Liquids in powder form to enhance mixing homogeneity for low fat/water containing food composites

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Liquids in powder form to enhance mixing homogeneity for low fat/water containing food composites

A dissertation submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

Doctor of Sciences

presented by

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Liquids in powder form to enhance mixing homogeneity for low fat/water containing food composites

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Dedicated to my grandmother Nadja Carlsson, for inspiring me to step out of my comfort zone.
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# Notation

## Latin Letters

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<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$m^2$</td>
<td>area</td>
</tr>
<tr>
<td>$C_g'$</td>
<td>% (w/w)</td>
<td>maximum freeze concentration</td>
</tr>
<tr>
<td>$d$</td>
<td>m</td>
<td>diameter</td>
</tr>
<tr>
<td>$F$</td>
<td>N</td>
<td>force</td>
</tr>
<tr>
<td>$ff_c$</td>
<td>-</td>
<td>flowability</td>
</tr>
<tr>
<td>$k$</td>
<td>°C</td>
<td>number of samples</td>
</tr>
<tr>
<td>$m_w$</td>
<td>g</td>
<td>sample wet weight</td>
</tr>
<tr>
<td>$m_d$</td>
<td>g</td>
<td>sample dry weight</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>$m^3/s$</td>
<td>volume flow rate</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td>ideal value</td>
</tr>
<tr>
<td>$P$</td>
<td>Pa</td>
<td>atomizing pressure</td>
</tr>
<tr>
<td>$q_0$</td>
<td>$\mu m^{-1}$</td>
<td>number based size frequency</td>
</tr>
<tr>
<td>$q_3$</td>
<td>$\mu m^{-1}$</td>
<td>volume based size frequency</td>
</tr>
<tr>
<td>$r$</td>
<td></td>
<td>regression coefficient</td>
</tr>
<tr>
<td>$s$</td>
<td></td>
<td>standard deviation</td>
</tr>
<tr>
<td>$s^2$</td>
<td></td>
<td>empirical variance</td>
</tr>
<tr>
<td>$T$</td>
<td>°C</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>°C</td>
<td>onset temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>°C</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>°C</td>
<td>melting temperature</td>
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<td>$t$</td>
<td>s</td>
<td>time</td>
</tr>
<tr>
<td>$t_c$</td>
<td>s</td>
<td>critical mixing time</td>
</tr>
<tr>
<td>$\bar{X}$</td>
<td></td>
<td>average value</td>
</tr>
<tr>
<td>$X_i$</td>
<td></td>
<td>measured property</td>
</tr>
<tr>
<td>$x$</td>
<td>$\mu$m</td>
<td>particle diameter</td>
</tr>
<tr>
<td>$x_{50,0}$</td>
<td>$\mu$m</td>
<td>number based median particle diameter</td>
</tr>
<tr>
<td>$x_{50,3}$</td>
<td>$\mu$m</td>
<td>volume based median particle diameter</td>
</tr>
</tbody>
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### Greek Letters

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<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
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<tbody>
<tr>
<td>$\varepsilon$</td>
<td>F/m</td>
<td>permittivity (complex dielectric constant)</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>F/m</td>
<td>permittivity of vacuum</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>-</td>
<td>relative permittivity of the material</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>kg/$m^3$</td>
<td>particle density</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>kg/$m^3$</td>
<td>bulk density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Pa</td>
<td>normal stress</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>Pa</td>
<td>consolidation stress</td>
</tr>
<tr>
<td>$\sigma_c$</td>
<td>Pa</td>
<td>unconfined yield stress</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Pa</td>
<td>shear stress</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>Pa</td>
<td>cohesion</td>
</tr>
<tr>
<td>$\phi_w$</td>
<td>Pa</td>
<td>wall normal load</td>
</tr>
<tr>
<td>$\phi_e$</td>
<td>°</td>
<td>effective angle of internal friction</td>
</tr>
<tr>
<td>$\phi_x$</td>
<td>°</td>
<td>wall friction angle</td>
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</tbody>
</table>

### Abbreviations

<table>
<thead>
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<th>Symbol</th>
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<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>cryo-SEM</td>
<td>Cryo Scanning Electron Microscopy</td>
</tr>
<tr>
<td>CL</td>
<td>Cooking Loss</td>
</tr>
<tr>
<td>CoV</td>
<td>Coefficient of Variation</td>
</tr>
<tr>
<td>CoV\textsubscript{N}</td>
<td>Normalized Coefficient of Variation</td>
</tr>
<tr>
<td>CT</td>
<td>Computer Tomography</td>
</tr>
<tr>
<td>db</td>
<td>dry base</td>
</tr>
<tr>
<td>DE</td>
<td>Dextrose Equivalent</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter</td>
</tr>
<tr>
<td>EM</td>
<td>Electromagnetic</td>
</tr>
<tr>
<td>FPE</td>
<td>Laboratory of Food Process Engineering (Lebensmittelverfahrenstechnik, LMVT)</td>
</tr>
<tr>
<td>FT-NIRS</td>
<td>Fourier Transformation-Near InfraRed Spectrometer</td>
</tr>
<tr>
<td>MC</td>
<td>Moisture Content</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>MWRT</td>
<td>Microwave Resonance Technique</td>
</tr>
<tr>
<td>PL</td>
<td>Powder-Liquid</td>
</tr>
<tr>
<td>RST</td>
<td>Ring Shear Tester</td>
</tr>
<tr>
<td>PLS</td>
<td>Partial Least Square</td>
</tr>
<tr>
<td>SEE</td>
<td>Standard Error of Estimation</td>
</tr>
<tr>
<td>SEP</td>
<td>Standard Error of Prediction</td>
</tr>
<tr>
<td>SFC</td>
<td>Solid Fat Content</td>
</tr>
<tr>
<td>S</td>
<td>Saturated</td>
</tr>
<tr>
<td>US</td>
<td>Un-Saturated</td>
</tr>
<tr>
<td>wb</td>
<td>wet base</td>
</tr>
<tr>
<td>WU</td>
<td>Water Uptake</td>
</tr>
</tbody>
</table>
Abstract

Mixing powder with a small fraction of liquid is a process step used in a wide range of industries. Adding the liquid homogeneously is, however, not a trivial task due to liquid enriched lump formation. With conventional mixing techniques, de-agglomeration post treatment is necessary either by mechanical treatment using so-called delumpers or by adding more liquid. The high-energy input using mechanical treatment, however, can result in the loss of functionality of sensitive materials. When adding more liquid, other negative effects might ensue. In food systems, e.g. confectionery products, an increase in fat content generally results in high caloric foods. Surplus water often requires an additional time and energy consuming drying step to obtain the end product, in which a low moisture content is generally desirable (due to storage/stability reasons). This can for example be seen in pasta manufacturing. To mitigate these drawbacks, a new approach for adding liquid to powders has been developed. The liquid is transformed into a solid powder by spray chilling, forming a so-called powder-liquid, to be mixed with the bulk powder. The aim of this work was to evaluate the powder-liquid mixing process in comparison to conventional techniques, where the liquid is sprayed into the powders during mixing. Fat and water based powder-liquids were produced and characterized in terms of particle size distribution, particle morphology, flow properties and stability. The particle size distribution of the powder-liquids can be controlled by the spray chilling parameters. Spherical fat and water based powder-liquids were produced, of which the water based powder-liquids were generated in a state with glassy shell and lamellae structure. Flow measurements of the pure fat-based powder-liquids revealed that their flow properties varied with the particle size distribution and temperature, which influence the solid fat content in the powder-liquids. In mixtures of powder-liquids and model powders, the flow properties varied with the powder-liquid concentration. The mixing quality was quantified by near infrared spectroscopy (NIRS), colorimetry and moisture content analysis after various mixing times, using the variation coefficient (CoV). The results demonstrated that both fat and water based powder-liquids mixed faster in comparison to the sprayed liquid. For low liquid fractions (≤10 wt%) the powder-liquids also lead to a higher degree of homogeneity in the final mixture. In addition, all three analysis methods were proven to give a good assessment of the mixing homogeneity of the various mixtures.
Zusammenfassung

Zusammenfassung

fett- als auch wasserbasierte Powder-Liquids im Vergleich zur eingesprühten Flüssigkeit bei Verwendung konventioneller industrieller Pulvermischertechnologie schneller mischen. Für kleine Flüssigkeitsanteile ($\leq 10$ wt%) führt das Powder-Liquid-Verfahren auch zu einem höheren Grad an Homogenität in der endgültigen Mischung. Darüber hinaus wurde dargelegt, dass sich alle drei Analysemethoden zur akkuraten Bestimmung der Mischgüte eignen.
1 Introduction

Mixing powders with small fractions of liquid is a frequently used processing step in a wide range of industries, such as the food, pharmaceutical and chemical (Černák et al., 1986). Besides as active ingredient in e.g. dough production, confectionery masses, cremes and gels, liquid is added to powders in order to bind dust, avoid segregation, produce or enhance granulation, coat particles with a liquid, or simply increase the weight by adding a cheap ingredient such as water.

When adding liquid to powder, the main tasks are in general to add the liquid and mix uniformly within capacity and mixing time of the mixer, and to avoid inhomogeneity due to liquid enriched lumps or agglomerates (Weinekötter and Gericke, 2000). There are several ways to add the liquid to the powders, such as pouring it into the powder-filled mixer, atomize it and spray the droplets onto the powder, or adding it as a vapor, which condensates when it comes in contact with the powder. Many times a combination of these techniques is used, such as spraying and the use of delumpers (Weinekötter and Gericke, 2000). Nevertheless, in case of adding small liquid fractions, lumping by local agglomerate formation is a typical known effect that clearly restricts the mixing homogeneity. As a consequence, in a number of related industrial food applications, liquids like fat or water are added in excess to guarantee a homogeneous mixture as prerequisite for further down stream processing. For the end product such intermediately required high liquid fractions may not be desirable. In fat-based food product systems, subsequent fat reduction is in general not possible, with the result of high caloric products of minor nutritional preference. An exemplary fat-based food system is milk chocolate confectionery, in which cocoa, sugar and milk powder are mixed with melted cocoa butter. In the case of a watery liquid phase, subsequent re-drying could be applied, which however significantly reduces the overall energy efficiency of such product manufacturing. In food industry, pasta is an example for water based systems with high water content for homogeneous dough making, and low water content in the consumer end product. In the production of pasta, semolina powder is mixed with water (Kratzer, 2007; Zweifel, 2001). Processing equipment and pasta producers have put major effort into more sustainable processing solutions, but with limited effect so far Bahu (1991); Ozgener and Ozgener (2006); Wang (2008). In both of these food systems, addition of small liquid fractions leads to lump formation and clogging, which is generally compensated by addition of larger liquid fractions. However, it would be desirable to (i) reduce
calorie density in chocolate confectionery or (ii) reduce drying energy consumption in the pasta manufacturing process.

Therefore, a new approach for mixing liquid into powder has been developed within this thesis, where the liquid is transformed into the solid state by spray chilling prior to mixing. Some fundamental aspects of the approach, like the spray chilling process, have been investigated in previous work within the Laboratory of Food Process Engineering at ETH Zurich (Windhab, 1995). Spray chilling is a technique to solidify liquids by dispersing them into a cold gas stream, in which the droplets are solidified to particles. The liquid is hereafter added to the bulk powders in a powdery state, as so called powder-liquid. By mixing the liquid in the form of a powder, the goal is to obtain an improvement in mixing quality; first of all for a homogeneous distribution of the liquid, but also for insertion of functional components, such as nutrients or active ingredients, for production of homogeneous food composites with low water or fat.

The aim of this work was to evaluate the powder-liquid mixing process in comparison to conventional mixing techniques, such as directly spraying the liquid into the powders during mixing. Following, the objectives were to (i) produce stable fat and water based powder-liquids by spray chilling, (ii) characterize the powder-liquids, model powder and their mixtures in terms of particle size distribution, particle morphology, flow properties, stability and mechanical properties, and (iii) mix the powders and analyze the mixing quality, testing different analysis methods with the main focus on near infrared spectroscopy (NIRS).
2 Background

2.1 Spray chilling and powder-liquid formation

Spray chilling, also called spray cooling, spray congealing or prilling, is a technique widely used in food and pharmaceutical industries to solidify liquids (Dubey et al., 2010; Okuro et al., 2013; Wagner, 1997). The liquid is dispersed into a cold gas stream by a spraying process, in which the droplets are solidified into particles. Hereby, fat melts, aqueous solutions and emulsions can all be transformed into free-flowing powders (Wagner, 1997), forming so called powder-liquids. Spray chilling can also be used for encapsulation of functional components, such as nutrients or active ingredients (Dubey and Windhab, 2013; Okuro et al., 2013; Zimmermann et al., 2004). An alternative way of producing solidified liquid particles is by grinding or crushing of solidified liquid, such as ice, which in previous studies was used for production of so called undeveloped dough (Campos et al., 1996). There is a WHO (World Health Organization) recommendation (WHO, 2006) for e.g. wheat flour fortification with iron in order to reduce iron deficiency anemia, which is not only a problem in developing countries. However, the flour milling industries are quite reluctant to follow these guidelines and take the extra effort (Hurrell et al., 2010). Physiologically relevant iron compounds can be inserted into the powder-liquid before the spray chilling step. Thus powder-liquids could serve as a new processing track to facilitate any type of food fortification with micro-nutrients or nutritionally valuable components.

As indicated by the name, spray chilling is an integrated process of atomization followed by chilling. A spray is defined as the flow of a liquid into a surrounding gaseous medium to form droplets. The disintegration of the liquid starts due to the very high density difference between gas and liquid and the velocity of the liquid jet, with or without additional air flow. Some important spray characteristics are the droplet size and size distribution, drop velocity distribution, spray density (number of droplets per unit volume), spatial drop distribution, spray angle, and length of jet cores (Dumouchel, 2008). In general, the spray process can be defined in three main steps, (i) the ejection of a liquid flow, (ii) the primary break up mechanism and, (iii) the secondary atomization (Dumouchel, 2008). More information on different types of spray and atomization of liquids is given by Ashgriz (2011); Dubey (2013);
Dumouchel (2008); Lasheras et al. (1998); Lefebvre (1989); Sirignano and Mehring (2000).

The second part of the spray chilling process, i.e., the chilling, also defines the final powder properties. In case of aqueous solutions, recent studies by Windhab et al. (2004) demonstrated that the physical state of the produced powder-liquids is of importance for the storage stability. Water based powder-liquids stayed free flowing for months, when being produced in a glassy state and stored at 2°C below their glass transition temperature (Windhab et al., 2004). Keeping the powder-liquid free flowing during storage is important in order to allow further processing. By cooling an aqueous solution rapidly, amorphous structures (glassy state) will prevail over crystalline structures. The inner structure of the solidified droplet will differ depending on the cooling gradient acting in the droplet and at the droplet surface. The cooling gradient depends on the actual cooling temperature, droplet size, relative velocity of the droplet and the surrounding cooling gas flow. The droplet size, in turn, is a function of the spraying parameters, such as atomizing pressure and feed rate of the liquid, its physical properties and the nozzle type used. For aqueous sugars and/or oligo-/polysaccharides solutions (as used in this work) the physical state, in respect to temperature and cooling gradient, also depend on the solid concentration (Windhab et al., 2004).

Figure 2.1(a) shows the possible physical states of a water droplet during the spray chilling process, depending on the cooling gradient and the solid concentration. During the spray chilling process, the outer shell of the droplet experiences a fast drop in temperature and thus exhibits a considerable temperature gradient. Subsequently, it cools rapidly and solidifies from a liquid to a glassy state type I (path 1; liquid to glass). The core of the droplet shows a much slower cooling rate, so that ice crystals have time to form (path 2). With increasing amount of ice crystals, the solid concentration around the crystals increases (path 2 to 3). When the maximum freeze concentration, $C_g'$, of the solution is reached, it either forms a rubber (point 3) or, if further cooled, a glass type II (point 4; rubber to glass). Glass type II forms lamella structures around the ice particles (Windhab et al., 2004). Figure 2.1(b) demonstrates the cross section of a spray chilled water droplet analyzed with cryo-scanning-electron microscopy (SEM), showing the glassy shell layer (type I) and lamella (type II).

### 2.2 Powder flow

In contrast to liquids and solids, the flow properties of powders cannot be described with the same rheological relations due to the different behavior. However, characterization of the physical properties of powders and their flow behavior are of major relevance to industry as they affect the powder behavior during storage, handling and
Figure 2.1: (a) Physical states of a water droplet during the spray chilling process, dependent on cooling rate (y-axis) and solid concentration (x-axis). $T_m$ points the melting temperature, $T'_g$ the glass transition temperature and $C'_g$ the maximum freeze concentration of the solution. (b) SEM image of a spray chilled water based powder-liquid, with an enlargement of the shell layer (1) and lamella (4), according to the respective point in (a) (adapted from Windhab et al. (2004)).
processing (Knowlton et al., 1994; Teunou et al., 1999). The flow of powders depends on several parameters, such as their composition, particle size and size distribution, moisture content, particle shape, surface properties and temperature (Ganesan et al., 2008; Juliano and Barbosa-Canovas, 2010; Schulze, 2008).

