



CHALMERS
UNIVERSITY OF TECHNOLOGY

Evaluation of Natural Anti-caking Agents in Spices and Spice Blends

For a Consumer-friendly Labeling of Spice Products

Master's thesis in the Master Degree Program in Biotechnology

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Abstract

Caking, whereby free flowing particles aggregate to form lumps is a common problem during handling and storage of food powders. Seasoning companies have experienced consumer dissatisfaction related to difficulties emptying the spice jar or get lumps of spices when emptying a bag with a spice blend. One way of preventing the caking development is to add a small amount of anti-caking agent. One of the most widely used anti-caking agent is silicon dioxide, labeled as E 551. During the past years, the consumer's demand for products with fewer additives has increased. This project focused on finding natural anti-caking agents that could replace silicon dioxide in spice products, to get a consumer- friendly labeling while also solving the caking problem.

The caking development was studied in the easily caked Lemon juice powder and Red Onion Seasoning mix containing native potato starch, inulin and a rice fiber as natural anti-caking agents. The replacing alternatives were evaluated based on how they affect the sorption isotherm, glass transition and flowability, as well as sensory properties of the host powders. Moisture sorption isotherms as well as glass transition analysis clarified that water has a large impact on the caking development in the hygroscopic host powders.

Glass transition measurements in combination with the flowability analysis, demonstrated that 5 % native potato starch, at lower relative humidities theoretically could be used as a silicon dioxide replacer. It was shown that the glass transition temperature of Lemon juice powder was increased while adding 5 % native potato starch, which theoretically indicates less stickiness, and consequently reduced risk of caking. Further, Lemon juice powder containing 5 % native potato starch presented flow function in the free flowing area, which further promotes its use as a natural anti-caking/ flow agent. The result from the sensory analysis confirmed that there is no significant difference between products containing 1.7 % silicon dioxide and 5 % native potato starch.

Keywords

Natural anti-caking agent, Stickiness, Caking, Cohesiveness, Silicon dioxide, Moisture sorption isotherm, Glass transition, Flowability, Sensory evaluation

Sammanfattning

Ett vanligt förekommande problem vid hantering och lagring av ingredienser i pulverform är klumpbildning. Detta kan påverka konsumenten genom att kryddan eller kryddblandningen innehåller klumpar då den öppnas och framförallt genom att kryddorna blir väldigt hårda vid förvaring. För att undvika klumpbildning, tillsätts ofta en liten mängd klumpförebyggande medel. Ett vanligt förekommande klumpförebyggande medel är kiseldioxid, vilken deklarerar som E 551 i ingrediensförteckningen. Det har blivit allt vanligare att konsumenter efterfrågar produkter med färre tillsatser. Syftet med det här projektet var att hitta naturliga substanser som skulle kunna ersätta kiseldioxid i kryddor och kryddblandningar och därmed, i kombination med att undvika klumpbildning, bidra till en mer konsument vänlig märkning av produkterna.

Klumpbildning studerades i Citronjuice pulver och en kryddblandning för picklad rödlök, eftersom dessa produkter var kända, både från produktion och ifrån konsument, för att lätt bilda klumpar och hårdna. Inulin, obehandlad potatisstärkelse samt potatis fiber utvärderades som naturliga ersättare till kiseldioxid baserat på hur det påverkade kryddans förmåga att absorbera fukt, temperatur vid vilken klumpbildning sker, flödesförmåga och smak. Generellt konstaterades att fukt har en stor påverkan på klumpbildning i de utvalda kryddorna.

Tillsats av 5 % obehandlad potatisstärkelse resulterade i högre stabilitet och, teoretiskt, lägre risk för klumpbildning vid rumstemperatur vilket tyder på att obehandlad potatisstärkelse skulle kunna fungera som en potentiell, naturlig ersättare till kiseldioxid. Kryddorna visade även god flödesförmåga vid tillsats av 5 % obehandlad potatisstärkelse vilket ytterligare förstärker dess förmåga att fungera som ett naturligt klumpförebyggande medel. Ingen skillnad i smak noterades då 1.7 % kiseldioxid ersattes med 5 % potatisstärkelse.

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1 Introduction

Nowadays, many food ingredients in the market are supplied in powdered form to facilitate use and processing, as well as to improve the stability of the ingredients by reducing the amount of water [1]. Caking, whereby free-flowing particles aggregate to form lumps, of food powders is a common problem which can contribute to reduced product quality, functionality and shortened shelf-life [2,3]. It can occur during processing, handling or storage and could therefore be a problem both in the production lines and for the consumers [2]. Employees working in the spice factory describe difficulties when handling caked raw materials [4, 5]. Additional process steps, in which the powder is delumped, is often needed before the raw material can be added into the silos or hoppers [5].

The spice company has occasional times, experienced criticisms from consumers complaining about lump formation or that the spices become very hard while stored [6]. Powders which contain a large amount of water-soluble amorphous substances are particularly sensitive to caking since they are hygroscopic, meaning that they absorb water during storage in an environment with high relative humidity [7]. The increased water content often leads to product stickiness and caking as a result of decreased viscosity and facilitated inter-particle interaction [8].

For amorphous substances, the glass transition temperature (T_g) plays an important role when predicting stickiness and caking of powders during different environmental conditions [3]. The glass transition temperature defines the temperature at which hard amorphous solids transform into soft, rubbery materials [9]. Above the T_g point, the viscosity of the material decreases with increasing temperature [3]. Decreased viscosity increases molecular mobility and favors inter-particle interaction, leading to increased cohesion, formation of lumps and decreased flowability of the powder [3]. The difference between the storage temperature of the powder and the T_g point is often the driving force for caking of amorphous powder [3].

From a consumer perspective, the formation of lumps and the reduced flowability of the powder can lead to difficulties in emptying the spice jar or get lumps with spices when emptying a bag with a spice blend. In order to facilitate the handling of the powder during production and to prevent consumers' dissatisfaction, anti-caking agents/ flow agents, which can prevent caking and improve the flowability of spices and spice blends are often added [10]. Anti-caking agents can prevent caking by several mechanisms, e.g. compete with the host powder for moisture, create moisture protective barriers on the surface of hygroscopic particles, coat surfaces to eliminate inter-particle interactions or increase the T_g point [2, 11].

Today, one of the most widely used anti-caking agent is silicon dioxide, labeled as E551 under the food ingredient list [10]. During the past years, the consumer's demand for products with fewer additives has increased [6]. One ambition is to reduce the amount of additives in spice products, and it is therefore of high interest to find natural anti-caking agents that can replace silicon dioxide. This could for many spice products, contribute to a labeling completely without chemical additives with E-number [10]. Companies like RIBUS offers producers to replace their synthetically produced anti-caking agents with natural or organic certified ingredients like rice-based concentrate to get a clean, consumer-friendly labeling while also solving the anti-caking challenges [12].

1.1 Aim

The aim of this project was to investigate if the anti-caking agent silicon dioxide (E551) could be replaced by natural alternatives with similar or improved anti-caking capacity, in order to reduce the amount of additives and get a consumer-friendly labeling of spice products. The replacing alternatives should be suitable for food, sensorial accepted but also environmentally and economically sustainable. Sorption isotherms, glass transition and powder flowability was evaluated as well as sensory properties, in order to determine whether a replacement is possible, and if so, provide guidelines for safe storage conditions and the amount of anti-caking needed to avoid caking.

1.2 Objectives

After finding three natural substances, which potentially could be used as silicon dioxide replacers, the objectives of the project are:

1. To evaluate how the natural anti-caking agents affect the hygroscopicity of the host powder by characterizing the moisture sorption isotherm.
2. To evaluate if any of the natural anti-caking agents functioning by increasing the glass transition temperature of the host powder.
3. To evaluate how the natural anti-caking agents affect the flow behavior of the host powder.
4. To evaluate if the natural anti-caking agents affect the sensorial properties of the host powder.

1.3 Limitations

This project will focus on finding natural anti-caking agents that can replace silicon dioxide in spice products, contributing to a more consumer friendly-labeling. The mechanisms of caking will be discussed theoretically, but the project is not, on a microscopic level aimed to determine the mechanisms in which silicon dioxide and the potential replacers prevent caking. The evaluation of the anti-caking agents will be done for a limited number of raw materials that has shown to be easily caked. The anti-caking capacity of the natural substances will be evaluated in relation to moisture absorption and mechanical stress. The effect of other factors like, temperature and particle size, known to affect stickiness and caking of food powders will be discussed, but not investigated.

This project will discuss caking and its consequences from a consumer perspective rather than a production perspective. Consumer's insecurity concerning additives and difficulties in emptying the spice jar or get lumps with spices when emptying a bag with spice blend are the main questions to resolve. There are many ways of controlling the caking development, but this study will only evaluate the possibility to prevent caking by using anti-caking agents. Other ways like, optimization of process and storage conditions will not be examined.

2 Theoretical Background

The theoretical background includes a description of the main factors known to play an important role in the caking phenomena. The influence of environmental conditions like temperature and humidity will be discussed, as well as material properties like particle size. As mentioned in the introduction, caking strongly affects the flowability of food powder. Section 2.2 provides a general description of the flow properties of bulk solids, which will be useful when discussing shear cell techniques. The main mechanisms of caking will be described in section 2.3, followed by a description of how anti-caking agents can be used to control the caking development. Methods that are commonly being used for the characterization of caking will be thoroughly discussed in section 2.4, and the final section includes an overview of the raw material used in the study.

2.1 Factors Affecting Stickiness and Caking of Food Powders

There are several factors, both internal and external, affecting stickiness and caking of food powders. The following chapter will initially define fundamental concepts like stickiness and glass transition temperature, while continuing discussing the main material properties and processing parameters known to play an important role in the caking development.

2.1.2 Stickiness

The American Society has defined a sticky material for Testing and Materials (ASTM) as a material in which an appreciable force is needed to separate from it immediately after contact [13]. Stickiness is often the first step of caking [14]. It is an instantaneous process compared to caking, which occurs over time [14]. Stickiness can also be described as the tendency of powder particles to stick to each other, or to chemically dissimilar surfaces like equipment and packages [15]. The term describes therefore two different interactions, cohesion (particle-particle stickiness) and adhesion (particle-wall stickiness) [16]. Particle cohesion is an internal property and a measure of the inter-particle forces required to keep the surfaces of two particles stick to each other [16]. The attractive forces holding particles together depends on the surface composition of the individual particles, and the physical process by which the particles interact [16,17].

Stickiness may have both positive and negative effects [15]. Cohesion stickiness is beneficial in granulation or controlled agglomeration in which the cohesiveness of the particles is used to agglomerates individual particles into granules [15,16]. In the majority of processes, the stickiness is considered undesirable since it gives rise to caking, formation of lumps, of food powders at high temperature and/or humidities [15, 16]. Adhesion stickiness is an interfacial property and describes the forces holding a particle surface to another material [15]. Particles sticking on walls lead to product loss [18].

2.1.3 Glass Transition Temperature

Glass transition temperature (T_g) has been used as an indicator for molecular mobility, food stability and to predict the behavior of different food systems [19,20]. In drying of food products, the T_g value is one of the most crucial factors to consider. Textural properties like stickiness and caking could be related to the glass transition theory [19].

Many food solids are often in their amorphous metastable state as a result of rapid removal of water by drying or freezing [21]. The amorphous matrix can exist either as a stable, viscous glassy state or as a more liquid-like, rubbery state [21]. The glass transition temperature is defined as the temperature at a given moisture content in which amorphous system changes from a glassy stable

state, to a rubbery state [19]. The glass transition temperature is specific for each material and depends on intra-solubility, plasticizing and the ability of the food components to form a homogenous solution [20,21]. Molecules in the amorphous state of a solid are randomly distributed and mobile, compared to in a crystal in which the molecules are in geometric arrangement with low mobility [19]. The backbone of the molecular structure in their glassy state is normally frozen and food solids in the glassy state have similar properties to hard plastic or crisp crackers [19,20]. Above the T_g point, the molecular mobility rapidly increasing as a result of decreased viscosity of the food materials [3, 20]. The high molecular mobility of the particles allows surface deformation and interaction between particles, leading to stickiness and increased cohesiveness [22]. The temperature at which food materials starts to become sticky has been referred to as the sticky point temperature, and is about 10-20 °C higher than the glass transition temperature [1], see Fig.1. This could also be explained in surface energy terms since the transformation from the glassy state to the rubbery state leads to increased surface energy of the food system. If the food material is not converted to the glassy state, the food particles will remain in a high energy sticky state in which they are highly prone to stick to another high-energy solid surface [23].

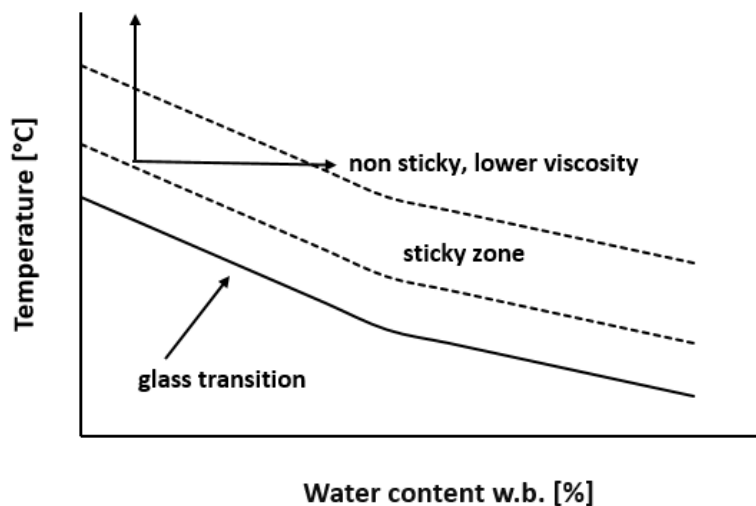


Fig.1. Glass transition and sticky zone for an amorphous compound. The sticky point temperature is about 10-20°C higher than the glass transition temperature.

2.1.4 Glass Transition Related Cohesion

Environmental conditions like temperature and humidity have, in addition to compression, been identified as the key external factors causing stickiness and caking of food powders [24]. Processing and storage of foods can lead to changes as a result of physical processes and chemical reactions [25]. The mobility of the food components have been identified, among other, as a major factor controlling the rate of these reactions [25]. As discussed in section 2.1.3, glass transition temperatures of food components provide a boundary between regions of low mobility in the glass phase, and increasing mobility in the rubbery phase, and is therefore of high relevance in controlling molecular mobility [25]. The difference between the environmental temperature (T) and the glass transition temperature of the material (T_g), has been identified as the driving force for stickiness and caking development [24]. Food powders containing compounds with high hygroscopicity, experience stickiness and caking at temperature above the glass transition temperature as a result of phase transition of amorphous compounds from a glassy to a rubbery state [26].

Inter-particle cohesion depends on viscosity and molecular mobility of the material which both could be related to the positive temperature difference between $T-T_g$ [22]. With increasing positive values of $T-T_g$, the viscosity of the material drops to approximately 10^{-6-8} Pa.s., causing high molecular mobility and a highly viscous flow between randomly distributed molecules in the amorphous matrix [24,27]. Foster, Bronlund & Paterson [26], found that the rate of change in cohesion, mainly stickiness of amorphous sugar powders could be linked to the $T-T_g$ value. In general, their results showed that the development of powder cohesiveness with time, increased with increasing $T-T_g$ values. For $T-T_g$ values about 10°C , the rate of change in cohesiveness during a time period of 16 hours was slow, while for $T-T_g$ values of $16-22^\circ\text{C}$, the cohesion rate increased with time. A positive difference greater than 22°C for amorphous sucrose, resulted in stickiness almost instantaneously. Fitzpatrick et al., [28] also demonstrated the effect of the positive temperature difference between the powder exposure temperature and the glass transitions temperature on the cake strength of skim milk powder. $T-T_g$ values of 0°C or less than 10°C resulted in low or negligible cake strength. As the temperature difference exceeded 20°C , the cake strength increased to over 1N.

The difference $T-T_g$ can easily be increased to positive values because of increasing powder storage temperature [24]. Glass transition as a result of elevated temperature is often referred to as thermal plasticization and is critical for food powder processing in countries with a hot and humid climate, and temperature fluctuations between day and night [24,29]. Glass transition related cohesion of amorphous, hygro-sensitive powders could also occur because of increasing water content, a phenomena known as water plasticization [29]. The influence of water on glass transition related cohesion will be further discussed in the following section.

2.1.5 Water

Several studies have shown that the main factors affecting stickiness and caking in amorphous foods are water plasticization on particle surfaces and temperature [24,30]. Being part of the atmosphere, an increase in relative humidity could lead to an increased amount of water being absorbed on the particle surface or into the bulk [31]. Water absorption may occur if there is a temperature gradient in the environment in which the powder is stored, since moisture will migrate from warmer regions towards colder regions [32]. Hygroscopicity can be described as the ability of a material to absorb water from a humid environment, and the effect of water in the physicochemical properties of food materials at different water content can be referred to as hygro-sensitivity [7,33]. Food systems containing carbohydrates and proteins are more affected by water compared to lipids [29]. Since moisture absorption and/ or migration has been identified as the key element for stickiness and caking, it is essential to know the hygroscopicity of the powder components to be able to determine the powder stability and predict the caking behavior [22,33]. Powders with low hygroscopicity, moisture content and degree of caking, as well as high solubility are often considered as stable powders [33].

The caking development and flow behavior of food powders could be difficult to predict since they often consist of compounds with different characteristics [22]. Amorphous and crystalline compounds are different in their hygroscopicity [7]. Compare to crystalline compounds, amorphous water-soluble compounds do not dissolve in water since they already have a liquid like supra molecular structure [7]. Instead, water migrates into the amorphous matrix where it has a plasticizing effect on the amorphous structure [7]. Water plasticization refers to the process of softening and increasing the flexibility of a polymer, leading to undesired textural behavior like

stickiness, caking and collapse of food systems [31]. Softening of the solids, allowing the particles to deform and come into closer proximity, which could increase the bonding strength [32].

Water plasticization can also be described as the process of lowering the glass transition temperature of amorphous food powders, which have been well recognized as a major factor causing stickiness and caking problems in many food powders [26,31]. Water plasticization of amorphous structure increase the difference between $T-T_g$, which discussed above, results in increased molecular mobility, decreased viscosity and increased reactions rates [21]. The hygroscopicity of dehydrated sugar foods can be related to the glass transition temperature [33]. The higher the powder T_g , the lower is its hygroscopicity [33]. Roos & Karel [21] showed that the glass transition temperature of amorphous food materials with high carbohydrate content, decreased with increasing water content. A linear relationship between water activity and glass transition temperature was also demonstrated in the same study. Plasticization of water, even at fairly low moisture content, has shown to depress T_g below the typical storage temperature of powders [34]. Roos [35] points out the importance of understanding the relationship between glass transition and water activity, in controlling the stability of dairy powders. Liquid bridging as a result of water absorption will be discussed in section 2.3.1.

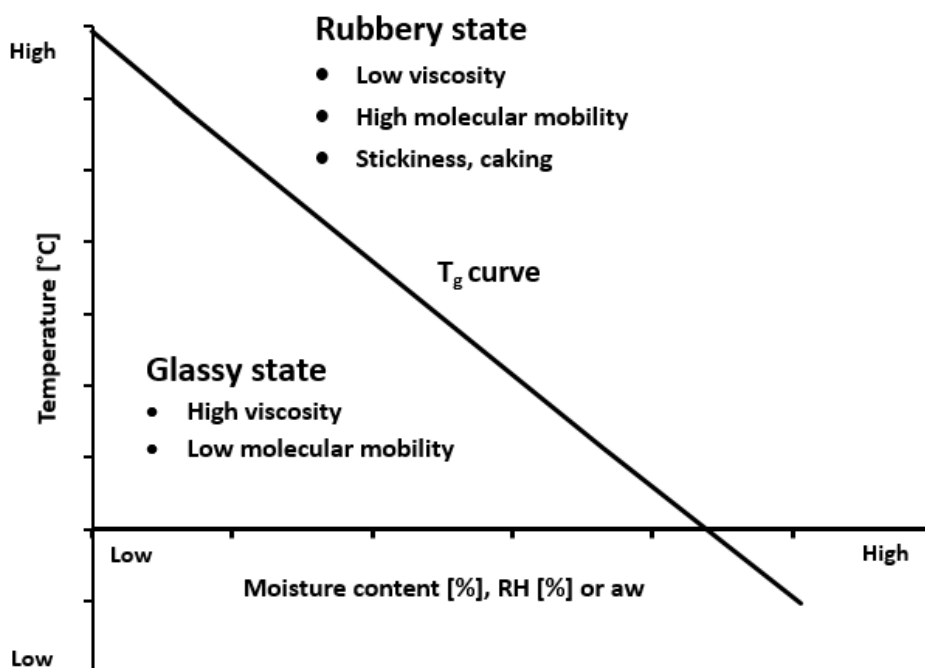


Fig.2. Glass transition temperature (T_g) as a function of moisture content [%], relative humidity [%] or water activity. Glass transition temperatures of food components provide a boundary between regions of low mobility in the glass phase, and increasing mobility in the rubbery phase. Water plasticization has shown to depress T_g below the typical storage temperature of food powders.

2.1.6 Pressure and Compression

So far, the influence of temperature and humidity on the caking and flow behavior of food powders have been discussed, but Teunou et al., [36] highlighted the importance of pressure on the flowability of food powders as well. Barbosa-Cánovas et al., [37] also described that compressibility negatively influences the flowing capacity of powders. Powder flow has been defined by Peleg [38] as the relative movement of particles among neighboring particles or along the container wall surface. The driving force for unaided flow is gravitation [38]. Food powders can be compacted

unintentionally by mechanical compression during handling or transportation [37]. For logistical reasons, free-flowing powders are often stored during prolonged periods [39]. Unless the powder is non-cohesive like dry sand, the state of compaction strongly affects the flowability of the powder [37]. For powders, containing soluble components, stored at high humidity and temperature, there is a marked influence of pressure on caking [31].

