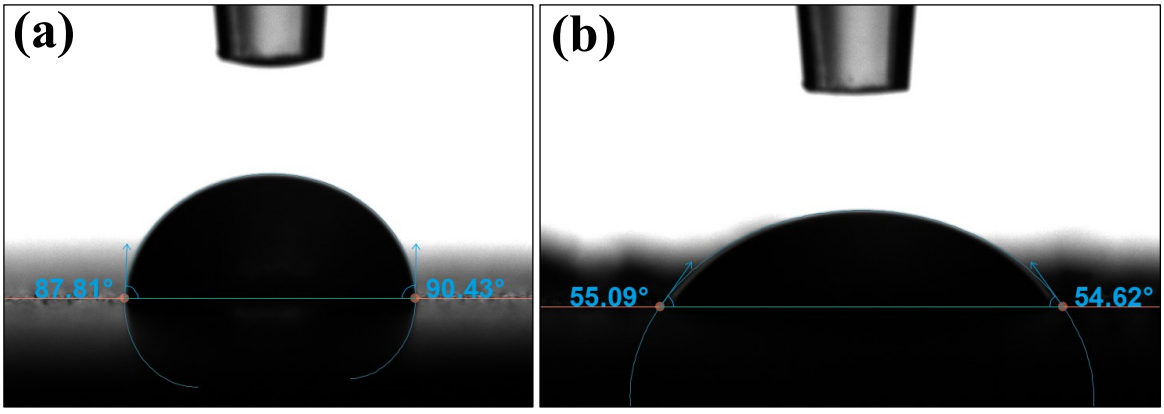


Figure 25. Contact angle measurement image for fresh Eila (a) WMP and (b) SMP

For the 2-month period caking test samples, contact angle analysis gave highly variating results (Table 5). The contact angle did not increase linearly in either WMP or SMP samples. WMP (l-moist) samples had higher contact angles in almost every condition compared to higher moisture content samples. The only exception was the WMP (l-moist) sample under consolidation which exhibited a lower contact angle after 8 weeks when compared to WMP (h-moist) low T and high T samples.

Table 5. Contact angle (°) results for Eila WMP and SMP samples taken every 2-weeks (wk=week)

| **Sample** | **Contact angle (°) of Eila WMP and Eila SMP** | | | | |
|---|---|---|---|---|---|
| | **0 wk** | **2 wk** | **4 wk** | **6 wk** | **8 wk** |
| WMP (l-moist) low T | 85.0±3.4 | 87.3±1.7 | 85.6±2.3 | 80.3±2.1 | 86.5±0.2 |
| WMP (l-moist) high T | 85.0±3.4 | 87.1±0.7 | 82.9±0.8 | 88.0±2.8 | 89.7±0.9 |
| WMP (h-moist) low T | 85.0±3.4 | 79.0±1.2 | 82.0±1.1 | 77.7±1.1 | 79.4±1.3 |
| WMP (h-moist) high T | 85.0±3.4 | 82.4±0.3 | 82.7±2.3 | 78.3±1.0 | 79.7±0.6 |
| WMP (l-moist) consolidation + low T | 85.0±3.4 | 81.7±0.6 | 82.7±1.2 | 87.6±2.1 | 78.9±0.9 |
| WMP (h-moist) consolidation + low T | 85.0±3.4 | 75.7±1.1 | 76.7±3.8 | 75.3±3.1 | 72.3±1.8 |
| SMP (l-moist) low T | 57.3±0.5 | 67.1±0.4 | 56.3±0.8 | 43.2±0.1 | 60.0±3.9 |
| SMP (l-moist) high T | 57.3±0.5 | 73.0±3.9 | 77.8±0 | 56.6±1.8 | 56.7±2.7 |
| SMP (h-moist) low T | 57.3±0.5 | 62.6±0.9 | 56.0±3.7 | 58.0±1.0 | 66.7±0.7 |
| SMP (h-moist) high T | 57.3±0.5 | 65.8±0.9 | 68.5±1.1 | 60.8±1.2 | 61.3±1.3 |
| SMP (l-moist) consolidation + low T | 57.3±0.5 | 57.4±0.5 | 60.7±2.1 | 65.7±0.9 | 62.2±1.1 |
| SMP (h-moist) consolidation + low T | 57.3±0.5 | 66.2±2.3 | 65.3±1.4 | 66.9±0.4 | 65.0±1.3 |

SMP samples had a significantly lower contact angle compared to WMP. It is important to note, that all SMP samples except the ones under consolidation broke after they were pressed into tablets. This breakage affected the measurements because a rougher powder surface absorbed moisture differently compared to an intact tablet. This led to inconsistencies and potential inaccuracies in the SMP results. Main effect screener plots are presented in detail in Figure 7 and 8 of Appendix III.

This analysis method had weaknesses that contributed to the results. When the powders were pressed into tablets, there was a possibility that the pressure could cause fat migration towards the surface which would affect the measurements. Additionally, the pressure may

be insufficient, leading to the breaking of SMP samples causing surface roughness. Other analysis methods such as dispersibility tests could examine the wettability better. Due to the limited amount of powder sample, the contact angle was measured with this method in this analysis.

## 7.7 Thermal behaviour of fat and $T_g$

DSC was used to analyze the thermal behaviour of fat in WMP samples as well as the $T_g$ of SMP samples. The fat crystallisation could be examined from the cooling profile and the $T_g$ could be examined from the second heating profile.

As WAXS analysis indicated, WMP powders underwent crystallisation which presumably would also be seen as changes in the thermal behavior of fat. Figure 26 shows the crystallisation profiles of the milk fat in WMP from different conditions with the peak positions. Fresh WMP (l-moist) and WMP (h-moist) under consolidation at low T after 8 weeks exhibited two peaks in their melting profile. According to Kim et al. (2005), these peaks represent low-melting triglyceride chains as they are at their characteristic peak positions. As stated earlier, triglycerides consist of different-length fatty acids (C4-C18) (Jeantet et al., 2016). This low-melting triglyceride means shorter or less saturated fatty acid chains which melt at lower temperatures compared to middle- and high-melting chains (Tham et al., 2017). When these melting profiles are compared to WMP (acc. bag) and WMP (acc. dish) profiles, there is a clear indication that some physical changes have happened. Two peak melting profiles had changed into broader one peak profile where the peak position was at a higher temperature. The storage temperature was higher (35 °C) at the accelerated caking test which could mean that the fat molecules might have recrystallized into a more stable form which could show as a single broader peak in the DSC curve. The peak position was closer to the middle-melting triglyceride chain characteristic temperature with these WMP (acc. bag) and WMP (acc. dish) samples. These shifts in the peak position clearly indicated significant changes happening in the fat crystallisation kinetics.

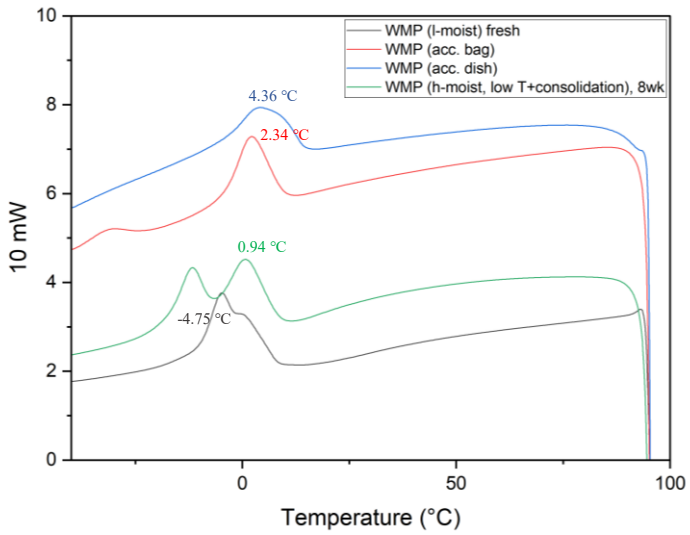


Figure 26. Fat crystallisation temperature with different Eila WMP at different conditions

Table 6 presents the fat crystallisation temperatures of WMP samples from different conditions. The peak position in the melting profile indicated the crystallisation temperature and as observed from the Figure 26, the peak shifted to higher temperatures over time and under varying conditions. The initial crystallisation temperature was different between the l-moist and h-moist 0-week samples due to their different moisture content. Fat might have undergone changes already during the incubation to the higher moisture content.

The crystallisation temperature changed towards higher temperatures during this 2-month caking test at all conditions. Lower moisture content samples had a more drastic change compared to higher moisture content samples. Nevertheless, higher moisture content samples had higher crystallisation temperatures after 8 weeks of storage. The difference was not severe but still noteworthy. It seems that initial moisture content had the most effect on fat crystallisation temperature whereas consolidation did not have any significant effect on it.

Table 6. Fat crystallisation temperature of WMP at different conditions analysed every 2-weeks (wk=week)

| Sample | Fat crystallisation temperature (°C) | | | | |
|---|---|---|---|---|---|
| | 0 wk | 2 wk | 4 wk | 6 wk | 8 wk |
| WMP (l-moist) low T | -4.75 | 0.25 | 0.10 | 0.87 | 0.86 |
| WMP (l-moist) high T | -4.75 | 0.42 | -0.088 | -0.52 | 0.67 |
| WMP (h-moist) low T | 1.27 | 1.61 | 1.76 | 2.22 | 2.31 |
| WMP (h-moist) high T | 1.27 | 1.26 | 1.24 | 1.27 | 1.69 |
| WMP (l-moist) consolidation + low T | -4.75 | 0.084 | 0.28 | 0.029 | 0.38 |
| WMP (h-moist) consolidation + low T | 1.27 | 2.07 | 1.96 | 1.86 | 0.94 |

Due to the absence of fat in SMP, DSC was used to analyse the $T_g$ of SMP samples. $T_g$ is influenced by changes in water activity (aw), moisture content, and temperature (T). Figure 27 presents the $T_g$ results for SMP under various conditions. Lower moisture content SMP samples exhibited higher $T_g$ compared to those with higher moisture content. The higher moisture content decreased $T_g$ because water acts as a plasticizer, increasing molecular mobility within the particles (Phosanam et al., 2021). These changes in glass transition temperature over 8 weeks suggested ongoing physical transformations within the particles, although these changes were not severe.