Jenike (1964, 1980) developed a shear cell for measuring flow properties of powders. Later on, new ring shear devices were designed by e.g. Felder (1990) and Schulze (1994). With such shear tests the yield locus of a powder is obtained, which represents the stress necessary to initiate flow after consolidation. For each yield locus the stress state in the powder is represented by a Mohr stress circle, illustrated in Figure 2.2, defining the unconfined yield strength $\sigma_c$ and consolidation stress $\sigma_1$. Furthermore, the flowability $ff_c$ is defined as the ratio of the consolidation stress $\sigma_1$ and the unconfined yield strength $\sigma_c$ (Eq. 2.1) (Schulze, 2008).

$$ff_c = \frac{\sigma_1}{\sigma_c}$$

(2.1)

The lower the $ff_c$ value, the more cohesive is the powder. In Figure 2.3, a related classification of flowability is given.

Figure 2.2: Yield locus and Mohr stress circles presented in a normal stress $\sigma$/shear stress $\tau$ diagram. The Mohr stress circles define the consolidation stress $\sigma_1$ and unconfined yield stress $\sigma_c$. With known yield locus, corresponding flow properties such as effective angle of internal friction $\phi_e$ and cohesion $\tau_c$ can be determined (adapted from Schulze (2008)).

For powder silo design (Jenike, 1964, 1980; Schulze, 2008), or other applications such as extrusion of powders (Althaus, 2010; Althaus and Windhab, 2011, 2012), further characteristic flow properties can be derived if the yield locus is known. In Figure 2.2, the effective angle of internal friction $\phi_e$ is shown, illustrated by the angle of the
effective yield locus. Cohesion $\tau_c$ is defined as the shear stress value where the yield locus intersects the $\tau$-axis (Schulze, 2008), i.e., the shear strength of the powder at zero normal stress (Fitzpatrick et al., 2004). Physically, cohesion can be related to the stickiness of powders and the force with which two particles attract each other (Adhikari et al., 2001).

For design of technical equipment in which the flow of powders along solid walls is important, the wall yield locus and the corresponding wall friction angle $\phi_x$ have to be determined. These are measured with a wall yield loci test and quantify the adhesive strength between the powder and the corresponding wall material. The higher the wall friction angle, the more difficult it is to move the powder along the wall, and i.e., the steeper the wall in a funnel/silo need to be inclined for the powder to flow under gravity force (Schulze, 2008).

Ring shear testers are well known for assessing flow properties of powders. Althaus (Althaus, 2010; Althaus and Windhab, 2012) applied ring shear tests to measure the flow properties of wet powders. Within this thesis the flow measurements are extended to powder-liquid systems.

### 2.3 Powder mixing

Mixing of powders is a frequently used operation in several industries, such as the food, pharmaceutical, and cosmetic industry (Poux et al., 1991). A few articles summarizing the state of the art in the field of powder mixing have been published...
during the last 50 years, such as Weidenbaum (1958); Williams (1968); Fan et al. (1970); Cooke et al. (1976); Sommer (1988); Fan et al. (1990); Poux et al. (1991); Kaye (1997); Weinekötter and Gericke (2000); Fan (2001).

2.3.1 Mixing mechanisms

Three major mechanisms have been identified to contribute to powder mixing: mixing by convection, mixing by diffusion and shear mixing (Fan, 2001; Poux et al., 1991). Mixing by convection involves bulk movement produced e.g., by agitators, pumps or rotating devices. Mixing by diffusion is induced by the random movement of particles. For fluids this is caused by Brownian motion, whereas motion of solid particles has to be stimulated by an external force. Diffusion of particles can thus only occur when the mixture is in motion (Fan, 2001; Weinekötter and Gericke, 2000). Finally, shear mixing is caused by slipping planes of particles. The powder mixing process is influenced by the powder properties, such as particle size distribution, particle shape, particle density, surface characteristics, moisture content, flowability and angle of repose, as well as friability, i.e the tendency of a material to break into smaller pieces (Poux et al., 1991; Sommer, 1988).

Powder mixing often entails demixing or segregation, meaning separation of the particles that are being mixed. Segregation can occur by differences in particle size, shape, density, surface characteristics and resilience, where differences in particle size have the highest impact due to adhesive forces. As for mixing, there are different mechanisms for segregation. The most frequent one is percolation, meaning movement of small particles from the top to the bottom through a bed of larger particles. Following, floating is the rise of larger particles due to vibration. Demixing can also occur by agglomeration of the particles, caused by e.g., humidity and electrostatic charges or during flow, called trajectory segregation (Fan, 2001; Poux et al., 1991; Weinekötter and Gericke, 2000). Due to demixing and segregation, care has to be taken not to “overmix” a powder mixture. It is common that the mixing quality increases to reach an optimum, and then falls off again before reaching equilibrium (Williams, 1968). Free-flowing powders with differences in particle size and density tend to segregate to a higher extent than cohesive powders (Poux et al., 1991). Hence, wet powders have a much lower tendency to segregate compared to dry powders, as they form liquid bridges binding the powders together. For fine particles, with a particle size below 30 µm, the tendency to segregate decreases due to their cohesive forces (Sommer, 1988; Weinekötter and Gericke, 2000; Williams, 1968).

Powder mixers can be divided into batch-, continuous-, and semi-batch mixers. Furthermore, they can be classified as active or passive (Fan, 2001). Within these classes, there are a large number of different mixers, such as tumblers, screw mixers, paddle mixers, pneumatic mixers and silo mixers. In this work, tumbler- and
paddle/ploughshare mixers were used. A tumbler mixer is typically a vessel in which the mixture is being rotated. Paddle mixers have a rotating shaft, usually vertical, with paddles, shovels or ploughshares. These mixers operate at higher rotation speeds compared to tumbler or screw mixers (Sommer, 1988). Depending of what type of mixer, different mixing mechanisms are acting (Fan, 2001). Mixers based on convective mixing have a lower tendency for segregation compared to those where diffusion or shear are the dominating mixing mechanisms (Poux et al., 1991). For the tumbler and paddle/ploughshare mixers used in this work, the acting mechanisms are shear and diffusion.

### 2.3.2 Mixing powder with liquid

Mixing of solids can be extended to systems where the powders are mixed with small amounts of liquid. As for mixing of pure solids, this is a common process in industry and is used e.g., in the food, pharmaceutical, chemical, plastics, composites and ceramic industries (Černák et al., 1986). Liquids are added to powders either as an added active ingredient, to bind dust together, to avoid segregation, to produce or enhance granulation, to coat particles with a layer of liquid or to simply increase the weight by using a cheap ingredient such as water. When adding liquid to powders there are in general two tasks to accomplish, (i) to add and uniformly mix the liquid with the powders within the capacity and mixing time of the mixer, and (ii) to avoid inconsistencies caused by liquid enriched lumps or agglomerates. Achieving a homogeneous mixture is, however, not an easy task, and often liquid enriched lumps need to be homogenized by mechanical treatments (Weinekötter and Gericke, 2000). Subsequent mechanical treatment can decrease the functionality of sensitive powders. An alternative way is to add a larger amount of liquid to the mixture to generate a suspension/paste with an evenly distributed high water fraction. However, in general, a low moisture content is required in the final product to enhance storage stability, for which a dehydration step is required (Wang, 2008). This can be seen in the production of dried pasta, where about 20 wt% water is added to produce pasta dough with a total moisture content of typically 30 wt% (Kill, 2007; Kratzer, 2007). After processing, the pasta product is dried to a maximum moisture content of typically 12.5 wt.%, corresponding to a water activity $a_w$ lower than 0.65, in order to ensure microbiological safety (Kill, 2007; Zweifel, 2001). Drying is the most time and energy consuming process. It requires also large investment costs for pasta dryers with drying air temperature and humidity control, otherwise quality defects such as cracks or broken pasta product results.

There are several ways to add liquid to powders, such as pouring the liquid into the mixer when already filled with the powders, atomizing the liquid and spray the droplets onto the powders, pouring the liquid and dispersing it within the powders.
by high shear or impact forces, or adding the liquid as vapor that condensates when it comes in contact with the powders. Often a combination of these processes is used, such as spraying and the use of delumpers (Weinekötter and Gericke, 2000). In this work, a new process of adding the liquid in the form of a powder-liquid is evaluated.

The wetting of powders can be characterized by different states, depending on the amount of added liquid (Goldszal and Bousquet, 2001).

- **Pendular state**: liquid bridges are formed between individual particles, forming agglomerates.
- **Funicular state**: addition of more liquid so the inter-particle space begins to be filled within the agglomerates.
- **Capillary state**: when the spaces between the particles are entirely filled, i.e., the agglomerates are saturated.
- **Dispersion**: when more liquid is added, liquid bridges between the agglomerates are formed and when all space between the agglomerates is filled, a solid-liquid dispersion state is obtained.

After the liquid has been added to the powders, there can still be some confusion about the nomenclature. Wet solids are all types of bulk solids that have a significant liquid content, including pastes, cakes, slurries, wet powders etc. Wet powders are partially saturated bulk solids, with different proportions of particles bound by liquid bridges and saturated particle clusters (Althaus, 2010). Furthermore, a paste is defined as a liquid-saturated, dense assemblies of particles that can hold an external shape until it is subjected to pressure. With increasing liquid content, the paste transforms first into slurry, and with even more liquid into a suspension of particles in a liquid (Kaye, 1997).

### 2.3.3 Mixing statistics

In an ideal mixture all particles are distributed equally, e.g., like a checkerboard. This is however rarely the case in real mixtures, for which the best possible result is random mixing, meaning the particles are randomly distributed. In order to characterize the quality of a mixture, a suitable measure has to be fixed. The properties in real mixtures, such as concentration, always differ from the ideal value, i.e., nominal concentration $P$. This deviation, the *variance*, is used as a measure to describe the quality of the mixture. The variance describes the mixture as a whole, for which the characteristic property is required everywhere in the mixture. Knowledge about the mixture can be acquired by sampling, further described in the the next section. In mixing theory, two variances are commonly used, being (i) the theoretical variance and (ii) the empirical variance (Sommer, 1988).
The theoretical variance $\sigma^2$ is based on theoretical assumptions of the mixture and is described by Eq. (2.2).

$$\sigma_{tot}^2(t) = \sigma_M^2 + \sigma_Z^2 + (1 - \frac{g}{G}) \cdot \sigma_{syst}^2(t)$$ (2.2)

The three terms composing the variance are $\sigma_M^2$, the variance of the precision of measurement, $\sigma_Z^2$, the variance of random mixing, representing the optimal case for solids, and $\sigma_{syst}^2$, the variance characterizing the mixture, which itself can be used to assess the mixing quality. The term $\frac{g}{G}$ is the ratio between the particle size and the sample size. If they are equal, the measured property depends only on the particle component and not on the mixing homogeneity (Sommer, 1988).

The empirical variance $s^2$ quantifies how much the measured property $X_i$ deviates from the ideal value $P$ for a finite number of samples $k$ (Eq. 2.3, 2.4). According to Eq. (2.4) the mean value $\bar{X}$ (Eq. 2.5) is used, if the nominal value $P$ is unknown (Hauser et al., 1990; Sommer, 1979, 1988).

$$s^2(X) = \frac{1}{k} \sum_{i=1}^{k} (X_i - P)^2$$ (2.3)

$$s^2(X) = \frac{1}{k} \sum_{i=1}^{k} (X_i - \bar{X})^2$$ (2.4)

$$\bar{X} = \frac{1}{k} \sum_{i=1}^{k} X_i$$ (2.5)

The variation coefficient (CoV) can be calculated as the ratio of the standard deviation $s$ and the nominal value $P$ (e.g. target concentration), or the mean value $\bar{X}$, giving a relative deviation of the mixing efficiency (Eq. 2.6) (Daumann et al., 2011; Sommer, 1982).

$$CoV = \frac{s}{\bar{X}}$$ (2.6)

Compared to the empirical variance or standard deviation, the variation coefficient is a good measure for comparing mixtures of different concentrations. Since the standard deviation depends on the sample size and does not account for concentration differences, it can give misleading results (Williams, 1968). Especially with small concentrations, the standard deviation tends to decrease due to the lower concentration values. This can otherwise hide the fact that the mixing quality tends to become worse with decreasing target concentration (Weinekötter, 2007). In food and pharmaceutical industries, the variation coefficient should generally be below 0.06 for
a homogeneous and satisfying mixing quality (Berthiaux et al., 2008; Marikh et al., 2008).

2.3.4 Powder sampling

Powder sampling is an important procedure to determine the quality of a mixture. The sample size, number of samples, sample location, and sampling method must all be examined to give a representative measure. The sample size should preferably correspond to the size that is of importance for the use of the powder mixture (Poux et al., 1991; Williams, 1968). Danckwerts (1953) defined this as the scale of scrutiny. The variance, used as a measure for mixing quality, is highly dependent on the sample size. The smaller the sample size is, the larger the variance will be. Consider for example the two extremes, where the smallest sample size would be the size of the individual particles in the mixture, and the largest sample size would be the same size as the entire mixture itself. These would of course give very different results for a measured variance, as the variance decreases with increasing sample size. Also the number of samples is of great importance for the reliability of the measured mixing quality. Taking a large number of samples can cause disturbances that modify the structure of the mixture, while a small number of samples gives a less accurate value of the homogeneity. Generally, twenty to forty samples of a mixture give correct information on the mixture homogeneity. Samples must be taken from different points in the mixer to give an overall measure of the mixing process. The sampling should preferably be carried out systematically, following different schemes that vary with the type of mixer. The most common method for sampling is to use so called thief probes. The principle is that a cylindrical rod is inserted into the mixture, where a small volume of the material falls into one or several openings in the rod. These are then closed before removing the filled rod from the mixture (Poux et al., 1991).

2.3.5 Evaluation of mixing quality

With a defined measure of mixing quality, there are various techniques that can be used to analyze powder mixtures with respect to their mixing homogeneity. In general, the methods for analyzing mixing quality can be divided into off and on line procedures. For off-line procedures a specified powder volume is taken manually from the mixture, either randomly or systematically. Many times the volume is too large and has to be split into smaller samples before analysis. Some methods also require that the powders are prepared beforehand. On-line analysis include in-line and in situ procedures. The main advantage with these is that the sampling and analysis is automated. Automatic procedures allow for a larger number of samples, giving more statistically reliable data. Nevertheless, on-line procedures often require to be
2 Background

Mixing of powders usually includes chemically differing components being mixed. Chemical analyses of powder mixtures are, however, very expensive, which is one of the reasons that physics based methods are more commonly used to analyze mixing quality. Differing physical properties can, e.g., be size, shape, moisture or color. Some widely used techniques are measuring electrical conductivity, e.g., for salt/sugar mixtures, examination of the differences in the granular structure of the components, reflection measurements of components with different colors, and identification of tracer particles by radioactivity (Weinekötter and Gericke, 2000).

In addition, near infrared spectroscopy (NIRS) is a frequently used analysis method, which is used to quantify the quality of the mixtures in this work. NIRS is fast and non-invasive, which makes it applicable to on-line analysis, and it is used in several areas of industry, such as food, pharmaceutical and chemical. Spectra of a sample can be measured in a few seconds by reflectance or transmittance and the absorption information is extracted by mathematical processing of the spectral data (Osbourne et al., 1986, 1993). NIRS has previously been successfully used to analyze powder mixtures, e.g., for determining the mixing quality of a sugar, cocoa powder and cocoa butter mixture for cold-extrusion of chocolate (Kropp, 2002), for qualitative (El-Hagrassy et al., 2006; Wargo and Drennen, 1996), and quantitative (Rubinovitz, 2002) models for the prediction of blend homogeneity of pharmaceutical powder blends, and for on-line monitoring of blending processes (Bucké et al., 2008).

As mentioned above, reflection measurements can be applied in case of colored components (Weinekötter and Gericke, 2000). In literature, there are several reports on using image analysis to assess the mixing quality of binary or multicomponent mixtures (Aït Aissa et al., 2010; Barra, 2000; Berthiaux et al., 2006; Daumann and Nirschl, 2008; Daumann et al., 2009; ReaLepe and Velázquez, 2003; Shenoy et al., 2014). However, not much is reported on using simple colorimetry. With colorimetry the reflection or transmission of light from an object is measured in order to obtain a numerical description of its color. For manufacturers producing colored products, color measurement is already an essential tool in quality control (Pathare et al., 2013). In this work, the application of colorimetry is further extended to the quality control of binary powder mixtures and compared to NIRS measurements.
3 Materials and methods

Mixing quality of fat- and water based powder-liquids mixed with model powders were analyzed by near-infrared spectroscopy (NIRS), colorimetry, and moisture analysis. The powder-liquids and model powders were further characterized in terms of particle size distribution, morphology, flow and surface properties, of which the methods are all described in the following chapter.

3.1 Raw materials

In the following section, the materials used to produce fat and water based powder-liquids are described, as well as the model powders with which the powder-liquids were mixed.