As mentioned in section 2.1.2, caking occurs over time, meaning that the influence of pressure or compression has a time factor [31,37]. Pressure or external compression of the powder bed e.g. during storage, brings particle together, leading to increased surface area contact and enhanced inter-particle attraction [31,39]. The powder bed will develop strength with measurable mechanical properties like compressive breaking strength [38]. The compressive breaking strength, also defined as the unconfined yield strength, and the mechanism of inter-particle interaction will be discussed further on. The effect of external compression can be seen in stockpiles in which powder at the bottom of the stack is transformed into lumps or cemented [31]. According to Tenou et al., [36] the cohesiveness of a powder depends, in general, on the size of the consolidation load. The results from their study showed that the higher the consolidation load, the greater the cohesiveness of the powder.

2.1.7 Sticky Food

Spray drying is a fast convective drying process, involving the conversion of material in liquid or slurry form, to dry powder by spraying it into a hot drying medium [17,18]. The technique is suitable for heat sensitive materials since the drying process is so rapid that the materials are only subjected to high temperatures for a short time [40]. It is the most common technique to obtain food powders like milk powders and fruit juice powders [17]. In the dehydration process drops are formed by atomization and the spray is mixed with hot air, which provide energy for evaporation of water from the liquid droplets [17,18]. Drops and air exchange heat and water which lead water vapor to be transferred from the drop surface to the surrounding air. Consequently, dried particles and cooled, humidified air are leaved behind [18].

Spray dried powders have longer shelf life, reduced volume and weight [17]. They are also easier to handle and transport, which make them more beneficial compare to their liquid ones [17]. But not all foods are easily spray dried. Spray dried foods can be divided into two categories, non-sticky and sticky- food [17]. Egg powders, dairy powders and solutions of maltodextrin, gums and proteins are examples of non-sticky foods, which remain free flowing after the drying process [17]. At the opposite, sugar and acid rich food particles tend to get stick on the drying wall or to each another, forming a paste like structure, which could lead to operational problem and low product yield [17,33]. Peleg [38] divided food powders into non-cohesive and cohesive powders based on the strength of the inter-particle forces. For non-cohesive food powders, the interparticle forces are negligible while for cohesive powders they play a significant role.

Amorphous low molecular weight substances like glucose, fructose and citric acid, have high hygroscopicity and low glass transition temperature which contribute to the sticky issue of spray drying [17,33]. According to Bhusari, Muzaffar & Kumar, [33] the glass transition temperature of fructose and glucose is about 5 and 31°C respectively, while Lu & Zografis [41] showed that dry citric acid has a T_g value of 11°C. In a food drying process, the liquid or rubbery food is transformed into the glassy state due to the removal of water [17]. But at spray drying temperatures higher than the T_g value of the powder, the material will not go through this phase transition, leading to the formation of soft particles with high-energy sticky surfaces [17]. As discussed in section 2.1.3, food material in

the rubbery, high energy state will stick to another high energy solid surface, which could lead to operational problems and low product yield [17].



Fig.3. Lump formation in Lemon juice powder. Food powders having high hygroscopicity and low glass transition temperature are particularly sensitive to caking.

2.1.8 Particle Size

Particle size has been identified as an important physical property affecting caking and flow behavior of food powders [36]. Small, fine particles have been considered as more subjected to cohesion than larger, coarser particles [32,36]. Generally, powders larger than 200 μm are free flowing while the flow of smaller particles is more difficult [36]. Particles of micro or nano size have very high surface to volume ratio, which make them highly influenced by electrostatic or molecular forces [31]. For particles below 10 microns size, the interparticle distance become small enough to make Van der Waals's forces significant.

Rumpf [42] was the first to claim that particle size influences the strength of the powder, and he stated that the particle size is inversely proportional to the tensile strength of the powder. In a study made by Specht [42], it was demonstrated that the yield strength (see section 2.2), increases as the particle size decreases. The smaller particle size, the larger surface area and larger number of contact points, which makes it easier for water to migrate and bridging to occur between powder particles [42]. The bridging between particles is described in section 2.3. For particles on a micro meter scale, the molecular forces could deform the bodies, resulting in increased contact area and more intimate contact [13]. It should be noticed that coarser powders might also be prone to cake in the case of a broad particle size distribution [32]. The non-uniformity of particle size could contribute to more contact points between larger particles and the surrounding smaller ones [32].

2.2 Flow Properties of Bulk Solids

The flowability of a powder can be defined as a behavioral characterization of its ability to flow [43]. The flowability of fine-grained bulk solids depends mainly on the adhesive forces acting between particles, but also on particle size distribution, particle shape, and chemical composition of the particles, moisture and temperature [44]. The major forces acting between fine-grained dry bulk solids, are van der Waals forces and electrostatic forces as a result of electric dipoles between atoms and molecules, or different electric potentials between particles surfaces [44]. A powder with "good

flow behavior” is defined as a bulk solid that flows out from a silo or a hopper due to the force of gravity alone [44]. The powder does not consolidate much and flows without flow promoting devices [44]. A powder showing flow obstructions or consolidating during storage is characterized as “poorly flowing” [44]. Generally, larger particles often flow more easily than fine particles since the gravity and inertia are greater than the inter-particle adhesive forces [43]. The magnitude of the load necessary for getting a bulk solid flowing is an important measure of flowability [44]. One way of characterizing bulk solids response to loading or determining time consolidation, is through the uniaxial compression test [44].

2.2.1 Uniaxial Compression Test

In the uniaxial compression test (Fig. 3) a hollow cylinder with removal wall is filled with a fine-grained bulk solid [44,45]. The bulk solid is compressed and consolidated by applying a normal stress (σ_1) - the consolidation stress or major principal stress –in the vertical direction. The more compression of the bulk solid, the more the volume of the bulk solid is reduced and thus the bulk density is increased [44]. In general, for an easy-flowing dry bulk solid, the bulk density will increase very little while for a cohesive and poorly flowing powder, there will be a much larger increase in bulk density when consolidation stress is applied [44,46]. According to Xanthakis, Ruud van Ommen & Ahrné [46], higher differences in bulk densities of nanopowders under progressive increase of consolidation stress, corresponds to flow functions in the very cohesive zone (Fig.5). Due to compression and consolidation of the bulk solid, there will also be an increase in strength of the bulk solid specimen (powder cake).

After applying the consolidation stress, the sample stress is released and the walls of the cylinder are removed [44,45]. The consolidated sample is then loaded with an increasing normal stress until it breaks, also known as fail [44,45]. The stress at which the powder cake fail is referred to as compressive strength, cohesive strength or unconfined yield strength (σ_c), and is a measure of the flow capability of the powder [44,45]. The unconfined yield strength corresponds to the strength of the bulk specimen after it has been compressed by the major principal stress [47]. For a powder to flow, the force acting on it must be greater than the unconfined yield strength σ_1 [47]. A bulk solid with high unconfined yield strength is characterized by its poor flow [45]. The failure is often referred to as the “incipient flow” since the powder cake starts to flow at this moment [44].

An additional property related to the flowability of a bulk solid is the effective angle of internal friction, which gives an indication about the inter-particle interactions [46]. A large effective angle of internal friction indicates greater particle-particle interactions [46]. The pattern was demonstrated by Xanthakis, Ruud van Ommen & Ahrné [46], which reported that powder with higher internal friction angles also showed higher compressibility values, as well as more cohesive behavior in the flow function analysis.

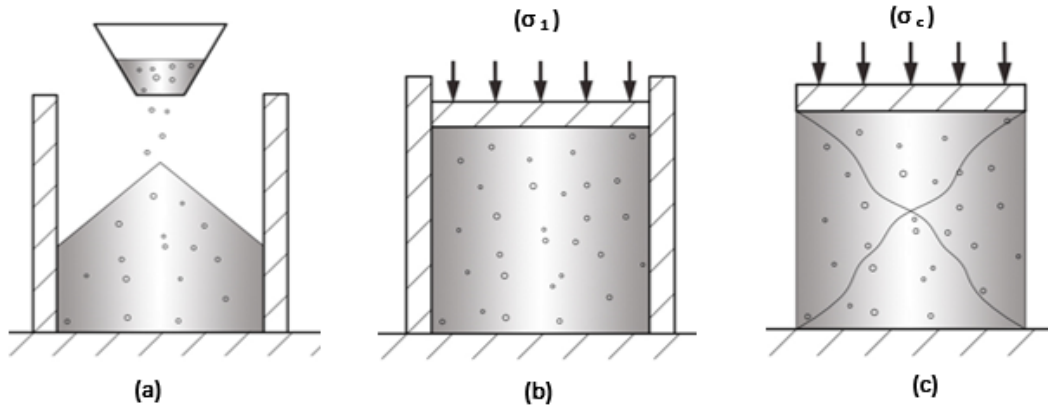


Fig. 3. Uniaxial compression test. A hollow cylinder with removal wall is filled with a fine-grained bulk solid (a). The bulk solid is compressed and consolidated by applying a normal stress (σ_1) - the consolidation stress or major principal stress - in the vertical direction (b). After applying the consolidation stress, the sample stress is released and the walls of the cylinder are removed. The consolidated sample is then loaded with an increasing normal stress until it breaks, also known as fail (c).

2.2.2 Numerical Characterization of Flowability

The unconfined yield strength (σ_c), in relation to the consolidation stress (σ_1), and the storage time (t), is often used to define the flowability of bulk solids [44]. Some bulk solids will gain strength while stored under compression, referred to as time consolidation or caking [44]. By applying the consolidation stress (σ_1), during a defined period of time, time consolidation can be determined using the uniaxial compression test. Numerically, flowability of bulk solids is evaluated using the flow index ff_c , which is a correlation between the consolidation stress (σ_1), and the unconfined yield strength (σ_c) according to the following equation [44]:

$$ff_c = \frac{\sigma_1}{\sigma_c} \quad (1)$$

A free-flowing powder is characterized by a high ff_c value (Table 1). The greater the ratio between the consolidation stresses applied to a powder and the unconfined yield strength (σ_c), the higher flowability of the bulk solid [44]. The lower the ff_c , the higher cohesiveness and poorer flow of the powder (Table 1). The curve representing the unconfined yield strength (σ_c), as a function of the consolidation stress (σ), together with the boundaries as classified in Table 1, can be illustrated in a flow function diagram (Fig.5). The flow function shows the relationship between the compressive stress applied for consolidating the powder, and the strength that the powder cake obtain [44]. Today, shear testers are often used instead of the uniaxial compression test to measure unconfined yield strength, bulk density and effective angle of internal friction [44]. The shear tester is further discussed in section 2.5.3.

Table 1. The flow index (ff_c) describing the ratio of consolidation stress (σ_1), to unconfined yield strength (σ_c), defines flow behavior as follows:

Flow function $ff_c = \sigma_1/\sigma_c$	Powder behavior
$ff_c < 1$	not flowing
$1 < ff_c < 2$	very cohesive
$2 < ff_c < 4$	cohesive
$4 < ff_c < 10$	easy-flowing
$ff_c > 10$	free-flowing

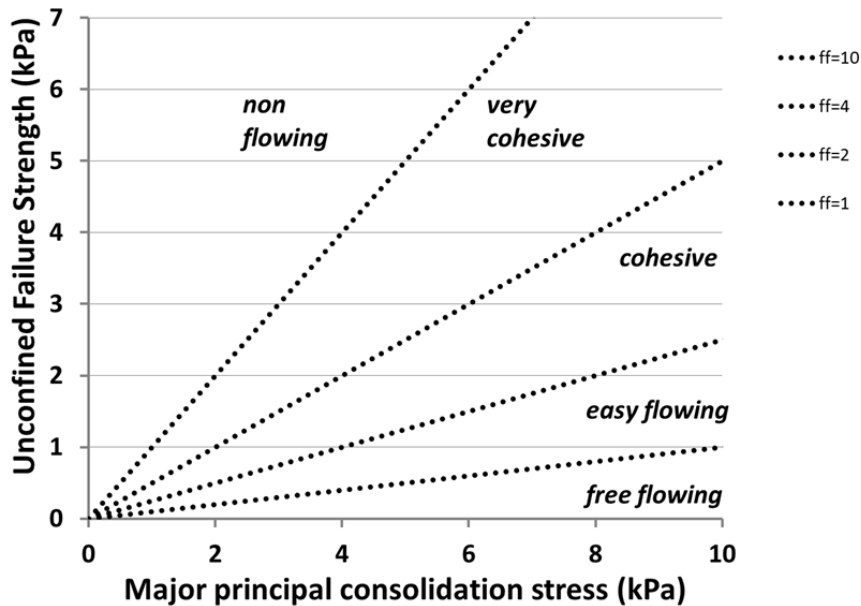


Fig.5. Flow function diagram. The dotted lines representing constant values of flowability. The higher ff_c value, the higher flowability of the powder.

2.3 Different Mechanisms of Caking

The previous section clarifies that changes, involving stickiness and caking, in a particulate system depends on many factors. The following section will focus on the mechanisms of caking and the forces causes primary particles to stick together. It is well known that the mechanisms involved are liquid bridging, solid bridging, inter-particle attractive forces and mechanical interlocking [37]. The cohesive strength of a powder can be due to more than one mechanism depending on the environmental conditions in the powder system [37,42]. According to Haider et al., [24] $T-T_g$ is an important parameter, not only for the caking probability, but also in determining which caking mechanism acting on a defined time scale. Humidity cycling or humidity caking, in which powders are exposed to high relative humidity followed by low relative humidity can lead to the formation of liquid bridges which are converted into solid bridges as a result of water evaporation [22,37]. As already mentioned, moisture migration caking is among the most common mechanism of caking [39,48]. In this chapter, caking of both amorphous and crystalline components will be discussed since the mechanism of bridging differs between the two structures.

2.3.1 Liquid Bridging

Crystalline substances seems to have low affinity for absorbing water at lower water activity, while at a critical relative humidity they start to rapidly absorb water [49]. Billings et al., [50] reported that the critical water activity for initiation of caking was 0.8 for bulk sucrose. The formation of liquid bridges starts with wetting and moisture absorption on the particle surfaces, causing plasticization [48,51]. The underlying mechanisms of liquid bridging dealing with capillary condensation in the pores formed at the contact point between two neighboring particles [50]. Condensation will occur if the pressure in the pores is lower than the surrounding atmosphere. In that case, the saturated vapour pressure above the liquid phase is less than the vapour pressure of the bulk air at the same temperature. If the pressure is lowered enough, the vapour pressure will be greater than the saturated partial pressure above the capillary (pore) surface, resulting in condensation, partial surface dissolution of soluble components, and inter-particle liquid bridges [49,50].

The strength of the liquid bridges, containing the dissolved substances, will mainly depend on the capillary forces [49]. Evaporation of water e.g. during drying can increase the force holding the particles together by, leaving behind the dissolved solids in the bridge [37,49,50]. In some cases, crystallization of the dissolved solids in the liquid can occur, leading to solid crystal liquids between the particles [49]. Specht [42] points out that the mechanism of solid bridge formation is the key to cake formation. Solid bridging can occur in several ways, and the mechanism for crystalline substances is different to that of amorphous substances [49]. Amorphous materials seem to form solid bridges by either sinter together or by visco-elastic deformation [52,53].

2.3.2 Sintering

A powder cake is formed due to several solid bridges holding particles together [42]. For amorphous materials, sintering is mainly responsible for the solid bridging [52]. Sintering can be described as the process in which particles move into the gap between neighboring particles, forming viscous bridges [49,53]. This happens for amorphous food powders at elevated humidity or temperatures since the molecules are able to flow above the glass transition temperature [49,52], see section 2.1.3. Hence, the rate of sinter bridge development depends on the stickiness, i.e. molecular mobility and viscosity of the material which, as familiar, could be related to the positive difference between the powder storage temperature and the glass transition temperature [49,53].

The driving force for sintering is surface tension and/or external forces [49]. All materials aim to reduce the free surface area, which could be associated to the free energy of the system [7,54]. When two amorphous, spherical particles adhere to each other, they can be considered as one single particle [7,54]. Molecules are transported to the contact point between the particles and while closing the gap between the particles, the free specific surface energy of the system is reduced [7,49,54]. Sintering is driven by the difference between the capillary pressure at the contact point between the particles and the Laplace pressure (the pressure difference between the inside and outside of the curved surface of the particles) in the volume of the two initial particles [7,55]. The process could also be driven by external forces and leads to the formation of material bridges between amorphous particles, through viscous material flow [53,56].

The adhesion forces between single particles are depending on the diameter and the viscosity of the bridge [53]. While going through the sticky zone with increasing temperature or water content (Fig.1), the stickiness of the powder increasing to a maximum value [22]. In the initial phase, decreased viscosity first accelerates the sintering and the strength of the powder cake due to enhanced molecular mobility and facilitated inter-particle adhesion [7,31]. The growing diameter of the sinter bridges increasing the strength of the powder cake, but with progressive moisture migration or elevated temperature, the stickiness of the powder as well as the viscosity of the sinter bridges decrease again, resulting in reduced strength of the powder cake [7,22,53]. This change in kinetics often occur when the sinter bridge diameter reaching the magnitude of the particle diameter [53]. Particles missing a stabilizing inner structure lose the structure and shape, causing a collapse of the powder structure [7]. Open pores in the powder package disappear, resulting in a highly viscous, amorphous melt [7].

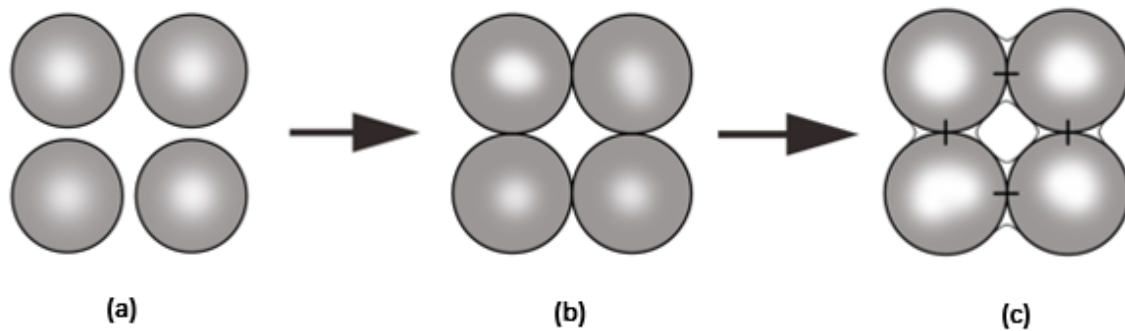


Fig.4. Sintering of an amorphous compound. In the initial phase (a), the particles are free flowing. At elevated temperature or humidity, the particles move into the gap between neighboring particles (b). While going through the sticky zone, the sintering and strength of the powder cake increase, due to increased molecular mobility and facilitated inter-particle interactions (c).

2.3.3 Viscoelastic Deformation

Increasing adhesive forces between single particles are common for any caking mechanism and could either be linked to the development of material bridges, as in the case of sintering, or increasing van der Waals forces between particles [52]. A mechanism responsible for increasing the inter-particle adhesive forces for amorphous food powders is viscoelastic deformation, leading to flattening of the contact site [53,57]. Polymers in the amorphous state have elastic properties because they are in a statistical conformation called random coils, which can be elongated during exposure to external stress [58]. When the stress is released, the material will partly relax [59]. Viscoelastic deformation could contribute to increasing van der Waals forces through increasing number of contact points, increasing contact area and decreasing distances between neighboring particles [52,59]. According to Aguilera et al., [52] viscoelastic deformation could enhance the development of sinter bridges. Whether viscoelastic deformation or sintering is the mechanism responsible for the adhesive forces will depend on mechanical properties like water content and temperature, but also on process time and compressive forces [24,52].

Haider et al., [24] discuss the effect of $T-T_g$ on the rheological behavior of amorphous hygroscopic substances, and how this will determine the flattening and sintering kinetics as well as the transitions between the two mechanisms. Rheology describes the deformation and flow of particles under defined conditions [60]. For low $T-T_g$ values, at the onset of the rubbery state, viscoelastic deformation in combination with increasing van der Waals forces, will be the most relevant caking mechanism [24]. Increasing parameters like $T-T_g$ values or compressive forces or deformation could lead to a transition from viscoelastic surface flattening to viscous flow sintering on a short time scale [24]. Berberner & Löffler [57] discuss the function of time by argue that there exists a characteristic time $t=t^*$, at which the contact circle radius for the same material and the same force, is the same for both flattening and sintering. Below this characteristic time, flattening will be the dominating mechanisms while above, sintering governs the interparticle interactions [57].

2.3.4 Mechanical Interlocking

The particle size, particle shape and particle size distribution play an important role in determining the dominating caking mechanism [61]. For particles with irregular and uneven size and shape, mechanical interlocking will be the dominating caking mechanism [14]. During compaction or vibration, particles will repose and interlock with each other causing reduced flowability [14,62]. Generally, particles with irregular shape have poorer flow properties compared to those with a more

spherical morphology, which easier glance past one another [62], see Fig. 5. The strength of the bond will depend on the roughness and distortion of the particles, as well as the degree of compaction [14]. Mechanical interlocking can cause otherwise cohesion less particles to form stable arches at a converging section in a container [63].

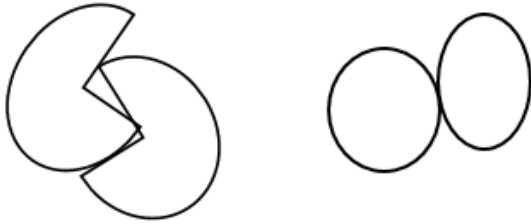


Fig. 5. Mechanical interlocking for particles with irregular shape and size. Particles with a more spherical morphology easier glance past one other.

2.4 Prevention of Stickiness and Caking

As familiar, there are many factors, both external and internal, affecting stickiness and caking of food powders. When assessing a caking problem, the powder properties known to affect stickiness and caking must be considered, as well as the environmental conditions and the handling of the food powder [32]. Characterization methods involving sorption isotherm, glass transition and flow analysis, can help identify and control those critical factors, see section 2.5. By correlating variables like temperature, relative humidity and particle size distribution with their effect on the bulk material's cohesive strength using a shear tester, it is possible to identify the most critical parameters [32]. An additional way of controlling the caking behavior of food powders is by adding a small amount of anti-caking agent [32].