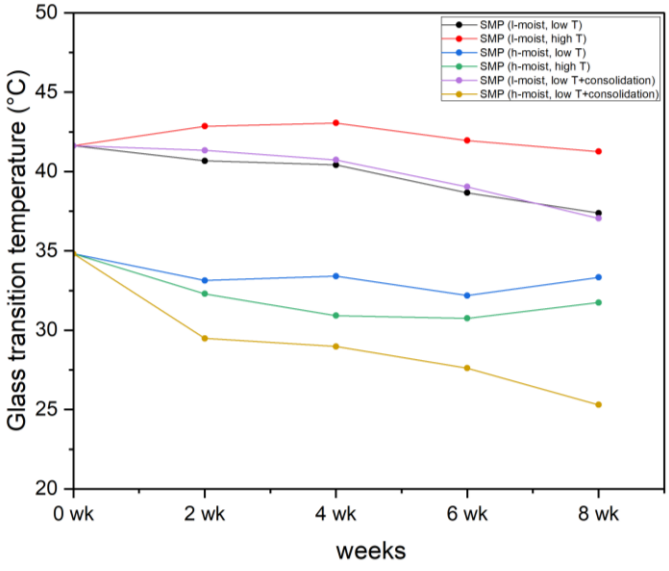


Figure 27. Glass transition temperature of SMP at different conditions analysed every 2-weeks (wk=week)

Shrestha et al. (2007) determined the $T_g$ for anhydrous lactose hydrolysed SMP to be 47 ℃ whereas Jouppila & Roos (1994) determined it to be 49 ℃. Now SMP had lower $T_g$ due to its initial moisture content of 0.98%. Jouppila & Roos (1994) studied that 1.5 % water content lowered the $T_g$ to 26 ℃ when powders were stored at 24 ℃. This study also studied the $T_g$ of Eila SMP with a water content of 2.56 % but the $T_g$ decreased only to ~35 ℃. Although higher moisture contents generally lead to a greater reduction in $T_g$, variations in composition and production processes can influence the $T_g$, leading to different outcomes.

## 7.8 Particle size analysis

Particle size was examined at three different intervals: 0-week, 4-week, and 8-week (Table 7). The D(0.5) value indicates the median particle size, meaning that 50 % of the sample's particles are smaller than the size presented (Pugliese et al., 2017). WMP particles were larger than SMP mostly due to the fat content as it acts as a binder between the particles. Bhandari (2024) stated that powder particle size is in the range of 10-250 µm whereas Jeantet et al. (2016) stated that the optimal particle size for obtaining the best dispersibility is 200 µm. This study exhibited particle sizes in the range of 120-134 µm for SMP and 126-138 µm for WMP samples, consistent with other findings.

All SMP samples from different conditions and times were not statistically different whereas WMP samples exhibited some significantly different particle sizes. 0-week and 4-week samples were not statistically different and only the WMP (h-moist) high T sample was statistically different from all other samples. These results indicated, that during this 2-month period caking test, particle size remained almost unchanged. Minitab main effect screener was used to analyse which variable (moisture, T, time, or consolidation) had the strongest effect on the particle size. For both WMP and SMP samples, time had the largest effect on it whereas initial moisture, temperature, and consolidation had only a small effect on it. The detailed effect plots are presented in Figure 9 and 10 of Appendix III.

Table 7. Average particle sizes during 2-month caking test analysed every 4-weeks (wk=week). Sample with the same letter are not statistically different (WMP and SMP done separately) (one-way ANOVA) followed by Tukey's test ($p < 0.05$).

| **Sample** | **D(0.5) µm** | | |
|---|---|---|---|
| | **0 wk** | **4 wk** | **8 wk** |
| WMP (l-moist) low T | 126.4$^{c}$ | 130.6$^{abc}$ | 132.4$^{abc}$ |
| WMP (l-moist) high T | 126.4$^{c}$ | 131.5$^{abc}$ | 134.6$^{ab}$ |
| WMP (h-moist) low T | 126.4$^{c}$ | 129.3$^{bc}$ | 128.3$^{bc}$ |
| WMP (h-moist) high T | 126.4$^{c}$ | 129.6$^{bc}$ | 137.9$^{a}$ |
| WMP (l-moist) consolidation + low T | 126.4$^{c}$ | 128.6$^{bc}$ | 129.5$^{bc}$ |
| WMP (h-moist) consolidation + low T | 126.4$^{c}$ | 132.9$^{abc}$ | 135.5$^{ab}$ |
| SMP (l-moist) low T | 120.7$^{a}$ | 123.6$^{a}$ | 128.1$^{a}$ |
| SMP (l-moist) high T | 120.7$^{a}$ | 119.9$^{a}$ | 129.7$^{a}$ |
| SMP (h-moist) low T | 120.7$^{a}$ | 117.1$^{a}$ | 134.1$^{a}$ |
| SMP (h-moist) high T | 120.7$^{a}$ | 119.5$^{a}$ | 129.8$^{a}$ |
| SMP (l-moist) consolidation + low T | 120.7$^{a}$ | 126.9$^{a}$ | 127.6$^{a}$ |
| SMP (h-moist) consolidation + low T | 120.7$^{a}$ | 137.8$^{a}$ | 122.5$^{a}$ |

In addition to powder particle size, the fat droplet particle size was also examined in WMP samples. Before the measurements, all non-fat components, such as proteins and carbohydrates, were dissolved from the sample to ensure reliable results for fat droplet size. Figure 28 presents the fat droplet size distribution to all WMP samples from the 2-month period caking test. Two different peaks could be identified from the results. First, more intensive, peak illustrated the fat droplet size whereas the other broader peak illustrated aggregates that were not dissolved. According to Malvern Panalytical (2020), fat globule particles should be observed at 1-2 µm whereas in these results the fat globule particles were observed below 1 µm. Casein micelles should be observed below 0.25 µm and particles near 10 µm are determined to be aggregates of fat globules. According to Jeantet et al. (2016), fat globules are measured between 0.2 and 15 µm but they state that the homogenization process decreases this diameter. These Eila WMP samples had undergone a homogenization process, which would explain why the fat globule sizes were smaller in this analysis. There was no significant difference in the peak intensity or in the peak position when 2-week samples and 8-week samples were compared. This means that the fat particle size remained

approximately the same after 2-month of storage at every condition. Based on these results, temperature, initial moisture and consolidation did not affect fat globule size distribution.