3.1.1 Fat based system

Fat based powder-liquids were prepared from palm stearin fat (Florin AG, Switzerland) in a spray-chilling process. Palm stearin fat was used as material for the powder-liquids due to its high melting temperature (40-60°C) and thus being a stable solid at ambient temperature. Sunflower oil (Florin AG, Switzerland) was used as analogous liquid for mixing trials comparing powder-liquid mixing to spraying liquid directly into the powders during mixing. Colorimetric measurements was used to evaluate the mixing quality, which required coloring of fat and oil (palm stearin fat, sunflower oil). For this, 0.3wt% of a lipophilic magenta dye CY1 (Geiger et al., 2008), was added to the fat and oil prior to admixture. As these mixing experiments were carried out at ambient temperature conditions, sunflower oil with a melting temperature of about −17°C was used as sprayed liquid, analogous to the palm stearin fat powder-liquids. The differences in fatty acid composition of palm stearin fat and sunflower oil; and their influence on the material (fat/oil) physical properties are given in Table 3.1.

\[^{1}\text{1-Ethyl-2-[3-(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)-1-propenyl]-3,3-dimethyl-3H-indolium perchlorate}\]
3 Materials and methods

Table 3.1: Material properties of the palm stearin fat and sunflower oil, used in the fat based systems. Data was taken from the product sheets of each material coming from Florin AG.

<table>
<thead>
<tr>
<th></th>
<th>Palm stearin fat</th>
<th>Sunflower oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmatic acid C16:0 [%]</td>
<td>78 – 85</td>
<td>5.5 – 7.0</td>
</tr>
<tr>
<td>Stearic acid C18:0 [%]</td>
<td>3 – 6</td>
<td>3.0 – 5.0</td>
</tr>
<tr>
<td>Oleic acid C18:1 [%]</td>
<td>9 – 13</td>
<td>22.0 – 32.0</td>
</tr>
<tr>
<td>Linoleic acid C18:2 [%]</td>
<td>1 – 3</td>
<td>56.0 – 66.0</td>
</tr>
<tr>
<td>Solid fat content, 20°C [%]</td>
<td>85 – 90</td>
<td>–</td>
</tr>
<tr>
<td>Melting point [°C]</td>
<td>40 – 60</td>
<td>-(15 – 20)</td>
</tr>
<tr>
<td>Viscosity [mPas]</td>
<td>107</td>
<td>49</td>
</tr>
</tbody>
</table>

3.1.2 Water based system

Water based powder-liquids were produced from a starch solution, prepared by mixing 10 wt% GlucidexIT6 (DE6) in deionized water. A 10 wt% DE6-water solution has a glass transition temperature around −8.3°C (Wagner, 1997). DE6 is hydrolyzed starch with six dextrose equivalents, kindly provided by Sugro AG (Basel, Switzerland).

3.1.3 Model powders

Different flours were used as model powders to mix with the fat and water based powder-liquids. The flours used were wheat flour type 400, biscuit flour type 10, and fine durum wheat semolina. All flours were provided from SwissMill (Zurich, Switzerland). Table 3.2 states the contents of the flours.

3.1.4 Powders for surface properties assessment

The powder materials used for stickiness and/or wettability testing are stated below, where DE stands for dextrose equivalent.

- Skimmed milk powder (MSK)
- Maltodextrin 17-20 DE (DE17-20)
- Maltodextrin 12 DE (DE12)
- Maltodextrin DE6 (DE6)
Table 3.2: Material properties of the wheat flour type 400, biscuit flour type 10, and fine durum wheat semolina used as model powders for the fat and water based powder-liquid systems. Data was taken from the product sheets of each material coming from SwissMill, and represent the content in 100 g product.

<table>
<thead>
<tr>
<th></th>
<th>Wheat 400</th>
<th>Biscuit 10</th>
<th>Semolina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat [g]</td>
<td>1.1</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbohydrates [g]</td>
<td>71.0</td>
<td>72.5</td>
<td>68.0</td>
</tr>
<tr>
<td>Protein [g]</td>
<td>11.5</td>
<td>10.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Moisture content [wt%]</td>
<td>13.5 – 15.0</td>
<td>12.5 – 14.0</td>
<td>13.5 – 14.5</td>
</tr>
</tbody>
</table>

- Partially hydrolyzed alcalase (protein)

All powders were kindly provided by Nestlé Product Technology Center (Konolfingen, Switzerland).

3.2 Spray chilling and powder-liquid production

Fat and water based powder-liquids were produced by spray chilling of melted and colored palm stearin fat and a 10 wt% DE6-water solution, respectively. The spray chilling process was performed in a cooling tower with a height of 3.7 m and a diameter of 1 m, built at the Laboratory of Food Process Engineering, ETH Zurich (Switzerland). The temperature in the cooling tower was regulated by spraying in and evaporating liquid nitrogen, to keep a temperature of −5/−30°C for the fat and −60°C for the water based system, respectively. The melted and colored palm stearin fat, as well as the DE6-water solution, were sprayed with an air-assist atomizing nozzle with external mixing characteristics (fluid cap PF2850DF-SS: 0.7 mm, air cap PA120-SS: 3 mm, Spraying Systems Co., USA). Several batches were produced for different studies on fat and water based powder-liquids, in order to evaluate different methods for mixing quality analysis as well as the mixing procedure itself. A detailed overview of the process parameters for the different studies can be found in Table 3.3.
Table 3.3: Process parameters in spray chilling of powder-liquid from palm stearin fat and DE6-water solution.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Experiments</th>
<th>Feed rate [mL/s]</th>
<th>Atomizing pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Method-evaluation (I)</td>
<td>2.3</td>
<td>4.6</td>
</tr>
<tr>
<td>1.2</td>
<td>Method-evaluation (II)</td>
<td>2.3</td>
<td>4.1</td>
</tr>
<tr>
<td>2</td>
<td>Mixing-evaluation</td>
<td>2.7</td>
<td>4.1</td>
</tr>
<tr>
<td>Water system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Method/mixing-evaluation</td>
<td>3.6</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>Mixing-evaluation</td>
<td>2.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

3.3 Powder characterization

Characterization of the physical properties of powders and their flow behavior are of major relevance to industry as they affect the powder behavior during storage, handling and processing (Knowlton et al., 1994; Teunou et al., 1999). In the following section the methods for assessing the physical-, surface-, and flow properties of the powder-liquids, model powders and their mixtures are described.

3.3.1 Laser diffraction particle size analyzer

The particle size distribution of fat based powder-liquids and flours were measured with a laser diffraction particle size analyzer LS 13 320 Beckman Coulter (Krefeld, Germany). A 5 mW diode laser was used as light source, emitting coherent light of 780 nm. Determination of the particle size distribution was made by the control software (Version 5.04.28, Beckman Coulter Inc., USA), using the Fraunhofer diffraction model. A universal liquid module was used with isopropanol as continuous phase. All measurements were carried out in triplicates.

3.3.2 Sieve analyzer

The particle size distribution of water based powder-liquids for method/mixing-evaluation (batch 3) and the flours were measured by sieve analysis. A column of sieves with mesh sizes in the range of 56-1000 µm were used for the sieving. Samples of 60 g powder-liquid were sieved at an amplitude of 3 mm/g for 5 min at −15°C in
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pre-cooled sieves. The flours were sieved in batches of 200 g at ambient temperature. Each measurement were carried out in triplicate.

3.3.3 Light microscopy

The powder morphology of fat based powder-liquids and wheat flour was studied with a Diaphot, Nikon (Mellville, USA) light microscope. Pictures were taken with an attached camera (DS Fi-1, Nikon, Mellville, USA; Soft-ware: NIS-Elements D 3.0) at 40x magnification. Iso-propanol was used as disperse phase for the measurements.

Analysis of water based powder-liquids (batch 4) and semolina was performed with an inverse microscope TMS-F, Nikon (Mellville, USA), connected to a CCD-video camera. The powder-liquids were analyzed in a cold stage cabinet (Microbox, Brouwer) at −15°C, from which the microscope could be operated through arm-holes. In addition to morphology, the particle size diameter of the powders was measured by image analysis using ImageJ to calculate their size distribution. As for the fat based powder-liquids and wheat flour, semolina was dispersed in iso-propanol for the measurements. The water based powder liquids were measured without liquid and cover glass.

3.3.4 Computer tomography

The morphology of water based powder-liquids (batch 3) was measured with a Scanco µCT40 (micro computed X-ray tomograph) in a climate chamber at −20°C, at the WSL Institute for Snow and Avalanche Research SLF (Davos, Switzerland). The tomograph was equipped with a microfocus X-ray source that was operated at 75 kV acceleration voltage. For the analysis, the powder-liquid was filled into a cylindrical sample holder \((d = 10 \text{ mm})\) and placed into the µCT. The µCT was programmed to scan 800 slices per sample.

3.3.5 Cryo-scanning electron microscopy

The inner structure of water based powder-liquids was investigated by cryo-scanning electron microscopy, SEM (Zeiss Gemini 1530 FEG, ETH Zurich Microscopy center). The samples were dispersed in glycerol/sugar-solution and frozen in liquid nitrogen, before they were cut in half (freeze-etched by BAF 060 device) to measure their inner structure.
3.3.6 Moisture content analysis

The moisture content of the flours used as model powders were measured by a halogen moisture analyzer HR73 (Mettler Toledo). Hereto the moisture content in the sample is determined by using the thermogravimetric principle. The moisture content in samples of 1 g were determined by program 3 (based on weight loss per unit of time) at 130°C. The moisture content (MC) was calculated by the ratio of lost water from initial wet weight \( m_w \) and final dry weight \( m_d \), described in Eq. (3.1).

\[
MC = \frac{m_w - m_d}{m_d}
\]  

(3.1)

3.3.7 Gas pycnometer

The powder particle density of fat based powder-liquids and wheat flour was measured with an Accupyc 1330 helium pycnometer (Micromeritics Instrument Corporation, USA).

3.3.8 Ring shear tester

The flow properties and bulk density of fat based powder-liquids, wheat flour and their mixtures were measured with a ring shear tester (RST-XS, Dr. Dietmar Schulze Schüttgutmesstechnik, Wolfenbüttel, Germany). Both yield loci and wall yield loci were determined at ambient temperature of 22°C. Yield loci were determined with the shear cell type XS-Mr, which has a cross-sectional area (of the annular internal volume for the sample) of 24 cm², an internal height of 13 mm, and a sample volume of approximately 30 cm³. The applied preshear stresses were 2, 5, 10 and 20 kPa, with resulting consolidation stresses \( \sigma_1 \) between 4 and 40 kPa. Wall yield loci was determined with the shear cell type XS-WM. A wall material sample of lathed, disc-shaped brass was inserted into the cell with its surface about 4 mm below the upper edge of the cell. The samples were tested for wall normal loads \( \sigma_w \) between 0.5 kPa and 8 kPa. In addition, the yield loci of a selected powder-liquid fraction (batch 1.1) and its mixtures were determined in a cooled room at 8°C for a preshear stress of 2 kPa (corresponding to a consolidation stress of \( \sigma_1 \approx 4 \) kPa). All measurements were performed in triplicates.
3.3.9 Texture analyzer

The flow properties of water based powder-liquids (batch 3), wheat flour and their mixtures were measured with a texture analyzer (TA-XT2, Stable Micro Systems, UK) at −15°C. Flowability of the powders was determined by a uniaxial compression test, depicted in Figure 3.1a. For the test, 10 g powder sample was filled in a hollow cylinder with removable walls (Figure 3.1b) and consolidated with a force ranging from 50−250 N (Figure 3.1a). The cylinder walls were removed and the force needed for the powder to break, i.e. flow, was determined in a breaking test (Figure 3.1c). With known contact area $A = 490.6 \text{ mm}^2$ and force $F$, the consolidation stress $\sigma_1$ and unconfined yield strength $\sigma_c$ could be calculated from Eq. (3.2) to determine the flowability $f_f$ from Eq. (2.1).

$$\sigma = \frac{F}{A} \quad (3.2)$$

![Figure 3.1: Scheme of the (a) uniaxial compression test, (b) hollow cylinder with removable wall before compression, and (c) compressed powder before breaking test.](image)

3.3.10 High resolution penetrometer

A high resolution penetrometer, called SnowMicroPen, was used to analyze the texture and stability of water based powder liquids. The measurements were performed at the WSL Institute for Snow and Avalanche Research SLF (Davos, Switzerland), where the SnowMicroPen mainly is used to analyze micro structure of snow, as reported by Schneebeli et al. (1999). The SnowMicroPen, depicted in Figure 3.2a, consisted of a measuring tip (5 mm diameter with a 60° tip angle), connected to a high resolution force transducer. The force transducer was housed in a drive cone and rod of 16 mm diameter, driven by a constant speed rotary motor. The range of
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the force transducer was between 0-500 N, with a resolution of 0.01 N. For the measurement, water based powder-liquid was sieved into boxes and stored for 0-40 min prior to measurement. For each sample (filled box), the force of the SnowMicroPen to penetrate the sample was measured (Figure 3.2b). Each sample was measured four times. The penetration velocity was held at 20 mm/s, and the penetration force was acquired every 4 µm. For the results, the force to penetrate a distance of 2 cm was acquired for different storage times.

Figure 3.2: Scheme of the (a) SnowMicroPen setup and (b) sample box with water based powder-liquid after penetration test.

3.3.11 Differential scanning calorimetry

The melting behavior of fat based powder-liquids was characterized with a DSC (differential scanning calorimeter) 822e from Mettler-Toledo GmbH (Greifensee, Switzerland; software Stare). The DSC was calibrated with indium \((m = 6.169 \text{ mg}, \text{onset temperature } T_c = 156.3 - 156.9 \degree C; \text{reference sample})\). Samples of approximately 5 mg powder-liquid were measured in aluminum crucibles. In order to avoid water condensation, nitrogen was used as purge gas with a flow rate of 20 ml/min. The samples were placed in the measuring chamber at 0\degree C and heated up linearly by 5\degree C/min to a final temperature of 80\degree C. The measurements were performed in triplicate.

In addition, DSC was used to measure the glass transition temperature \(T_g\) of the DE6-water solution that was used for preparing water based powder-liquids. Approximately 5 mg solution with various DE6 concentration (10-60 wt%) were cooled directly to \(-50\degree C\) for 10 min, before it was heated up linearly with a heating rate of 5\degree C/min to a final temperature of 10\degree C. Each measurement was performed in triplicates. The glass transition temperature \(T_g\) was determined with the software Stare (Mettler-Toledo GmbH, Greifensee, Switzerland).
3.3.12 Nuclear magnetic resonance (NMR)

Solid fat content (SFC) of fat based powder-liquids was analyzed by NMR Minis-peq mq-20 (Bruker Optik GmbH, Ettlingen, Germany; Software: version 2.58 Rev. 12/NT/XP). The samples were filled in NMR tubes of 10 mm diameter (PC 0704, Bruker Optics) and conditioned in a tempered water bath for half an hour before measurement. SFC was measured by the AOCS official direct method (AOC, 1999b) and calculated using Eq. (3.3), where $S_S$ is the solid fat signal and $S_L$ the liquid fat signal (Padar, 2007). All measurements were performed five times at 8°C and 22°C, respectively.

$$SFC = \frac{S_S}{S_S + S_L}$$ (3.3)

3.4 Powder surface properties assessment

In addition to spray chilling, powders can be produced by spray drying, in which, contrary to spray chilling, moisture is removed to produce a dry solid powder. Fouling, i.e. adhesion of powder to the spray tower wall, is a major limitation for increasing the output in spray drying processes. When not correctly prevented, fouling can lead to complete blockage of the outlet and cause large negative economic consequences. It is therefore essential to understand and control the adhesive behavior of powders, such as stickiness, in order to optimize the spray drying process (Gianfrancesco et al., 2015). Skim milk powder is a typical product produced by spray drying, for which reconstitution is of high importance. Wettability is in turn one of the main parameters affecting reconstitution of powders. Powder stickiness and wettability measurements of skim milk powder (MSK), selected maltodextrins (DE17-20, DE12, DE6) and protein powder (alcalase) were performed at Nestlé Product Technology Center (Konolfingen, Switzerland), and are presented in this section.

3.4.1 Powder stickiness

Powder stickiness was assessed with a rheometer (Physica Rheolab MC 1, Anton Paar, Austria) adapted for powder testing. The adapted rheometer, depicted in Figure 3.3, consisted of a double jacketed chamber (Figure 3.3a) connected to an oil bath (Julabo, GSE 1278, Germany) and a stirrer (Figure 3.3b). The rotational speed of the stirrer and temperature of the oil bath was controlled by the software Rheoplus. Various rotational speed (50-1200 rpm) and filling degrees (20-40 %) were evaluated, but no significant difference was seen. Earlier tests on skim milk powder did however
show that a stirring rate of 120 rpm gave a good measure of the sticky point that corresponded to calculated values (Suter, 2013). Furthermore, a 30\% filling degree made sure to cover the stirrer blade fully and the temperature sensor to touch the sample in order to measure the sample temperature properly. A constant rotational speed of 120 rpm and filling degree of 30\% was thus selected to be used for the trials. The torque was measured over time with progressively increasing temperature from 45-120°C. The sticky point could thus be detected by a clear increase in torque. For each sticky point, at least three replicates were measured. To measure the stickiness with increased moisture content, samples were placed in air tight desiccators filled with Magnesium Chloride, $a_w = 0.328$, and Magnesium Nitrate, $a_w = 0.529$, respectively. In addition, some samples were dried in a vacuum oven (Heraeus vacutherm) at 55°C and 200 mBar in order to measure the sticky point at lower moisture content. Initial moisture content was measured with a halogen moisture analyzer (Mettler Toledo, Switzerland; Program 3, 105°C). Moisture content after equilibration in the desiccators and vacuum oven was measured by weight and calculated.