2.4.1 Anti-caking Agents

Anti-caking agents, also referred to as flow conditioners, gliadants or lubricants, are substances added to prevent caking and improve the flowability of food powders [2,37,64]. Anti-caking agents are very fine powders with a particle size of about 0.1-30 μm , and can be divided into inorganic and organic substances [14,64]. Silicon dioxide, calcium phosphates and magnesium silicates are examples of inorganic powders commonly used in dairy powders and salts [14]. For shredded cheese products and dried fruit pieces, organic anti-caking agents like microcrystalline cellulose, vegetable fibers and starches are more widely used [14]. To be allowed in food powders, the anti-caking agent needs to be inert, safe in specified amount and classified as "generally regarded as safe" (GRAS) [37]. To fulfill the criteria of good manufacturing practice (GMP), the substance should also be used in the lowest level as possible and prepared and handled in the same way as the food ingredient [14]. The additives can be listed either as nutrient or as a food ingredient [37]. Studies have shown that the optimal performance of anti-caking agents were achieved when added in an amount of 1-3 % [37].

Kono, Huang & Xi [64] reported that the mechanism of the flow conditioners depends on the structure of the bulk powder in which the flow aid is dispersed. Generally, anti-caking agents have shown to compete with host powder for moisture, acting as a moisture barrier or physical barrier between particles or increasing the T_g value [37]. A key factor to minimize the risk of caking is the strict control of moisture content at low temperatures [37]. Anti-caking agents often have strong water absorptive ability and in combination with the capacity to absorb a lot of water without experiences stickiness, they can compete with the host powders for the available water [14,37]. Due

to more surface area per unit weight, they absorb water faster than the host powder, which leads to reduced hygroscopicity, and consequently reduced risk of caking [14,37]. The fine powders often stick to, or coat the larger particles and the effect of competing with the host powders for moisture has shown to have the largest effect when the anti-caking agent completely covers the surface of the host powder [37]. By coating the powder particles, anti-caking agents may also function by giving the powder a water-repellant character [65], see Fig.6.

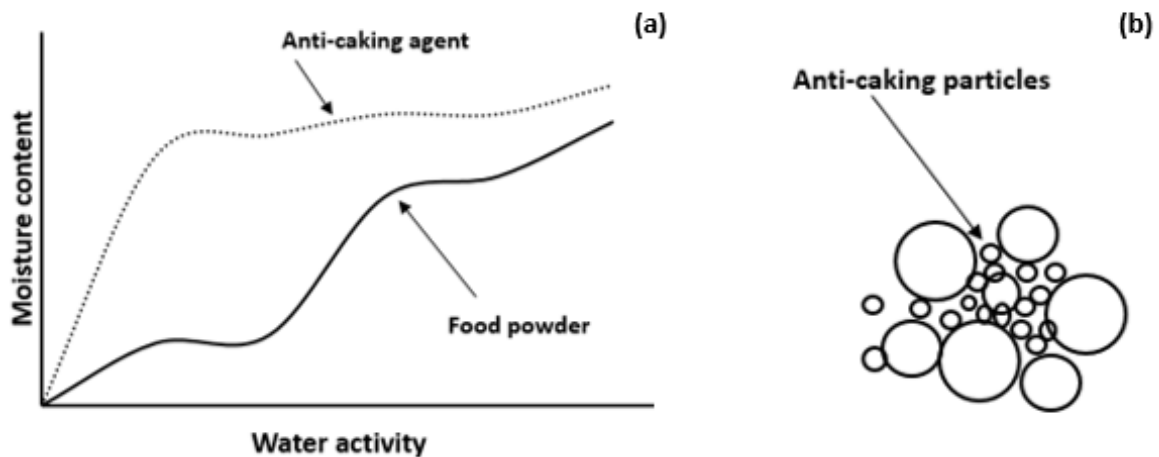


Fig.6. Anti-caking agents have shown to compete with the host powder for the available water (a) or acting as a moisture or physical barrier between particles (b). They have the ability to absorb a lot of water without experience stickiness.

A consequence of the small particle size of anti-caking agents is that they are very cohesive and have a strong tendency to cake when not mixed with another powder [66]. On the other hand, they are easily absorb on the surface of larger particles in powder mixes and by doing so, they acting as a surface roughness or physical barrier between powder particles, preventing particle surfaces from adhere to each other [14,37,66]. By covering the powder particles surfaces, they increase the minimum contact distance between the interacting particles, leading to reduced contact area and consequently reduced molecular attractive forces like van der Waals forces [66]. Silicon dioxide, the most common anti-caking agent, has shown to be strongly adsorbed at surfaces of larger particles, behaving like a surface roughness [66]. When incorporated between larger particles, anti-caking agent could also interfere with liquid bridges, thus weaken the caking bonds and reduce the cohesiveness of the powder or prevent the formation of crystal growth [37,67]. York [68] reported that there exists a saturation condition, that is to say, an optimum concentration of anti-caking agent, above the flowability of the host powder could not be further improved. The optimum concentration depends on the average size of the anti-caking particles in relation to the host powder, as well as the physical and chemical nature of the additive [68].

The importance of glass transition on the caking tendency has been discussed several times in this paper. In the case anti-caking agents are chosen among high molecular weight ingredients like starch, having high T_g , they could function by increasing T_g of the powder, resulting in improved stability of the powder mix [11]. According to Das & Jaja [9], isolated protein or maltodextrin are often added to fruit juices to increase the T_g value, and overcome the problem of stickiness during drying. Potato starch as an anti-caking agent has been successfully used in shredded Mozzarella cheese [69].

2.4.2 Natural Anti-caking Agents

As stated in the very beginning of this paper, the consumer demand for products with fewer additives has increased during the past years. Nowadays, it is possible to replace the synthetically produced anti-caking agents like silicon dioxide with natural ingredients, leading to a cleaner labeling while also solving caking and flow related problems [12]. Companies like RIBUS offers “The Synthetics Replacer”, NU-Flow, which effectively replaces synthetics like silicon dioxide in system requiring anti-caking agents [12]. NU-FLOW is made from rice hulls or rice husks and contains about 18-20% silica and 70 % fiber. Steve Peirce, the owner of the company, stated to Food Engineering magazine, that the uniform distribution of silica embedded in the fibers, allows the two components to work together, and that the fibers provide good water and oil absorption capacity [70]. NU-FLOW has been used as one-to-one replacer to silicon dioxide and can be labeled simply as “rice concentrate” in the food ingredient list [12].

2.5 Methods for Characterization of Stickiness and Caking

Boonyai, Bhandari & Howes [30], divided stickiness measurements techniques into direct and indirect methods. It is well known that moisture is one of the key factors affecting stickiness, caking and flowability of hygroscopic food powders [36,71]. Moisture sorption isotherms, together with glass transition temperature profiles using a differential scanning calorimetry (DSC) are common, indirect methods for predicting the stability of powders [30,71]. Flowability analysis using Shear cell techniques, is an example of a direct method used for the quantification of cohesion and adhesion of food powders under controlled consolidation levels [30,61]. A general description of the moisture sorption isotherm, glass transition approach and flowability analysis will be given in the following section. Sensory analysis, using objective methods like triangle test, will be discussed thoroughly in the final section.

2.5.1 Moisture Sorption Isotherm

A moisture sorption isotherm can be used to describe the behavior of a food powder towards the humid air when stored in an environment with different relative humidities at a given temperature [36,51]. It is a useful tool when optimizing process and storage conditions in order to minimize moisture caking [61]. In graphical form, the sorption isotherm shows the relationship between water content and water activity in a food product [51]. As seen in Fig. 7, the water could be absorbed in one or several layer [51]. The shape of the curve will provide useful information about the type of interaction between the material and the humid surrounding [61].

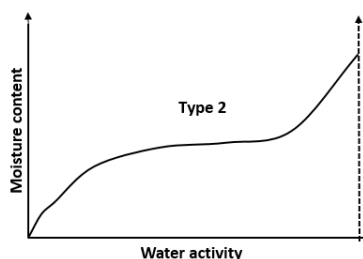


Fig.7. Five different types of isotherms have been classified while the most common is the nonlinear, sigmoidal isotherm (Type 2).

Five different types of sorption isotherms have been classified while the most common is the nonlinear, sigmoidal isotherm [71], illustrated in **Fel! Hittar inte referenskälla..** If the food material contains crystalline components, the shape of the sorption curve is characterized as type 3 [72], see Fig. 7. As mentioned, amorphous and crystalline components behave differently when exposed to an environment with high humidity or temperature [7]. As seen in Fig. 7, crystalline components do not absorb water until high relative humidities, and the shape of the sorption curve also indicates that only a small amount of moisture is needed to localize regions of high water activity in which liquid bridging could occur [61].

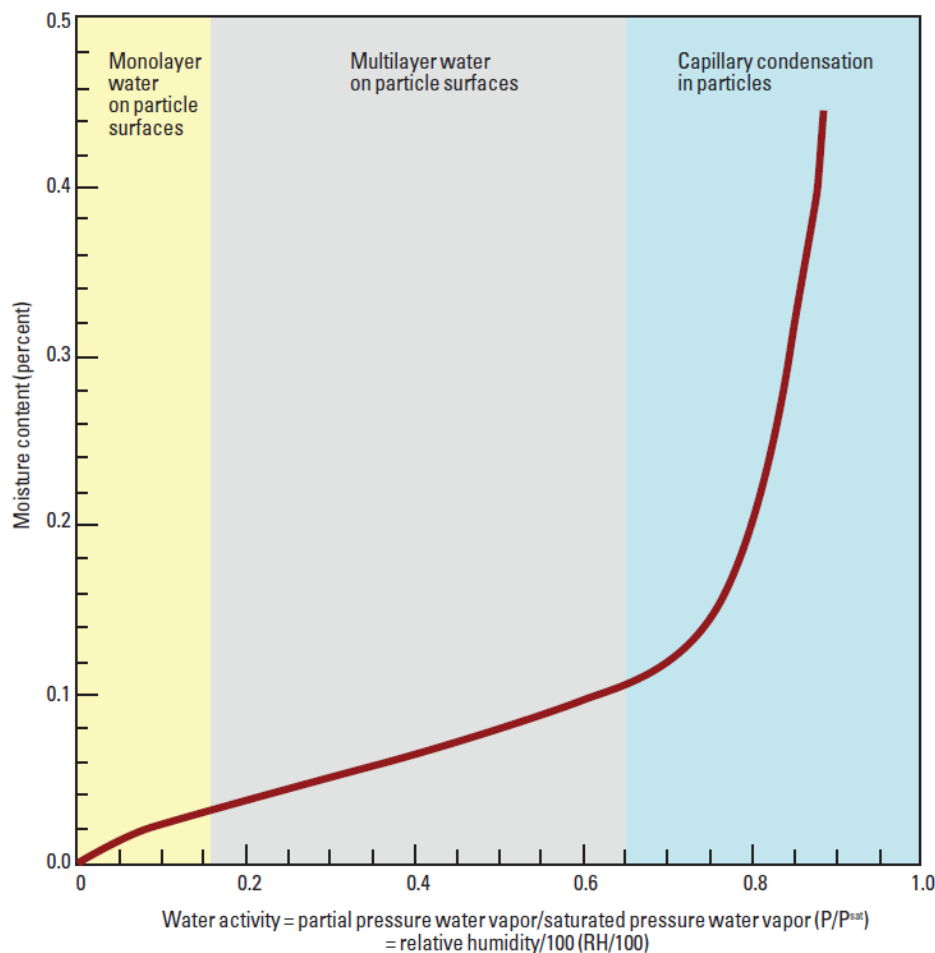


Fig. 7. Sorption isotherm for a crystalline material. The shape of the isotherm indicates that only a small amount of water is needed to reach regions of high water activity. As seen, water can be absorbed in one or several layers. Pictures taken from Jenike & Johanson [61].

In the sorption isotherm analysis, small samples of the material are placed in humidity chambers or desiccators and exposed to constant temperature and a range of different relative humidities [61]. The sample will absorb or release water until it reach equilibrium with the air, that is to say when its water activity is similar to the relative humidity in the air [24]. The change in weight at each relative humidity, obtained by comparing the weight before and after drying, representing the total moisture content as a function of the relative humidity in equilibrium with the material [61].

2.5.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique measuring how physical properties of a sample changes along temperature and time [73]. The technique is frequently used in industries like food, pharmaceuticals and paper [74]. The device determines the temperature and heat flow associated with phase transitions like glass transition, melt and crystallization, as a function of temperature and time [73]. Based on a temperature difference between a sample and a reference material, DSC measuring a heat quantity corresponding to the amount of energy absorbed or released by the sample while heated [73]. The result from the DSC analysis is presented in a thermogram, showing the heat flow as a function of temperature. There exists two different types of DSCs: heat flux DSC and power compensated DSCs [73].

The heat flux DSC consists of two pans, the sample pan and an empty reference pan, placed on a thermoelectric disc, surrounded by a furnace [73]. The furnace is heated at a linear rate, and the energy is transferred through the thermoelectric disc to the sample pan and reference pan [73]. Due to different C_p values, the sample pan will be heated more slowly compared to the reference pan, resulting in a temperature difference [73]. C_p of a material can be described as the amount of energy (J/g, J/mol or calories/ g) a material can hold, and it is known, for all material, to increase with temperature [74]. The input energy required to compensate for the temperature difference between the sample and the reference, would be the amount of energy absorbed or released by the molecule in the sample [73]. The temperature difference is measured by area thermocouples and the heat flow is calculated according to the thermal equivalent of Ohms law:

$$q = \Delta T / R \quad (2)$$

where q is thermal heat flow, ΔT is the temperature difference between the sample and reference and R is the resistance of thermal electric disc [73].

As already mentioned, the structure of an amorphous material like glass, is random. While heating, the heat capacity increases and eventually, the material will contain enough energy to be mobile [74]. The energy required will be higher than the energy corresponding to the baseline, resulting in a step change or peak in the thermogram [74], see Fig. 10. The temperature range in which the step change occur, is referred to as the glass transition [74]. In the heat flux DSC, peaks corresponding to energy requiring, endothermic, events will point down since the sample will absorb energy and be cooler than the furnace [74]. The glass transition temperature can be defined as the onset, mid or end points of the glass transition, while the most common is to define the midpoint temperature as the glass transition temperature [9], see Fig. 10.

2.5.3 Shear Cell Techniques

Shear testers are often used in advanced solid technology to study powder flowability, i.e. to evaluate how the unconfined yield strength (cake strength) of the powder varies with consolidation stress [3,44]. The technique provides a quantitative measure of the shear stress required to break the powder cake at different consolidation load [3]. The method provides information about the cohesion between particles, but is more commonly used to evaluate the flow behavior of powders, rather than the stickiness of the powder [30]. Brookfield POWDER FLOW TESTER (PFD) is an

instrument based on the shear cell technique, which can be used to characterize powder flow properties under different consolidation loads [75].

In the PFD, the sample powder, is loaded into an annular shear cell which consists of a trough [75]. Before starting the test, the weight of the powder sample is measured. The main principle behind the PFD is to drive a compression lid vertically downward into the annular shear cell to apply a defined force and consequently a specific consolidation stress within the powder sample [76]. The compaction stress applied to the powder sample is controlled by a beam load cell [75]. As the uniaxial compression test, described in section 2.2.1, the shear test is a two-step procedure. In the initial step, the powder is pre-consolidated by applying the vertical normal stress [31,44]. Further, the compaction lid is fixed, while the annular shear cell is rotated at a defined speed which due to friction between particles causing a measurable shear stress in the bulk solid [44,75]. The torque resistance of the powder sample in the shear cell moving against the powder in the fixed lid is measured by a calibrated reaction torque sensor [75].

The process is repeated and successively greater loads are applied to the lid, leading to that the powder sample is exposed to increasing consolidation stress [76]. At each consolidation stress, a particular shear stress causing failure will be obtained [31]. The shear stress as a function of consolidation stress can be presented in a yield locus curve in which parameters like consolidation stress, unconfined yield strength and effective angle of internal friction can be determined [31,44]. Subsequently flowability can be derived from the acquired parameters [75]. A detailed description of the determination of these parameters from the yield locus curve is found elsewhere [44].

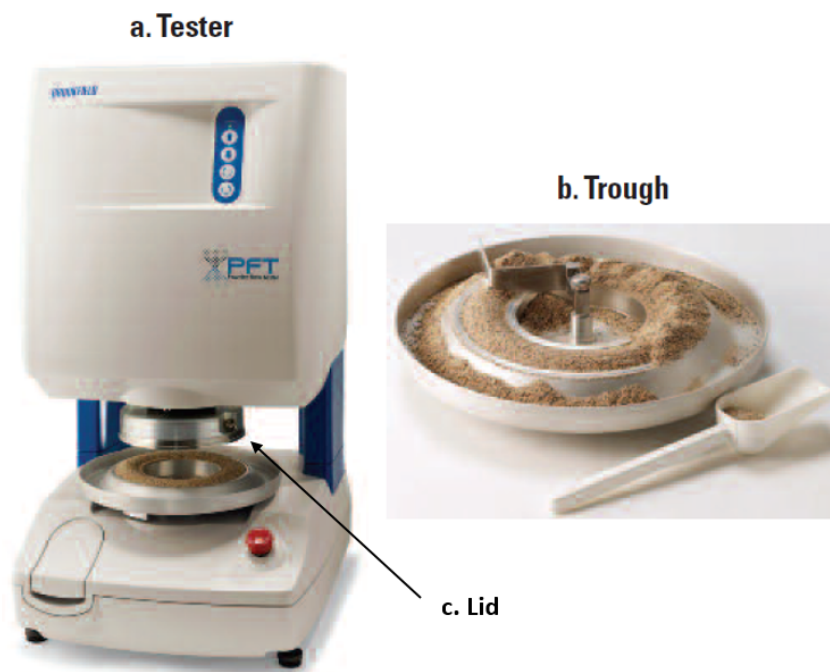


Fig.8. The Brookfield POWDER FLOW TESTER (PFD). The compression lid is drawn vertically downward into the annular shear cell to apply a defined force and consequently a specific consolidation stress within the powder sample. Picture redrawn from Brookfield Engineering Laboratories [76].

2.5.4 Sensory Analysis

Sensory evaluation is often defined as a method used to evaluate products based on how they are perceived through the sense of sight, smell, touch, taste and hearing [77]. Sensory and consumer testing have during the past years become an important role in R & D and marketing for understanding human behavior and provide guidelines for development and commercial strategy [77]. A sensory test could be either objective or subjective. Objective test methods are used to determine whether there are differences between products and if so, identify the nature and magnitude of the difference. Determination whether there exists a difference between samples are done in the discrimination test methods, while the descriptive test methods aiming to identify the nature and magnitude of the sensory difference [77]. Description tests are used in combination with statistical data analysis to define if the samples are view to be different. On the other hand, subjective test methods providing subjective data like liking and preference. One commonly used objective test, belonging to the discrimination test methods is the triangle test [77].

2.5.5. Triangle test

Triangle test is a sensory evaluation aiming to determine if there exists a difference between samples [77]. The conclusion after performing a triangle test is that there either exists a significance difference between samples or that it does not exist a significance difference between samples. Before introducing the test, a significance level, e.g. $p = 0.05$, should be determined. The test belonging to what is referred to as overall difference tests, in which all information, like aroma and appearance, can be used to make the decision [77]. In the triangle test, the assessors get three samples labeled with three-digit codes, and are told that two are the same and one is different. The task is then, after tasting the samples in a provided order, to separate the odd sample from the two similar samples. The three samples can be presented in six different orders according to the following experimental design [77]:

Table 1. Experimental design for the six possible orders of presentation in the triangle test.

AAB	BBA
ABA	BAB
BAA	ABB

The size of the panel used depends on the aim and significance of the test, but a standard practice is to use each presentation order an equal number of times and with a panel size of about 24-30 participants [77]. The data can be analyzed either manually or by software packages. While using the software packages, the probability of making a type I error, that is to say a “false positive”, is calculated and compared with the significance level. Assuming a panel of 30 assessors. The minimum numbers of correct responses to be able to reject the null hypothesis of “no difference between samples”, at a significance level of 5 %, is 15. If the minimum numbers of right responses are fulfilled, and the probability of making a type 1 error is less than the significance level of the test, it can be concluded that there exists a significance difference between the samples [77].

2.6 Raw Material

Low molecular weight sugars and organic acids are referred to as sticky food, see section 2.1.7. The fruit powder Lemon juice powder and the spice blend Red onion seasoning mix, both contain a large amount of sticky ingredients. These products are known to be highly problematic when it comes to caking [5]. The powders have shown to be problematic during production and storage,

but also for the consumers. A short description of the products and the containing ingredients, as well as the potential natural replacers to silicon dioxide, will be given in the following sections.

2.6.1 Lemon Juice Powder

Lemon juice powder can be found in several Asian spices and spice blends. The organoleptic properties of Lemon powder has been described as a light beige, homogenous, fine powder with a citrus flavor [78]. The powder is produced with low temperature spray drying and the final product contains 50 % lemon juice and 50% maltodextrin, with a particle size of about 0.5 mm. More than half of the nutrients constitutes of carbohydrates, of which more than 20% is sugar [78]. Paterson & Bröckel [79] determined, using HPLC, the sugar and fruit acid composition of filtered and pasteurised lemonjuice. Their result showed that the lemon juice contained, in excess of the fruit sugars, about 20 % citric acid. Due to the presence of low molecular weight sugars and organic acids, having high hygroscopicity and low glass transition temperature, there is a big challenge preventing stickiness and caking problems during processing and storage of products containing Lemon powder.

2.6.2 Red Onion Seasoning Mix

Red onion seasoning mix is a spice blend containing sugar, salt, citric acid, lime juice powder, silicon dioxide and oregano, used for pickled onion. Red Onion seasoning is complicated by the fact that it contains many different components, both amorphous and crystalline, which makes the stickiness, caking and flow behavior difficult to predict.

2.6.2.1 Sugar: Free Flowing Crystals of Sucrose

The major ingredient in the Red onion seasoning is white, purified sucrose in free flowing crystals with a mean value of 0.45-0.55 mm [80]. To avoid lumping, the product should be stored at a stable temperature, not below 10 °C and at a relative humidity of 40-65 %. Sucrose might be labelled as sugar or white sugar in the food ingredient list [80].