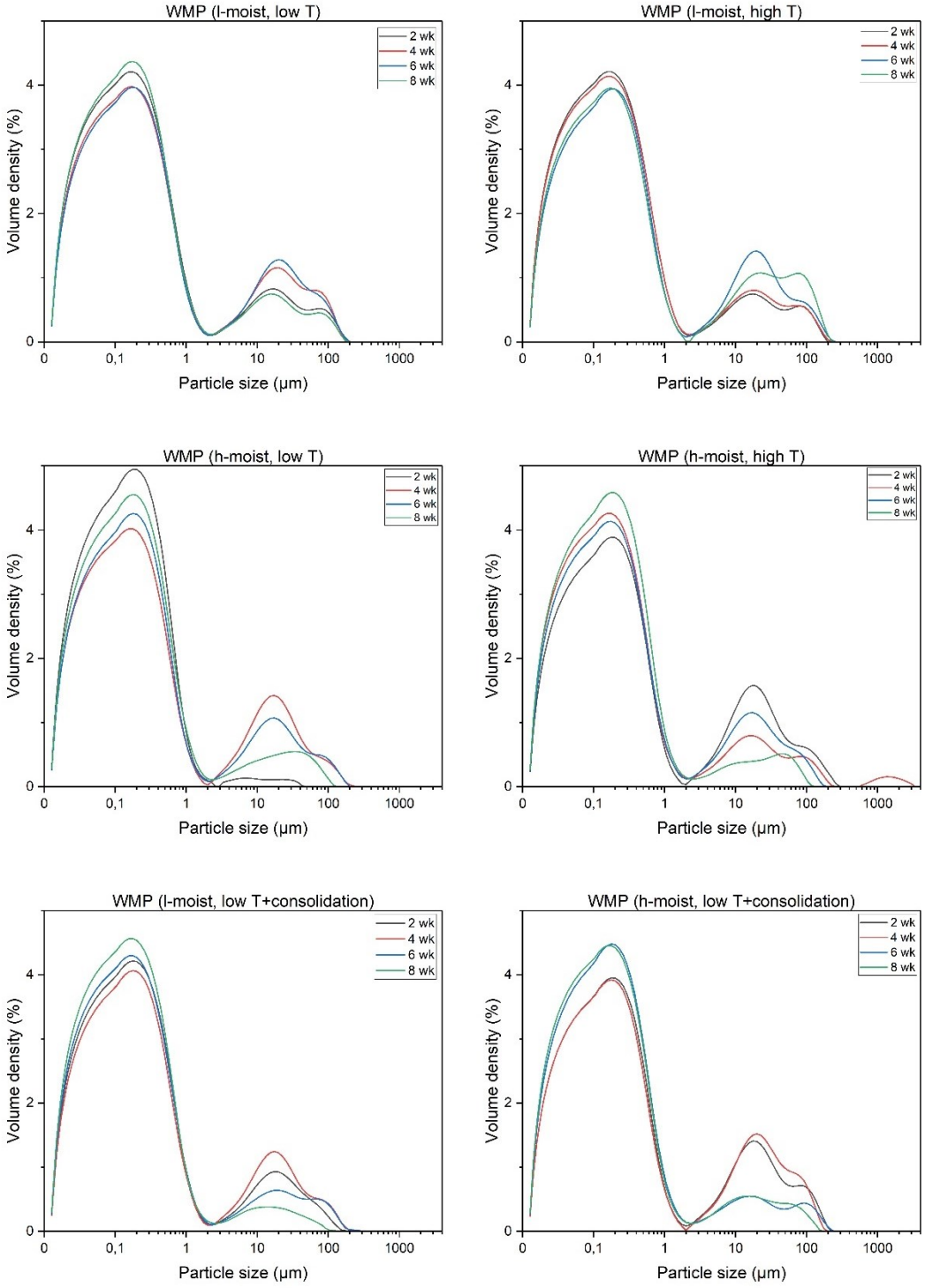


Figure 28. Particle size distribution of fat droplets in WMP samples analysed every 2 weeks (wk=week)

Fat particle size distribution was also examined in WMP (acc. bag) and WMP (acc. dish) samples (Figure 29). Surprisingly, WMP (acc. bag) exhibited minimal changes in the fat particle size when compared to fresh WMP (l-moist). It was expected to have a more significant difference due to its higher moisture content and temperature exposure.

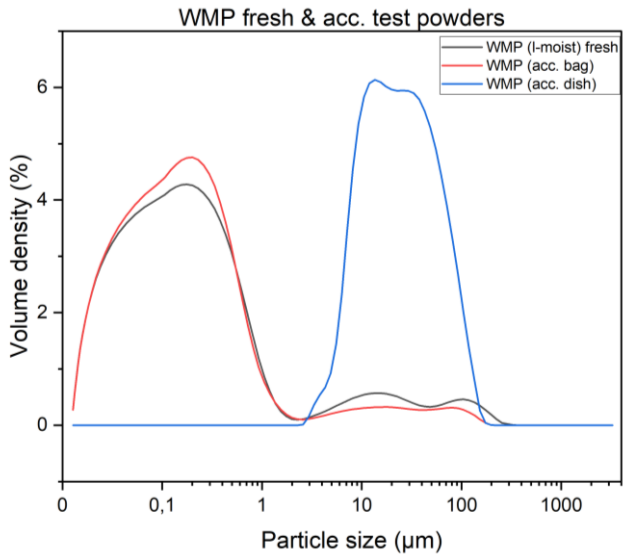


Figure 29. Particle size distribution of fat droplets in fresh WMP (l-moist), WMP (acc. bag) & WMP (acc. dish)

WMP (acc. dish) peak shifted towards the characteristic peak position of fat aggregates (Malvern Panalytical, 2020). The change was severe when compared to WMP (l-moist) fresh powder where there were no fat aggregates present. These findings indicated that the fat particle size in WMP remained stable under milder storage conditions, with noticeable changes occurring only under severe environmental conditions.

## 7.9 Flowability of Eila SMP and WMP

Powder flowability was analysed using a rheometer. Flow function illustrates the strength that a powder develops at an exposed surface for a given consolidation stress, and it is often used to classify powder flowability (Fitzpatrick, 2013). Table 8 presents the classification of

flowability based on flow function ($ff_c$). Powder is free flowing if the flow function is > 10 and it starts to get cohesive when the value is between 2 and 4.

Table 8. Powder flowability based on flow function ($ff_c$) (adapted from Fitzpatrick, 2013)

| Flow function | Flow description |
|---|---|
| $ff_c < 1$ | hard |
| $1 < ff_c < 2$ | very cohesive |
| $2 < ff_c < 4$ | cohesive |
| $4 < ff_c < 10$ | easy flowing |
| $10 < ff_c$ | free flowing |

When the flowability results for Eila SMP and Eila WMP (Table 9) were compared to these flow function classifications, the results indicated that the powders would change from cohesive powder to more easy flowing powder during time. These results contrasted with earlier studies done for example by Brockbank et al. (2015) where the flowability decreased after caking. It is uncertain if these results differ due to the uncertainty of the analysis method or because of some other factors. It is also possible, that the flowability improves temporarily before becoming properly sticky. This could happen because the powder initially absorbs a small amount of moisture, which coats the particles and enhances flowability. However, as the powder continues to absorb more moisture, the particles start to agglomerate, leading to stickiness. Particle size is one of the most affecting factors influencing flowability and generally, bigger particles flow more easily, while smaller particles can lead to poorer flow characteristics, such as increased cohesion and potential for caking. There was an increase in particle size over time, and the flowability results showed an increase as well.

Table 9. Flow function ($ff_c$) of Eila SMP and Eila WMP analysed every 2-weeks (wk=week)

| Sample | Flow function ($ff_c$) of Eila WMP and Eila SMP | | | | |
|---|---|---|---|---|---|
| | 0 wk | 2 wk | 4 wk | 6 wk | 8 wk |
| WMP (l-moist) low T | 2.21 | 2.39 | 2.02 | 2.73 | 2.24 |
| WMP (l-moist) high T | 2.21 | 2.52 | 2.19 | 2.88 | 2.53 |
| WMP (h-moist) low T | 1.92 | 2.67 | 2.66 | 2.53 | 2.32 |
| WMP (h-moist) high T | 1.92 | 2.71 | 3.2 | 2.69 | 3.81 |
| WMP (l-moist) consolidation + low T | 1.92 | 2.53 | 2.89 | 2.84 | 2.60 |
| WMP (h-moist) consolidation + low T | 2.21 | 2.01 | 2.84 | 2.61 | 3.32 |
| SMP (l-moist) low T | 4.59 | 3.67 | 4.09 | 3.53 | 4.18 |
| SMP (l-moist) high T | 4.59 | 4.43 | 3.93 | 5.07 | 3.47 |
| SMP (h-moist) low T | 3.78 | 4.03 | 7.37 | 6.61 | 3.33 |
| SMP (h-moist) high T | 3.78 | 3.19 | 3.52 | 5.21 | 4.99 |
| SMP (l-moist) consolidation + low T | 3.78 | 3.48 | 5.95 | 5.25 | 6.49 |
| SMP (h-moist) consolidation + low T | 4.59 | 3.19 | 7.81 | 5.53 | 5.67 |

The median flow function value for all SMP samples at 0 weeks was 4.2 and at 8 weeks was 4.6. For WMP at 0 weeks it was 2.1 and at 8 weeks it was 2.6. This indicates that SMP samples remained easy flowing for the whole 2-month period whereas WMP samples remained cohesive. In addition to flow function, the unconfined yield strength ($\sigma_c$) was obtained from the data results. Hartmann & Palzer (2011) stated that if the $\sigma_c$ exceeds 1000 Pa, the sample was considered as caked. The unconfined yield strength was above 1000 Pa in all WMP samples during the whole 2-month period when SMP samples remained under 1000 Pa the whole time which would indicate that all WMP samples were already caked whereas SMP samples remained flowing.

## 7.10 Summary of findings

A variety of analyses was done to study the caking in Eila SMP and Eila WMP powders. The analysis results from different methods showed consistency.

### 7.10.1 Factors influencing caking

Kim et al. (2008), Phosanam et al. (2021) and Ryabova et al. (2023), among other researchers, have stated that moisture content, temperature, time, and consolidation are the most important factors influencing caking in milk powders. In this study, those factors and their significance were examined. Main effect screener determined which factors affected the results whereas the 2-sample t test and ANOVA (one-way analysis of variance followed by Tukey's test ($p < 0.05$)) determined if the differences were statistically significant. The results concluded that different factors had different influences on powder properties with different analysis methods.

Initial moisture content affected the crystallinity (%), peak absorption (A), and contact angle (°) resulting in both Eila SMP and WMP samples. Even though the initial moisture contents were well below the maximum allowable moisture content of 5 % (Council directive 2001/114/EC), significant changes were observed between the samples with different initial moistures. Temperature affected the crystallinity (%), cake strength (g), and contact angle (°) results in both Eila SMP and WMP samples whereas consolidation affected the crystallinity (%), cake strength (g) results in both Eila SMP and WMP samples. Consolidation also impacted contact angle (°) results in WMP samples. Time had an effect on cake strength (g) and particle size results in both Eila SMP and WMP samples.

Table 10 presents the P-values from 2-sample t test made to identify if there were significant differences in the crystallisation results between the different initial moistures and between the two different temperatures and between consolidation. Results indicate that there was a significant difference (p-value $\leq 0.05$) between the initial moistures in Eila WMP samples. Low and high temperatures and different consolidations did not have any significant differences between them. This indicates that initial moisture levels had a significant effect on powder properties and their caking kinetics. It is important to note, that the determination of initial moisture in the early process stage plays a major role in preventing caking and crystallisation. This result on its own already indicated that even minor changes in the moisture content influenced the onset of caking.