Figure 3.3: Image of the adapted rheometer for testing of powder stickiness, with the (a) double jacketed sample holder, (b) stirrer, and (c) test-setup.

3.4.2 Powder wettability

In this section, the methodology for the contact angle measurements and commercial wetting test is explained.

Contact angle

Powder contact angles were measured according to the methodology developed by Dupas (2013). Powder samples were prepared by spin coating of 20 wt\% powder-water solutions. About 1 mL of the solution was placed on a glass cover slip (Menzel-Gläser, 24×40 mm, Germany) and run in the spin coater (Laurell Technologies Corporation,
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US), depicted in Figure 3.4a. A dynamic program was used with increasing rotational speed (500 rpm for 10 s, 4000 rpm for 30 s). The glass micro slide was let to rest for at least one day before further measurement. A 1 µL water droplet was placed on each coated glass dish by a syringe (Figure 3.4b,c) and analyzed with a Krüss Drop Shape Analyzer DSA30 (Germany). Uncoated (pure) glass dishes were used as reference. The contact angle $\Theta$ (Figure 3.4d) was filmed and evaluated over time with the DSA30 software.

Figure 3.4: Scheme of the contact angle measurement with (a) spin coater, (b) drop shape analyzer, (c) drop inserted by the syringe and (d) contact angle $\Theta$ of a water droplet on a pure glass surface.

Commercial wettability test

For comparison with an alternative method, a commercial wetting test already used in industry was performed. The test consists of pouring 25 g of powder into 150 mL water and to take the time the powder needs to wet, i.e. sink, or alternatively estimate how much powder is still un-wetted after 120 s. Figure 3.5 illustrates the wetting test.

3.5 Mixing and sampling

Several mixing trials were performed in order to evaluate the powder-liquid mixing method itself, as well as to compare it with other mixing procedures. Due to the different requirements needed for fat and water based systems, different mixing equipment was used, explained further in the following section.
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Reference mixtures for NIRS calibration

Reference mixtures of various concentrations fat based powder-liquids (0–100 wt%) and wheat flour were prepared in a home-built free-fall tumble mixer, demonstrated in Figure 3.6, for the near infrared spectrometry (NIRS) calibration. The powder-liquid was sieved (for decompaction reasons) into the beaker on top of the wheat flour in total batches of 50 g. The beaker was mounted on the aluminum frame of the tumble mixer. A tumbling movement of the beaker around the axis of the shaft was induced by rotation of the shaft leads at 30 rpm. The applied mixing time of 15 min was split into two parts. After 10 min the mixture was manually mixed with a spoon to destroy eventual lumps, prior to the last 5 min of mixing in the tumble mixer. All mixtures were prepared at ambient temperature of 22°C.

Reference mixtures of water based powder-liquid and wheat flour/semolina were prepared by manually mixing the powders in a 500 ml plastic beaker at −15°C. The powder-liquids were sieved onto the flour prior to mixing and the mixtures were prepared in batches of 50 g with various powder-liquid concentration (0-100 wt%).

Method evaluation (powder-liquid mixing) of fat based systems

Mixtures of fat based powder-liquids and wheat flour were prepared in a DFML 20 powder-speedmixer (Bühler AG, Uzwil, Switzerland) with a filling volume of 20 L. Fractions of 5, 10, 15, and 20 wt% sieved powder-liquid (for decompaction reasons) was given into the wheat flour. Each mixture was produced only once for two powder-liquid fractions (PL \( x_{50,3} \)). The powder mixtures were analyzed by near infrared
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![Figure 3.6: Colored fat based powder-liquid and wheat flour in a plastic beaker mounted on a home-built free fall tumble mixer.](image)

spectroscopy (NIRS) and colorimetry for different mixing times (0-1800 s). At every selected mixing time interval, 4 samples of 50 g each were systematically taken from the mixture (Figure 3.7a) with a thief probe. Each sample was measured five times (Figure 3.7b), resulting in $k = 20$ measurements, of 16% data-inaccuracy that was calculated by using Eq. (3.4) (Squires, 2001). A detailed sampling scheme is given in Figure 3.7.

$$\frac{\Delta s}{s} = \frac{1}{\sqrt{2(k - 1)}}$$ (3.4)

**Mixing-procedure evaluation (powder-liquid vs. sprayed liquid) of fat based systems**

The mixtures were prepared in a MRMA-1000 paddle mixer (Bühler AG, Uzwil, Switzerland) in batches of 180 kg by (i) mixing 5 wt% sieved fat based powder-liquid (for decompaction reasons, from palm stearin fat) or (ii) spraying 5 wt% sunflower oil into biscuit flour, respectively. The mixtures were produced in triplicates for each mixing procedure. The mixing quality was measured by colorimetry for different mixing times (0 – 300 s). At every selected mixing time interval, 10 samples of 10 g each were systematically taken (Figure 3.8a and Figure 3.8b) with a thief probe, measured three times (Figure 3.8c) and thus resulting in $k = 30$ measurements, of 13% data-inaccuracy (Eq. 3.4). A detailed sampling scheme is given in Figure 3.8.
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Figure 3.7: Judication of (a) sampling positions in the DFML 20 speedmixer used for evaluating the quantification methods and (b) measuring domains for each sub-sample for NIR spectroscopy and colorimetry, respectively. Real dimensions are not taken into account.

Figure 3.8: Scheme of (a) sampling positions in the MRMA-1000 paddle mixer seen from above and (b) from the side, and (c) measure points of each sample with the colorimeter. Scale is not taken into account.
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Method evaluation (powder-liquid mixing) of water based systems

The following powder-liquid mixtures were prepared by manually mixing the produced water based powder-liquids with wheat flour in a 500 ml plastic beaker at $-15^\circ$C. Mixtures for flow measurements and studies on the variation of the powder-liquid concentration (5−20 wt%) were made in batches of 200 g. All powder-liquid mixtures were prepared in triplicates. The mixture were divided in four samples of 50 g each that were measured at five locations by NIRS and moisture analysis, giving in total $k = 20$ measurements per mixture and mixing time (16 % data-inaccuracy, Eq. 3.4).

Mixing-procedure evaluation (powder-liquid vs. sprayed liquid) of water based systems

The mixing of water based powder-liquids with wheat flour was performed in a Ploughshare Laboratory Mixer L5 (Lödige Process Technology, Germany), demonstrated in Figure 3.9a. The mixtures were prepared in batches of 1.5 kg (rotational speed of 260 rpm at $-10^\circ$C), and compared to mixtures that were produced by directly spraying the 10 wt% DE6-water solution onto the flour with a pressure nozzle (1 bar at ambient temperature). In addition, mixtures of various concentration (5-20 wt%) water based powder-liquid and sprayed DE6-water solution were prepared in the Lödige mixer with semolina as model powder, at a rotational speed of 60 rpm in $-15^\circ$C. The corresponding amount DE6-solution were sprayed into the mixture at 0.5 bar at ambient temperature. All mixtures were prepared in triplicates. For analysis, samples of 50 g were systematically taken at each mixing time according to the sample scheme in Figure 3.9b, and analyzed by NIRS at five locations for each sample, giving in total $k = 25$ measurements (14 % data-inaccuracy, Eq. 3.4).

3.6 Evaluation of mixing quality

The fat and water based powder-liquid mixtures were evaluated by near infrared spectroscopy (NIRS), colorimetry and moisture analysis, described in the following section.

3.6.1 Near-infrared spectroscopy (NIRS)

In order to evaluate the mixing quality by NIRS, it had to be calibrated with reference mixtures of known powder-liquid concentration. The NIRS calibration and analysis of mixing quality are described in the following section.
Figure 3.9: Scheme of (a) the Lödige Ploughshare Laboratory Mixer L5, and (b) sampling positions in the mixer for each mixture and time occasion.

**NIRS calibration**

The Fourier Transformation Near Infrared spectrometer NIRFlex N-500 (Büchi, Flawil, Switzerland) was calibrated with minimum 60 reference mixtures, containing 0−100 wt% fat and water based powder-liquid in wheat flour and semolina, respectively. The reference mixtures were prepared as described in the Mixing and sampling-section. For each reference mixture, the whole mixture was scanned with the NIR spectrometer three times, providing in total minimum 180 spectra for the calibration. With the NIRCAl software, the spectra were divided into 2/3 calibration set and 1/3 validation set. Using chemometrics and principal component analysis, partial least squares (PLS) regression was applied to calculate statistical data to validate the calibration.

To further evaluate the calibrations, four reference samples of each mixture were re-measured to test the accuracy of the calibration. These samples were measured five times each that gave in total $k = 20$ measurements, for which the average concentration and standard deviations were calculated.

**NIRS analysis**

Mixing quality of powder-liquid/powder and sprayed liquid/powder mixtures was analyzed with a Fourier Transformation Near Infrared spectrometer NIRFlex N-500 of Büchi (Flawil, Switzerland) using NIRCAl software suite version 1.4. A Büchi solids device with a rotating cylinder was used for diffuse reflection measurements at ambient temperature (22°C). Recorded wave numbers were 12 500 cm$^{-1}$ to 4000 cm$^{-1}$ with a resolution of 8 cm$^{-1}$, and an absolute wave number accuracy of ±2 cm$^{-1}$.
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The sample dimensions of the NIRFlex Solids petri dish holder was 100 mm with an illumination spot diameter of $D = 9$ mm, giving an approximated sample area of $A = 64$ mm$^2$. The mixing quality was evaluated as a result of the variation coefficient (CoV) given by Eq. (2.6).

For a better comparison of NIRS and colorimetry measurements of fat based powder-liquids, the NIRS results were normalized by dividing CoV with the estimated sample area $A = 64$ mm$^2$ (Eq. 3.5).

$$CoV_N = \frac{CoV}{A}$$

3.6.2 Colorimetry

Mixing quality of fat based powder-liquid/powder and sprayed liquid/powder mixtures were analyzed at ambient temperature (22°C) with a portable tri-stimulus colorimeter (Chroma-Meter CR-300, Minolta AG, Dietikon, Switzerland) with a measuring diameter of $D = 8$ mm, corresponding to a measuring area of $A = 50$ mm$^2$. The CIE (Commission Internationale de l’ Eclairage) $L^*, a^*, b^*$ colorimetry system (Schuck et al., 2012) was used for color determination. $L^*$ indicates lightness, and its values range from 0 (an ideal black object) to 100 (an ideal white object). Positive $a^*$ values indicate red direction, negative $a^*$ value is the green direction, positive $b^*$ values are the yellow direction, and negative $b^*$ values are the blue direction (Argyri et al., 2014). The instrument was calibrated by using a white plate with coordinates $L^* = 96.98$, $a^* = -0.02$ and $b^* = 1.93$ prior to each measurement trial. The mixing quality was evaluated as a result of the variation coefficient (CoV) (Eq. 2.6) from the $a^*$ value measurements.

For a better comparison of NIRS and colorimeter measurements of the fat based powder-liquid mixtures, the colorimeter results were normalized by dividing CoV with the sample area $A = 50$ mm$^2$ (Eq. 3.5).

3.6.3 Moisture content analysis

Mixing quality of water based powder-liquid mixtures was, in addition to NIRS, analyzed by a halogen moisture analyzer HR73 (Mettler Toledo). Hereto the moisture content in the mixtures are determined by using the thermogravimetric principle. The moisture content in samples of 1 g were determined by program 3 (based on weight loss per unit of time) at 130°C. The moisture content (MC) was calculated by Eq. 3.1.
3.7 Testing of model products

Pasta model products were produced to see how the mixing procedure influence final product properties, comparing the powder-liquid mixing with conventional mixing techniques. Mechanical properties and cooking loss were measured on pasta tablets produced as described below.

3.7.1 Mechanical properties

Mechanical properties of pasta model products were measured by a Zwick/Roell universal testing machine (Zwick Z010, Zwick GmbH & Co. KG, Ulm, Germany) with testXpert software. Pasta tablets were prepared by pressing water based powder-liquid/semolina and sprayed DE6-water solution/semolina mixtures into a tablet. For each sample, 5 g of the mixture was filled in a hollow cylinder (20 mm diameter) and compressed with a punch by applying a force of 3 kN (Figure 3.10). Prior to further testing, the tablets were removed from the cylinder and let to rest for 7-10 min. To test the stability, the tablets were placed on a flat table and compressed by a punch with an increasing force until the breaking point of the tablet was reached. The tests were performed on mixtures with 5-20 wt% added powder liquid vs. sprayed liquid that was mixed with semolina for 10 min to have a good mixing quality. All mixtures were let to rest 16 h at ambient temperature (22°C) in order to have a comparable state of the mixtures. For each mixture, 20 tests were performed from which the average breaking strength $F$ and standard deviation were calculated, in order to compare the results from the two mixing procedures.

![Figure 3.10: Schematic illustration of the mechanical test performed on pasta model products.](image)

3.7.2 Cooking loss and water uptake

Pasta tablets were produced as described above from semolina mixtures with 10 wt% added powder-liquid/sprayed liquid. About 1 g semolina mixture was used for each
tablet, of which seven tablets were produced and tested for each mixture. Cooking loss and water uptake were measured on the tablets the day after production. The tablets were boiled for 8 min and after cooling, the mass \( m_w \) of the cooked tablets were weighed and the dry matter \( m_d \) was determined after drying. Cooking loss (CL) and water uptake (WU) were calculated according to Eq. (3.6) and (3.7) (Kratzer, 2007).

\[
CL = \frac{m_{d,uncooked} - m_{d,cooked}}{m_{d,uncooked}} \cdot 100
\]  

\[
WU = \frac{m_{m,cooked} - m_{d,cooked}}{m_{d,cooked}} \cdot 100
\]

3.8 Water distribution in powder systems

For better understanding of what happens in the powder-liquid mixtures during melting, sorption isotherms of semolina was assessed at low temperatures, and the distribution of water based powder-liquid in model powders was analyzed by microwave resonance technique measurements.

3.8.1 Sorption isotherms

In literature, sorption isotherms on durum wheat semolina are already reported, e.g., for investigation of the influence of different temperature (Pollatos et al., 2013) and various particle size (Murrieta-Pazos et al., 2014). These works, however, were performed at a temperature of 25°C or higher. To fill the knowledge gap on how semolina behaves at lower temperatures, a gravimetric method was used to determine the sorption behavior of semolina at temperatures between 4-22°C. Completely dehumidified semolina in the size range 250-355 µm were placed in tared sample cups and weighed (about 1.2 g). The samples were placed in sealed vessels with over-saturated salt solutions (LiCl, MgCl2, K2CO3, Mg(NO3)2, NaCl, KCl, K2SO4) of various water activity \( a_w \) and let to equilibrate for three days at each temperature. The measurements were performed in triplicate.

3.8.2 Microwave resonance technique

Resonators using microwave (MW) resonance frequencies can be a good tool to assess moisture and density. MW sensors are based on the principle that an electromagnetic
(EM) wave propagating in a material will be affected by the fundamental EM constants (permittivity and permeability). Variations in the physical parameters change these constants and can be detected using this kind of sensor (Nyfors and Vainikainen, 1994). Moist materials can be seen as a dielectric medium with the complex dielectric constant (permittivity) \( \varepsilon \) described by Eq. (3.8), with \( \varepsilon_0 \) being the permittivity of vacuum, and \( \varepsilon_r \) describing the real and imaginary part of the permittivity, respectively.

\[
\varepsilon = \varepsilon_0 (\varepsilon_r' - j\varepsilon_r'')
\]

In the MW region, the EM wave used for the measurement can penetrate deep into the material, which allows for measurement of the whole sample and not only the surface moisture. MW measurements are also relatively independent from salt and mineral fractions due to that the ionic conductivity of salts dissolved in water does not have an influence in this frequency range (Hauschild, 2005). In other areas such as geophysical exploration or biomedical imaging, MW sensors are commonly used, and previous attempts have been made to monitor water distribution in soils (Zhang et al., 2011).

Water in liquid state has a permittivity value of \( \varepsilon_r \approx 80 \) below 5 GHz, while dry solids have a much lower permittivity (\( \varepsilon_r < 10 \)). Moreover, water molecules in ice form changes completely its EM behavior with an \( \varepsilon_r \approx 3 \) and very low losses at MW frequency regime (Nyfors and Vainikainen, 1994). These facts in combination with the low cost of MW sensors compared with other sensing techniques such as magnetic resonance imaging (MRI), make them a perfect candidate for this type of application. In this study, microwave resonant technique (MWRT) was used to analyze the melting of powder-liquid (PL) mixtures.

**Preparation of powder-liquid mixtures**

PL mixtures were prepared by mixing 5 wt% and 20 wt% powder-liquid (\( \leq 125 \mu m \)) with semolina (size fraction 250-355 \( \mu m \)) and glass powders (70-110 \( \mu m \)), respectively. The PL samples were prepared in cylindrical sample cups (height: 7 cm, diameter: 2 cm) at \(-15^\circ C\) and stored on dry ice until the MWRT analysis. Three replica of each sample were prepared to test the robustness of the measurement technique.