2.6.2.2 Salt: Crystalline Sodium Chloride

The second major component in the Red onion seasoning mix is common salt which consists of white, crystalline sodium chloride [81]. The salt is highly dispersed and completely soluble. Fitzpatrick et al., [22] studied the caking behavior of crystalline, common salt during exposure to a relative humidity of 100 %, and found that the salt readily absorbed water and caked, however the cake strength was very weak.

2.6.2.3 Lime Juice Powder

Lime juice powder is a free flowing, fine powdered product produced by low temperature spray drying [82]. The powder consists, like Lemon juice powder of 50 % fruit solids and 50 % maltodextrin, and is characterized by high hygroscopicity and thermoplasticity. The particle size is about 0.5 mm and the moisture content less than 5%. Due to the presence of citric acid, the acidity is about 25-38 % [82]. The powder is often used as a taste giving components in spice blends [10]. According to the product specification, the product should be protected from light, moisture and oxygen and it is recommended to store the sample at 4-18 °C, at a relative humidity of not more than 60% [82].

2.6.2.4 Citric Acid

Red Onion seasoning mix consists of about 9 % citric acid, and it is mainly used for its taste giving and antioxidant capacity [10]. Being a metal chelator, citric acid protect lipids from oxidizing [83]. Citric acid appears as a white, completely soluble and crystalline powder [84].

2.6.2.5 Silicon Dioxide

The anti-caking agent used in the Red Onion seasoning mix is silicon dioxide, labelled as E551 [10]. Silicon dioxide is a hydrophilic silica that combining high absorption capacity, with good flowability [85]. The silica has a particle size of 13.5 μm , giving a high specific surface area. The silica is inert but due to the very high specific surface area, it could absorb moisture and volatile organic substances from the surrounding atmosphere. The producer recommends therefore storing the powder in sealed containers in a dry, cool place, protected from volatile organic substances [85].

2.6.2.6 Oregano

A small amount of 100 % pure Oregano leaves, are added in the Red Onion seasoning to provide flavor [10,86].

2.6.3 Natural Alternatives

As discussed in section 2.4.2, anti-caking agents may due to their high water absorption capacity, function by competing with the host powder for moisture, reduce inter-particle interactions or increasing the glass transition temperature. The following section will provide a general description of three, potential replacer to silicon dioxide, which seems to have one or a few of the anti-caking properties described above.

2.6.3.1 Orybran

The rice fiber Orybran is produced from brown rice by removing the external layers of the rice kernel until the kernel's core, resulting in a particle size of about 300-425 μm [87]. The kernel's core consists mainly of starch, giving the product a carbohydrate content of about 30 %. Being an important source of proteins and noble fats, and also bringing a high concentration of dietary fibers (30%) [87]. Orybran is marketed as a health promoting ingredient. It is suggested to be used in products like high fiber content breakfast cereals, bread and baby food, and can be labeled simply as stabilized rice bran [87]. As discussed above, the rice fiber NU-FLOW, is already manufactured as a potential replacer to silicon dioxide [12]. Similarities between NU-FLOW and Orybran regarding the high fiber content, makes also Orybran to a potential replacer to silicon dioxide.

2.6.3.2 Native Potato Starch

Native potato starch is a multifunctional ingredient, widely used in food applications and manufacturing process [88]. The product is among other thing, used as a texturing agent, water binder and thickener, and has been applied in food products like biscuits, microwaveable soups and cooked sausages. The starch content is about 80% and the moisture content in the range of 17-21 % [88]. According to Livsmedelsverket [89], native potato starch is not considered as a food additive. Being a high molecular weight ingredient with high glass transition temperature, it could potentially be used as anti-caking agent, functioning by increasing T_g of the powder mix [11]. As already mentioned, potato starch has been successfully used as an anti-caking agents in shredded mozzarella cheese [69].

2.6.3.3 Fibruline

Fibruline is a soluble dietary fiber consisting of inulin, a non-digestible oligosaccharide built up of fructose and glucose units [90]. Being extracted from the chicory roots by a natural process, it is a natural source food ingredient. Fibruline is a fine granulated white powder with a particle size of less than 500µm [90]. Having a neutral or slightly sweet taste, it is commonly used in the dairy, bakery and confectionary industry, but can also be added to powder blends and beverages. Due to a dietary fiber content of over 80%, it may function as a fiber enrichment [90]. As with native potato starch, Inulin is either not classified as a food additive and can e.g. be labeled as (Chicory) Inulin, Chicory (Vegetable) fiber or (Chicory) Fructo-Oligosaccharide [89,90]. Fibruline is considered as a potential natural anti-caking agent due to its high fiber content, and possibly high water absorption capacity.

3 Materials and Methods

The following sections will describe the materials and methods used to evaluate the silicon dioxide replacers: Fibruline, potato starch and Orybran, based on how they affect the moisture sorption isotherm, glass transition, flowability and sensory properties of the host powders Lemon juice powder and Red Onion seasoning mix.

3.1 Preparation of Raw Materials

The working materials in the study were powders obtained from Santa Maria AB, and a fiber producing supplier. The easily caked pure Lemon powder, and the spice blend Red Onion seasoning mix were investigated. Details about the powders can be found in section 2.6. The caking behavior of each powder was analyzed without addition of anti-caking agent, with silicon dioxide and with the three potential replacers according to Table 2. The amount of anti-caking used corresponded to the amount of silicon dioxide used in the Red Onion seasoning mix at the present situation. The working samples of Lemon powder was prepared by adding 1.7 % of each anti-caking agent to the raw material according to Table 2. The powders were mixed using an electric hand mixer and a food processor. Red Onion seasoning mix was prepared by mixing according to the recipe obtained from Santa Maria AB. The raw materials were added in geometric progression and the amount of anti-caking agent added corresponded to 1.7 % (Table 2). The powders were vacuum packed in plastic bags and stored in room temperature for further analysis. In parallel to the DSC measurements and flow functions tests, additional samples of Lemon powder containing 5 % of the natural anti-caking agents, and Lemon powder with 10 % of native potato starch were prepared in the same way as described above.

Table 2. Working samples of Lemon powder and Red Onion seasoning mix. Sample 1a and 2a, contains no additive while sample 1b-1e, and 2b-2e contains 1.7 % anti-caking agent.

Lemon powder	
1a	Lemon powder- No additive
1b	Lemon powder- 1.7 % Silicon dioxide
1c	Lemon powder- 1.7 % Fibruline
1d	Lemon powder- 1.7 % Potato starch
1e	Lemon powder- 1.7 % Orybran
Red Onion seasoning mix	
2a	Red Onion seasoning mix- No additive
2b	Red Onion seasoning mix- 1.7 % Silicon dioxide
2c	Red Onion seasoning mix- 1.7 % Fibruline
2d	Red Onion seasoning mix- 1.7 % Potato starch
2e	Red onion seasoning mix- 1.7 % Orybran

3.2 Moisture Content and Sorption Isotherm Analysis

Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) were equilibrated, according to the method described by Descamps et al., [3] at various relative humidities in desiccators containing saturated salt solutions with known relative humidities (Table 3). The salt solutions were prepared by adding potassium acetate (CH_3COOK), potassium carbonate (K_2CO_3) and ammonium nitrate (NH_4NO_3) to water until the solutions become saturated, in other words until the water activity of each salt solutions measured around 0.23, 0.43 and 0.62. The water activity was measured using an Aqua Lab Water Activity Meter 3TE, calibrated with standard solutions. Approximately 10-15 g of Lemon powder (1a-1e) respectively Red Onion seasoning mix (2a-2e), were taken from the vacuum bags, placed in petri dishes and stored in the desiccators at circa 23, 43 and 62 % relative humidity, with the lid partly open. All samples were stored in the desiccators in duplicate (Fig. 9).

Table 3. Relative humidities obtained by a saturated solutions of potassium acetate (CH_3COOK), potassium carbonate (K_2CO_3) and ammonium nitrate (NH_4NO_3)

Relative humidity [%]	Salt solution
23	CH_3COOK
43	K_2CO_3
62	NH_4NO_3

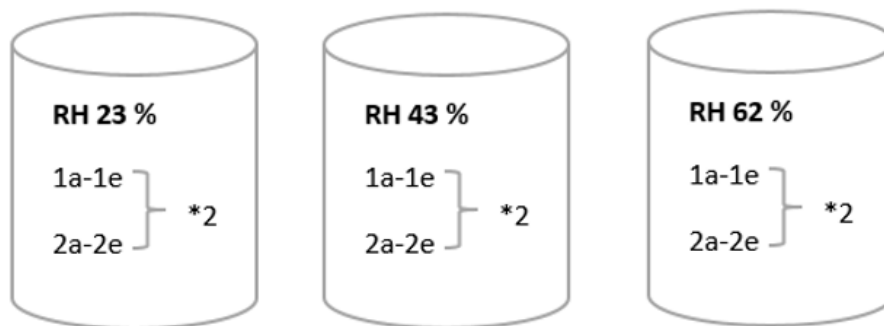


Fig. 9. Experimental setup for equilibration of Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) in the desiccators. Each sample was stored in duplicate at 23, 43 and 62 % relative humidity.

The water activity of the powders were measured regularly to verify if the powders reached equilibrium with the atmosphere in the desiccators. To speed up the process of equilibrating the samples, they were after two days of storage in the desiccators, placed in a climate chamber Vötsch VCL 4010, at 23, 43 and 62 % relative humidity. The samples were allowed to equilibrate in the climate chamber at each relative humidity for about two additional days, and when the water activity of the powders were in the range of 0.23, 0.43 and 0.62, they were considered as equilibrated. The appearance of the powders after storage at each relative humidity was noticed.

After storage in the climate chamber, the moisture content of the powders were measured by comparing the weight of the samples before and after drying it overnight at 70 °C in a vacuum oven. Approximately 3 g of each samples were dried in the vacuum oven. The moisture content (m.c.) wet basis, of each sample (s) was calculated according to the following equation:

$$m. c. = \frac{S_{\text{before drying}} - S_{\text{after drying}}}{S_{\text{before drying}}} \quad (3)$$

where $S_{\text{before drying}}$ corresponds to the weight of each sample after storage in the climate chamber, and $S_{\text{after drying}}$ corresponds to the weight of each sample after drying it overnight at 70 °C in the vacuum oven.

The results were presented in moisture sorption isotherm presenting moisture content, wet basis, as a function of water activity at each relative humidity. The remaining samples were stored in the desiccators for further DSC measurements.

3.3 Determination of Glass Transition Temperature (T_g)

The glass transition temperature was measured using a differential scanning calorimetry (DSC) from Mettler Toledo. The instrument was calibrated with 6.37 mg of indium placed in a sealed aluminum pan of 40 μl . During the measurements, nitrogen was used as carrier gas, and an empty aluminum pan was used as a reference. T_g measurements were performed using a similar method to the one described by Patersen & Bröckel [2]. The calorimetric measurements were done with a heating rate of 5 °C / 60 s from -40°C to 75 °C. Glass transition temperatures were measured in duplicate for Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) at various water activities, obtained by storage in the desiccators at circa 23, 43 and 62 % relative humidity. The same measurements were done in duplicate for Lemon powder containing 5 % of Fibruline, native potato starch and Orybran, and Lemon powder containing 10 % of native potato starch. Glass transition temperature was also measured for the anti-caking agents separately after storage in their package at room temperature. Owing to the high T_g value of potato starch, the up scan was done from 0 °C to 180 °C with a heating rate of 5 °C / 60 s. The effect of water on the glass transition of lime juice powder, was analyzed by measuring T_g at a high respectively low water activity.

All T_g measurements were followed by water activity measurements. Thermograms obtained from the DSC analysis, were analyzed for the onset, mid and endpoints of glass transition. The midpoint temperature of the thermogram was considered as the glass transition temperature. Two baselines, tangents to the curve at the onset and endpoint were used to find the midpoint of glass transition, which was further determined by the DSC program. The two replicates for each sample were analyzed for the same onset and endpoints temperature. The results of the DSC measurements were presented in graphs showing glass transition temperature as a function of water activity at each relative humidity.

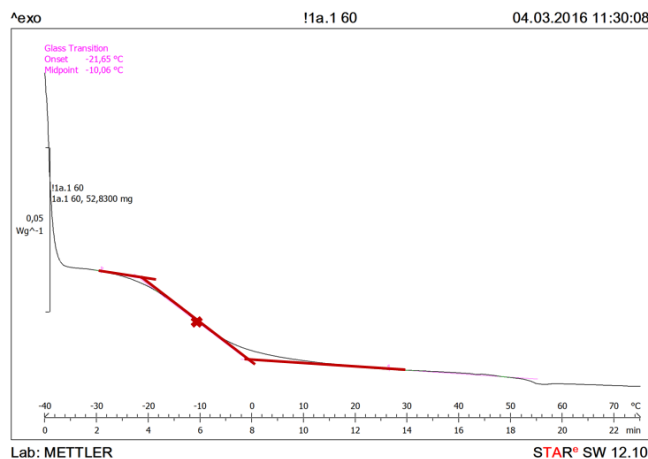


Fig. 10. Example of a thermogram obtained from the DSC analysis of Lemon powder. The thermogram was analyzed for the onset, midpoint and endpoint of glass transition. The midpoint temperature was considered as the glass transition temperature (red cross).

3.4 Determination of Flow Properties

The flow behavior of the powders were determined by using a powder flow tester (PFT) from Brookfield Engineering Laboratories Inc, connected to a PC provided with Powder FLOW Pro V1.2 software (Fig.8). The PFT complies with the shear test technique described in section 2.5.3. The flow function, bulk density and effective angle of wall friction were performed using a standard flow function, bulk density and wall friction program. The powders were carefully loaded in the shear cell with the use of a powder scoop to minimize compaction during sample preparation. Flow properties were accomplished in duplicate for Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) according to Table 2, and for the anti-caking agents separately. The measurements were done for samples stored in their sealed package in room temperature, at a relative humidity of circa 20-25 %. Additional measurements were done in duplicate for Lemon powder, containing 5 % of Fibruline, native potato starch and Orybran, as well as for Lemon powder containing 10 % of native potato starch. The water activity of the samples were measured in parallel to the flow functions test to confirm that the water activity was around 0.20-0.25. The standard programs measured the flow functions, bulk densities and effective angles of internal friction over five major principal consolidation stresses in the range of 0.3-25 kPa. The flow function test results were exported into excel and presented in a flow function diagram, showing the straight lines representing constant values of flowability, and the unconfined yield strength versus the major principal consolidation stress. An illustration of the flow function diagram can be found in section 2.2.2. Bulk densities and effective angles of internal friction were presented as a function of the major principal consolidation stress.

3.5 Sensory Analysis

Sensory analysis using a discriminative triangle test, was performed for Lemon yoghurt containing Lemon powder with 1.7 % silicon dioxide (sample 1) respectively 5 % native potato starch (sample 2). 1000 g Turkish yoghurt was mixed with 40 g Lemon juice powder. The product information and the experimental design for the triangle test can be seen in Table 4 and in Appendix 1. Sample 1 was labeled with the codes 739 and 548, while the codes of sample B were 305 and 491. The aim of the sensory analysis was to detect whether or not there exists a significant difference between the two samples. The significance level of the sensory test was set to 5 %.

The test panel, consisting of 22 assessors, were provided with three samples among 739, 548, 305 and 491, in a randomized order and was told that two of the samples were the same and one different from the other. After tasting the samples in the provided order, the panel was asked to identify the odd samples. The panel was allowed to use all information, e.g. to make the decision. After performing the test, the data was analyzed statically using EyeQuestion Sensory Software.

Sensory analysis aiming to indicate whether or not a detectable difference exists between two samples was also performed for two variations of pickled onion based on Red Onion seasoning mix containing 1.7 % silicon dioxide (sample 3) and 5 % native potato starch (sample 4). Product information as well as experimental design are found in Table 4 and Appendix 1. Four medium sized red onions were sliced thinly and mixed thoroughly with 50 g seasoning, and leaved at rest for one hour. 21 assessors tasted the samples labeled 135, 603, 904 and 274 in a provided order, and were asked to pick out the odd sample from the rest. The significance level of the test was set to 5 % and the results were analyzed by Eye Question Sensory Software.

Table 4. Codes and descriptions of the samples used in the triangle test.

	1	2	3	4
Codes	739,548	305, 491	135, 603	904, 274
Description 1	Lemon yoghurt	Lemon yoghurt	Pickled Red Onion	Pickled Red Onion
Description 2	1.7% silicon dioxide	5 % native potato starch	1.7 % silicon dioxide	5 % native potato starch

4 Results

The following sections present the results from the moisture sorption isotherm, DSC measurements and flowability analysis for Lemon powder (1a-1e) and Red Onion seasoning (2a-2e), as well as the anti-caking agents silicon dioxide, Fibruline, native potato starch and Orybran. The final section presents the result from the sensory analysis of Lemon powder and Red Onion seasoning containing 1.7 % silicon dioxide and 5 % native potato starch.

4.1 Moisture Sorption Isotherm

Fig.11, shows the appearance of Lemon powder 1a-1e, after storage at 23, 43 and 62 % relative humidity. As seen, Lemon powder containing silicon dioxide (1b) is the only powder not showing any cohesiveness after storage at 23 % relative humidity. Initial cohesiveness, that is to say, formation of lumps, can be seen for the other samples, however the cake strength is very weak. Lemon powder with Orybran (1e) as anti-caking agent, indicates the most cohesive behavior. The second and third row in Fig.11 show the appearance of the powders after storage at 43 respectively 62 % relative humidity. Lemon powder with silicon dioxide (2b) is after storage at 43 % still the only free flowing powder, while the other samples demonstrate a slightly increased cake strength compared to storage at 23 % relative humidity. As seen in the middle row, Lemon powder with Fibruline (1c) and native potato starch (1d), behave very similarly while exposed to 43 % relative humidity. After storage at 62 %, all powders form a very hard cake. The cake strength of Lemon powder with silicon dioxide (2b) is slightly lower compared to sample 1a, 1c-1e. As seen in the bottom row, all samples except Lemon powder with silicon dioxide (1b) change color after storage at 62 % relative humidity.

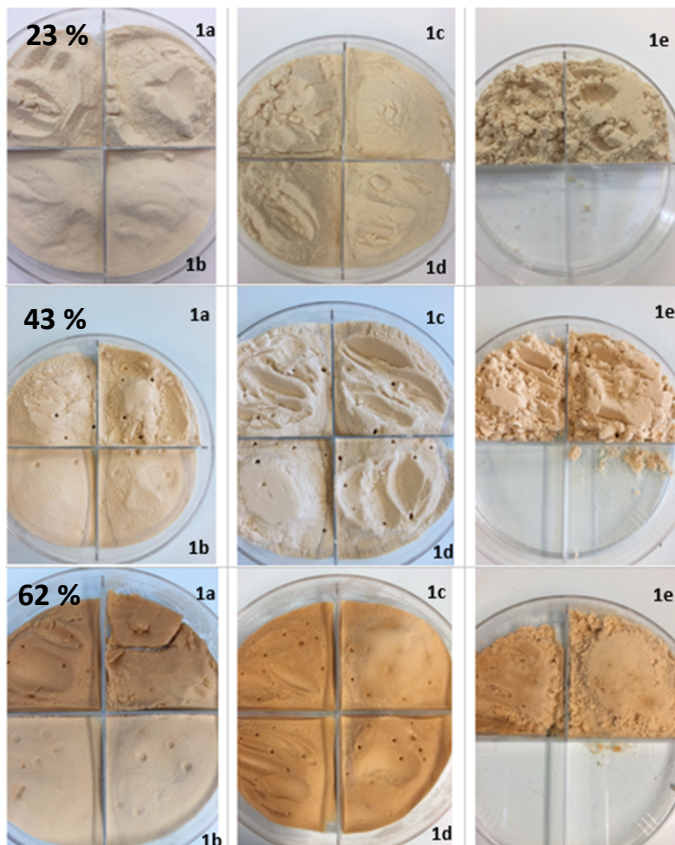


Fig.11. Appearance of Lemon powder (1a-1e) after storage at 23, 43 and 62 % relative humidity (down to top). 1a-No additive, 1b-Silicon dioxide, 1c-Fibruline, 1d-Potato starch and 1e-Orybran.

The appearance of Red Onion seasoning mix after storage at 23, 43 and 62 % relative humidity can be seen in Fig. 12. Small lumps of lime powder are seen after storage at 23 % relative humidity for sample 1a, 1c and 1d, while Red Onion seasoning mix containing silicon dioxide (2b) and Orybran (2e) not show any cohesiveness. Similar behavior can be seen after storage at 43 % relative humidity. Lumps of lime powder are found in sample 1a, 1c and 1d, however the largest lumps are seen in Red Onion seasoning mix without additive (2a). The only free flowing powder after storage at 62 % relative humidity is Red Onion seasoning mix with silicon dioxide (2b). Sample 1a, 1c-1e are turned into hard cakes in which wet lumps of lime powder can be found. The largest number of lumps can still be seen in sample 2a. The cake strength of Red Onion seasoning mix with potato starch (2d) is slightly lower compared to Red Onion seasoning mix with Fibruline (2c). The appearance of Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) after storage at about 62 % relative humidity for about 7 weeks in the desiccators is shown in Fig. 13. All samples of Lemon powder are turned into an extremely hard, dark brown cake whether all samples of Red Onion seasoning mix are dissolved and turned into a pasty mass.