Table 10. P-values from 2-sample t test regarding factor differences in FTIR analysis

| Samples | P-value for initial moisture | P-value for temperature | P-value for consolidation |
|---|---|---|---|
| Eila Pro WMP (all) | P < 0.001 | P = 0.641 | P = 0.916 |
| Eila Pro SMP (all) | P = 0.138 | P = 0.685 | P = 0.129 |

There was no statistically significant difference on either factor (p-value ≤ 0.05) regarding crystallinity (%) in both Eila WMP and SMP (Table 11). All factors affected crystallinity (%) but the differences in temperature and moisture content did not influence the onset of caking.

Table 11. P-values from 2-sample t test regarding factor differences in crystallinity (%)

| Samples | P-value for initial moisture | P-value for temperature | P-value for consolidation |
|---|---|---|---|
| Eila Pro WMP (all) | P = 0.349 | P = 0.229 | P = 0.790 |
| Eila Pro SMP (all) | P = 0.603 | P = 0.344 | P = 0.532 |

Specifically, the difference between the two temperatures was observed to impact cake strength as the significant difference (p-value ≤ 0.05) was noted in cake strength, whereas initial moistures did not exhibit any significant difference (Table 12). Özkan et al. (2003) concluded that pressure impacts caking time, and Ryabova et al. (2023) found that consolidation increased caking. When the cake strength was analysed using a consolidation kit, it was confirmed that consolidation indeed increased cake strength significantly. After 8 weeks under 10 kPa consolidation, the powder cake needed immense force to break down. In conclusion, consolidation stress induced severe caking.

Table 12. P-values from 2-sample t test done regarding factor differences in cake strength

| Samples | P-value for initial moisture | P-value for temperature |
|---|---|---|
| Eila Pro WMP (all) | P = 0.897 | P < 0.001 |
| Eila Pro SMP (all) | P = 0.138 | P = 0.019 |

In addition to cake strength, there were significant differences noted between the two temperatures as well as between the two initial moistures and consolidation when the contact angle (°) was analysed. P-values from this 2-sample t test are presented in Table 13 for

contact angle measurement results. In WMP samples, all factors (T, initial moisture, and consolidation) had a significant difference between them. These results indicate that minor changes in temperature and moisture content influenced the onset of caking since the initial moisture contents and temperature differences in the storage conditions were relatively small.

Table 13. P-values from 2-sample t test regarding factor differences in contact angle (°) analysis

| Samples | P-value for initial moisture | P-value for temperature | P-value for consolidation |
|---|---|---|---|
| Eila Pro WMP (all) | $P < 0.001$ | $P = 0.004$ | $P = 0.002$ |
| Eila Pro SMP (all) | $P = 0.124$ | $P = 0.217$ | $P = 0.143$ |

Fitzpatrick et al. (2007) stated that regarding the temperature and RH, the cake strength increased as the time of exposure increased. This study came to the same conclusion, identifying time as the most significant factor in the formation of cake strength in both WMP and SMP samples. Temperature was the second most influential factor, with results indicating that higher temperatures increased the cake strength, consistent with the findings of Hartmann & Palzer (2011). Initial moisture had a minimal effect on cake strength in WMP while it significantly affected SMP. This supports the notion that SMP needs to absorb more moisture before forming cakes.

Time also had the most effect on contact angle (°) in SMP samples as well as on particle size in both WMP and SMP. Particle size increase can occur due to natural attraction forces between the particles and if moisture is absorbed, it only increases the size growth. Proper storage, handling, and processing adjustments are essential to maintain the quality and usability of the powder over time.

### 7.10.2 Induction time for caking

Caking was already noticeable within 2 weeks in consolidated SMP (h-moist) and in consolidated WMP (h-moist) samples after 6 weeks of storage at low T. WMP (h-moist) stored at high T also exhibited visible lumping after 6 weeks of storage. These observed

lumps were already hard but still breakable. The cake strength of the WMP (h-moist) sample at high T was approximately 100 g after 6 weeks of storage. Given that the ideal cake strength is 0 g and severely caked WMP had a cake strength of 252 g, this indicated that the WMP (h-moist) sample at high T was already severely caked after 6 weeks.

To assess the severity of caking under milder transport and storage conditions, the low moisture samples at low T should be investigated. Based on these results, the highest cake strength after 8 weeks of storage for SMP (l-moist) at low T was 4.5 g whereas WMP (l-moist) at low T was 21.5 g. These samples exhibited the lowest increase in crystallinity compared to other 2-month test samples and the composition analysis (FTIR) showed no significant differences between 0 weeks and 8 weeks in both samples. In addition, there was no significant difference in particle size distribution between the samples after 0 and 8 weeks. WMP (l-moist) sample stored at low T had the highest free fat content of 1.2 % when compared to other 2-month period caking test samples, and the fat crystallisation temperature also shifted over 8 weeks. Overall, some changes occurred in these WMP (l-moist) and SMP (l-moist) samples stored at low T, but severe caking was not observed during the 2-month period. In practice, these milk powders are transported and stored for longer periods, so further investigations are needed to determine the induction time for severe caking under milder conditions.

# 8 Conclusions and recommendations

Milk powders are exposed to changing conditions during long-distance transport, leading to physical and structural changes that can ultimately result in caking. The objective of this thesis was to determine the induction time for severe caking in lactose-free milk powders under transport and storage conditions and to assess whether minor changes in temperature and moisture content affect caking. This thesis also aimed to identify the component responsible for hard cake formation and to determine if consolidation stress induced severe caking.

The literature identifies moisture absorption and temperature increase as the main factors contributing to caking. Milk powders, especially lactose-free milk powders, are extremely

hygroscopic and prone to absorb moisture from the environment which increases particle mobility and leads to caking. Based on the results obtained from this study, lactose-free SMP and WMP do not experience significant caking at their milder storage and transportation conditions, however physical changes in particle properties and structure were already noticeable. Minor changes in temperature and moisture content were found to affect caking, emphasizing the importance of maintaining optimal conditions.

Carbohydrates were identified as the main cause of hard cake formation, with cake strength results indicating that SMP formed harder cakes than WMP. The absence of fat in SMP means carbohydrates and protein are responsible for cake formation. SMP also contains higher amount of carbohydrates and proteins which resulted in higher caking. The used analysis methods did not concentrate on protein alterations but because proteins undergo denaturation and other physical changes at high temperatures (70 ℃), it is reasonable to state that carbohydrates are the main cause for the formation of hard lumps. Lactose-free SMP and WMP samples experienced crystallisation and formation of hard cakes even though Maillard reactions did not take place and additionally, carbohydrate was identified as the component that crystallised during caking, further supporting the conclusion that carbohydrates are the main cause of hard cakes. The crystallinity (%) was higher in SMP samples and higher $a_w$ samples examined higher crystallinity. High temperatures, severe moisture absorption and crystallisation can lead to increased Maillard reactions, noticeable when powders were exposed to 75 % RH at an accelerated caking test.

Consolidation stress was found to induce caking, although significant effects require severe pressure. However, visible caking was observed in lactose-free SMP and WMP samples after 2 and 6 weeks of storage at low T, respectively. Consolidation stress was found to increase the contact angle (°) in WMP samples as well as cake strength. Effect of consolidation in caking must be taken into account in storage and transport conditions.

These results aligned with previous studies on moisture and temperature's roles in caking, but this thesis provided new insights into lactose-free milk powders. This thesis achieved its objectives by identifying the induction time for severe caking and highlighting that even minor temperature and initial moisture content changes impacted caking in lactose-free milk powders. Carbohydrates were identified as the main component to form hard cakes and consolidation stress was identified to induce caking. This study gives new insights into the properties of lactose-free milk powders, and it is thereby significant for the dairy industry.

This study had some limitations. For example, the amount of powder sample (10 g) limited the usage of some analysis techniques which would have required high amounts of sample. For this reason, moisture content (%) could not be observed during the 2-month period. The focus of these analysis methods was primarily on carbohydrate and fat content. Future research should explore the role of proteins in caking, especially under varying temperature conditions. Additionally, longer period caking test at milder storage and transport conditions should be exploited to further research the induction time for severe caking. Since carbohydrates were identified as the primary component to cause of hard cakes, their role and possible modifications should be investigated more. Overall, this research contributes to a deeper understanding of caking mechanisms in lactose-free milk powders, with potential benefits for improving product quality and shelf life in the dairy industry.

# References

Anandharamakrishnan, C. 2017. Handbook of drying for dairy products. Chichester, England: Wiley Blackwell.

Bhandari, B. 2024. Handbook of food powders: Processes and properties. 2nd edition. Cambridge, Elsevier.

Boland, M., Thompson, A. & Harjinder. S. 2014. The Whey Proteins in Milk: Thermal Denaturation, Physical Interactions, and Effects on the Functional Properties of Milk. Milk proteins - From expression to food. 2nd edition. Elsevier.

Brockbank, K., Armstrong, B., Chandorkar, Y. & Freeman, T. Understanding powder caking as a consequence of a range of mechanisms by means of powder rheometry. Particulate science and technology. Vol 33, no. 1, p. 102-108.

Carpin, M., Bertelsen, H., Bech, J.K., Jeantet, R., Risbo, J. & Schuck, P. 2016. Caking of lactose: A critical review. Trends in food science & technology. Vol 53, p. 1-12.

Council directive 2001/114/EC relating to certain partly or wholly dehydrated preserved milk for human consumption. 2013. Official Journal L15, p. 19

CODEX STAN 207–1999.

Cuq, B., Mandato, S., Jeantet, R., Saleh, K., & Ruiz, T. 2013. Agglomeration/Granulation in Food Powder Production. In Handbook of food powders: Processes and properties. 2nd edition. Cambridge, Elsevier.