**Microwave resonant technique measurements**

An MWRT previously introduced in Nohlert et al. (2014) was used for the study. The new technique is very similar to the well-known cavity perturbation measure-
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In this case, information from multiple resonant modes is integrated to provide three-dimensional spatial resolution. The PL melting process is dynamically monitored using the MWRT. The cold sample is introduced in a cylindrical cavity resonator (Balanis, 1989) and the resonant frequencies and temperature of the sample are measured at regular time intervals until the sample reaches room temperature. The measurement setup is depicted in Figure 3.11. It consists of a cylindrical cavity resonator, an Agilent E8361A Vector Network Analyzer (VNA) and an optical fiber thermometer consisting of a Reflex signal conditioner and T1 sensor probe from Neoptix. The resonant frequencies of the cavity are extracted from the measured $S$ parameters using a signal processing identification algorithm (McKelvey et al., 1996; Nohlert et al., 2014). The optical fiber thermometer allows to measure the temperature of the sample without disturbing the EM field distribution inside the resonator.

Figure 3.11: Image of the MWRT system during measurement of the melting of a PL mixture (cylindrical cavity resonator: $r = 51$ mm and $h = 90$ mm, sample: $r = 13$ mm and $h = 70$ mm.)
The three dimensional permittivity distribution inside the resonator cavity can be estimated with the following procedure (Nohlert et al., 2014). The cavity volume is divided into \(N\) different regions, and the permittivity of each region is obtained from the variation of the resonant frequencies of \(M\) different modes by solving an overdetermined system of equations \((M > N)\):

\[
\Delta \omega = S \Delta \epsilon
\]

where \(\Delta \omega_m = \omega_{m, \text{sample}} - \omega_{m, \text{ref}}/\omega_{m, \text{ref}}\) is the variation in the complex resonant frequency of the \(m\)-th mode of the cavity with respect to the empty cavity \((\omega_{m, \text{ref}})\), \(\Delta \epsilon_n = \epsilon_n - \epsilon_{n, \text{ref}}\) is the variation in the complex permittivity of the \(n\)-th region in the cavity, and \(S\) is an \(M\) by \(N\) sensitivity matrix where each element corresponds to:

\[
S_{mn} = -\int_{V_n} |\vec{E}_{m, \text{ref}}|^2 dV_n \frac{2}{V} \int_V |\vec{E}_{m, \text{ref}}|^2 dV
\]

which is the ratio of the electric energy in the \(n\)-th region and twice the electric energy stored in the cavity for the \(m\)-th resonant mode, where \(\vec{E}_m\) is the electric field distribution of the \(m\)-th resonant mode.

This procedure will provide with an estimation of the effective permittivity in the \(n\)-th region of the cavity, since several approximations are introduced in the development. First, the permittivity is assumed to be constant with frequency. Second, Eq. 3.10 is an approximate formula that assumes that the field distribution in the cavity is approximately the same for the perturbed and unperturbed cavity. These approximations greatly simplifies the reconstruction procedure and are sufficient to provide qualitative information about the permittivity distribution in the cavity. For a more detailed derivation of the perturbation theory and the limits of the approximations the reader is referred to Harrington (1961).

Prior to measurement, the PL samples were kept cold in a polystyrene box filled with dry ice. The sample was then introduced in the resonator cavity and the measurement was run for a total of 90 min to allow the sample to reach room temperature. Measurements were performed every 30 s. For all measurements, a total of \(M = 8\) resonant modes were used and the cavity was divided in \(N = 2\) regions.
4 Results and discussion

The following chapter presents the results of the powder characterization, surface properties assessment, mixing trials and mechanical testing. For each section, the results are presented for the fat and water based systems separately.

4.1 Powder characteristics

Powder characteristics, such as particle size, shape and density, influence the flow properties of powder and powder-liquids, as well as their mixture-homogeneity. In the following section, the characteristics of the fat and water based powder-liquids, model powders and their mixtures are presented.

4.1.1 Fat based powder-liquids and model powders

In this subsection the characteristics of the fat based powder-liquids and the model powders used for the fat based systems are presented.

Particle size distribution and morphology (fat systems)

Laser diffraction studies on the particle size distribution revealed rather broad multimodal size distributions (1-200 µm) of the flours used as model powder for the fat based system (Figure 4.1, Table 4.1). Wheat flour type 400 showed a bimodal size distribution with a median particle diameter $x_{50,3}$ of 43 µm and a span, $\frac{x_{90,3} - x_{10,3}}{x_{50,3}}$, of 2.5. Biscuit flour type 10 showed a multimodal size distribution of a median particle diameter $x_{50,3}$ of 23 µm with a span of 4.1. In comparison, the fat based powder-liquids, manufactured by spray chilling of palm stearin fat, had a rather monodispers and fairly narrow distribution. While their span stayed almost constant, the particle size differed strongly with the spray process parameters used (Table 4.1), with median particle diameters $x_{50,3}$ of 25 µm, 53 µm and 132 µm. An increase in the liquid feed rate increased the particle size (cp. batch 1.2 vs. 2), whereas, an increase in the atomizing pressure caused its decrease (cp. batch 1.1 vs. 1.2). Along with increasing...
4 Results and discussion

Table 4.1: Powder characteristics, feed rate \( \dot{m} \), atomizing pressure \( P \), median particle diameter \( x_{50,3} \), span, particle \( \rho_p \) and bulk \( \rho_b \) density, in respect to process parameters in spray chilling process for powder-liquids. (* Data not available.)

<table>
<thead>
<tr>
<th>Powder-liquid from palm stearin fat</th>
<th>( \dot{m} ) [mL/s]</th>
<th>( P ) [bar]</th>
<th>( x_{50,3} ) [( \mu m )]</th>
<th>span [-]</th>
<th>( \rho_p ) [kg/m(^3)]</th>
<th>( \rho_b ) [kg/m(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1.1</td>
<td>2.3</td>
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<td>25</td>
<td>1.9</td>
<td>1040</td>
<td>300</td>
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<td>4.1</td>
<td>53</td>
<td>1.9</td>
<td>1010</td>
<td>370</td>
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<td>1.4</td>
<td>520</td>
<td>*</td>
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<td>Flour</td>
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<tr>
<td>Wheat 400</td>
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<td>-</td>
<td>43</td>
<td>2.5</td>
<td>1490</td>
<td>680</td>
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<tr>
<td>Biscuit 10</td>
<td>-</td>
<td>-</td>
<td>23</td>
<td>4.1</td>
<td>*</td>
<td>620</td>
</tr>
</tbody>
</table>

particle size, a change in particle- and bulk density was seen from gas pycnometer and ring shear tests (Table 4.1), with somewhat lower particle density and increasing bulk density with the larger size fraction. These observations go along with analogue studies given in literature (Ilić et al., 2009), where the parameter-influence on the spray chilling process was studied in more detail.

Figure 4.1: Size distribution of the (a) flours and (b) fat based powder-liquids for two mixing trials.

In Figure 4.2 light microscopy images of the flours and fat based powder-liquids are presented that demonstrate their morphology. The powder-liquids were in general more roundly shaped; while wheat flour showed a more irregular and biscuit flour again a more round particle structure.
Flow properties of single powders (fat systems)

In Figure 4.3, the flow properties acquired with the ring shear tester are depicted for wheat flour and two fat based powder-liquid fractions (I/II). Wheat flour had a flowability, \( ff_c \) value, ranging between 3.3 to 6.8 for the tested consolidation stresses \( (\sigma_1 = 4 \text{ kPa} - 40 \text{ kPa}) \), which according to Schulze is classified as cohesive to easy-flowing. The \( ff_c \) values of the two powder-liquid fractions were clearly lower. Size fraction I \( (x_{50,3} = 25 \mu m) \) had a flowability value of \( ff_c = 1.1 - 1.2 \) and size fraction II \( (x_{50,3} = 53 \mu m) \) of \( ff_c = 1.5 - 1.8 \). Thus, both can be classified as very cohesive. The powder-liquid fraction I with the smaller particle size showed a rather lower flowability. This is expected to come from the increasing impact of Van der Waals forces, due to the larger volume specific surface area of the smaller particles (Schulze, 2008). Figure 4.3(a) shows an almost linear increase in flowability of the three powders with increasing consolidation stress \( \sigma_1 \), in which the wheat flour exhibited the highest flowability. Furthermore, the difference in flowability between the powders, increased with increasing consolidation stress \( \sigma_1 \).

In Figure 4.3(b), the cohesion \( \tau_c \), depending from the consolidation stress \( \sigma_1 \) is presented. Cohesion is defined as the shear stress of the powder at zero normal stress (Fitzpatrick et al., 2004), and can be related to the stickiness of powders and the force with which two particles hold together (Adhikari et al., 2001). Of the tested
Figure 4.3: Flow properties and flowability $f_f$ of the wheat flour and the two powder-liquid (PL) fractions: (a) instantaneous flow function, (b) effective angle of internal friction $\phi_e$ (c) cohesion $\tau_c$ and (d) wall friction angle $\phi_w$ (n=3).
powders, the cohesion was clearly lower for single wheat flour, $\tau_c = 209 \text{ Pa} - 1289 \text{ Pa}$, when compared with the powder-liquid fractions. Furthermore, it was higher for the powder-liquid with the smaller size fraction (I), $\tau_c = 967 \text{ Pa} - 8686 \text{ Pa}$, compared to the powder-liquid with the larger size fraction (II), $\tau_c = 596 \text{ Pa} - 5292 \text{ Pa}$. As for the flowability, the cohesion increased linearly with increasing consolidation stress $\sigma_1$.

In Figure 4.3(c), the effective angle of internal friction $\phi_e$ of the powders is presented. It is related to a characteristic shear to normal stress ratio at which the powder will start flowing. Together with the wall friction angle $\phi_x$, it can be used for designing processing equipment and apparatuses (e.g. silos). In general, the larger the friction angle the steeper the silo walls need to be, ensuring an optimal powder flow. The effective angle of friction decreased for all powders with the consolidation stress $\sigma_1$, before it approached a plateau. Wheat flour had an effective angle of friction in the range of $\phi_e = 40.7^\circ - 35.2^\circ$, which was lower compared to both powder-liquid fractions. The powder-liquid fraction with the smaller particle size had a higher effective angle of friction, $\phi_e = 78.7^\circ - 61.9^\circ$, in comparison to its larger equivalent, $\phi_e = 58.4^\circ - 50.9^\circ$.

Figure 4.3(d) presents the wall friction angle $\phi_x$. Similar to the effective angle of internal friction in (c) it is related to a characteristic wall shear to normal stress ratio needed for the material to slip on a certain wall material. Once again, the wall friction was lower for the wheat flour, with $\phi_x = 20.9^\circ - 11.8^\circ$, in comparison to both powder-liquids. In addition for the wheat flour, the wall friction decreased with the normal stress $\sigma_1$ before it finally planed out. Whereas, for both powder-liquids it decreased only slightly and not that well defined. Moreover, $\phi_x$ was higher for the powder-liquid with the smaller size fraction (I), $\phi_x = 34.2^\circ - 32.2^\circ$, when compared to the powder-liquid with the larger size fraction (II), $\phi_x = 22.2^\circ - 17.7^\circ$.

The data analysis for flowability, cohesion, effective angle of internal friction and wall friction angle were consistent to each other. Thus, in the next section, only data of flowability, cohesion and effective angle of internal friction are presented, as they are of major interest for the powder flow processing.

**Flow properties of powder mixtures (fat systems)**

In Figure 4.4, the flow properties of fat based powder-liquids mixed with wheat flour at various consolidation stresses in the range of $\sigma_1 = 4 \text{kPa} - 40 \text{kPa}$ are presented. A summary of the corresponding flowability, cohesion and effective angle of internal friction values are given in Table 4.2.

Figure 4.4(a) shows the cohesion of the powder-liquid size fraction I mixtures. The cohesion was lower for all mixtures than for the single powder-liquids, but higher than for the single wheat flour. Furthermore, it increased among the mixtures with increasing concentration of powder-liquid. Consequently, the opposite trend was seen
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Figure 4.4: Cohesion $\tau_c$ and effective angle of (internal) friction $\phi_e$ of the two powder-liquid (PL) fractions, single and mixed with wheat flour (5 wt% to 15 wt%), in relation to the single wheat flour: (a) cohesion of PL size fraction I, (b) cohesion of PL size fraction II, (c) effective angle of internal friction of PL size fraction I, and (d) effective angle of internal friction of PL size fraction II.
Table 4.2: Flowability $f_r$, cohesion $\tau_c$ and effective angle of (internal) friction $\phi_e$ of the wheat flour and two fat based powder-liquid (PL) fractions, single and in mixtures, where the fraction of powder-liquid in wheat flour is denoted. The values correspond to the tested consolidation stresses $\sigma_1 = 4 \text{kPa} - 40 \text{kPa}$.

<table>
<thead>
<tr>
<th></th>
<th>$f_r$ [-]</th>
<th>$\tau_c$ [Pa]</th>
<th>$\phi_e$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat flour</td>
<td>3.3 - 6.8</td>
<td>209 - 1289</td>
<td>40.7 - 35.2</td>
</tr>
<tr>
<td>PL I – 25 μm</td>
<td>1.1 - 1.2</td>
<td>967 - 8686</td>
<td>78.7 - 61.9</td>
</tr>
<tr>
<td>5 wt%</td>
<td>2.4 - 3.9</td>
<td>391 - 2210</td>
<td>45.8 - 40.4</td>
</tr>
<tr>
<td>10 wt%</td>
<td>2.0 - 3.3</td>
<td>455 - 2631</td>
<td>50.4 - 42.3</td>
</tr>
<tr>
<td>15 wt%</td>
<td>2.0 - 2.7</td>
<td>465 - 3376</td>
<td>50.4 - 43.9</td>
</tr>
<tr>
<td>PL II – 53 μm</td>
<td>1.5 - 1.8</td>
<td>596 - 5292</td>
<td>58.4 - 50.9</td>
</tr>
<tr>
<td>5 wt%</td>
<td>2.9 - 5.6</td>
<td>320 - 1535</td>
<td>42.4 - 37.7</td>
</tr>
<tr>
<td>10 wt%</td>
<td>2.7 - 4.4</td>
<td>340 - 2032</td>
<td>43.5 - 38.1</td>
</tr>
<tr>
<td>15 wt%</td>
<td>2.2 - 3.2</td>
<td>416 - 2730</td>
<td>47.5 - 42.0</td>
</tr>
</tbody>
</table>

for the flowability, presented in Table 4.2. The mixtures had all a flowability between that of the single powder-liquids and wheat flour, which decreased with increasing powder-liquid concentration. All fraction I mixtures were classified as cohesive. In Figure 4.4(b), the cohesion of the size fraction II mixtures is presented. In comparison to fraction I, their cohesion was consistently lower, showing that the flow properties of the single powder-liquids influenced also the flow behavior of the mixtures. As seen before for fraction I, the cohesion of the fraction II mixtures increased with increasing concentration of powder-liquid. The opposite trend was seen for the flowability, which decreased with increasing concentration of powder-liquid. In comparison to the fraction I mixtures, they were classified as cohesive to easy-flowing.

Figure 4.4(c) shows the effective angle of internal friction of the powder-liquid size fraction I mixtures in relation to the single powders. For all fraction I mixtures the effective angle of internal friction was clearly lower than for the single powder-liquids, and higher than for the single wheat flour. In addition, the effective angle of internal friction of the mixtures increased with increasing concentration of powder-liquid. In Figure 4.4(d), the effective angle of internal friction of the powder-liquid size fraction II mixtures is presented. As for cohesion, they showed a lower effective angle of internal friction than corresponding fraction I mixtures. All fraction II mixtures also had a lower effective angle of internal friction compared to the single powder-liquids, but higher than that of the single wheat flour. In general, similar trends were seen for fraction II and fraction I. The effective angle of internal friction increased with increasing concentration of powder-liquid.
These results showed that both flowability, cohesion and effective angle of internal friction varied with the concentration of powder-liquid in the mixtures. Depending on the particle size of the powder-liquid, the cohesion and effective angle of internal friction were consistently higher and the flowability lower for the size fraction with lower particle sizes. The impact of the Van der Waals forces, acting between the particles, increases with smaller particle sizes due to larger specific surface area. This trend was equally seen in the single powders as well as for the mixtures.

**Flow properties at various temperatures (fat systems)**

In Figure 4.5, the flow measurements of the powder-liquid \( x_{50,3} = 25 \, \mu m \) size fraction mixtures (batch 1.1) carried out at low temperature of 8°C compared with those at 22°C, are presented. Figure 4.5(a) demonstrates that the single powder-liquids had a clearly higher flowability at 8°C when compared to 22°C. Different to this, the wheat flour showed no difference in flowability for these two temperatures. Concerning the powder mixtures, it was as in the previous section seen that the flowability decreased with increasing concentration of powder-liquid. In addition, all mixtures had a clearly higher flowability at 8°C compared to 22°C.