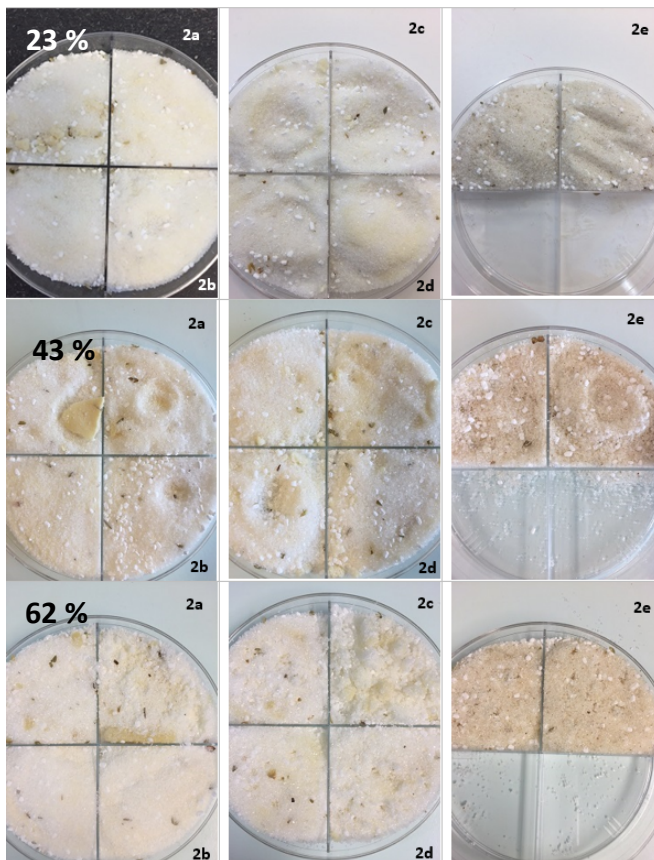


Fig. 12. Appearance of Red Onion seasoning mix (2a-2e) after storage at 23, 43 and 62 % relative humidity (down to top). 2a-No additive, 2b-Silicon dioxide, 2c-Fibruline, 2d-Potato starch and 2e-Orybran.



Fig. 13. Appearance of Lemon powder 1a-1e (left) and Red Onion seasoning mix 2a-2e (right) after storage at 62 % relative humidity for about 7 weeks.

Fig. 14-Fig. 17, shows the moisture sorption isotherm of Lemon powder (Fig. 14, Fig. 16) and Red Onion seasoning mix (Fig. 15, Fig. 17). Fig. 14-Fig. 15, present moisture content as a function of water activity (aw), obtained by equilibrating the samples in the climate chamber, while Fig. 16 -Fig. 17 show water content as a function of the relative humidity in the climate chamber. The shape of the moisture sorption isotherm of Lemon powder (Fig. 14) could be related to the nonlinear, sigmoidal isotherm (72), see section 2.5.1. As seen in Fig. 14, there is no significant difference in moisture content or water activity (aw), between Lemon powder 1a-1e, at aw about 0.23-0.35. The change in water content between aw 0.23-0.35 is very low or negligible. Above aw circa 0.35, the moisture content of the samples increases with increasing water activities, that is to say, the powders absorb more water when stored in an environment with high relative humidity (Fig. 14).

The average moisture content with standard deviations, of Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) at each relative humidity is presented in Fig. 16-Fig. 17. As seen in Fig. 14, the difference between water activity and moisture content between the samples are larger at 62 % relative humidity however larger standard deviations are demonstrated at 62 % compared to 23 and 42 % relative humidity (Fig. 16). The water activity of Lemon powder 1a-1c, is in the range of 0.48-0.5 while the water activity of Lemon powder 1d-1e, is circa 0.54 (Fig. 14). As seen in Fig. 14 and Fig. 16, the moisture content of Lemon powder 1a-1c, is higher compared to Lemon powder 1d-1e.

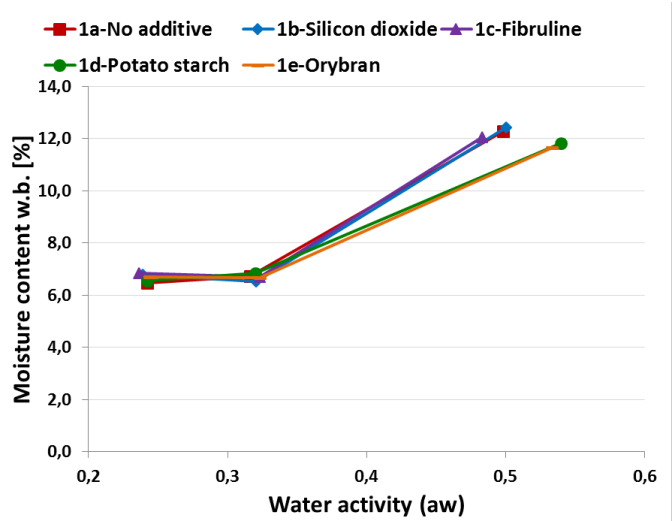


Fig. 14. Moisture sorption isotherm for Lemon powder without additive and with 1.7 % silicon dioxide, Fibruline, potato starch and Orybran. The result presented represent an average value based on one duplicate.

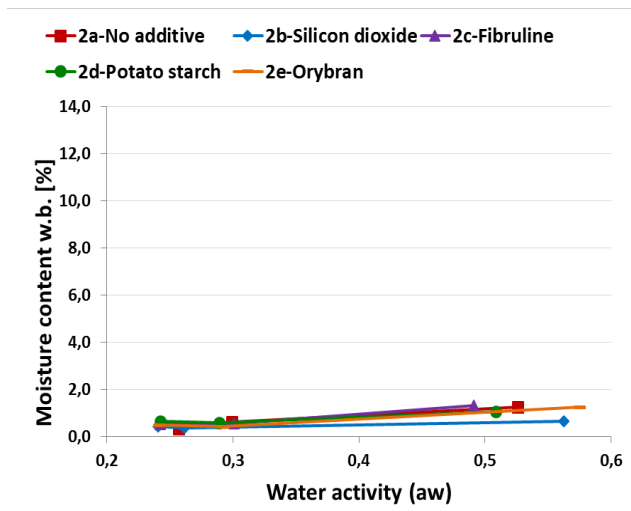


Fig. 15. Moisture sorption isotherm for Red Onion seasoning mix without additive and with 1.7 % silicon dioxide, Fibruline, potato starch and Orybran. The result presented represent an average value based on one duplicate.

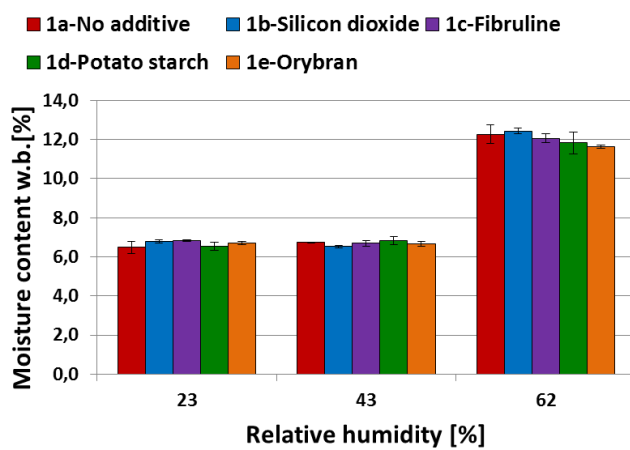


Fig. 16. Moisture content [%], wet basis, as a function of the relative humidity [%] in the climate chamber for Lemon powder (1a-1e).

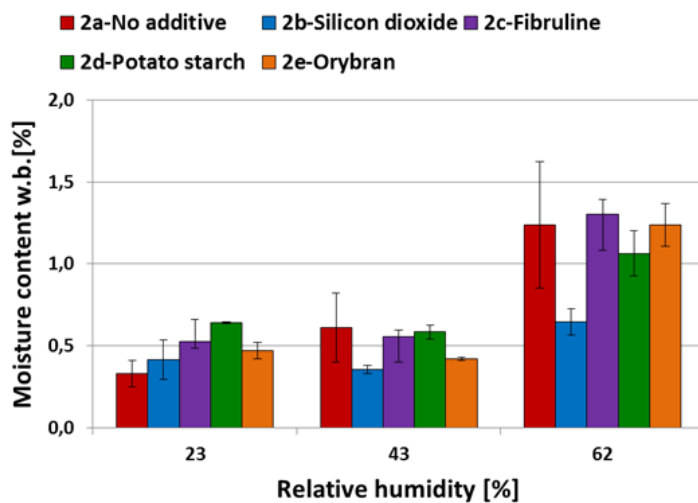


Fig. 17. Moisture content [%], wet basis, as a function of the relative humidity [%] in the climate chamber for Red Onion seasoning mix (2a-2e).

Fig. 18 shows a comparison between the moisture content of Lemon powder and Red Onion seasoning mix without additive. As seen, Lemon powder and Red Onion seasoning mix behave differently when exposed to humid environments (Fig. 18). The moisture content of Red Onion seasoning mix without additive is circa 10 % of the moisture content of Lemon powder without anti-caking agent at each relative humidity. The general shape of the moisture sorption isotherm (Fig. 15) shows, compared to Lemon powder (Fig. 14) that Red Onion seasoning do not absorb water until higher relative humidities, however the amount of water absorbed is very low. As seen in Fig. 15 and Fig. 17, the moisture content do not exceed 1.5 % for any of the different combinations of Red Onion seasoning. The moisture sorption isotherm shows that only a small amount of water is needed to reach regions of high water activity (Fig. 15).

As seen in Fig. 17 the change in moisture content while going from 23 to 43 % relative humidity is very low or negligible for sample 2b-2e, while higher for sample 2a, however a larger standard deviation is demonstrated for sample 2a at a relative humidity of 43 %. Generally, as seen when comparing Fig. 16 and Fig. 17, larger standard deviations are demonstrated for Lemon powder compared to Red Onion seasoning. The moisture content after storage at 62 % relative humidity is higher for sample 2a, 2c, 2d and 2e, compared to sample 2b, though large standard deviations within the duplicates are demonstrated (Fig. 15, Fig. 17) The water activity of sample 2a, 2c, 2d and 2e is in the range of circa 0.49-0.576, while the water activity of sample 2b is circa 0.56. Just like Lemon powder, the difference in water activity between the samples are larger at higher relative humidities (Fig. 15) The general trend according to Fig. 15 and Fig. 17, is that the moisture content of the samples increase while going from 23 to 62 % relative humidity.

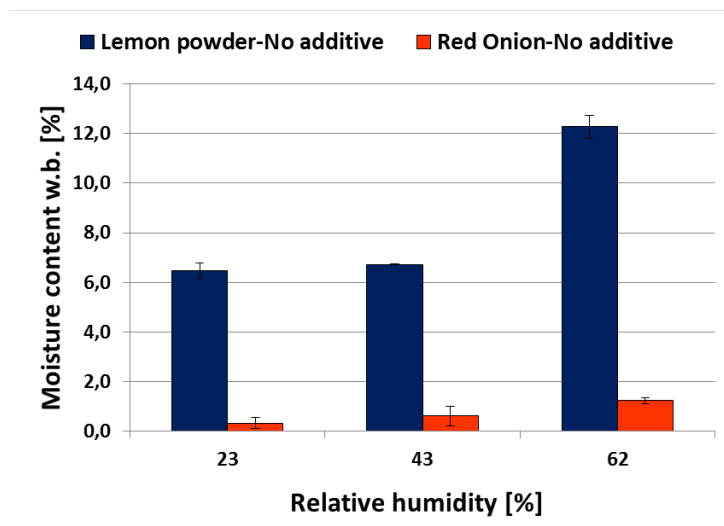


Fig. 18. Comparison between the moisture content [%], wet basis, for Lemon powder and Red Onion seasoning without additive after storage at 23, 43 and 62 % relative humidity.

4.2 Glass Transition Temperature

Fig. 19 shows the results from the DSC measurements of Lemon powder (1a-1e). Glass transition temperature is presented as a function of three different water activities, obtained by storage at 23, 43 and 62 % relative humidity. The effect of water plasticization is clearly demonstrated in Fig. 19 since the T_g value of all combinations of Lemon powder, decreases with increasing water activity. Generally, T_g of all samples decreases from about 25 to -10 °C while going from a water activity of about 0.25 to 0.46. The largest change in T_g , about 35 °C, is seen for sample 1b, however sample 1b also demonstrates the largest increase in water activity (Fig. 19). As seen in Fig. 19, sample 1a, 1b, 1c

and 1e show similar behavior, that is to say, the difference between T_g of the samples is low. Sample 1d, shows a lower T_g value compared to the others at a water activity of circa 0.4, but similar T_g values at lower respectively higher water activities.

Fig.20 presents T_g values as well as water activity of the natural anti-caking agents Fibruline, potato starch and Orybran after storage in their sealed package at room temperature. Fibruline and Orybran express lower T_g values of 57 respectively 55 °C, compared to potato starch which has a T_g value of 127 °C. As seen in Fig.20, the water activity of potato starch is higher than the water activity of Fibruline and Orybran. Glass transition temperature for silicon dioxide and Red Onion seasoning mix could not be determined due to the absence of glass transition in the thermogram (Fig. 21).

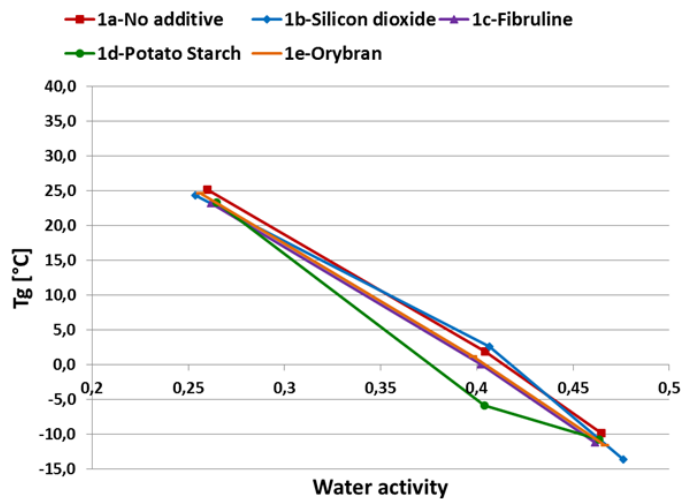


Fig. 19. Glass transition temperature [°C], obtained by DSC, as a function of water activity for Lemon powder without additive, and with 1.7 % of silicon dioxide, Fibruline, potato starch and Orybran. All measurements were done in duplicate, and the values presented represent the average value.

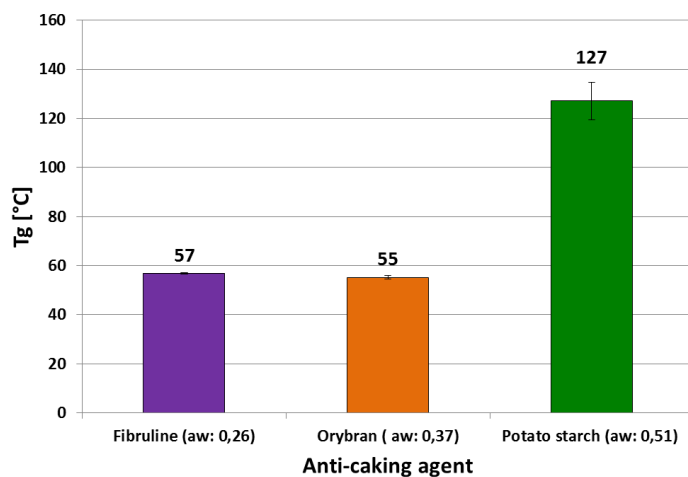


Fig.20. Glass transition temperature [°C], obtained by DSC, and water activity of the natural anti-caking agents Fibruline, Orybran and potato starch, after storage in their sealed package at room temperature.

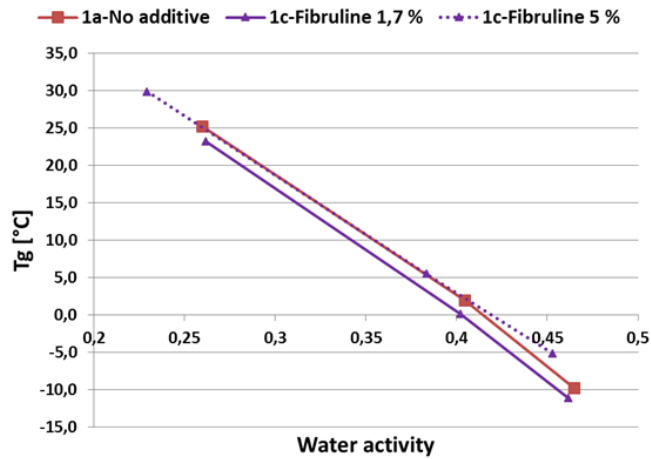


Fig. 22. Glass transition temperature [°C] as a function of water activity for Lemon powder without additive and with 1.7 respectively 5 % Fibruline.

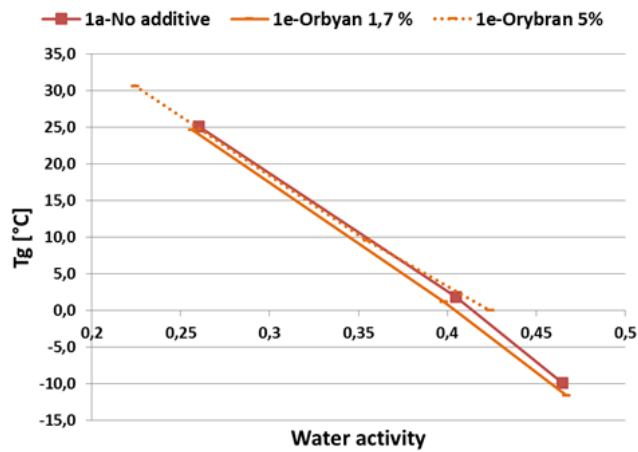


Fig. 23. Glass transition temperature [°C] as a function of water activity for Lemon powder without additive and with 1.7 respectively 5 % Orybran.

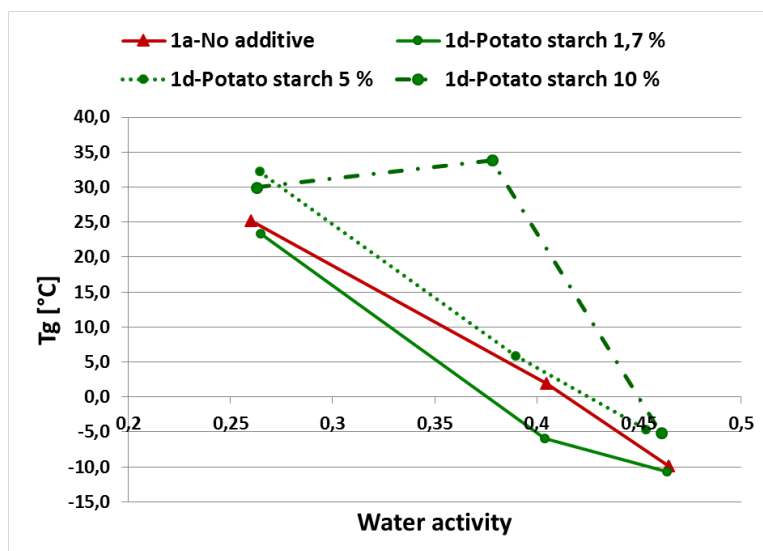


Fig. 24. Glass transition temperature [°C] as a function of water activities of Lemon powder without additive and with 1.5, 5 respectively 10 % potato starch.

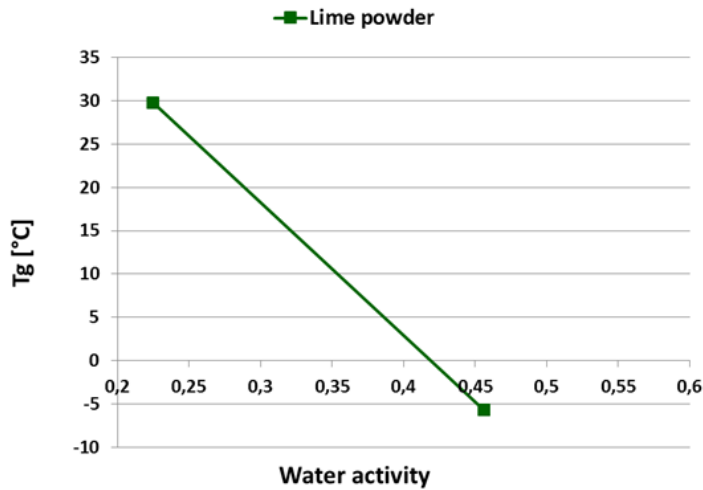


Fig.25. Glass transition temperature [°C] as a function of two different water activities for lime powder (one of the components in the Red onion seasoning mix).

4.3 Flow Properties

Fig. 26 and Fig. 27 show the flow function plots of Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e), at different levels of consolidation stresses. A flat curve, that is to say a high ff_c value, indicates an easily flowing powder, while a step curve, low ff_c value, indicates more difficulties in flow, see 2.2.2. As seen in Fig. 26, at a consolidation stress lower than circa 14 kPa, the flow function plot of sample 1a indicates flow behavior at the boundary between the easy and free flowing area. At consolidation stresses above circa 14 kPa, the powder presents slightly lower flowability, that is to say, flow function in the easy flowing area instead of the free flowing area. The flow function plot of sample 1b, indicates a free flowing powder at all levels of consolidation stresses. Sample 1c and 1d present, at consolidation stresses up to circa 14 kPa, flow functions at the boundary between the easy and free flowing area, while for consolidation stresses above circa 14 kPa, the powders show slightly improved flow by passing the free flowing area. The flowability of sample 1c and d, is almost identical, that is to say, the difference in terms of flow index (ff_c) is very low.

As seen in Fig. 26, the flow function plot of sample 1e, indicates a cohesive powder with difficulties in flow below consolidation stresses of circa 9 kPa. Above, the flow function plot indicates a more easily flowing powder. At consolidation stresses in the range of 0-13 kPa, the flow function plot is represented by a step curve, while for higher consolidation stresses, the flow function plot becomes more flat (Fig. 26). Generally, all combinations of Lemon powder, at the consolidation stresses applied, are represented by easy or free flowing powders (Fig. 26). Lemon powder with silicon dioxide as anti-caking agent/ flow agents seems to be the most easily flowing powder while Lemon powder with Orybran, appears to be the most cohesive powder, showing poorer flow (Fig. 26).