Dairy World. 2024. Milk powder, past and present. Dairy World LLC. [referred: 12.7.2024]. Available: The Evolution of Milk Powder: From Past to Present – Dairy World.

Du, Z., Xu, N., Yang, Y., Li, G., Tai, Z., Li, N. & Sun, Y. 2023. Study on internal structure of casein micelles in reconstituted skim milk powder. International journal of biological macromolecules. Vol 224, p.437-452.

Elintarviketeollisuusliitto ETL. 2024. Tilastoja elintarvikkeiden viennistä ja tuonnista. [referred 18.7.2024]. Available: Tilastoja elintarvikkeiden https://www.etl.fi/tilastot-ja-aineistot/tilastoja-elintarvikkeiden-viennista-ja-tuonnista/ viennistä ja tuonnista - ETL

Ermis, E. 2021. Food powders properties and characterization. 1st edition. Cham: Springer international publishing.

Fialho, T., Martins, E., Silva, C., Stephani, R., Tavares, G., Silveira, A., Perrone, I., Schuck, P., Oliveira, L. & Carvalho, A. 2018. Lactose-hydrolyzed milk powder: Physicochemical and technofunctional characterization. Drying technology. Vol 36, no. 36, p. 1688-1695.

Fialho, T., Nogueira, M., Moreau, A., Delaplace, G., Schuck, P., Perrone, I., Carvalho, A. & de Sa Peixoto Junior, P. 2019. Sugar type matters in spray drying: Homogeneous distribution in milk powder favors repulsive interactions between proteins. Food structure. Vol 22, p. 100132 -.

Fitzpatrick, J.J. 2013. `12 - Powder properties in food production systems´, in Handbook of Food Powders. Elsevier Ltd. p. 285-308.

Fitzpatrick, J.J, Descamps, N., O'Meara, K., Jones, C., Walsh, D. & Spitere, M. 2010. Comparing the caking behaviour of skim milk powder, amorphous maltodextrin and crystalline common salt. Powder Technology. Vol 204, p.131-137.

Fitzpatrick, J.J., Hodnett, M., Twomey, M., Cerqueira, P.S.M., O'Flynn, J. & Roos, Y.H. 2007. Glass transition and the flowability and caking of powders containing amorphous lactose. Powder Technology. Vol 178, p. 119-128.

Harju, M., Kallioinen, H. & Tossavainen, O. 2012. Lactose hydrolysis and other conversions in dairy products: Technological aspects. International dairy journal. Vol 22, p. 104-109.

Hartmann, M. & Palzer, S. 2011. Caking of amorphous powders - Material aspects, modelling and applications. Powder Technology. Vol 206, no 1, p.112-121.

Jeantet, R., Croguennec, T., Schuck, P. & Brule, G. 2016. Handbook of food science and technology 3. Food biochemistry and technology. London, England; ISTE.

Jouppila. K & Roos Y.H. 1994. Glass transitions and crystallization in milk powders. Journal of dairy science. Vol 77, no. 10. p. 2907-2915.

Kamyabi, M., Sotudeh-Gharebagh, R., Zarghami, R. & Saleh, K. 2017. Principles of viscous sintering in amorphous powders: A critical review. Chemical engineering research and design. Vol 125, p. 328-347.

Karaman, A.D., Özer, B., Pascall, M.A. & Alvarez, V. 2015. Recent advances in dairy packaging. Food reviews international. Vol 31, no.4, p. 295-318.

Kim, E.H.-J., Chen, X.D. & Pearce D. 2005. Melting characteristics of fat present on the surface of industrial spray-dried dairy powders. Colloids and surfaces, B, Biointerfaces. Vol 42, no. 1, p. 1-8.

Kim, E. H.-J., Chen, X.D. & Pearce D. 2008. Surface composition of industrial spray-dried milk powders. 3. Changes in the surface composition during long-term storage. Journal of food engineering. Vol 94, no. 2, p. 182–191.

Malvern Panalytical. 2020. Using Laser Diffraction to Measure the Size and Stability of Dairy Emulsions. AZoM. [referred: 10.7.2024]. Available: https://www.azom.com/article.aspx?ArticleID=13760.

Masum, A.K.M., Chanrapala, J., Huppertz, T. Adhikari, B. & Zisu, B. 2020. Influence of drying temperatures and storage parameters on the physicochemical properties of spray-dried infant milk formula powders. International dairy journal. Vol 105, p. 104696.

Mcmahon, D.J. & Brown, R.J. 1984. Composition, structure, and integrity of casein micelles: a review. Journal of dairy science. Vol 67, no. 3, p. 499-512

Mendoza, L. 2016. Caseins. 1st edition. Hauppauge: Nova Science Publishers, Incorporated.

Minitab. 2024. Minitab support. [web page]. [referred: 17.7.2024]. Available: https://support.minitab.com/en-us/minitab/

Murrieta-Pazos, I., Gaiani, C., Galet, L. & Scher, J. 2012. Composition gradient from surface to core in dairy powders: agglomeration effect. Food hydrocolloids. Vol 26, no 1, p. 149-158.

Naranjo, G.B., Gonzales, A.S.P., Leiva, G.E. & Malec, L.S. 2013. The kinetics of maillard reaction in lactose-hydrolysed milk powder and related systems containing carbohydrate mixtures. Food chemistry. Vol 144, no 4, p. 3790-3795.

Nasser, S., Peixoto, P., Moreau, A., Croguennec, T., Bray, F., Rolando, C., Tessier, F., Hedoux, A & Delaplace, G. 2018. Storage of Micellar Casein Powders with and without Lactose: Consequences on Color, Solubility, and Chemical Modifications. Journal of agricultural and food chemistry. Vol 66, no. 39, p. 10274-10282.

Novaes, S.S.C., Dantas, F.B.H., Alvim, I.D, de Oliveira Miguel, A.M.R., Dantas, S.T. & Alves, R.M.V. 2019. Stability of omega-3 enriched milk powder in different commercial packages stored under accelerated conditions of temperature and relative humidity. International dairy Journal. Vol 88, p. 1-9.

Palzer. St. 2011. Agglomeration of pharmaceutical, detergent, chemical and food powders — Similarities and differences of materials and processes. Powder technology. Vol 201, no 1, p. 2-17.

Phosanam, A., Chandrapala, J., Huppertz, T., Adhikari, B. & Zisu, B. 2020. Effect of storage conditions on physicochemical and microstructural properties of skim and whole milk powders. Powder technology. Vol 372, p. 394-403.

Phosanam, A., Chanrapala, J., Zisu, B. & Adhikari, B. 2021. Storage stability of powdered dairy ingredients: a review. Drying technology. Vol 39, no. 11, p. 1529-1553.

Pisecky, J. 2012. Handbook of milk powder manufacture. 2nd edition. Copenhagen, GEA Process engineering A/S.

Pugliese, A., Cabassi, G., Chiavaro, E., Paciulli, M., Carini, E. & Mucchetti, G. Physical characterization of whole and skim dried milk powders. Food scientists & Technologists. Vol 54, no. 11, p. 3433-3442.

Qi, X., malmos, K.G., van den Berg, F.W.J., Grumsen, F.B. & Bakalis, S. 2024. Crystal size, a key character of lactose crystallization affecting microstructure, surface chemistry and reconstitution of milk powder. Food Research International. Vol 177, 177113872–113872.

Roos, Y. H. 1993. Melting and glass transitions weight carbohydrates of low molecular weight carbohydrates. Carbohydrate Research. Vol 238, p. 39-48.

Roos, Y. H. 2002. Importance of glass transition and water activity to spray drying and stability of dairy powders. Le Lait. Vol 82, no.4, p. 475-484.

Roos, Y. H. 1995. Phase transition in foods. San Diego: Academic Press.

Ryabova, A.E., Semipyatny, V.K. & Galstyan, A.G. 2023. Effects of storage conditions on milk powder properties. Journal of dairy science. Vol 106, no. 10, p. 6741-6758.

Saji, R., Ramani. A., Gandhi, K., Seth, R. & Sharma, R. 2024. Application of FTIR spectroscopy in dairy products: A systematic review. Food and Humanity. Vol 2, no. 2, p. 100239

Schuck, P., Jeantet, R. & Dolivet, A. 2012. Analytical methods for food and dairy powders. 1st edition. Newark, John Wiley & Sons, Incorporated.

Schuck, P., Blanchard, E., Dolivet, A., Mejean, S., Onillon, E. & Jeantet, R. 2005. Water activity and glass transition in dairy ingredients. Le Lait, Vol 85, p.295-304.

Schulnies, F. & Kleinschmidt, T. 2018. Time consolidation of skim milk powder near the glass transition temperature. International dairy journal. Vol 85, p. 105-111.

Schulze, D. 2021. Powders and bulk solids: behaviour, characterization, storage and flow. 2nd edition. Cham, Switzerland: Springer.

Schulz, P. & Rizvi, S. 2023. Hydrolysis of lactose in milk: Current status and future products. Food reviews international. Vol39, no. 5, p. 2875-2894.

Shrestha, A.K., Howes, T., Adhikari, B.P. & Bhandari, B.R. 2007. Water sorption and glass transition properties of spray dried lactose hydrolysed skim milk powder. Food science & technology. Vol 40, no. 9, p. 1593-1600.

Tamime, A.Y. 2009. Dairy powders and concentrated products. 1st edition. Newark, John Wiley & Sons.

Tham, T.W.Y., Xu, X., Yeoh, A.T.H. & Zhou, W. 2017. Investigation of caking by fat bridging in aged infant formula. Food chemistry. 21830–39.