![Flowability and Cohesion Graph](image)

**Figure 4.5:** Depiction of (a) flowability \( ff \) and (b) cohesion \( \tau_c \) of the fat based powder-liquid (PL) size fraction I \( (x_{50,3} = 25 \, \mu m) \) mixed into wheat flour, measured at 8°C and 22°C, respectively. The average measured value is shown above each column.

In Figure 4.5(b), the cohesion of the powder mixtures is presented. As expected, the cohesion of the powder-liquids was lower at 8°C than at 22°C. No clear difference was seen at these temperatures in cohesion for the wheat flour, as also reflected by the flowability. All mixtures showed as well lower cohesion at 8°C compared with 22°C.
These results show that the influence of temperature on the flow behavior of fat based powder-liquids and powder-liquid mixtures, is an important parameter during processing, storage and handling of such food powders. In general, temperature fluctuations cannot be neglected.

**Thermal properties and solid fat content of fat based powder-liquids**

Due to the differences in flowability and cohesion of the single powder-liquids at 8°C and 22°C, a more detailed characterization of the thermal properties and solid fat content (SFC) was detected by DSC and NMR, respectively. In Figure 4.6(a) the DSC measurements of the fraction I powder-liquids upon temperature increase (0 – 80°C) is presented, in which the peak indicates the melting temperature range of the powder-liquids from 30°C to 60°C, with a peak maximum at 58°C. Consequently, the melting range was clearly higher than for the tested temperatures of 8°C and 22°C. Hence, the difference in flowability and cohesion that was observed during the temperature studies of powder-liquid fraction I (section 3.4) might be better explained by differences of solid/liquid fat content.

![Figure 4.6: (a) DSC curve showing the melting behavior (n=3) and (b) NMR measurement showing the solid fat content (SFC, n=5) of the powder-liquid size fraction I with $x_{50,3} = 25 \mu m$ at 8°C and 22°C, respectively.](image)

For this purpose NMR studies were done. Figure 4.6(b) summarizes the results of these related NMR studies, showing the solid fat content in the powder-liquid at 8°C and 22°C, respectively. There is a rather small but clear difference in solid fat content at the two temperatures. At 8°C the solid fat content was 80±0.3% compared to 78±0.2% at 22°C. It is expected that the difference of 2% in solid fat content makes the powder-liquids at 22°C more cohesive, and thus changes the flow behavior clearly. Furthermore, these results showed that NMR measurements allow for higher accuracy in determining the solid/liquid fat content in comparison to the DSC measurement.
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Additionally, with DSC, selected deviations in the baseline reconstruction may lead to larger differences of the solid/liquid fat content than measured by NMR.

4.1.2 Water based powder-liquids and model powders

The following subsection presents the particle size distribution, morphology and flow properties of the water based powder-liquid systems.

Particle size distribution and morphology (water systems)

The particle size distribution calculated from sieve analysis for the water based powder-liquid produced for method/mixing evaluation (batch 3 in Table 3.3) and wheat flour is presented in Figure 4.7. The volume based median of the powder-liquid $x_{50,3} = 360 \mu m$, was about seven times larger than that of the wheat flour, with $x_{50,3} = 50 \mu m$. As can be seen, the span of the powder-liquids (1.5) was wider than that of the wheat flour (1.0). This is directly coming from the spray chilling parameters in use. In general, lower atomizing pressures and higher volumetric flow rates cause powder-liquids of bigger particle size and span.

![Figure 4.7: Particle size distribution of water based powder-liquid (batch 3) and wheat flour, assessed by sieve analysis.](image)

The particle size distributions of water based powder-liquids (batch 4 in Table 3.3) and semolina, calculated by (a) number and (b) volume from light microscopy measurements, are presented in Figure 4.8. Number based calculations of the size distribution revealed a median based particle diameter of $x_{50,0} = 55 \mu m$ for the powder-liquid and $x_{50,0} = 24 \mu m$ for the semolina. The powder-liquids had a unimodal size distribution with a span of 1.4 and semolina a bimodal distribution with a span of 2.6. Conversion of the number based- to a volume based distribution gave, as expected and seen in
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Figure 4.8, a small increase of the size (shift of the curves to the right). The volume based calculations revealed thus a median based particle diameter of $x_{50.3} = 160 \mu m$ for the powder-liquid and $x_{50.3} = 230 \mu m$ for the semolina. The corresponding span was 1.4 (powder-liquid) and 0.7 (semolina), respectively. Comparing these results to the powder-liquids in Figure 4.7, it can be seen that the spray chilling parameters had a high influence on the size distribution also for water based powder-liquids, where a higher atomizing pressure and lower feed rate gave powder-liquids with smaller particle size and a somewhat more narrow span.

Figure 4.8: Particle size distribution of water based powder-liquid (batch 4) and semolina from microscopy measurements, calculated by (a) number and (b) volume.

To validate the comparison of particle size distributions between the various analysis methods, a direct comparison of laser diffraction, microscopy measurements and sieve analysis was made on semolina, presented in Figure 4.9. Comparing the results from laser diffraction and microscopy on a number basis (Figure 4.9a), almost no correlation could be seen between the methods. However, on a volume basis (Figure 4.9b), the comparison between laser diffraction and microscopy, as well as with sieve analysis, was much better. As expected, more information could be seen from laser diffraction measurements, showing clearly that the semolina had a bimodal distribution. This was also seen from the microscopy measurements, requiring that enough particles are analyzed for reliable results. In general, it is easier to measure more individual particles by laser diffraction, when this methods can be applied. No bimodal distribution was seen from the sieve analysis, where a limitation is the available sieves, as well as agglomeration of finer particles. The size distribution correlated however rather well, showing that the methods are comparable on a volume basis.

Complementary studies on the individual powder morphology by imaging techniques, depicted in Figure 4.10, revealed for both fractions of the powder-liquids a more spherical shape with isolated air inclusions (a, b). The air inclusions occur due to that
the dispersed liquid droplets freeze gradually from the outside during the spray chilling process. Once the ice starts to expand, the water inside the ice particle experience an over pressure that pushes towards the ice shell. If this pressure is high enough, the ice shell fractures and the liquid drains out of the shell. Subsequently, the drained liquid freezes and forms a small tail on the particle surface, visible in Figure 4.10b. CryoSEM (cryo-scanning electron microscopy) images of intersected powder-liquid particles (Figure 4.10c) revealed their internal morphology, confirming the lamella structure formation explained in section 2.1. In comparison to the powder-liquids, both wheat flour (Figure 4.11a) and semolina (Figure 4.11b) was more irregularly shaped. The wheat flour had clearly smaller particles compared to semolina, also seen from the particle size distribution.

Flow properties and stability of water based powder-liquids

Figure 4.12 shows the flowability $f_f$ of (a) single powder-liquids for various consolidation force ($F = 50–250$ N), and (b) mixtures with various powder-liquid to wheat flour ratios after a consolidation of $F = 50$ N, measured by a texture analyzer. The single powder-liquids showed a somewhat higher $f_f$ value for higher consolidation forces (Figure 4.12a). Compared to the single wheat flour, the powder-liquid had however a much lower flowability (Figure 4.12b). A reason for the cohesive behavior (low flowability) might come from uptake of moisture from the air during production. After spray chilling, the powder-liquids are quickly collected and transferred to a cooling room for storage prior to further usage, but are thus shortly exposed to the surrounding atmosphere of the pilot plant, in which the spray chilling takes place. As
Figure 4.10: Morphology of water based powder-liquid from (a) light microscopy measurement, (b) computer tomography capture, and (c) cryo-scanning electron microscopy image from the intersection of a powder-liquid particle.

Figure 4.11: Light microscopy capture of (a) wheat flour and (b) semolina, showing their morphology.
expected, the flowability of the mixtures thus decreased with increasing concentration of powder-liquid. This arises from the flow properties of the single components. Due to the more empirical method of determining flowability with a texture analyzer (TA), compared to for example a ring shear tester (RST), there are no classifications for the measured \( f_f \) values. However, the flowability of wheat flour assessed from TA, \( f_f = 55.7 \), can be compared to previous RST measurements in Section 4.1.1, with a flowability \( f_f = 3.3 \) at a consolidation stress of \( \sigma_1 = 4 \text{kPa} \), showing that the TA values are clearly higher.

Figure 4.12: Flowability \( f_f \) of (a) single water based powder-liquids and (b) single powder-liquids (100 wt%) and wheat flour (0 wt%), as well as their mixtures with denoted amount of added powder-liquid (5-20 wt%).

Previous work from Wagner (Windhab et al. (2004); Wagner (1997)) showed that water based powder-liquids stayed free-flowing for months when stored at least 2°C below their glass transition temperature (explained further in Section 2.1). To further test the short term stability of the powder-liquids, penetration tests were made with a SnowMicroPen at −20°C, presented in Figure 4.13. These results showed that the penetration force increased consistently with storage time. After the short term storage, the powder-liquids could however still be easily separated by sieving, why no bridge formation between the particles can have taken place.

**Thermal properties of water based powder-liquids**

With DSC (differential scanning calorimetry), the glass transition temperature \( T_g \) of water based powder-liquids where measured from DE6-water solutions of various concentrations. In Figure 4.14, the DSC measurements are presented, showing that the glass transition temperature increase with increasing DE6-concentration. The water based powder-liquids were produced from a 10 wt% DE6-water solution. The DSC signal of this measurement was however too low, and consequently it was estimated from a polynomial fit of the data extrapolated from the higher concentrations.
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Figure 4.13: Penetration force of SnowMicroPen measurements through a bed of water based powder-liquids with increasing storage time at $-20^\circ$C.

This provided a glass transition temperature around $-10.7^\circ$C, corresponding rather well to Wagners’ (Windhab et al. (2004); Wagner (1997)) previous measurements on the same system of $T_g$ around $-8.3^\circ$C. Storing and handling the powder-liquids at temperatures of $-15^\circ$C is thus sufficient to keep the powder-liquids stable.

Figure 4.14: Glass transition temperature of the DE6-water solutions used to produce the water based powder-liquids, for increasing DE6-concentration.

4.2 Powder surface properties

In the following section the results of the stickiness and wettability measurements are presented.

50
4.2.1 Powder stickiness

Powder stickiness was measured by an adapted rheometer, with which the stickiness of skim milk powder (MSK) first was tested to be compared to previous results. In Figure 4.15a, a typical measure of the torque and temperature over time is presented, where the increase in torque shows the sticky point of the powder for a certain moisture content.

![Figure 4.15: Torque measurements over time indicating the sticky point at a certain temperature for (a) skim milk (MSK) and (b) protein powder.](image)

By measuring the sticky point of the powder at several moisture contents, a sticky point curve was done that is presented in Figure 4.16, in relation to the glass transition temperature $T_g$ of MSK. A shift of the sticky point from the glass transition temperature was seen and measured to $17 \pm 2^\circ C$, which corresponds well to previous findings of Hennigs et al. (2001), reporting that a powder will stick when its temperature is about $20^\circ C$ higher than $T_g$.

The sticky point of maltodextrin with DE 17-20 was measured to around $120^\circ C$ for moisture contents between 3.7-5.6 wt% (wb), but due to the high glass transition temperature of the maltodextrin and limitations in heating temperature of the rheometer, it was not possible to measure it properly. Hence, no similar trend as for the skim milk powder could be seen.

The glass transition concept is valid only for pure carbohydrates, whereas the presence of other components like proteins and fats can lead to different adhesive mechanisms. It was therefore of extra interest to see if it was possible to measure the stickiness of a protein powder. However, as can be seen in Figure 4.15b, the torque fluctuated by increasing and decreasing, not giving a distinct sticky point as for the skim milk powder and maltodextrin.

To conclude, the adapted rheometer could successfully be used to assess the stickiness of skim milk powder. The results showed a sticky curve with a shift of $17 \pm 2^\circ C$.
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Figure 4.16: Sticky point curve for skim milk powder (MSK) at various moisture content. Above the glass transition temperature, which corresponds well with previous findings. Unfortunately, the oil bath used to heat the powder rheometer could not reach the high temperatures needed to measure the sticky point of the tested maltodextrins. It was thus difficult to see any similar trend as for the skim milk powder. The protein powder was more difficult to measure as it did not always show a clear sticky point. To assess the stickiness of such powders, the method needs to be further developed and more tests need to be performed. As recently reported by Gianfrancesco et al. (2015), further work on assessing the stickiness curve for various food model powders, showed that the powder rheometer is a useful tool to assess stickiness on carbohydrate-based products. Hence, it is a good complement to optimize the spray drying process in order to prevent fouling, not only having to use the glass transition temperature as a reference.

4.2.2 Powder wetting angle

Figure 4.17 demonstrates the measured contact angle over time of skim milk and maltodextrin powder films, as well as pure glass used as reference. For all powders, the contact angle decreased over time. As expected, the powders had a clearly lower contact angle, i.e. higher wettability, compared to the pure glass dishes, further illustrated in Figure 4.18. Skim milk (MSK) showed the highest wettability of the powders. Among the maltodextrins, the wettability increased with increasing DE number, for which the DE17-20 had the highest wettability and DE6 the lowest.

Table 4.3 shows the result of the commercial wetting test, in which the time to wet a certain amount of powder in water was estimated, alternatively the amount unwetted
4 Results and discussion

Figure 4.17: Contact angle $\Theta$ of skim milk powder (MSK) and various maltodextrin films coated on glass covers.

Figure 4.18: Contact angle $\Theta$ of a water droplet on (a) pure glass and (b) glass coated with maltodextrin DE12 after 3 s.
powder after 120 s. All measurements were performed in ambient temperature. The maltodextrin DE17-20 showed a clearly better wettability compared to the other powders. For the other maltodextrins, the wettability was, as for the contact angle measurements, decreasing with decreasing DE number. The skim milk powder (MSK) showed compared to the contact angle measurements the lowest wettability in this test, in contrary to the highest wettability. This is not too surprising though, since many factors such as bulk density, particle size and temperature also have to be taken into account.

Table 4.3: Wettability of skim milk powder (MSK) and various maltodextrins measured by a commercial wettability test.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Wetting time [s]</th>
<th>Unwetted powder [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSK</td>
<td>&gt;120</td>
<td>~ 90</td>
</tr>
<tr>
<td>DE 6</td>
<td>&gt;120</td>
<td>80 – 90</td>
</tr>
<tr>
<td>DE 12</td>
<td>&gt;120</td>
<td>50 – 60</td>
</tr>
<tr>
<td>DE 17-20</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

From the bulk density measurements, presented in Figure 4.19, it can be seen that the maltodextrin DE17-20 had a clearly higher bulk density compared to the other powders. Due to gravity, this can explain the clearly higher wettability of the DE17-20 compared to the other powders.

Figure 4.19: Bulk density of skim milk powder (MSK) and the tested maltodextrins.

To conclude, it worked well to measure the contact angle on the powder films. No direct correlation could be seen with the comparison of the commercial wetting test. For a better understanding of the meaning of the results, further tests needs to be done to relate the contact angle to actual wetting behavior and reconstitution of the powders.
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4.3 Mixing quality

In the following section the results of the near infrared (NIR) calibration and the mixing trials of fat and water based powder-liquids are presented.

4.3.1 Pre-evaluation of near infrared calibration

The Fourier Transformation Near Infrared (FT-NIR) spectrometer was calibrated as described in Section 3.6.1 (NIRS calibration). Table 4.4 presents the statistical data of the three calibrations for fat based powder-liquid/wheat flour, water based powder-liquid/wheat flour and water based powder-liquid/semolina. The standard error of estimation (SEE) and standard error of prediction (SEP) give the standard deviation of the calibrating set and the independent validation set. To ensure a good calibration, these should be as small as possible and close to each other. This was the case for all mixtures, even though the water based powder-liquid/wheat flour mixture showed a clearly higher value compared to the other mixtures. This might have come as a result of condensation on the measure glass, why extra care was taken into account for calibration of the water based powder-liquid/semolina mixtures. The systematic distortion BIAS for the validation set gives information on the average deviation of the predicted values from the true values and should therefore be as close to zero as possible. The BIAS for the calibration set is zero by definition, and was for the validation set low for all mixtures. In addition, the regression coefficient $r$ describes the accuracy of the PLS regression, or in other words how well the predicted values match the calibration values, and must be larger than 0.9 (Kropp, 2002), which it was for all mixtures.

Table 4.4: Statistical data for the NIR calibrations of fat based powder-liquid/wheat flour, water based powder-liquid/wheat flour and water based powder-liquid/semolina. The statistical data shows the BIAS, standard error of estimation (SEE) and standard error of prediction (SEP) for the calibration and validation spectra, respectively, as well as the regression coefficient $r$.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Calibration spectra</th>
<th>Validation spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BIAS</td>
<td>SEE</td>
</tr>
<tr>
<td>fat-PL/wheat</td>
<td>0</td>
<td>0.4655</td>
</tr>
<tr>
<td>water-PL/wheat</td>
<td>0</td>
<td>1.7019</td>
</tr>
<tr>
<td>water-PL/semolina</td>
<td>0</td>
<td>0.8782</td>
</tr>
</tbody>
</table>
Across-check of the calibration accuracy was performed on selected reference mixtures with various powder-liquid ratios of known concentration. Figure 4.20 demonstrates the data from the re-measured reference mixtures. The measured concentrations of the reference mixtures matched well with the true concentrations for all three calibrations. The standard deviations between the measurements were also low, although it was somewhat higher for the water based powder-liquid/wheat flour mixtures compared to the other calibrations. Together with the statistical data in Table 4.4, this shows that this calibration was not as good as the other two. All calibrations were however considered to be satisfying and could be used to quantify the mixing quality in the following trials.