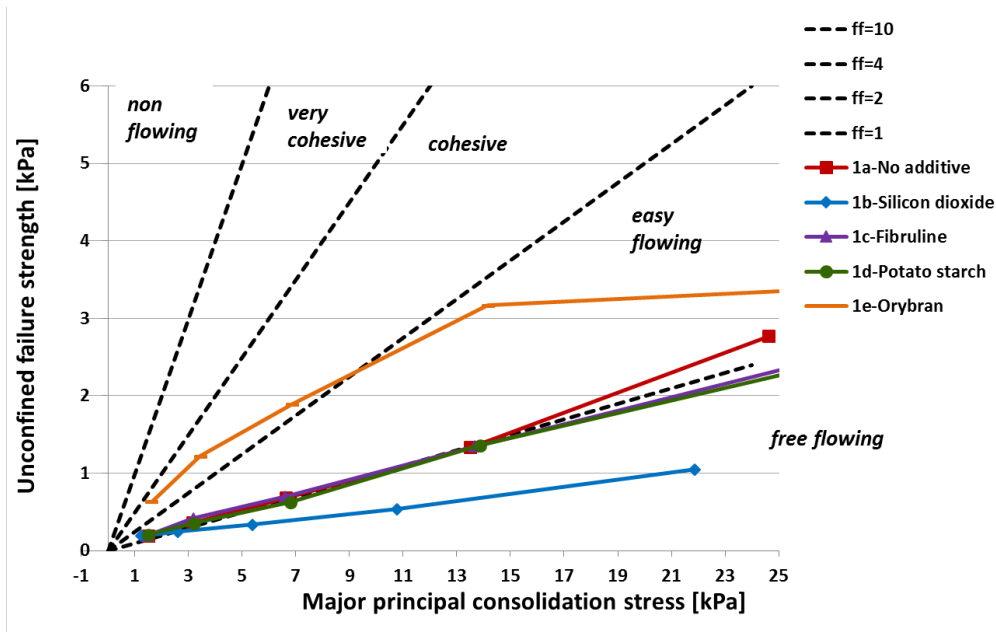


Fig. 26. Flow functions, determined with the use of a powder flow tester (PFT), of Lemon powder without additive, and with 1.7 % silicon dioxide, Fibruline, potato starch and Orybran, at different levels of major principal consolidation stress. All measurements were done in duplicate, and the values presented represent the average value.

As seen in Fig. 27, the flow function plots of Red onion seasoning mix (2b-2e) indicate free flowing powders at the consolidation stress applied. Among sample 2b-2e, sample 2c shows the highest flow index that is to say, the highest flowability, while 2b shows the lowest flow index, and consequently slightly lower flowability. The flow behavior of Red Onion seasoning mix without additive is different to the others (Fig. 27). At consolidation stresses below circa 12 kPa, the flow function plot is represented by a flat curve in the free flowing area while at consolidation stresses above circa 12 kPa, the unconfined yield strength increases with increasing consolidation stresses. At a consolidation level of circa 23 kPa, the flow function passes the easy flowing zone.

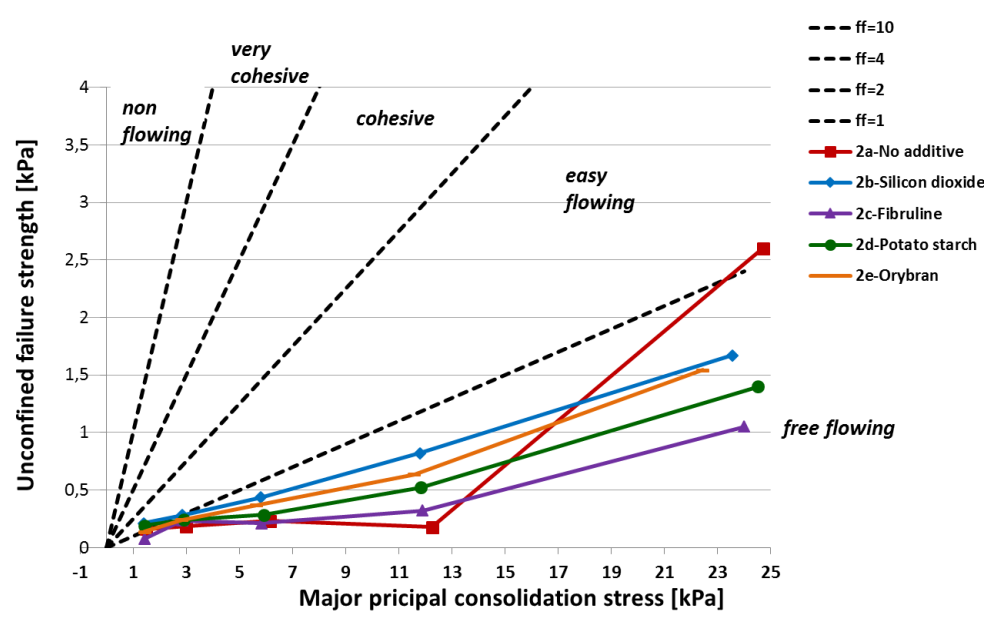


Fig. 27. Flow functions of Red Onion seasoning without additive, and with 1.7 % silicon dioxide, Fibruline, potato starch and Orybran, at different levels of major principal consolidation stress [kPa].

The flow function plots of silicon dioxide, Fibruline, potato starch and Orybran are shown in Fig. 28. Silicon dioxide presents at low levels of consolidation, flow function at the boundary between the cohesive and very cohesive area, while at consolidations stresses above circa 3 kPa, the flow function indicates a cohesive powder. As seen in Fig. 28, the flow index of sample 1b, varies with the consolidation stress applied. Orybran also shows difficulties in flow by having a flow function in the cohesive area at all consolidation stresses applied. Fibruline presents at consolidation stresses below circa 12 kPa, flow function in the free flowing area while above, the flow index increases. At a consolidation level of circa 17 kPa, the flow function passes the easy flowing area. The flow function of potato starch indicates at consolidation stresses below circa 7 kPa that the powder behaves as an easy flowing powder, while for increasing consolidation stresses, as a free flowing powder. Among the anti-caking agents, the flow function of potato starch indicates the most easily flowing powder, while the flow function of silicon dioxide illustrate the most cohesive powder at the consolidation stress applied (Fig. 28).

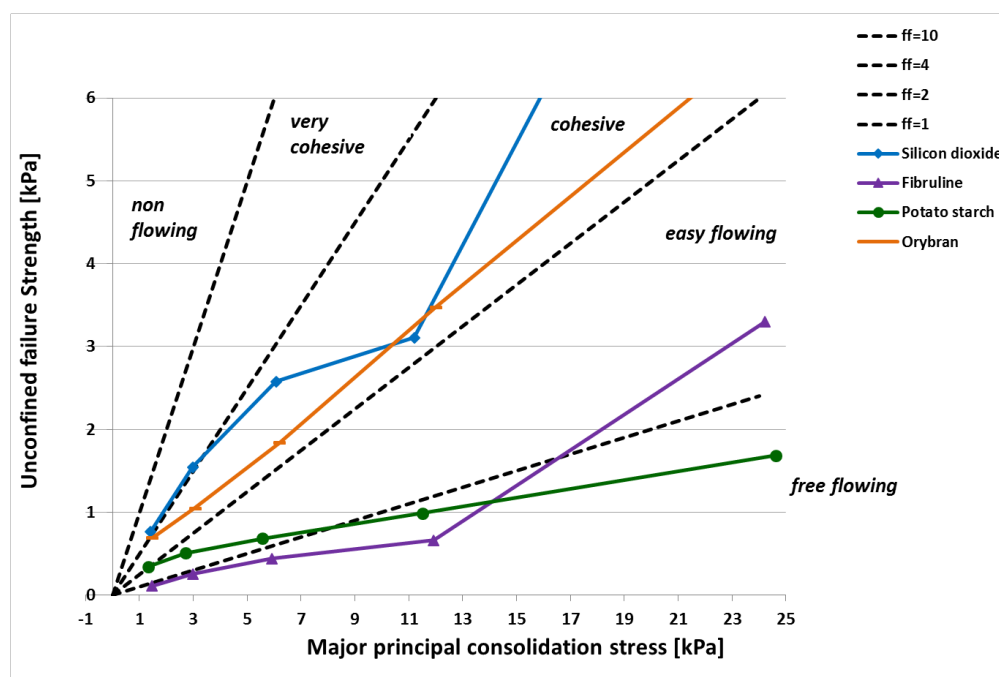


Fig. 28. Flow functions of silicon dioxide, Fibruline, potato starch and Orybran, at different levels of major principal consolidation stress [kPa].

Fig. 29 and Fig. 30, show how the flow functions of Lemon powder containing Fibruline respectively Orybran, change while increasing the amount of anti-caking agent from 1.7 to 5 %. The flow function of Lemon powder without additive is also presented in the same figures. As seen in Fig. 29 and Fig. 30, the flowability was not increased while increasing the amount of anti-caking agent added. Lemon powder containing 5 % of anti-caking agent present flow function in the same region as Lemon powder with 1.7 % anti-caking agent at consolidations levels below circa 14 kPa, while above, the powders with 5 % anti-caking agent show poorer flow than the powders containing less anti-caking agent. As seen in

Fig. 31, the flowability of Lemon powder was increased by increasing the amount of potato starch from 1.7 to 5 %. Lemon powder with 5 % potato starch presents flow function in the free flowing area at all consolidation stresses applied. The flow function indicates a more easily flowing powder than Lemon powder with 1.7 % potato starch at all consolidation stresses. When increasing the

amount of potato starch additional 5 %, the flow function was removed from the free flowing area to the cohesive area, indicating a powder with difficulties in flow (

Fig. 31). As seen in

Fig. 31, the flow function of Lemon powder containing 10 % of potato starch indicates lower flowability than both Lemon powder without additive and with 1.5 % potato starch at the different levels of consolidation. As seen in Fig. 32, a slightly improved flow was achieved while using 5 % potato starch as anti-caking agent, compared to 1.7 % silicon dioxide.

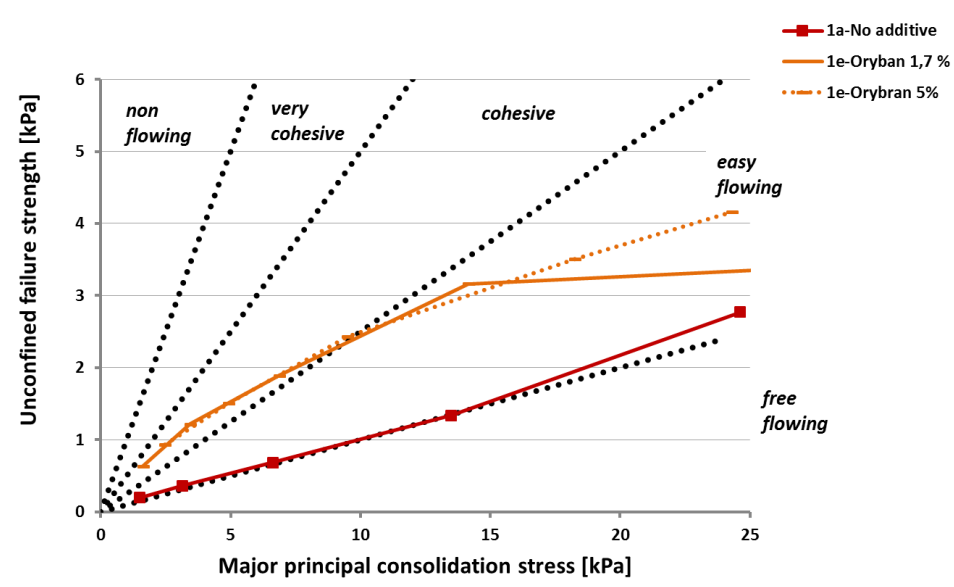


Fig. 29. Flow functions of Lemon powder without additive, and with 1.7 respectively 5 % Fibruline, at different levels of major principal consolidation stress [kPa].

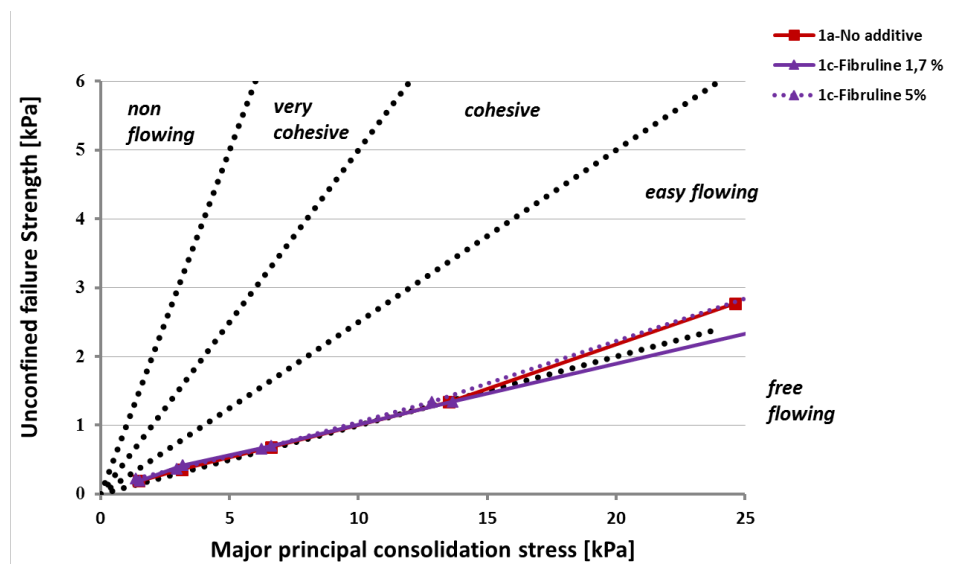


Fig. 30. Flow functions of Lemon powder without additive, and with 1. 7 respectively 5 % Fibruline, at different levels of major principal consolidation stress [kPa].

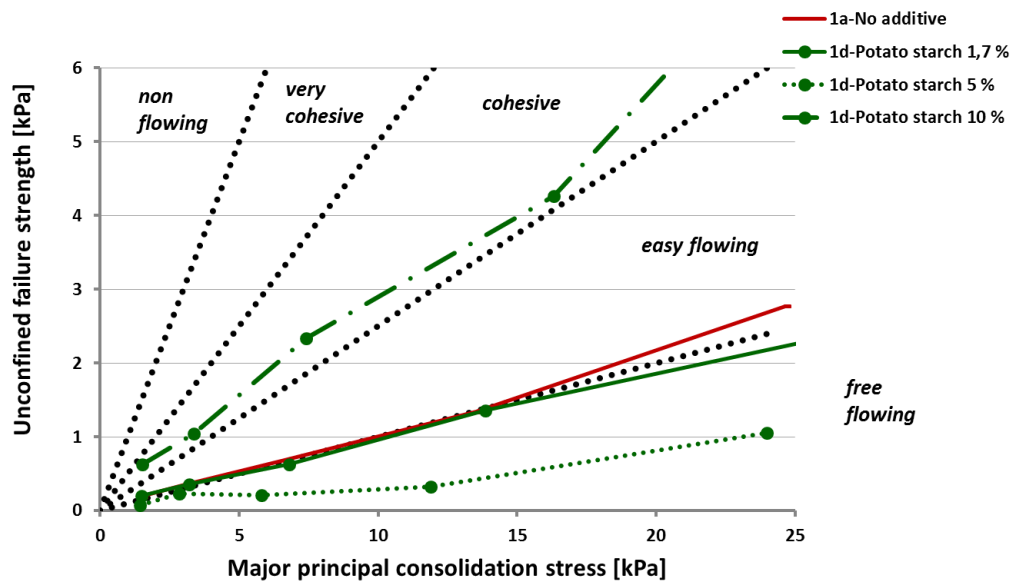


Fig. 31. Flow functions of Lemon powder without additive, with 1.7, 5 and 10 % potato starch, at different levels of major principal consolidation stress [kPa].

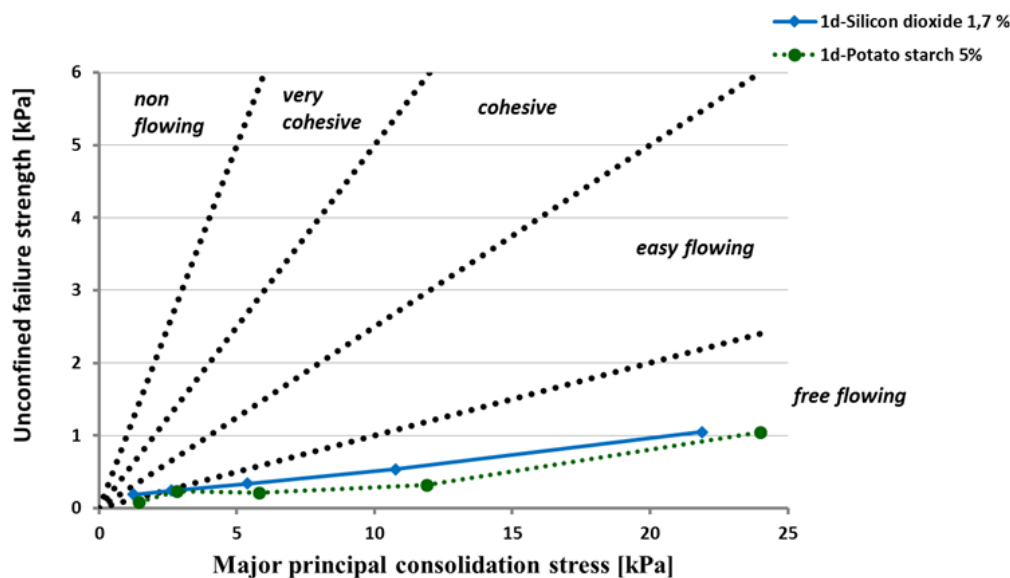


Fig. 32. Flow functions of Lemon powder with 1.7 % silicon dioxide and 5 % potato starch, at different levels of major principal consolidation stresses [kPa].

Fig. 33 and Fig. 34 show the bulk densities of Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) at different levels of major principal consolidation stress. The increase in bulk density under about 30 kPa is summarized in

Table 5. Theoretically, for an easy-flowing powder the bulk density will increase very little while for a cohesive powder there will be a much higher increase in bulk density, see section 2.2.1. As seen in Fig. 33 and Fig. 34 as well as in

Table 5, the highest increase in bulk density is obtained for Lemon powder without additive. Lemon powder containing Orybran shows the lowest increase in bulk density (Fig. 33,

Table 5). Red Onion seasoning mix with silicon dioxide and without additive shows the highest respectively lowest increase in bulk density at the different consolidation levels (Fig. 34,

Table 5). As seen in Fig. 35 and Table 6, the anti-caking agents showing the largest increase in bulk density during the consolidation stress applied, are potato starch and Orybran. Less compressibility is seen for Fibruline. Fig. 36 presents the result from the bulk density measurement for Lemon powder without additive, and with increasing amount of potato starch. As seen in Fig. 36 and Table 6, the most easily flowing powder based on the increase in bulk density, is Lemon powder containing 5 % potato starch. The most cohesive powder, that is to say the powder with the largest increase in bulk density is Lemon powder with 10 % of potato starch (Fig. 36, Table 6).

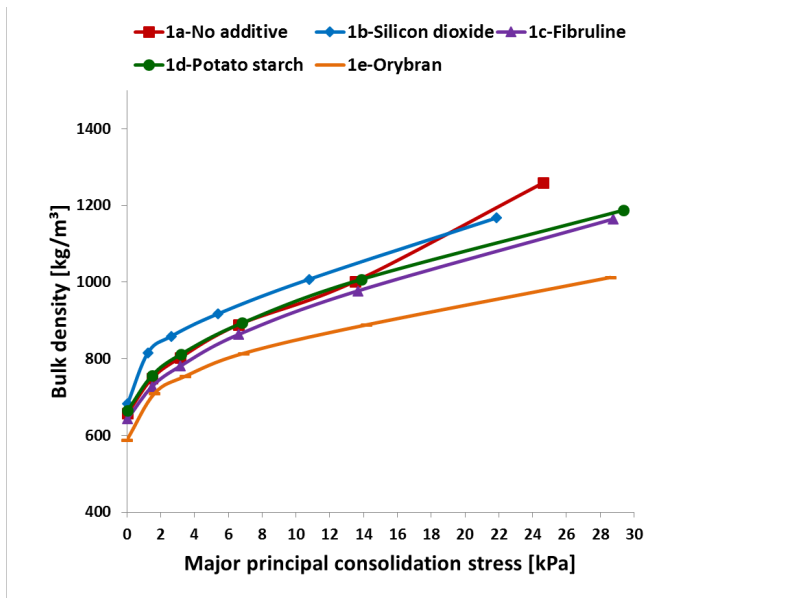


Fig. 33. Bulk densities [kg/m^3] determined with the use of a powder flow tester (PFT) of Lemon powder without additive and with 1.7 % of silicon dioxide, Fibruline, potato starch and Orybran at different levels of major principal consolidation stress [kPa].

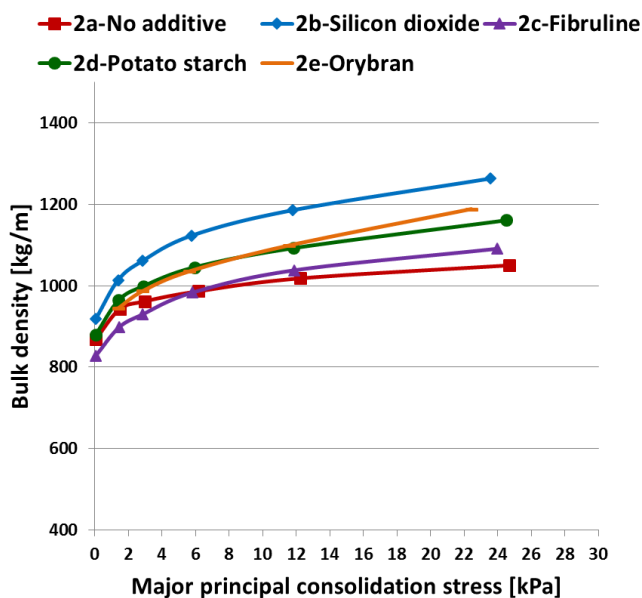


Fig. 34. Bulk densities [kg/m^3] of Red Onion seasoning mix without additive and with 1.7 % of silicon dioxide, Fibruline, potato starch and Orybran at different levels of major principal consolidation stress [kPa].

Table 5. Density difference ($\Delta\rho$), [kg/m^3] of Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) under circa 30 kPa of major principal consolidation stress.