Thomas, M., Scher, J., Desobry-Banon, S. & Desorby, S. 2004. Milk powders ageing: effect on physical and functional properties. Critical reviews in food science and nutrition, Vol 44, no. 5, p. 297-322.

Torres, J., Stephani, R., Tavares, G., Garvalho, A., Costa, R., Almeida, C., Almeida, M., Oliviera, L., Schuck, P. & Perrone, I. 2017. Technological aspects of lactose-hydrolyzed milk powder. Food research international. Vol 101, p. 45-53.

US8986768B2. 2015. Low-lactose and lactose-free milk product and process for production thereof. Valio Oy, Finland. (Tikanmäki, R. & Kallioinen, H.)

Valio. 2024a. Valio Eila PRO lactose free whole milk powder. [web page]. [referred: 19.3.2024]. Available: Valio Eila® PRO lactose free whole milk powder - valio.com

Valio. 2024b. Valio Eila Pro lactose free skim milk powder. [web page]. [referred: 19.3.2024]. Available: Valio Eila® PRO lactose free skimmed milk powder - valio.com

Yazdanpanah, N. & Langrish, T. A. G. 2013. Comparative study of deteriorative changes in the ageing of milk powder. Journal of food engineering. Vol 114, no.1, p.14-21.

Zafar, U., Vivacqua, V., Ghadiri, M. & Cleaver, J.A.S. 2017. A review of bulk powder caking. Powder Technology. Vol 313, p. 389-401.

Özkan, N., Withy, B. & Chen, X.D. 2003. Effects of time, temperature, and pressure on the cake formation of milk powders. Journal of food engineering. Vol 58, p. 355-361.

Appendix I Images of powder caking in Eila SMP and WMP

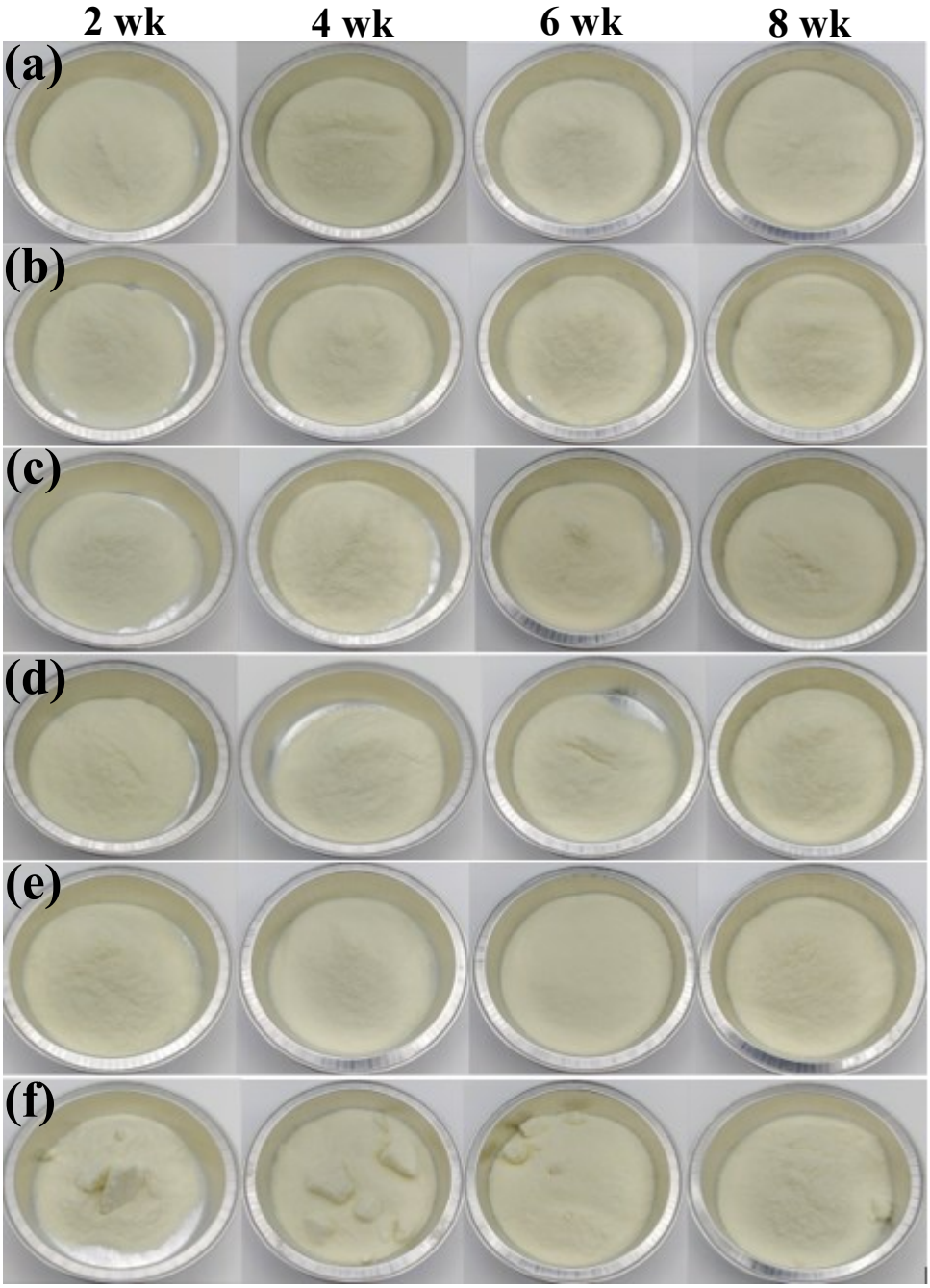


Figure 1. Powder caking in Eila (a) SMP (l-moist) at low T (b) SMP (l-moist) at high T (c) SMP (h-moist) at low T, (d) SMP (h-moist) at high T, (e) SMP (l-moist) under consolidation at low T, (f) SMP (h-moist) under consolidation at low T

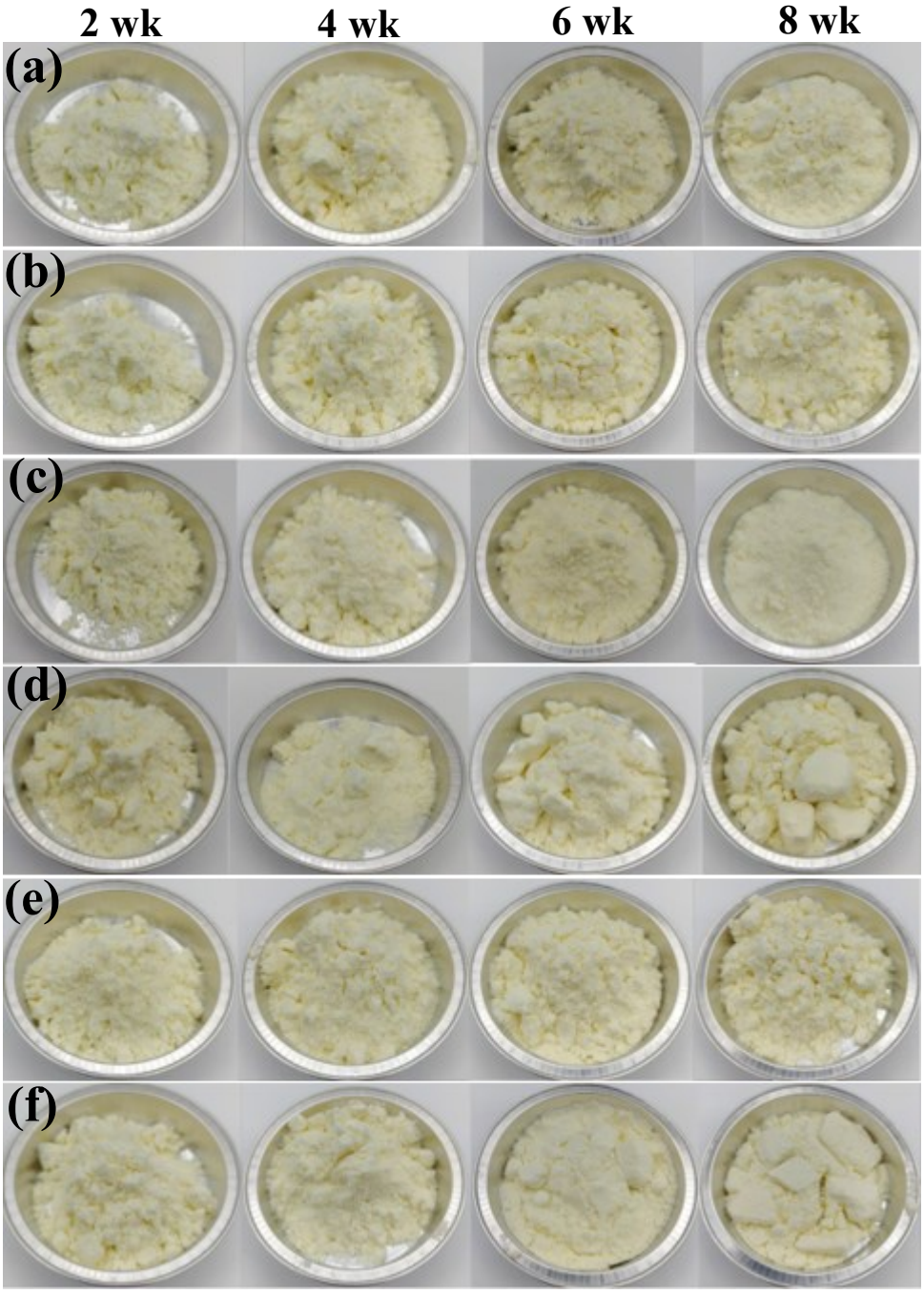


Figure 2. Powder caking in Eila (a) WMP (l-moist) at low T, (b) WMP (l-moist) at high T, (c) WMP (h-moist) at low T, (d) WMP (h-moist) at high T, (e) WMP (l-moist) under consolidation at low T, (f) WMP (h-moist) under consolidation at low T