Figure 4.20: Measured concentrations of (a) fat based powder-liquid in wheat flour, (b) water based powder-liquid in wheat flour, and (c) water based powder-liquid in semolina of selected reference mixtures as a function of the true concentration. The error bars indicate the standard deviation from the 20 measurements for each mixture.

4.3.2 Mixing quality of fat based systems

The following section the results of the mixing trials of fat based systems are presented.

Method evaluation (powder-liquid mixing)

Figure 4.21 depicts the mixing quality, represented by the normalized variation coefficient $CoV_N$, of powder-liquids (5, 10, 15 and 20 wt% palm stearin fat) that were mixed with wheat flour and studied by both NIRS and colorimetry method. Powder-liquids of two different size-fractions were compared ($25 \mu m$ and $53 \mu m$). Both methods, NIRS and colorimetry, revealed equivalent trends for the studied powder-liquid/powder mixtures. In general a decay function of variation coefficient ($CoV$) with time $t$ is observed. Hence, the mixing quality improves with decreasing variation coefficient.
and the mixture is considered to be homogeneous or to reach an equilibrium when the variation coefficient reaches its minimum, i.e. planes out into a plateau and mixing proceeds indefinitely. In some cases demixing can occur. This is however uncommon for cohesive powders, which was used in these trials, and was also not observed why it is not further discussed. The time-point at the beginning of the plateau represents the critical mixing time \( t_c \) that is needed to reach a homogeneous mixture (Poole et al., 1964).

Figure 4.21: Mixing quality over time represented by the normalized variation coefficient \( CoV_N \) (CoV divided by the sample area \( A \) of each method) for eight powder mixtures with four different powder-liquid amount (a-d) and two size fractions \( (x_{50,3} = 25\mu m \text{ and } x_{50,3} = 53\mu m) \), quantified with NIRS and colorimetry. The variation coefficient from the colorimetry measurements is calculated from the a-value.

Hence, \( t_c \) splits off the curve-behavior, or differently spoken the mixture-homogeneity, into two phases (e.g. Figure 4.21a) that are individually describable by power law functions: \( CoV_N = A t^z \), with \( A \) being the interception point with the y-axis at time zero and \( z \) the function slope in the log-log plot. Table 4.5, respectively Figure 4.22, rep-
4 Results and discussion

represents fit-data on NIRS 25 \( \mu \text{m} \) fraction for the four different powder-liquid (PL) concentrations. Fit-data on the other fraction (53 \( \mu \text{m} \)) and on colorimetry measurements were analogous but are not shown. However, for the four powder-liquid concentrations the mixture inhomogeneity was highest at the start of the mixing-experiments, showing a maximal normalized variation coefficient of about 0.03 \( \text{mm}^{-2} \). It decreased for all mixtures with the mixing time and, with some fluctuations, planed out after \( t_c = 20 - 30 \text{s} \) to a value of around 0.001 \( \text{mm}^{-2} \). Thereby, NIRS-data in comparison to colorimetry, and lower powder-liquid concentrations in comparison to higher ones (\( \leq 10 \text{ wt\% PL} \)) showed slightly higher plateau values (Figure 4.23). This might arise from the different method accuracies and/or higher influence of small powder-liquid concentrations on the mixture-homogeneity.

Table 4.5: Power law fits \((CoV_N = At^z)\) to data points of NIRS 25 \( \mu \text{m}\) fraction (1) before and (2) after critical mixing time \( t_c \).

<table>
<thead>
<tr>
<th>( c_{PL} )</th>
<th>1st fit ((A))</th>
<th>1st fit ((z))</th>
<th>2nd fit ((A))</th>
<th>2nd fit ((z))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt%</td>
<td>0.0309</td>
<td>-0.650</td>
<td>0.0028</td>
<td>0.0703</td>
</tr>
<tr>
<td>10 wt%</td>
<td>0.0195</td>
<td>-0.758</td>
<td>0.0026</td>
<td>-0.0750</td>
</tr>
<tr>
<td>15 wt%</td>
<td>0.0196</td>
<td>-0.764</td>
<td>0.0009</td>
<td>0.0533</td>
</tr>
<tr>
<td>20 wt%</td>
<td>0.0158</td>
<td>-0.727</td>
<td>0.0014</td>
<td>-0.1260</td>
</tr>
</tbody>
</table>

Figure 4.22: Data-visualization of (a) interception point \( A \) and (b) exponent \( z \) for power law fits \((CoV_N = At^z)\) to data points of NIRS 25 \( \mu \text{m} \) fraction (1) before and (2) after critical mixing time \( t_c \) (Figure 4.21).

Nevertheless, the results showed that NIRS and colorimetry are comparative methods that appear equivalently applicable for quantifying the mixing behavior of powder mixtures. The obtained data of NIRS and of colorimetry not only showed similar
Figure 4.23: Normalized variation coefficient $CoV_N$ after 300 s of mixing, in the plateau (mixture equilibrium) region, for the different powder-liquid concentrations, their two different fractions (25 vs. 53 $\mu$m) and methods (NIRS vs. colorimeter) used in the method-evaluation test. In addition, the $CoV_N$ of the 5 wt% powder-liquid mixture made in the mixing-evaluation test is presented in comparison to the colorimeter measurements of the 5 wt% mixtures in the method-evaluation test.
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trends for the same sample, their normalized variation coefficients also lay in the same range of magnitude, in respect to the maximum relative errors $\pm 16\%$. Furthermore, the two powder-liquid fractions of different size distribution ($x_{50,3}$: 25 $\mu$m and 53 $\mu$m) did not show any particular irregularities (Figure 4.21 and Figure 4.22). Thus, particle size and distribution of moderate differences (1:2 ratio) have a rather low contribution to the powder-liquid/powder mixing process, and will be discussed in more detail in the next section.

This study showed that a high homogeneity of powder-liquid/powder-mixtures is achievable in relatively short times. Moreover, the usage of powder-liquids proved to be a robust mixing approach, as slight variations in particle-size showed a rather low contribution on the critical mixing time $t_c$ and/or on the final mixture-homogeneity. Colorimetry gave a good estimation of the mixing kinetics of colored powder mixtures. Additionally, the colorimeter did not require any long calibration time and was compared to the NIRS easier to handle and to transport. Subsequently, it was used to investigate the mixing quality during the process evaluation of powder-liquid/powder vs. sprayed liquid/powder mixing-process, presented below.

**Mixing-procedure evaluation (powder-liquid vs. sprayed liquid)**

Dependent on the individual fatty acid composition (saturated (S) vs. unsaturated (US)) palm stearin fat ($S >> US$) and sunflower oil ($S << US$) appear to be either solid or liquid at room-temperature. The two different admixture-materials were used according to their physical properties (cf. Table 3.1) that either favored the powder-liquid usage or favored an optimized spraying process of similar particle- and droplet-size ($\sim 130 \mu$m) at ambient temperature. The transient evolution of mixing quality of the powder mixtures prepared by (i) mixing 5 wt% powder-liquid in biscuit flour or (ii) spraying 5 wt% liquid fat (sunflower oil) into biscuit flour, is presented in Figure 4.24 by the normalized variation coefficient $CoV_N$. A major difference between the two mixing-procedures can be seen in a delayed addition of the sunflower oil to avoid sudden lump-formation of liquid and powder. The automatized oil feed (50 g/s) of sunflower oil completed after 180 s, while the total mass of palm stearin powder-liquid was directly placed onto the flour top from start on. However, a similar mixing or rather homogenization behavior was observed. In case of powder-liquid a very fast drop of the normalized variation coefficient $CoV_N$ was found that within 60 s flattened out (from 0.02 to 0.002 mm$^{-2}$) and thus marked an evenly distributed powder/powder-mixture. In case of the sprayed oil, obviously no major improvement in the mixture homogeneity is obtainable during the liquid feed. The first probe was measured after 120 s of mixing, when 80 wt% of sunflower oil was inserted. From this moment onward the normalized variation coefficient decreased only marginally (from 0.15 to 0.09 mm$^{-2}$) until the oil-addition completed at approximately 180 s.
However, after the oil is fully sprayed-in and the data is corrected for this delay the mixture homogeneity reached its equilibrium rather progressively (300 s), following a power law function with coefficient $A = 0.57$ and power $z = -0.94$. Nevertheless, the normalized variation coefficient of the sprayed liquid/powder mixture appears always to be higher than for the powder-liquid/powder mixtures in the observed time range. Hence, the use of powder-liquids shows a couple of advantages concerning the mixing with powdery blends, such as blending different materials in the same state of matter in a ready to use condition, causing a better starting point (lower $CoV_N$) in the homogenization process, and altogether fastens the mixing and homogenization process.

![Figure 4.24: Mixing quality over time represented by the normalized variation coefficient $CoV_N$ (variation coefficient $CoV$ divided by the sample area $A$) for mixing 5 wt% powder-liquid in biscuit flour (patterned squares) or spraying 5 wt% liquid sunflower oil into biscuit flour (closed diamonds) with an automatized oil feed of 50 g/s. Open diamonds present delay-corrected (arrow) spray-data of sunflower oil and crosses power-law fit to the transient homogenization process.](image)

Furthermore, a longer equilibrium time was observed for the powder-liquid (5 wt%)/flour mixtures during the mixing-procedure evaluation ($\sim 60$ s) than seen in the method evaluation ($\sim 30$ s). It was expected to originate from one of the mixing quality in-
fluencing factors like the mixer type or the powder properties, such as particle shape and size, as well as cohesiveness, particle density and bulk density. Shenoy et al. (2015) found that bulk density differences has a larger influence on the mixture quality compared with particle size, correlating a particle size ratio $< 4.5$ with a very well mixing. Small bulk density ratios ($< 3.5$) were related with a very good mixture homogeneity, while higher ratios ($> 6$) even showed apparent segregation. Table 4.6 states calculated size- ($x_{50,3}$) and bulk density- ($\rho_b$) ratios dependent on the $CoV_N$ for all presented mixtures containing $5\text{wt}\%$ powder-liquid (PL). Our results confirm the general understanding of how mixture quality is influenced by several powder properties. Considering the particle size ratios, the biscuit 10 – PL 132 mixture should mix rather poorly in comparison to its wheat 400 – PL analogues. However, at the same time its bulk-density ratio favors a good mixing. Subsequently, a slightly higher $CoV_N$ value of the biscuit 10 – PL 132 mixture (cf. also Figure 4.23) was observed, which in turn does not diverge too strongly from the ones seen in the wheat 400 – powder liquid mixtures. This is due to the stronger influence of bulk density in comparison to the particle size. It goes along with the observations from the wheat 400 – powder liquid mixtures concerning their two different size fractions ($25\mu m$ and $53\mu m$). Here, the size ratios differ to each other, while the bulk density ratios are in the same range. As bulk-density is associated with the particle shape, the use of uniformly round-shaped powder-liquids (Figure 4.2) may support an optimal mixing performance.

Table 4.6: Particle size- ($x_{50,3,\text{flour}}$) and bulk density ($\rho_b$) ratios with the $CoV_N$ at 300s for all presented mixtures containing $5\text{wt}\%$ powder-liquid (PL).

<table>
<thead>
<tr>
<th></th>
<th>$x_{50,3,\text{PL}}$</th>
<th>$\rho_b,\text{PL}$</th>
<th>$x_{50,3,\text{flour}}$</th>
<th>$\rho_b,\text{flour}$</th>
<th>$CoV_N,300s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat 400 – PL 25</td>
<td>0.58</td>
<td>0.44</td>
<td>1.72</td>
<td>2.27</td>
<td>1.43</td>
</tr>
<tr>
<td>Wheat 400 – PL 53</td>
<td>1.23</td>
<td>0.54</td>
<td>0.81</td>
<td>1.84</td>
<td>1.96</td>
</tr>
<tr>
<td>Biscuit 10 – PL 132</td>
<td>5.74</td>
<td>0.84</td>
<td>0.17</td>
<td>0.19</td>
<td>2.01</td>
</tr>
</tbody>
</table>

4.3.3 Mixing quality of water based systems

In the following section, the results of the mixing trials of water based systems are presented.
Method evaluation (powder-liquid mixing)

Figure 4.25 demonstrates the mixing quality of water based powder-liquid/wheat flour mixtures (5–20 wt%), represented by the variation coefficient (CoV) of NIRS measurements. The mixtures become more homogeneous with decreasing variation coefficient, and are considered homogeneous at the point where the variation coefficient starts to plane out into a plateau. In food and pharmaceutical industries the variation coefficient should generally be below 0.06 for rather homogeneous and thus satisfying mixing quality (Berthiaux et al., 2008; Marikh et al., 2008).

All mixtures started with a variation coefficient of about 1, which decreased consistently with the mixing time and planed out around 0.1 after a critical mixing time $t_c$ of 30 s. Referring to the mixing criteria of 0.06, the homogeneity is not sufficient, showing that more efficient mixing equipment is needed. The mixture containing 20 wt% PL showed a tendency of slightly lower variation coefficient, but with no clear difference compared to the other mixtures (5-15 wt% PL). This result is rather surprising in consideration to the flowability studies of the pure PL, the pure wheat flour, and their mixtures presented in section 4.1.2 (Flow properties and stability of water based powder-liquids), which showed strong differences. As a quite good flowability was observed for the flour and a considerably lower one for the PL or for any of its mixtures, it would have been expected to see a difference also in the mixing behavior. This was however not the case. Thus, the differences in flow behavior were too small to significantly influence the mixing behavior.

![Figure 4.25: Mixing quality given by the variation coefficient (CoV) of powder mixtures made of wheat flour and water based powder-liquid (5, 10, 15 and 20 wt%).](image-url)
In addition to NIRS, the mixing behavior of the water-based powder-liquid mixtures was evaluated by moisture content (MC) analysis. Figure 4.26 shows the variation coefficient of the mixtures over mixing time for the two methods, respectively. NIRS and MC analysis indicate a similar mixing behavior, with a variation coefficient decreasing over time and that starts to plane out after about 30 s. Figure 4.27 demonstrates the mixing curve for each mixture (5, 10, 15 and 20 wt%) individually, confirming that the two methods show the same mixing trend but different absolute value of the variation coefficient. This can be explained by the different sample size between the two methods. In comparison to the evaluation of NIRS and colorimetry in section 4.3.2 (Method evaluation), the sample size between NIRS and MC analysis are more difficult to normalize due to the different measures (estimated area for NIRS, since the penetration depth of the beam is difficult to estimate, and volume/weight for MC analysis).

Figure 4.26: Mixing quality given by the variation coefficient (CoV) of powder mixtures made of wheat flour and water-based powder-liquid (5, 10, 15 and 20 wt%), analyzed by near infrared spectroscopy (NIRS) compared to moisture content (MC) analysis.

**Mixing-procedure evaluation (powder-liquid vs. sprayed liquid)**

To evaluate the powder-liquid mixing methodology, 10 wt% water was once added in form of solid powder-liquid, and once added by spraying the equivalent amount of water directly onto wheat flour. Figure 4.28 depicts the variation coefficient, or differently spoken the mixing quality, of the powder mixtures (solid powder-liquid/wheat flour and sprayed liquid/wheat flour).

The variation coefficient of both mixtures decreased fast with the mixing time, indicating a transient improvement of the mixture. Its plateau marks the mixture...
Figure 4.27: Mixing quality given by the variation coefficient (CoV) of powder mixtures made of wheat flour and water based powder-liquid (5, 10, 15 and 20 wt%), analyzed by near infrared spectroscopy (NIRS) compared to moisture content (MC) analysis.
equilibrium and thus best homogeneity. Nevertheless, both powder mixtures differed strongly in terms of the quality of mixing. The variation coefficient of the powder-liquid mix started around 1, as was seen also for the powder-liquid mixtures in Figure 4.25. It decreased to 0.07 after a rather short mixing time of only 10 s. Best homogeneous mixtures were reached after a critical mixing time $t_c$ of 30 s, when the variation coefficient reached a plateau value at around 0.05. This value matches the food and pharmaceutical criterion of a satisfying mixing quality, and in addition proves a better mixing capability for the L"odige mixer when facing the simple manual mixing.

However, for mixtures produced by directly spraying the liquid onto the wheat flour the variation coefficient was determined first after 10 s, after all liquid was inserted. Hence, a CoV of 0.2 was measured that further declined to 0.1 in the plateau region (30 s).

Worth to note is that incorporation of the sprayed-in liquid, besides the nozzle configuration and spray parameters (Lipp, 2008), highly depend on the number of spray nozzles being used, which was only one in this case. By taking into account that the sprayed liquid was inserted later into the mixture (correction indicated with open triangles in Figure 4.28), the sprayed liquid reached homogeneity at a $t_c$ of 10 s. However, after 10 s the variation coefficient was clearly lower for the powder-liquid mixtures throughout the whole mixing process as well as at the end of the mixing. This demonstrated that the powder-liquid mixing process lead to a better incorporation of the liquid into the solid bulk powder phase than when inserted by spraying.