Sample	$\Delta\rho$ [kg/m^3]
Lemon powder	
1a-No additive	601.3
1b-Silicon dioxide	485.0
1c-Fibruline	521.3
1d-Potato starch	523.3
1e-Orybran	423.9
Red Onion seasoning mix	
2a-No additive	182.0
2b-Silicon dioxide	345.6
2c-Fibruline	263.8
2d-Potato starch	281.3
2e-Orybran	329.2

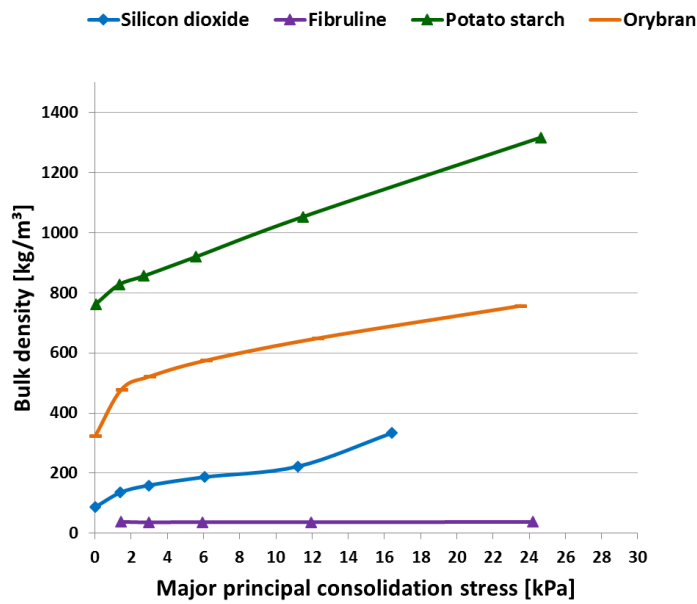


Fig. 35. Bulk densities [kg/m^3] of silicon dioxide, Fibruline, potato starch and Orybran at different levels of major principal consolidation stress [kPa].



Fig. 36. Bulk densities [kg/m^3] of Lemon powder without additive and with 1.7, 5 respectively 10 % of potato starch at different levels of major principal consolidation stress [kPa].

Table 6. Density difference ($\Delta\rho$), [kg/m^3] of Lemon powder without additive and with 1.7, 5 respectively 10 % of potato starch under ca. 30 kPa major principal consolidation stress.

Sample	$\Delta\rho$ (kg/m^3)
Lemon powder	
1a-No additive	601.3
1d-Potato starch 1,7 %	523.3
1d-Potato starch 5 %	210.8
1d-Potato starch 10 %	733.3
Anti-caking agent	
Silicon dioxide	247.1
Fibruline	184.3
Potato starch	553.9
Orybran	432.2

The results from the effective angle of internal friction for Lemon powder (1a-1e) and Red Onion seasoning mix (2a-2e) are presented in Fig. 37 and Fig. 38. As discussed in section 2.2.1, theoretically, the larger effective angle of internal friction, the greater inter-particle interaction. Sample 1b shows lower angle values, compared to sample 1a, 1c, 1d and 1e, under all the consolidation levels applied (Fig. 37). Generally, the decrease of the angle for Lemon powder (1a-1e) is very low or negligible (Fig. 37). The largest decrease (3.8°) is obtained for Lemon powder with silicon dioxide as anti-caking agent. Red Onion seasoning mix without additive shows generally the highest angle value, while Red Onion seasoning mix with silicon dioxide and Orybran show among the lowest values under all the applied levels of consolidation stress (Fig. 38). The largest decrease in effective angle of internal friction (3.45°) can be seen for sample 2c. Effective angles internal friction of the anti-caking agents separately, are presented in Fig. 39. Silicon dioxide and Orybran present larger decrease, about 24.2°

respectively 7.95 °, angle value, compared to Fibruline and potato starch under the consolidation stress applied. As seen in Fig. 40, the change in angle value was very low or negligible when the amount of potato starch was increased from 1.7 to 5 %, however an increase of about 10 °, under all the applied levels of consolidation stress, can be seen for Lemon powder with 10 % potato starch. The largest decrease in angle value corresponds to Lemon powder with 5 % potato starch.

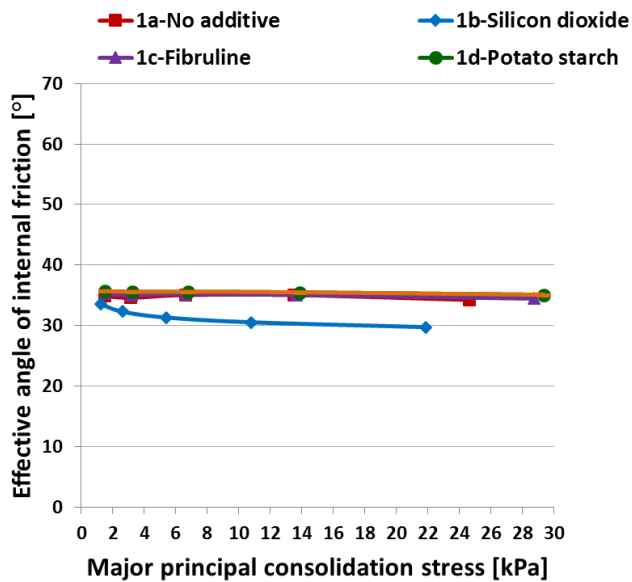


Fig. 37. Effective angles of wall friction [°], determined with the use of a powder flow tester (PFT), for Lemon powder without additive, and with 1.7 % silicon dioxide, Fibruline, potato starch and Orybran at different levels of major principal consolidation stress [kPa]. All measurements were done in duplicate, and the values presented represent the average value.

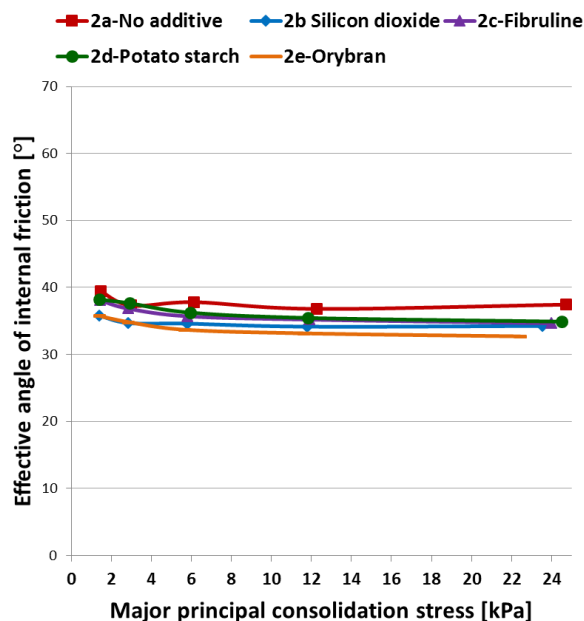


Fig. 38. Effective angles of wall friction [°] for Red Onion seasoning mix without additive, and with 1.7 % silicon dioxide, Fibruline, potato starch and Orybran at different levels of major principal consolidation stress [kPa].

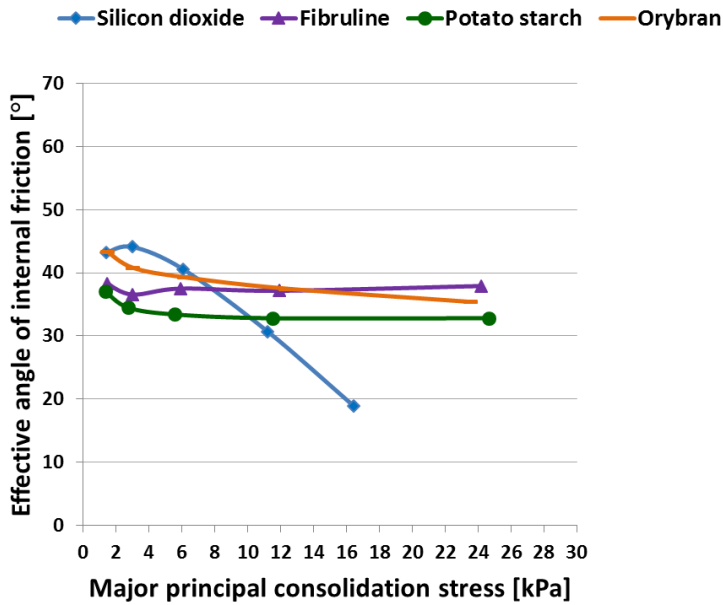


Fig. 39. Effective angles of wall friction [°] for silicon dioxide, Fibruline, potato starch and Orybran at different levels of consolidation stress [kPa].

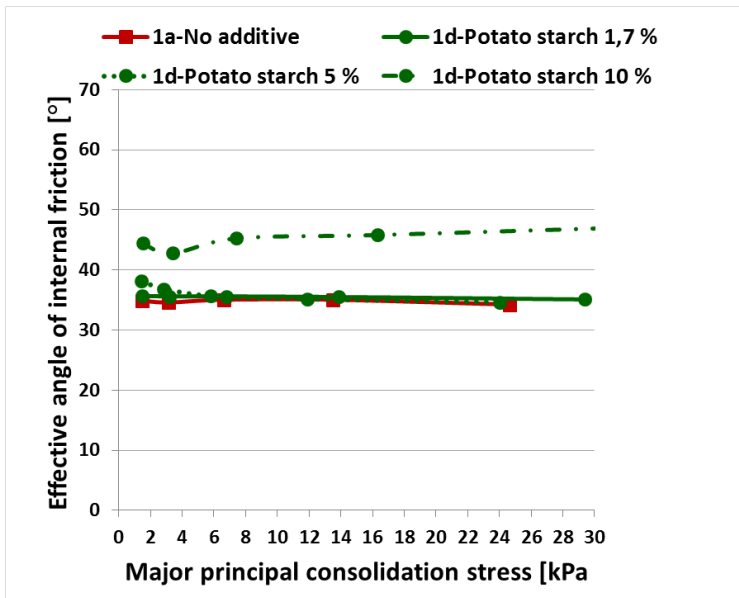


Fig. 40. Effective angles of wall friction [°] for Lemon powder without additive and with 1.7, 5 respectively 10 % potato starch at different levels of major principal consolidation stress [kPa].

4.4 Sensory analysis

Table 7 shows the results and statistical data analysis from the sensory analysis 1 and 2, of Lemon yoghurt with 1.7 % silicon dioxide and 5 % native potato starch, and pickled onion based on Red Onion seasoning mix with 1.7 % silicon dioxide and 5 % native potato starch. As seen in Table 7, the minimum numbers of incorrect responses to be able to reject the null hypothesis of “difference between samples”, with a panel of 22 assessors and a significance level of 5 %, is 12. In difference test number 1, 18 assessors did not managed to identify the odd sample from rest while 4 assessors succeeded to identify which sample that was different to the other. As seen in Table 7, the probability of making a type I error, that is to say a “false positive”, was calculated to 0.965, which is higher than the significant level, meaning that there is no significant difference between the samples.

The result from difference test 2, shows that 7 of 21 assessors identified the odd sample while 14 assessors did not identified the different sample. As the probability of making a type 1 error was higher than the significance level of 0.05, the null hypothesis of “difference between samples” could be rejected, that is to say, it can be concluded that there not exists a significant difference between the samples.

Table 7. Result and statistical data analysis from triangle test 1 and 2. No significant difference could be identified among Lemon yoghurt containing 1.7 % silicon dioxide and 5 % native potato starch, or pickled onion based on Red onion seasoning with 1.7 % silicon dioxide and 5 % native potato starch.

Test	Description	Correct	Incorrect	Total	Min 5%	P> =4	p< 5%
1	Lemon yoghurt	4	18	22	12	0.965	FALSE
2	Pickled onion	7	14	21	12	0.581	FALSE

5 Discussion

The following sections will discuss the results from the moisture sorption isotherms, DSC measurements and the flowability analysis. The results will be discussed based on the theoretically background, and compared with results from earlier studies.

5.1 Water

As discussed in section 2.4.1, anti-caking agents have the ability to absorb a large amount of water without experience stickiness. A powder with good anti-caking properties could be deviated from easily caked powders in the sorption isotherm graph by having a higher moisture content, but still having the same water activity. This could theoretically mean that the anti-caking agent functioning by competing with the host powder for the available water by binding it, making the powder less prone to cake as a result of water plasticization. The fact that the moisture content and water activity of sample 1a-1c at higher relative humidities, are higher respectively lower compared to sample 1d-1e, could theoretically indicate improved anti-caking properties (Fig. 14). This reasoning is not supported by the visual analysis of the powders after storage in the climate chamber that clearly demonstrates that Lemon powder without additive behaves much more cohesive than when silicon dioxide is added, already at lower relative humidities (Fig.11).

Beyond a slightly lower cake strength of sample 1b, it was not possible to separate the samples based on anti-caking properties after storage at 62 % relative humidities. When comparing the moisture content, the larger standard deviations seen for sample 1a and 1d after storage at 62 % relative humidity, should also be considered (Fig. 16). Even though there is a small difference in moisture absorption capacity, it is probably too low to result in improved anti-caking properties. The result from the moisture sorption isotherm indicates that longer time is needed for samples to equilibrate at higher relative humidities since the water activity of the powders differ. The purpose of the analysis was to evaluate if the potential anti-caking agents affect the hygroscopicity of the powder. It has been easier to evaluate the effect on the hygroscopicity if the powders had been completely equilibrated because then the comparison of moisture content had been made for samples having the same water activity.

The result from the moisture sorption analysis of Lemon powder (1a-1e) does not indicate that any of the anti-caking agent when added in an amount of 1.7 %, functioning by competing with the host powder for the available water. The natural anti-caking agents were chosen mainly due to their potential water absorption capacity, see section 2.6.3, making the result somewhat unexpected. One likely explanation is that the natural-anti caking agents are needed in higher amount to affect the caking behavior of the host powders. Assuming high water absorption capacity of the natural alternatives, another explanation dealing with the hygroscopicity of the powder surface. Water diffusion will probably be faster for a highly hygroscopic surface compared to a lower hygroscopic surface. It could be that the anti-caking agents were not completely distributed in the powder, resulting in a surface composition similar to Lemon powder without additive.

What is generally established from the analysis is that, Lemon powder as a raw material is highly hygroscopic and experience stickiness while stored in humid environments. The shape of the sorption isotherm shows that the raw material absorbing increasing amount of water during exposure to higher relative humidifies (Fig. 14). The fact that all powders were caked after storage at

62 % relative humidity (Fig.11), confirms that water absorption has a large impact on the stickiness and caking behavior of Lemon powder. The result is in agreement with the literature, saying that powders containing low molecular weight substances having high hygroscopicity, experience stickiness and caking while exposed to humid environments, see section 2.1.7. What also can be said from the moisture sorption isotherm (Fig. 14) in combination with the visual analysis (Fig.11) is that the powder behaves cohesive, that is to say that the caking development is initiated already at lower relative humidities. It is interesting to discuss the anti-caking properties of silicon dioxide. The moisture sorption isotherm for Lemon powder containing silicon dioxide is similar to the other powders in the range of 23-43 % relative humidity (Fig. 16). Still, it is the only free flowing powder at 43 % relative humidity. There are therefore reasons to suspect that silicon dioxide may function in another, or additional way than competing with the host powder for the available water. This is supported by the literature saying that silicon dioxide has shown to be strongly adsorbed at the surfaces of larger particles, behaving like a surface roughness, see section 2.4.1.

The result from the sorption isotherm of Red Onion seasoning mix without additive is in agreement with literature, and indicates the presence of crystalline components. As discussed in section 2.5.1, powders containing crystalline components do not absorb larger amount of water until higher relative humidities, and only a small amount of water is needed to reach region of high water activity. The shape of the moisture sorption isotherm for Red Onion seasoning mix confirms this behavior (Fig. 15). Billings et al., [50] reported that the critical water activity for initiation of caking was 0.8 for bulk sucrose. Red Onion seasoning mix 2a and 2c-2e, showed tendency to cake at lower water activities than 0.8, probably due to the presence of the amorphous, hygroscopic and easily caked lime powder. Small lumps of lime powder was seen for all samples except the ones containing silicon dioxide, which further supports its anti-caking capacity (Fig. 12)

As discussed with Lemon powder, the result from the sorption isotherm does not indicate improved anti-caking capacity for any of the samples (Fig. 15). The fact that Red Onion seasoning mix with silicon dioxide, was the only powder, not showing any lump formation after about two days of storage at 62 % relative humidity (Fig. 12) further indicating another or additional anti-caking mechanism than water absorption. One likely explanation to why the natural anti-caking agents when adding in 1.7 %, not prevent the lime powder in the seasoning from aggregating, dealing with the particle size of the anti-caking agents. Silicon dioxide has a particle size of 13.5 μ while e.g. Fibruline has a particle size of 500 μ , see section 2.6.2.5 and 2.6.3.3. Meyer & Zimmermann [66], explains the possibility of small anti-caking agents to be easily absorbed on larger particles, thereby reducing inter-particle interactions, see section 2.4.1. The larger particle size of Fibruline, could possibly impair the absorption capacity, leading to less surface roughness on the surface of the lime powder particles. A higher amount of Fibruline, could possibly improve the ability of the anti-caking agents to be absorbed on the host powders. Consequently, an improved surface roughness could probably also improve the water absorption and consequently prevention of inter-particle interactions like liquid bridges, see section 2.3.1.

As seen in Fig. 15 and Fig. 17, the moisture content do not exceeds 1.5 % for any of the different combinations of Red Onion seasoning mix. The moisture content for Red Onion seasoning mix without additive, compared to Lemon powder without additive seems realistic based on the amount of hygroscopic powders. Red onion seasoning mix contains beyond a high amount of sucrose, about 3 % lime powder and 9 % citric acid, which both are known as hygroscopic powders, see section

2.1.7. As mentioned in section 2.6.1, Lemon powder contains 50 % Lemon juice powder and 50 % maltodextrin. Since it is known that crystalline components do not absorb water until higher relative humidities, the moisture content for Red Onion seasoning mix without additive was therefore, at lower relative humidities, expected to be about 12 % of the moisture content of Lemon powder without additive. Fig. 18 shows that the moisture content of Red onion seasoning mix is about 10 % of Lemon powder. The higher water content of Lemon powder can consequently be explained by a more hygroscopic surface, resulting in faster water diffusion and consequently higher moisture content in the sample.

As mentioned in section 2.6.2, Red Onion seasoning mix is a multicomponent mixture of powders with different characteristics like particle size. The large standard deviations seen in Fig. 17 could probably be related to the multi component system. It is likely that the two measurements in each duplicate were done for samples having slightly different composition and consequently had adsorbed different amount of water. As discussed in section 2.6.2, the presence of many different components making it difficult to predict the caking behavior. As with the result from the sorption isotherm of Lemon powder, this analysis does not indicating anti-caking properties for any of the potential natural additives. The result from the moisture sorption isotherm in combination with the visual analysis of the powders after storage at different relative humidities, is still useful, since it confirms the knowledge about the different behavior of amorphous and crystalline components while exposed to water.

As discussed in section 2.1.2, caking occurs over time. The influence of time on the caking development is clearly demonstrated when comparing the appearance of the powders in Fig.11 and Fig. 12 with Fig. 13. While stored, Lemon powder continuing to gain strength, leading to extremely hard cakes after storage at high relative humidities for 7 weeks. No anti-caking capacity could be identified. The behavior of Red Onion seasoning mix after storage at high relative humidity for a longer time period could probably be related to the progressive moisture migration and further liquid bridge formation, discussed in section 2.3.1. Capillary condensation in the pores, resulting in partial dissolution of the soluble components and consequently inter-particle interactions could explain why the appearance.

5.2 Water plasticization

The result from the glass transition analysis for Lemon powder (Fig. 19), confirms that water has a plasticizing effect of amorphous food powders, see section 2.1.5. The fact that the T_g value decreasing linearly with increasing water activity, is in agreement with what was reported by Roos & Karel [21]. Since it is known that glass transition has a large impact on the stickiness and caking property for amorphous food powders, the aim of the DSC analysis was to evaluate if any of the potential silicon dioxide replacers could prevent caking by increasing the T_g value of the host powders. As discussed in section 2.1.4, the difference between the glass transition temperature of the powder, and the powder storage temperature is the main driving force for caking of amorphous food powders. By increasing T_g , the $T - T_g$ value decreasing, resulting in higher stability of the powder at the actual storage temperature. Water will still have a plasticizing effect, but the transformation from the glassy state to the rubbery state will, at a certain powder storage temperature, take place at a higher relative humidity compared to a powder with lower T_g value. Since all powders caked at a relative humidity of 62 % (Fig.11) it was not surprisingly that the T_g value decreased to temperatures far below the powder storage temperature of about 20 °C, at higher relative humidities (Fig. 19).

As discussed in section 2.4.2, high molecular weight substances like starch could function as anti-caking agents by increasing T_g of the host powder. One reason explaining the low difference between T_g of Lemon powder (1a-1e) after storage at 23 % respectively 62 % (Fig. 19) could be that the amount of anti-caking agent was too low to give any effect. As described in section 3.3, the water activity of the samples was measured in correlation with the DSC measurements, and are those presented in Fig. 19. Since only a small amount of sample was used in the analysis, T_g measurements could have been done for samples having higher respectively lower water activity than the ones presented. This could explain why the T_g value of sample 1d is different from the others after storage at 43 % relative humidity, but not after storage at 23 and 62 % relative humidity (Fig. 19). More measurements could have improved the result.

Assume that a spice jar containing Lemon powder is stored at a constant temperature of 20 °C. As seen in Fig. 24, the water activity in which the glass transition takes place at this temperature is about 0.28 respectively 0.33 for Lemon powder containing 1.7 and 5 % potato starch. An increase in relative humidity as a result of weather fluctuations will, as confirmed in the moisture sorption analysis (Fig. 14, Fig. 16), increase the moisture absorption and further water activity of the powders. At a water activity of 0.35, T_g of Lemon powder containing 1.7 respectively 5 %, will be decreased to 5 and 15 °C. As seen in Fig. 24, a glass transition temperature of about 5 and 15 °C, resulting in that each powder will be stored 15 respectively 5 °C above their glass transition temperature. According to Foster, Bronlund & Paterson [26], the development of powder cohesiveness, caking, increases with increasing $T - T_g$ values, see section 2.1.4. Based on this statement, adding 5 % potato starch will theoretically reduce the development of powder cohesiveness with time. Saying that Lemon powder containing 5 % potato starch showing improved anti-caking properties compared to Lemon powder without additive and with 1.7 % potato starch (Fig. 24), is also supported by what was stated by Fitzpatrick et al., [28], see section 2.1.4. It should be clarified that adding 5 % potato starch, theoretically and practically, does not show to completely solve the caking problem but it seems, at lower relative humidities, to improve the stability of hygroscopic food powders in a way that may delay caking.