Appendix II Cake strength (g) of Eila WMP and SMP

Table 1. Cake strength (g) of Eila WMP & SMP at different conditions analysed every 2-weeks (wk=week)

| **Sample** | **Cake strength (g) of Eila WMP and Eila SMP** | | | |
|---|---|---|---|---|
| | **2 wk** | **4 wk** | **6 wk** | **8 wk** |
| WMP (l-moist) low T | $6.1^{E}$ | $7.6^{E}$ | $11.9^{E}$ | $21.5^{D,E}$ |
| WMP (l-moist) high T | $15.1^{DE}$ | $12.7^{E}$ | $73.3^{BCD}$ | $157.6^{A}$ |
| WMP (h-moist) low T | $8.2^{E}$ | $12.6^{E}$ | $10.4^{E}$ | $28.0^{DE}$ |
| WMP (h-moist) high T | $20.0^{DE}$ | $35.8^{CDE}$ | $112.1^{AB}$ | $94.9^{ABC}$ |
| WMP (acc. dish) | - | - | - | 252.0 |
| WMP (consolidation kit) | 159.8 | 388.9 | 490.8 | 741.1 |
| SMP (l-moist) low T | $4.1^{B}$ | $3.5^{B}$ | $4.0^{B}$ | $4.5^{B}$ |
| SMP (l-moist) high T | $4.0^{B}$ | $5.2^{B}$ | $5.1^{B}$ | $44.0^{A}$ |
| SMP (h-moist) low T | $3.8^{B}$ | $4.3^{B}$ | $4.2^{B}$ | $5.2^{B}$ |
| SMP (h-moist) high T | $4.5^{B}$ | $4.7^{B}$ | $5.2^{B}$ | $11.0^{B}$ |
| SMP (acc. dish) | - | - | - | 578.7 |