For further evaluation of the powder-liquid mixing procedure, trials with water based powder-liquid compared to sprayed water were mixed with semolina. Concentrations of 5, 10, 15 and 20 wt% powder-liquid and corresponding sprayed water were mixed with semolina and the mixing quality of the mixtures were quantified by NIRS over time. Figure 4.29 depicts the variation coefficient of the NIRS measurements for the different mixture concentrations. For the powder-liquids (5-20 wt%), the variation coefficient started around 1 for all mixtures and decreased over time before planing out into a plateau around 0.05 after a critical mixing time $t_c$ of 60-300 s, indicating a homogeneous mixture. As mentioned in previous sections, this fulfills the mixing criteria of a variation coefficient below 0.06 (Berthiaux et al., 2008; Marikh et al., 2008). For the mixtures with liquid inserted by spraying, the plateau was not as distinct and the variation coefficient decreased slower over time, indicating that longer mixing times would be needed. For the mixtures with lower liquid concentrations (5 and 10 wt%), the variation coefficient was lower for the powder-liquid mixtures than for the sprayed liquid at the end of the mixing, i.e. after 1200 s. The variation coefficient for the mixtures with sprayed liquid was 0.10 and 0.06 for the 5 and 10 wt% mixtures, respectively, and thus not sufficient. However, the opposite trend was seen for the mixtures with higher liquid concentrations (15 and 20 wt%), for which the
Figure 4.28: Mixing quality of the powder mixtures when mixed with powder-liquids in comparison to when the liquid was sprayed into the mixture through a pressure nozzle. The sprayed liquid was inserted first after 10 s, corrected for in the graph.
variation coefficient of the sprayed liquid crossed the one of the powder-liquids and decreased to a lower end-value.

Figure 4.29: Mixing quality of semolina mixtures when mixed with powder-liquids in comparison to when the liquid was sprayed into the mixture through a pressure nozzle.

To better explain this behavior, Figure 4.30 depicts the mixing results by comparing the mixtures for the two mixing procedures separately. Whereas the variation coefficient planed out around 0.05 for all powder-liquid concentrations (Figure 4.30a), it differed more between the mixtures with the sprayed liquid. Figure 4.30b shows how the variation coefficient planed out to lower values with increasing liquid concentration, ranging from 0.10 for 5 wt% to 0.02 for 20 wt%. This confirms that it is normally easier to achieve a homogeneous mixture when mixing larger amounts of liquid into powder, why a better mixing homogeneity was obtained for higher liquid concentrations when inserting the liquid by spraying. As was seen, this is not directly applied to powder-liquid mixing, where the liquid stays in a powdery state during the whole mixing procedure and the mixing homogeneity thus stayed constant for all concentrations. This means that, although powder-liquid mixing is clearly more efficient to achieve a faster mixing compared to inserting the liquid by spraying, it gives a more homogeneous mixture only for low liquid concentrations (≤10 wt%).
4.4 Testing of model products

In the following section, the mechanical properties and cooking loss/water uptake of pasta model products are presented.

4.4.1 Mechanical properties

Figure 4.31 demonstrates the mechanical properties of the pasta model products produced from powder-liquid/semolina mixtures in comparison to sprayed liquid/semolina mixtures. For both methods, 5, 10, 15 and 20 wt% water were added in the form of powder-liquid or alternatively sprayed onto the semolina during mixing. Due to an initial moisture content of 12 wt% (wb) in the semolina, the resulting absolute moisture content in the mixtures were about 16, 22, 26 and 30 wt% (wb), where 30 wt% corresponds to the typical moisture content in a traditional pasta dough. Figure 4.31 shows the breaking strength of the tablets produced with various added moisture content from the two mixing methods. For each concentration, the mixtures produced from the powder-liquids (Figure 4.31a) had in general a higher breaking strength compared to the mixtures produced with the sprayed water (Figure 4.31b). Only the 5 wt% mixture showed the opposite behavior. Further comparison of the methods demonstrate that the breaking strength increased from the 5 wt% to the 10 wt% mixtures, before it constantly decreased in the mixtures with additional moisture (15,
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20 wt%). This behavior can be explained by a change in the structure of the semolina, from glassy- to rubbery state, which was discussed by Kratzer (2007). The main constituents of semolina are starch and proteins (gluten). For water contents less than 16 wt%, semolina can be regarded as a dry granular and flowable bulk solid in a glassy state. This explains the lower breaking strength of the 5 wt% mixtures, with an effective moisture content of 16 wt%, where the semolina is still in the glassy state. With increasing water content, the glassy constituents of the semolina become plasticized, reaching the glass to rubber transition regime at 16-20 wt% moisture content. In this transition region, first the protein is plasticized and, with increasing water content also the starch, before the product can be seen as a wet granular material. For the 10-20 wt% mixtures, with effective moisture content of 22-26 wt%, the semolina is thus in the rubbery state and, with increasing moisture content the degree of plasticity is increased, which resulted in a lower breaking strength of the tablets.

![Diagram](image-url)

Figure 4.31: Mechanical properties of semolina mixtures when mixed with powder-liquids in comparison to when the liquid was sprayed into the mixture through a pressure nozzle. The mixtures are defined by the added amount of liquid (5-20 wt%), corresponding to effective moisture contents of about 16, 22, 26 and 30 wt% (wb).

Although the breaking strength varied somewhat in absolute value between the mixtures from the two mixing methods, it clearly showed the same trend. For better understanding of the differences, further trials would be needed to investigate the influence of mechanical stress during the mixing.
4.4.2 Cooking loss and water uptake

Figure 4.32 presents the cooking loss and water uptake of model pasta tablets produced from semolina mixtures with 10 wt% added powder-liquid/sprayed liquid. The tablets produced from powder-liquids show a tendency of somewhat higher water uptake and slightly lower cooking loss. Cooking behavior of pasta is directly linked to its matrix structural properties and is an important quality criteria. Cooking loss can occur either from (i) leaching of polymeric material into the cooking water, or (ii) disintegration of the pasta strand during cooking (Kratzer, 2007). The tendency of somewhat higher cooking loss of the tablets produced with sprayed liquid might result from a less homogeneous mixture. This hypothesis is supported by the larger standard deviation in cooking loss between the samples produced by sprayed liquid. Kratzer (2007) reported differences in cooking loss seen in pasta depending on type of extrusion. Pasta strands produced from a cylindrical-plunger system had a less homogeneous structure and showed an increased cooking loss, possibly caused by disintegration of the pasta strand during cooking. The higher water uptake of the powder-liquid tablets suggests a less rigid structure that might come as a result of the lower mechanical impact during mixing and thus a weaker protein network formation. However, no major differences were seen, and the two mixing methods seem to give rather similar product properties. Further trials would need to be performed with investigation of the micro structure to draw any clear conclusions.

Figure 4.32: Cooking loss (CL) and water uptake (WU) of model pasta tablets produced from semolina mixtures with 10 wt% added powder-liquid/sprayed liquid.
4.5 Water distribution in powder systems

The following section presents the sorption isotherms of semolina, as well as the distribution of water based powder-liquids in model powders during melting, evaluated by microwave resonance technique.

4.5.1 Sorption isotherms

Sorption isotherms of semolina was measured at various temperatures by a gravimetric method, presented in Figure 4.33. The samples were let to equilibrate in sealed vessels filled with over-saturated salt solutions of various water activity $a_w$. The water uptake of semolina increases with increasing water activity in a slightly sigmoid shaped (S-shaped) curve. Sigmoid shapes are typical for food products containing bio-polymers like starch and protein (Kratzer, 2007). In addition, wheat and wheat-derived products often exhibit hysteresis (Hébrard et al., 2003). Comparing the water uptake at different temperatures, there is a clear trend that the water uptake decreases with increasing temperature. These results correspond well with literature. Pollatos et al. (2013) saw the same trend from investigating the sorption behavior of semolina at higher temperatures of 25-40°C. They found that the water uptake decreases at a given water activity with increasing temperature, suggesting that semolina becomes less hygroscopic at higher temperatures. Hence, semolina can absorb more water at lower temperatures. Pollatos et al. (2013) suggests that this might come from that at lower temperatures, water molecules possess a lower kinetic energy, which is insufficient to overcome the corresponding energy of sorption.

4.5.2 Microwave resonance technique

The water distribution of water based powder-liquids in semolina and glass powder was evaluated by a microwave resonance technique during melting. Figure 4.34 presents the real and imaginary parts of the reconstructed permittivity values $\varepsilon_{\text{eff}}$ of pure semolina and model glass powder. The permittivity of glass powder stayed constant during melting, as expected without water in the system. For the semolina, however, a slight increase of the real part, and distinct linear increase of the imaginary part of the permittivity were seen. This comes as a result of the moisture content available in semolina, for which the permittivity increases when the water goes from solid ice to liquid phase.

Figure 4.35 shows the reconstructed permittivity values $\varepsilon_{\text{eff}}$ of the semolina and glass powder mixed with powder-liquids. The transition of water from the ice to the liquid state can be clearly seen by the change in permittivity. This transition is much
Figure 4.33: Sorption isotherms of semolina at various temperatures, showing the water uptake as a function of the water activity.

smoother for the PL/semolina mixtures, since the water bounds to the material and a lower permittivity value is reconstructed. This is a typical behaviour of water bound in a hygroscopic material (Nyfors and Vainikainen, 1994). Clear differences were observed for the two cases for low/high amount of added powder-liquid. For the PL/glass mixtures, the presence of free water can be differentiated since the permittivity value becomes much higher and again clear differences between the two samples were observed for the different amount of PL added.

To conclude, it was possible to follow the melting dynamics of powder-liquids in semolina and glass mixtures by microwave resonance technique. The samples showed reproducible results and a distinct difference in permittivity between the samples. Due to the residual moisture content in pure semolina, a permittivity change was seen with temperature, whereas the permittivity of the pure glass sample stayed constant. In the PL mixtures, the state transition of the water from ice to liquid was clearly distinguished. It was also possible to distinguish between bound and unbound water, where the lower permittivity values of the PL/semolina mixtures indicated that the water was bound to the material. Our results show that MWRT can be a useful tool for assessing melting dynamics of moist material.
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Figure 4.34: Real and imaginary part of the reconstructed permittivity value $\varepsilon_{\text{eff}}$ of pure semolina and glass powder measured during melting.

Figure 4.35: Real and imaginary part of the reconstructed permittivity value $\varepsilon_{\text{eff}}$ of semolina and glass powder mixed with 5 wt% and 20 wt% powder-liquid measured during melting.
5 Conclusions

In this thesis, a new approach for mixing low fractions of liquid into powders using so-called powder-liquids was evaluated. Both fat and water based powder-liquids were produced and investigated in terms of powder characteristics and mixability with wheat flour and semolina, used as model powders.

Fat based powder-liquids were characterized in terms of particle size distribution, particle morphology, flow properties and thermal behavior. The particle size distribution of the powder-liquid was controlled by varying the atomizing pressure during the spray chilling process, producing roundly shaped powder-liquid particles. A ring shear tester could be applied to measure the flow properties of fat based powder-liquids and powder-liquid mixtures. A clear difference in flow behavior was seen between the fat based powder-liquids and wheat flour, which were used as model powder, as well as between different size fractions of the powder-liquids. Wheat flour had a consistently higher flowability and lower cohesion, effective angle of internal friction, and wall friction angle, compared to the powder-liquids. Furthermore, powder-liquids with a smaller particle size (\(x_{50,3}=25 \, \mu\text{m}\)) had a lower flowability and higher cohesion, effective angle of internal friction and wall friction angle compared to the powder-liquids with the larger particle size (\(x_{50,3}=53 \, \mu\text{m}\)). Mixtures of powder-liquid and wheat flour showed clear functional dependencies of cohesion and friction angle as a function of the powder-liquid concentration. This tendency was seen for both size fractions. The flow measurements also showed a clear temperature dependence for the powder-liquids. The flowability was higher at lower temperatures for the single powder-liquids, as well as for the mixtures of powder-liquid and wheat flour. Subsequently, the opposite behavior was seen in cohesion, which was consistently lower at lower temperature. This can be explained with the somewhat higher solid fat content in the powder-liquids at lower temperature. No clear difference was however seen for the single wheat flour. These results showed the influence of particle size and temperature on the flow behavior of powder-liquids and powder-liquid mixtures. In addition, it was proven that ring shear testing is also applicable to uncommon powders, as in form of powder-liquids.

Water based powder-liquids were characterized in terms of particle size distribution, morphology, powder flow properties and stability. The water based powder-liquid particles were, beside roundly shaped, sometimes hollow and were produced partly
(outer shell and internal lamellae structure) in a glassy state. Wheat flour and semolina that were used as dry model powder, had both a more irregular particle shape. Also water based powder-liquids had a much lower flowability compared to wheat flour. In this case, it is expected to come from the sticky behavior of the water based powder-liquid surface, being exposed to higher temperature and moisture in the surrounding air during production/transportation. In mixtures with different ratios of powder-liquid and wheat flour, the flowability subsequently decreased with increasing concentration of the powder-liquid. Short term stability tests of the powder-liquids showed that they tend to clog together already after short storage periods (≤40 min). However, they could easily be separated again by sieving, showing that they did not strongly sinter.

NIRS and colorimetry could both be applied in order to quantify the mixing quality of fat based powder-liquid mixtures (5-20 wt% added powder-liquid). The normalized variation coefficient from the two methods demonstrated not only similar mixing kinetics, their normalized variation coefficients also lay in the same range with respect to the maximum relative errors. Lower powder-liquid concentrations in comparison to higher ones showed slightly higher plateau of the variation coefficient, which might arise from higher influence of small powder-liquid concentrations on the mixture-homogeneity. The mixing results showed that colorimetry is as reliable as NIRS measurements and hence can be a first choice validation method in industry. The colorimeter did not require any long calibration before use and was in addition easy to handle and transport. Consequently, colorimetry was used to evaluate the powder-liquid mixing process in comparison with spraying the liquid into the base powder (5 wt% added powder-liquid/sprayed oil). Even after correcting the time delay of the sprayed oil, the powder-liquids mixed faster and had a higher degree of homogeneity throughout the whole mixing process until the end. Comparing the different size fractions of powder-liquid, with respect to their particle size and bulk density ratios towards the flour, it was seen that the differences were too small to have a significant impact on the mixing quality.

The mixing quality of water based powder-liquid mixtures could be quantified by NIRS and moisture content analysis. No clear difference in mixing behavior was seen between the mixtures of various powder-liquid concentrations (5-20 wt%) mixed with wheat flour. A comparison between NIRS and moisture content analysis showed similar mixing behavior but due to difficulties in normalization of the sample size, they showed slightly different values. The comparison in mixing quality between adding water in the form of powder-liquid and spraying it directly (10 wt%) into the wheat flour during mixing in a powder mixer, showed a clear advantage for the powder-liquids. From the moment when all water was inserted, the powder-liquid mixtures had a lower variation coefficient, indicating a better mixing quality, throughout the whole mixing procedure as well as in the final mixture. Further mixing trials were performed with semolina, varying the added moisture between 5-20 wt% powder-
liquid and sprayed water, respectively. For all mixture concentrations, the powder-liquids mixed faster and gave a homogeneous mixture in a shorter time compared to the sprayed-in liquid case. In addition, the mixing quality was stable between the various powder-liquid concentrations and gave a sufficient mixing quality in all cases. For the mixtures to which liquid was directly added by spraying, the mixing quality was clearly worse for the lower liquid concentrations ($\leq 10$ wt%). With higher liquid concentrations, the mixing quality improved for the mixtures with sprayed liquid, whereas for low liquid concentrations, the powder-liquid mixing proved to be more efficient.

Mechanical testing of pasta model products, produced from wet semolina mixtures by alternately adding the moisture in the form of powder-liquid or sprayed liquid showed similar behavior for the two methods. A clear shift in material properties was seen when the semolina went from a glassy to a rubbery state with increasing moisture content. The tested methods gave also similar behavior in cooking loss and water uptake of the pasta tablets.

To conclude, the results show that powder-liquids can be of real great advantage to prepare homogeneous mixtures of powders with a low fraction of liquid. Fat and water based powder-liquids could be produced and characterized successfully. For added liquid contents $\leq 10$ wt%, both fat and water based powder-liquids gave clearly better mixing quality of the mixtures compared to directly spraying the liquid into the dry powders during mixing. Such powder-liquid mixtures can be further processed by e.g. tableting or extrusion to produce homogeneous products with high stability and reduced amount of fat/water. This can in turn allow for new low calorie foods, or reduce the caloric density in already existing products such as chocolate, or alternatively allow for new approaches to produce different type of pasta or other sintered foods more energy-efficient partially due to reduced drying costs. Initial trials were made to produce model products from powder-liquid mixtures for the proof of feasibility with encompassing results, but further trials are required to investigate their applicability in different type of food and/or pharmaceutical systems, where also the insertion of functional components would be of additional interest. Loading the powder-liquid particles with functional components impacting on sensory (flavour, aroma) or nutritional characteristics could be facilitated and ensure their homogeneous mixing into the powder matrix even for very low concentrations of such functional components.
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