As discussed in section 2.4, adding a small amount of anti-caking agent is one way of controlling the caking development. The result from both the sorption isotherm (Fig. 14, Fig. 15) analysis and DSC measurements (Fig. 19), clearly emphasizing the importance of controlling external factors like relative humidity as well, when handling hygroscopic food powders. This project was not aimed to optimize process and storage conditions, but what can be said is that the effect of adding 5 % potato starch, will probably be even higher in combination with optimized process and storage conditions. It is clearly in Fig. 24, that controlling, that is to say, reducing the relative humidity in the environment in which the powder is produced or stored, will further stabilize and delay the caking development. From a consumer perspective, the evaluation of moisture absorption and glass transition of hygroscopic food powders, further explains the importance of storing the spices in a dry, low humid environment.

The reason to why the T_g value of Lemon powder was not increased by adding 5 % Fibruline and Orybran, is probably due to the lower T_g values of those substances compared to potato starch (Fig. 20, Fig. 22, Fig. 23). The diverged T_g value of Lemon powder with 10 % potato starch (Fig. 24), could be owing to an incomplete mixing of Lemon powder and potato starch. The small amount of powder used for the DSC analysis, might contribute, in combination with an incomplete mixing, to that the two replicates were not representative for the powder mix. Since the measured T_g value is

higher than the expected value, it seems like the DSC analysis was done for samples having a higher amount of starch. This is the most likely explanation since the standard deviation between the two replicates were low.

The aim of measuring glass transition temperature of lime powder, was to confirm what was suspected namely that lime powder is the most sensitive, in terms of water plasticization, component in the Red Onion seasoning mix. The result from the DSC analysis of lime powder (Fig.25), showed that the fruit powder behave very similarly to Lemon powder while exposed to different relative humidities. The result was expected since large lumps of lime powder have been identified in the Red Onion seasoning mix already at lower relative humidities (Fig. 12), and also since both powders are composed by low molecular weight substances, having high hygroscopicity and low glass transition temperatures, see section 2.1.7. By knowing the similarities between the fruit powders, makes it supportable to anticipate the caking properties of Red Onion seasoning mix based on the DSC analysis of Lemon powder. This is useful, since no results were obtained from the DSC measurements of Red onion seasoning mix. Based on the results from the T_g analysis of lime powder (Fig.25) and Lemon powder with 5 % starch (Fig. 24), it seems like potato starch could delay the cohesiveness development, especially the formation of lumps of lime powder, also in the Red Onion seasoning mix.

5.3 Flowability

The result from the flowability analysis of Lemon powder without additive, and with silicon dioxide (Fig. 26), confirms that the flow behavior of food powders can be improved by adding a small amount of anti-caking/ flow agent, see section 2.4. The change in bulk density for Lemon powder without additive and with silicon dioxide (Fig. 33,

Table 5), is in agreement with what was reported by Xanthakis, Ruud van Ommen & Ahrné [46], namely that a free flowing powder shows lower change in bulk density compared to a more cohesive powder, see section 2.2.1. Xanthakis, Ruud van Ommen & Ahrné [46] also found that the effective angle of friction was lower for those powders showing lower increase in bulk density as well as improved flow properties. Fig. 26, Fig. 33,

Table 5 and Fig. 37, confirms that the same relationship is seen for Lemon powder without additive, and with silicon dioxide.

The cohesiveness of silicon dioxide (Fig. 28) is in agreement with what was reported by Meyer & Zimmermann [66], namely that anti-caking agents due to their smaller size are easily caked, see section 2.4.1. The reason to why Lemon powder with silicon dioxide presents flow function in the free flowing area, is probably due to, what was also explained by Meyer & Zimmermann [66], the ability of anti-caking agents to act as a surface roughness thereby preventing inter-particle interactions, see section 2.4.1. Since silicon dioxide did not show any tendency of either absorbing a large amount of water (Fig. 14, Fig. 15), nor increasing the T_g value of the host powder (Fig. 19) , the surface roughness theory seems like the most likely. By comparing Fig. 26 and Fig. 28, it can be seen that the poorer flow of Lemon powder with Orybran, almost certainly is due to the cohesiveness of Orybran itself. Based on the difficulties in flow, the increase in bulk density was expected to be as highest for Lemon powder 1e. As seen in Fig. 26 and

Table 5, the relationship between compressibility and flow behavior, discussed by Xanthakis, Ruud van Ommen & Ahrné [46], could not be seen when using Orybran as anti-caking agent.

Generally, the results from the flow functions and bulk density measurements for the anti-caking agents (Fig. 28, Fig. 35 and Table 6) could not be correlated based on what was described by Xanthakis, Ruud van Ommen & Ahrné [46]. One could think of differences like water activity as a likely explanation to the difficulties in correlating the flow function, compressibility and effective angle of wall friction measurements. As could be seen from the glass transition analysis for Fibruline, Orybran and potato starch (Fig.20), potato starch has a higher water activity compared to Fibruline and Orybran after storage in their sealed packages at room temperature. As discussed several times in this paper, water has a large impact on the caking development in food powders. The high compressibility of potato starch could be due to the higher amount of unbounded, free water, in the powder matrix and consequently facilitated liquid bridging. The higher compressibility of potato starch does not necessarily have to affect its ability to flow while applying increasing consolidation stresses.

The fact that potato starch, both when added in Lemon powder (Fig. 26) and while analyzed separately (Fig. 28), does not show any difficulties in flow, further promotes that it, at lower relative humidities, theoretically could be used as a silicon dioxide replacer. Further, the change in bulk density when added in Lemon powder (Fig. 33) could be correlated to the flow behavior. (Fig. 26). The question remaining after the first flowability analysis was if the flow of Lemon powder could be further improved by increasing the amount of potato starch.

Generally, Red Onion seasoning (2a-2e) present flow functions in the free flowing area (Fig. 27). The low flowability seen for Lemon powder when using Orybran (Fig. 26) as anti-caking agent could not be seen when the rice fiber was used in the Red Onion seasoning mix. One explanation could be related to what was described by Mehos & Clement [32], namely that non-uniformity of particle size could increase the number of contact points between smaller and larger particles, see section 2.1.8. One theory is that Orybran is more easily absorbed on the larger crystalline components in the Red Onion seasoning, thereby preventing interactions between the rice particles. Generally, the results show that the higher flowability (Fig. 27), the smaller increase in bulk density (Fig. 34,

Table 5), the smaller effective angle of wall friction (Fig. 38), which as discussed above is in agreement with earlier studies. Kono, Huang & Xi [64] reported that the mechanism of the flow conditioners depends on the structure of the bulk powder in which the flow aid is dispersed, see section 2.4.1. The fact that potato starch when adding in 1.7 % shows high flowability both when added in the amorphous Lemon powder (Fig. 26) and the multicomponent Red Onion seasoning mix containing particles with different characteristics (Fig. 27), demonstrates that it could potentially be used as a silicon dioxide replacer in a wide range of spice products.

Generally, Red Onion seasoning mix (2a-2e) shows slightly improved flow compared to Lemon powder (1a-1e). As discussed in section 2.1.8, particle size has been identified as an important physical property affecting the caking and flow behavior of food powders. One theory is that the generally larger particle size of the components in the Red Onion seasoning mix compared to Lemon powder, contributing to the improved flow behavior. This theory is supported by Teunou, Fitzpatrick & Synnott [36] saying that powders larger than 200 μm are free flowing while the flowability of smaller particles are more difficult, see section 2.1.8. Sucrose, which is the main component in the Red Onion seasoning mix, has a particle size of 0.45-0.55 mm while Lemon powder has a particle size of about 0, 5 mm, see section 2.6.1 and 2.6.2.1. The fact that the improved flow of Red Onion seasoning mix could be related to the size of the anti-caking agent in relation to the host powder is

also supported to what was described by York [68], see section 2.4.1.

Just like in the glass transition analysis, no improvements were seen when increasing the amount of Fibruline and Orybran from 1.7 to 5 % (Fig. 29, Fig. 30). The results were not unexpected partially due to the glass transition analysis showing that the stability of the powders were not changed when increasing the amount of anti-caking agent (Fig. 22, Fig. 23). But also since the flow function of especially Orybran, indicated that Orybran is highly cohesive itself (Fig. 28). Adding 5 % potato starch was expected to increase the flowability of Lemon powder since potato starch has not shown to be as cohesive as Orybran. Further, the result from the glass transition analysis, indicating theoretically higher stability of the Lemon powder with 5 % (Fig. 24), also contributed to the expected increased flowability. As seen in

Fig. 31 and Fig. 32, Lemon powder with 5 % potato starch presents flow function in the free flowing area, and demonstrates even better flow behavior than Lemon powder containing silicon dioxide. While increasing the amount to 10 %, the flow was strongly impaired (

Fig. 31), which further verifies what was concluded by York [68], that there exists an highest acceptable level above which anti-caking agents start to impair the flowability of the powder. The difficulties in flow, could be related to both increased bulk density (Fig. 36, Table 6) as well as increased effective angle of internal friction (Fig. 40), indicating higher compressibility and larger inter-particle interactions compared to Lemon powder with 5 % potato starch.

One possible explanation to the increased flowability while using 5 % potato starch compared to 1.7 %, is that potato starch compared to silicon dioxide, is not that effectively absorbed on larger particles, resulting in that a higher amount is needed to get the same effect as with silicon dioxide. As pointed in section 2.4.1, the effect of coating has shown to be highest when the anti-caking agents completely cover the surface of the powders. The likely situation when increasing the amount from 5 to 10 % is probably that the surface of the host powders at a certain amount of potato starch became saturated. Another explanation dealing with the increased glass transition temperature for Lemon powder with 5 %. As seen in Fig. 24, Lemon powder with 5 % potato starch will, at a certain water activity and storage temperature, theoretically always be more stable, that is to say, less sticky and less cohesive than Lemon powder with 1.7 % starch. As stated in literature as well as showed in this study (

Fig. 31, Fig. 36, Table 6, Fig. 40), a powder showing less compressibility, that is to say, a smaller increase in bulk density, lower effective angle of wall friction, will generally show better flow compared to a cohesive powder, see section 2.2.1.

6 Conclusions and Future Work

Caking, whereby free flowing particles aggregate to form lumps, is a common problem during handling and storage of food powders. Powders containing a high amount of low molecular weight sugars and organic acids, having high hygroscopicity and low glass transition temperature, have shown to be particularly sensitive to caking. Lemon juice powder and Red Onion seasoning mix, are known to be highly problematic when it comes to caking, both in the production but also for the consumers.

According to literature, there are many factors, both external and internal, affecting the caking development. This study focused mainly on the moisture induced caking, and the result from the moisture sorption isotherms and glass transition measurements, demonstrated that water has a large impact on the caking behavior of Lemon juice powder and Red Onion seasoning mix. Mechanically induced caking was also evaluated in the flowability analysis, and showed generally that the cohesiveness of a powder, affects its ability to flow.

The aim of this study was to evaluate potential, natural anti-caking agents, which could replace silicon dioxide in spice products, contributing to a more consumer-friendly labeling while also solving the caking problem. What was generally concluded, especially after exposing the powders to humid environments, was that silicon dioxide as anti-caking agent, is highly effective in preventing caking in the easily caked Lemon juice powder and Red Onion seasoning mix. Fibruline, native potato starch and Orybran, referred to as natural anti-caking agents, were evaluated based on the ability to affect the hygroscopicity, glass transition and flowability of the host powders.

The results from the DSC measurements in combination with the flow function tests, demonstrated that 5 % native potato starch, at lower relative humidities theoretically could be used as a silicon dioxide replacer. It was shown that the glass transition temperature of Lemon juice powder was increased while adding 5 % native potato starch, which theoretically indicates less stickiness and consequently reduced risk of caking. Further, Lemon juice powder containing 5 % native potato starch presents flow function in the free flowing area, even better than silicon dioxide, which further promotes its use as a natural anti-caking/ flow agent. The result from the sensory analysis confirmed that there is no significant difference between products containing 1.7% silicon dioxide and 5% native potato starch.

It should be remembered that the visual appearance of Lemon juice powder with 5 % native potato starch, after exposing to higher relative humidities, does still indicate the initiation of cohesiveness. The cohesiveness at higher relative humidities was seen also for powders containing silicon dioxide, which further clarifies that caking of powders containing hygroscopic substances, probably needs to be controlled in additional way beyond adding anti-caking agents, to completely avoid the caking development. The results from this study shows that there is a strong relation between the environment in which the powder is stored, and the caking development, which further points the importance of controlling process and storage conditions. From a consumer perspective, which was the main focus in this study, this could be easily done by keeping the spices in a dry, low humid environment for a not too long period of time.

An important learning through the project is that caking occurs over time, that is to say, the longer the powder is stored, the more it will gain strength. The time factor is less problematic for powders stored in bags since they are often opened and emptied once, compared to powders stored in spice

jars that are opened several times while often stored for a longer time period. Once opened, the powder starts to equilibrate with the surrounding air, resulting in water migration. One recommendation is, initially, to replace silicon dioxide with 5 % native potato starch for those powders stored in bags, and evaluate, from a consumer perspective, its ability to prevent the formation of lumps. The advantage of having a consumer- friendly labeling needs to be weighed against the quality of the product.

Another way of facilitating the anti-caking capacity of native potato starch is to initially replace it in those spices containing granulates instead of very fine powders. It was shown from this study that Lemon juice powder was generally more easily caked and shows slightly poorer flowability than Red Onion seasoning mix, which could be related to what is stated in literature concerning the effect of particle size on the caking behavior. Compared to optimization of process and storage conditions, changes related to particle size is an easier, not that extensive way of preventing the caking development.

As stated in the very beginning of this paper, one ambition is to reduce the amount of additives, but also sugar and salt, in spice products. This could indirect affect the caking development by reducing the amount of hygroscopic substances, which is known, both from the literature and from this study, to be most sensitive to caking. Adding 5 % native potato starch could at the moment, be a way of, not preventing, but delaying the caking development in spices and spice blends.

A next step of this study could be the investigation of the influence of adding 5 % native potato starch on both single and multicomponent powder caking along medium and long term storage under ambient conditions. In combination with the ongoing ambition to reduce the amount of e.g. sugar, changes related to particle size and future attempts to optimize process and storage conditions, the natural anti-caking could for many spice products contribute to a labeling completely without chemical additives, while also solving the caking problem. Native potato starch fulfills the requirements for the replacing alternative, namely that it should be safe, suitable for food and sensorial accepted, but also environmental and economically sustainable.

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Appendix 1

Table 8 shows the experimental design for the sensory analysis of Lemon yoghurt containing 1.7 % silicon dioxide and 5 % native potato starch, and Pickled Onion based on Red Onion seasoning mix with 1.7 % silicon dioxide and 5 % native potato starch. Each assessor got one tray with three samples of Lemon yoghurt, and three samples of Pickled Onion according to Table 8.

Table 8. Experimental design for the sensory analysis.

Sample 1	Lemon yoghurt, 1,7% silicon dioxide	739, 548
Sample 2	Lemon yoghurt, 5% starch	305, 491
Sample 3	Pickled Red Onion, 1,7% silicon dioxide	135, 603
Sample 4	Pickled Red Onion, 5% starch	904, 274

Set	Sample	Sample	Sample	Sample	Sample	Sample
1-325	739-1	305-2	548-1	135-3	904-4	274-4
2-459	491-2	548-1	739-1	904-4	274-4	603-3
3-791	548-1	739-1	305-2	904-4	135-3	603-3
4-489	548-1	491-2	305-2	135-3	603-3	274-4
5-214	491-2	305-2	739-1	274-4	135-3	904-4
6-183	305-2	548-1	491-2	603-3	274-4	135-3
7-563	491-2	739-1	548-1	135-3	274-4	904-4
8-560	491-2	548-1	305-2	274-4	904-4	603-3
9-492	548-1	305-2	491-2	603-3	904-4	135-3
10-310	739-1	491-2	548-1	135-3	603-3	904-4
11-127	548-1	739-1	491-2	904-4	135-3	274-4
12-457	305-2	491-2	739-1	904-4	603-3	135-3
13-480	305-2	739-1	491-2	274-4	904-4	135-3
14-586	739-1	548-1	305-2	603-3	904-4	274-4
15-376	739-1	491-2	305-2	274-4	603-3	904-4
16-803	548-1	491-2	739-1	135-3	904-4	603-3
17-875	305-2	739-1	548-1	274-4	603-3	135-3
18-829	305-2	491-2	548-1	603-3	135-3	274-4
19-495	548-1	739-1	305-2	135-3	603-3	274-4
20-734	548-1	491-2	305-2	603-3	274-4	135-3
21-249	739-1	305-2	548-1	274-4	135-3	904-4
22-840	305-2	548-1	491-2	904-4	135-3	603-3
23-895	491-2	305-2	739-1	904-4	274-4	603-3
24-129	491-2	548-1	739-1	135-3	904-4	274-4
25-704	491-2	739-1	305-2	135-3	274-4	603-3
26-529	739-1	548-1	491-2	904-4	274-4	135-3
27-879	305-2	548-1	739-1	603-3	135-3	904-4
28-813	739-1	305-2	491-2	274-4	135-3	603-3
29-483	491-2	305-2	548-1	904-4	603-3	274-4
30-931	548-1	305-2	739-1	603-3	274-4	904-4

Appendix 2

Fig.41 shows an example of the thermograms obtained from the DSC analysis of Lemon powder. As seen in Fig.41, the thermograms were, for each duplicate, analyzed for the same onset and endpoint temperatures.

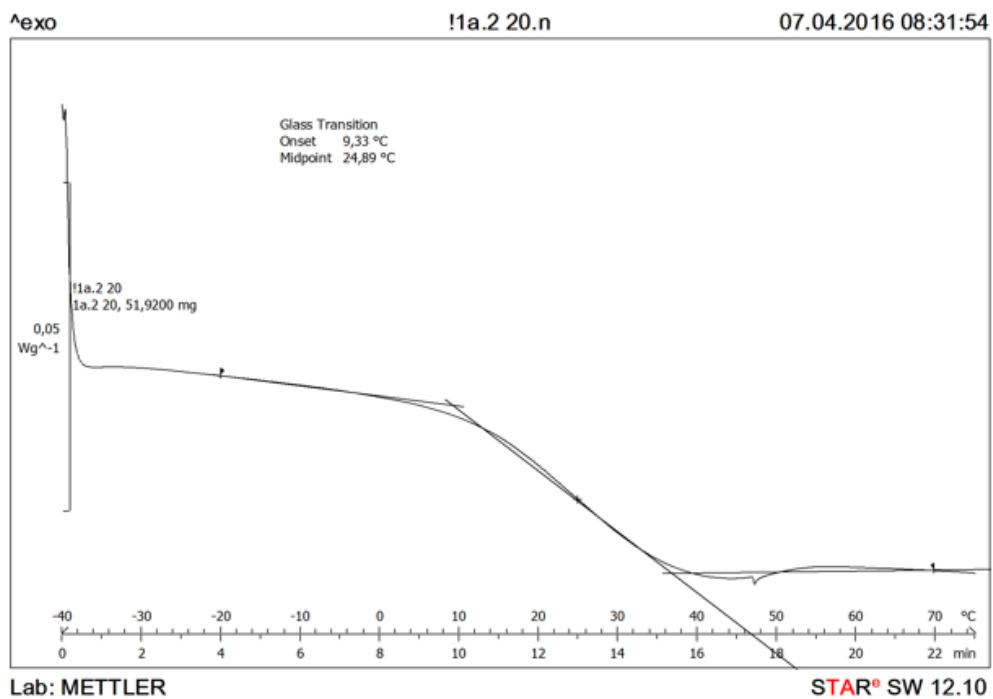
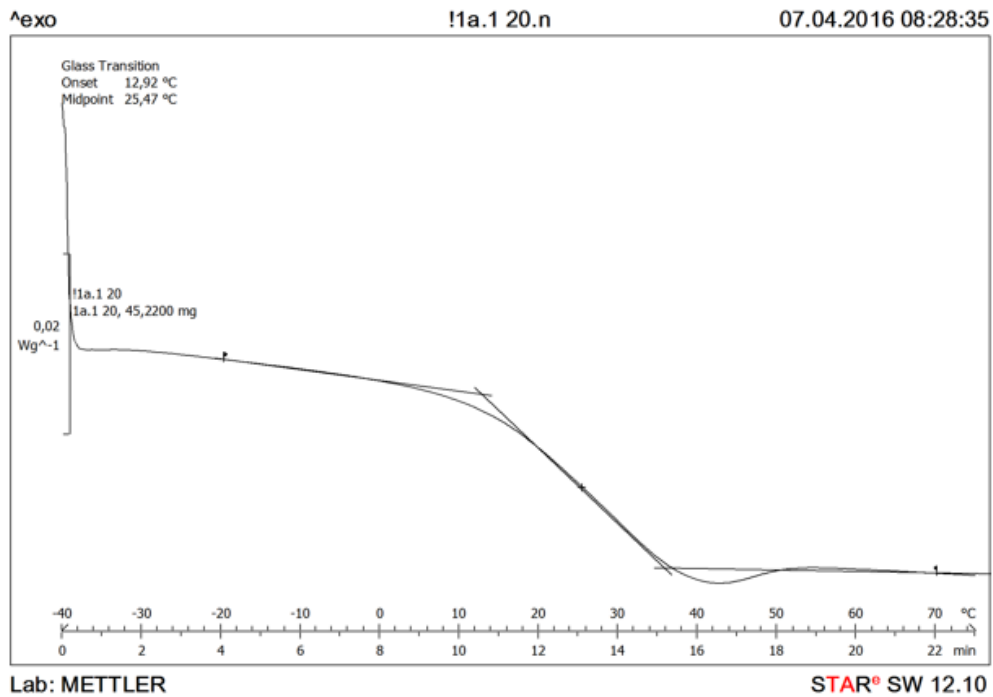


Fig.41. Thermograms obtained from the DSC analysis of Lemon powder without additive after storage at 23 % relative humidity.