Appendix III Main effects screener plots

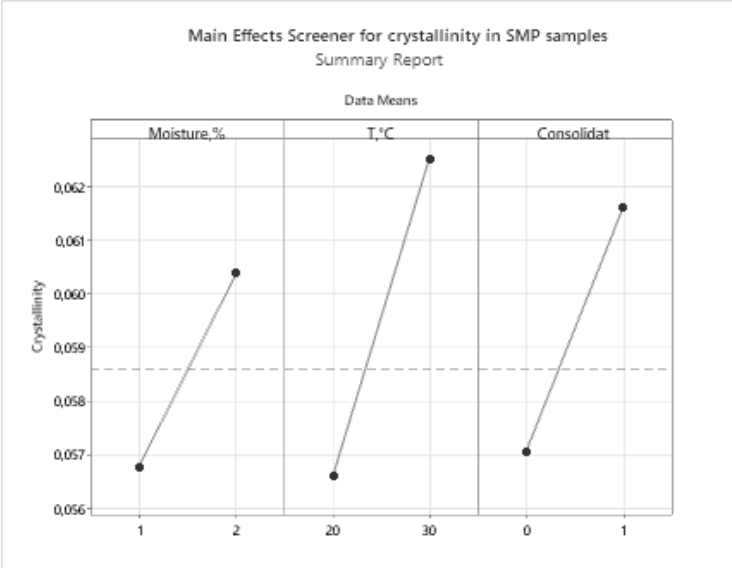


Figure 1. Main effect screener for crystallinity in SMP samples

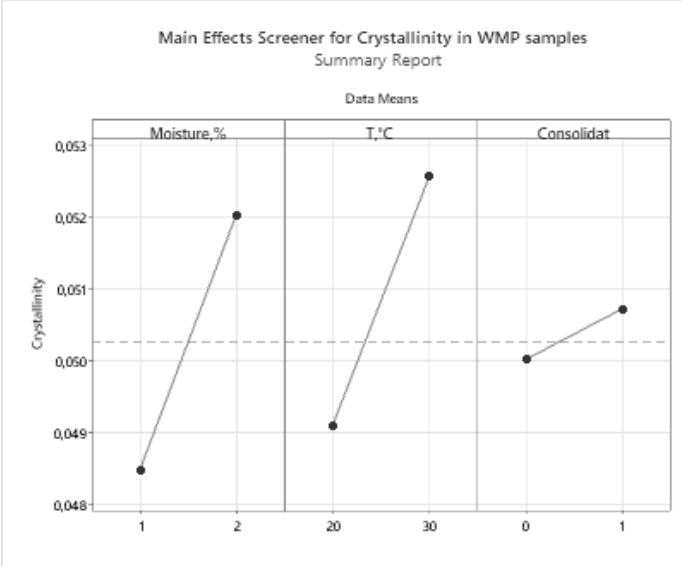


Figure 2. Main effect screener for crystallinity in WMP samples

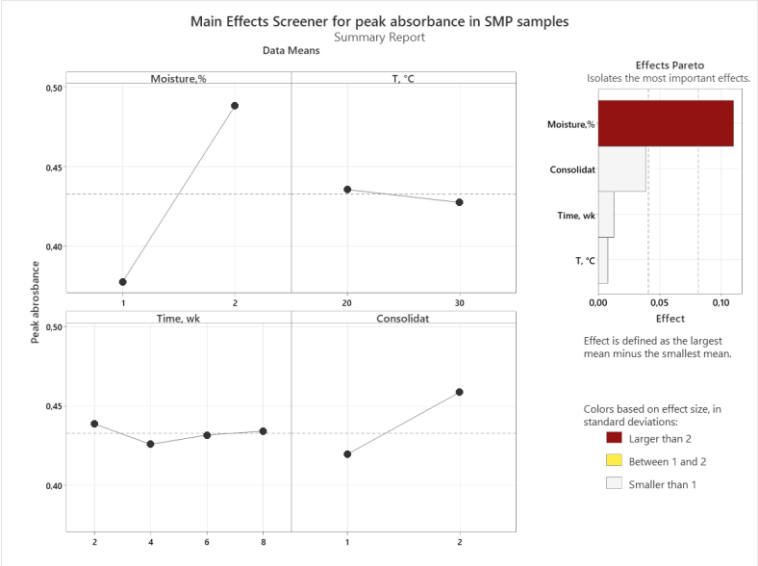


Figure 3. Main effect screener for peak absorbance in SMP samples

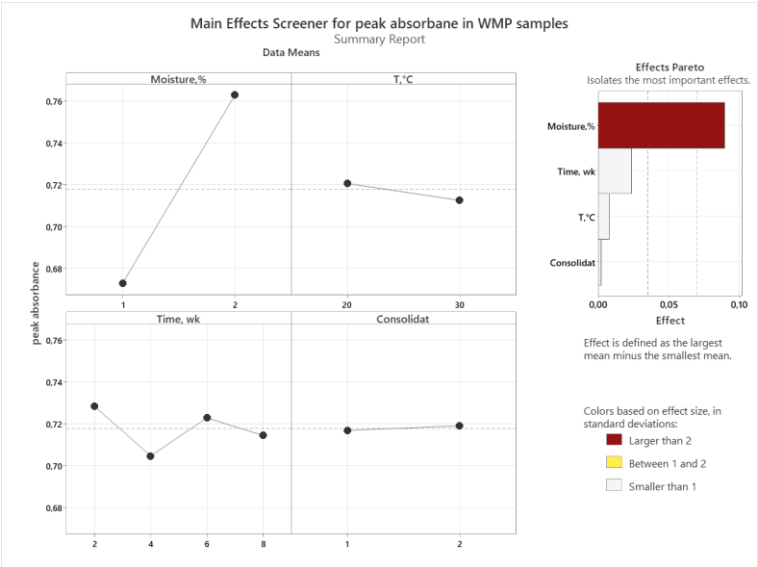


Figure 4. Main effect screener for peak absorbance in WMP samples

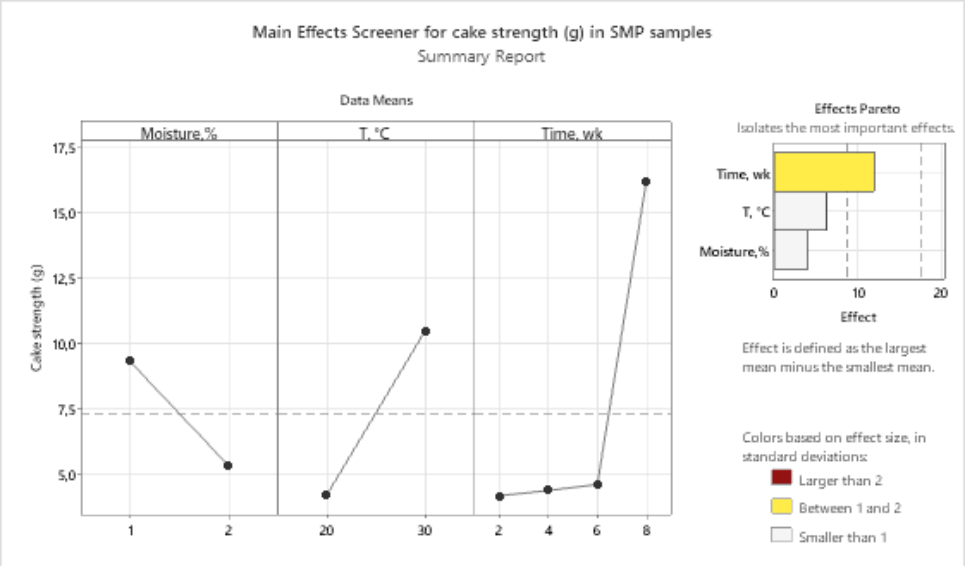


Figure 5. Main effect screener for cake strength (g) in SMP samples

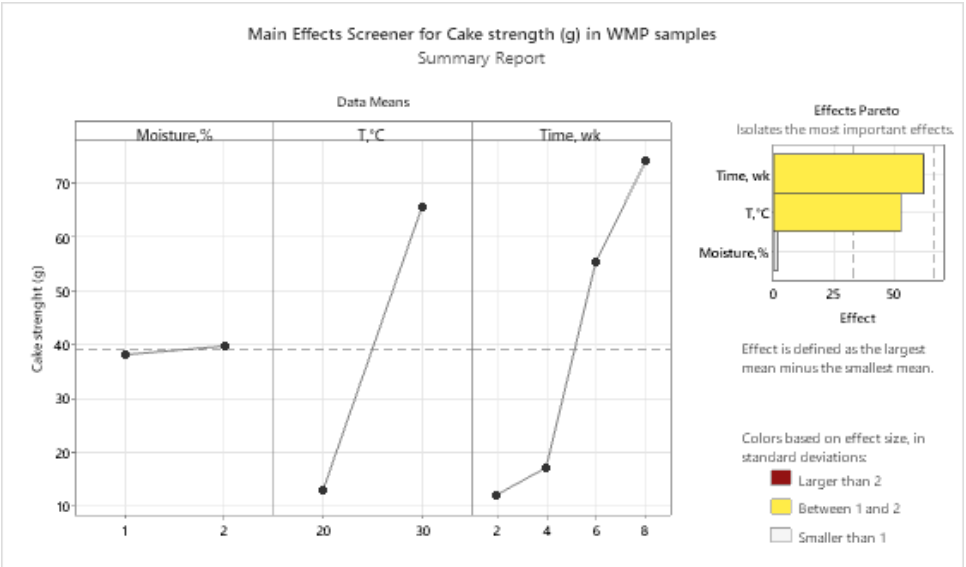


Figure 6. Main effect screener for cake strength (g) in WMP samples

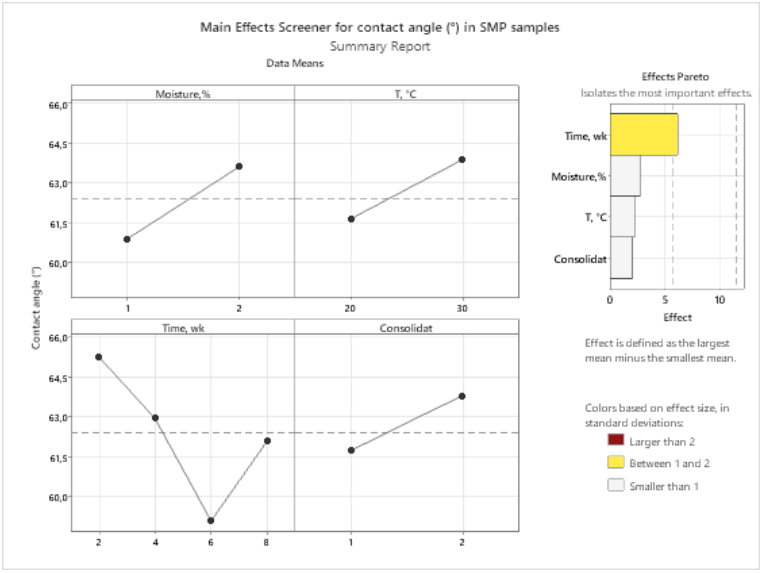


Figure 7. Main effect screener for contact angle (°) in SMP samples

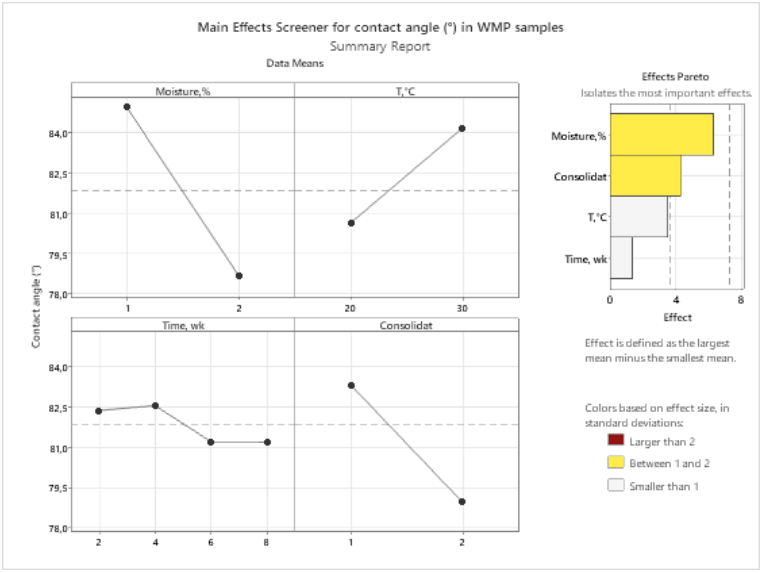


Figure 8. Main effect screener for contact angle (°) in WMP samples

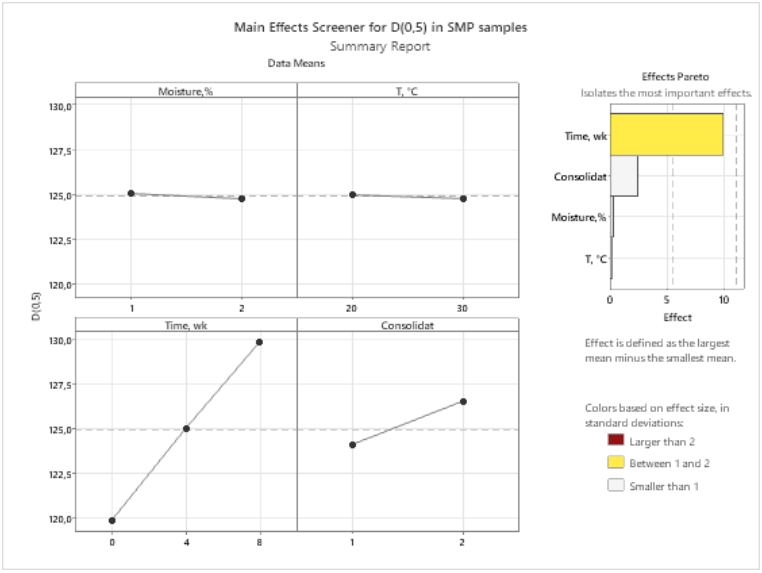


Figure 9. Main effect screener for D(0.5) in SMP samples

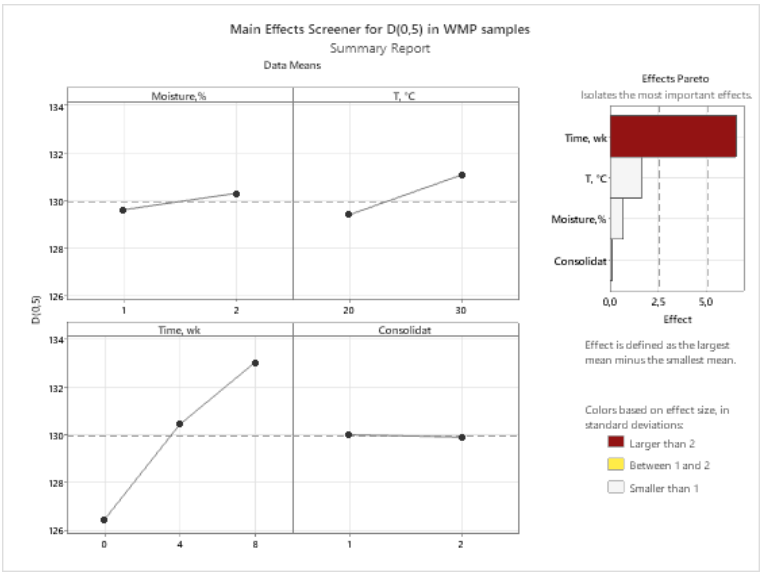


Figure 10. Main effect screener for D(0.5) in WMP samples

Appendix IV Free fat (%) of Eila WMP

Table 1. Free fat (%) of Eila WMP at different conditions analysed every 2-weeks (wk=week)

| **Sample** | **Free fat (%) for Eila WMP** | | | | |
|---|---|---|---|---|---|
| | **0 wk** | **2 wk** | **4 wk** | **6 wk** | **8 wk** |
| WMP (l-moist) low T | 0.949 | 0.903 | 1.050 | 1.025 | 1.231 |
| WMP (l-moist) high T | 0.949 | 0.918 | 0.997 | 0.867 | 1.201 |
| WMP (h-moist) low T | 0.949 | 0.915 | 0.971 | 0.954 | 1.147 |
| WMP (h-moist) high T | 0.949 | 0.784 | 0.761 | 0.943 | 0.818 |
| WMP (l-moist) consolidation + low T | 0.949 | 0.983 | 1.058 | 0.901 | 0.910 |
| WMP (h-moist) consolidation + low T | 0.949 | 0.754 | 0.985 | 0.883 | 0.862 |
| WMP (consolidation kit) | - | - | - | - | 1.702 |
| WMP (acc. dish) | - | - | - | - | 1.580 |