1. Introduction

The number of consumers of plant-based milk alternatives (PBMA) is increasing due to health, environmental, ethical and animal welfare concerns (Cardello et al., 2022). Plant-based products have a beneficial effect on health by providing nutrients and secondary plant substances (Gonder, 2016). Furthermore, PBMA are a more environmentally friendly product compared to conventional cow's milk. A soy-based milk alternative, for example, results in 3.2 times lower CO_2 emissions and 22.4 times lower water consumption during production compared to cow's milk (Bocksch, 2020). Consequently, the industrial relevance of PBMA products is increasing at an annual growth rate of 12.5% and global sales of $24.6 billion are forecasted of 2025 (Reyes-Jurado et al., 2021). Particularly the powder form is characterized by better physical and chemical stability, easy weighing, efficient transport and a smaller storage volume compared to the liquid product (Cuq et al., 2011). The plant-based powders can also be incorporated into numerous food systems, such as sweets, instant products and infant formula. However, in comparison to conventional dairy milk powder, PBMA present certain challenges, including shelf-life, dispersion stability and reconstitution which can be usually linked to the behavior of the plant-based ingredients. On the example of reconstitution, PBMA powders tend to form lumps which have to be avoided as incomplete rehydration of the powder is not acceptable to the consumer during product use. To optimize the dissolution process, the PBMA particles are structured by forming typically agglomerates. During agglomeration, primary particles are combined to form larger, porous secondary particles that have a blackberry-like particle structure. The agglomerate structure enables a defined stability, dissolution behavior and flowability of the product (Palzer, 2006; Palzer et al., 2012).

To produce a targeted particle design with optimized reconstitution properties, the influence of the material on the formation, structure and characteristics of the agglomerated powders was investigated in this thesis. The focus was set on the plant protein and fiber component in the complex PBMA formulation, since no literature data is available to date. Moreover, no studies have been conducted on the production process for powdered PBMA products, which is subdivided into emulsion production, spray drying and fluidized bed agglomeration. As the individual process steps influence the product in addition to the material properties, a detailed analysis was performed and knowledge generated for a targeted particle design. To understand the structuring as a function of the surface composition of the particles at the micro-level, numerical methods were used to model and analyze particle binding. The results obtained were transferred to the macro-mechanism in the fluidized bed and various product structures were generated by setting defined process parameters. In further investigations, a correlation between the particle structure, size and dissolution behavior of the powders was established, which enables a transfer to industrial production regardless of used production plant and scale. Additionally, the reconstitution was analyzed experimentally and modeled to identify additional influencing parameters of the complex material system.

1.1 Properties of food emulsion

Often PBMA are emulsions that are intended to resemble the physical and sensory properties of cow’s milk (McClements & Grossmann, 2021). Thereby PBMA belong to the oil-in-water (O/W) emulsions, in which the dispersed oil phase is present as droplets in the aqueous continuous phase (Leal-Calderon et al., 2007). Depending on the raw material source, the used vegetable oils have different melting behavior, viscosity values and interfacial tensions, which influence the droplet formation and stability of the disperse phase in the emulsion. Plant-based emulsifiers such as proteins, polysaccharides, phospholipids and biosurfactants are incorporated into PBMA to facilitate emulsion production (McClements et al., 2019). In particular, proteins are often used as emulsifier systems due to their structuring, texturizing, foaming and nutritional properties. Based on the amphiphilic structure, the protein molecules adsorb at the phase interface and stabilize the dispersed oil droplets by introducing electrostatic and steric repulsive forces lowering the interfacial tension (McClements & Grossmann, 2021). Adsorption at the interface occurs with unfolding of the proteins, thus promoting interaction with other adsorbed molecules. The formed viscoelastic protein layers can generate multilayers through the adsorption of reversibly bound molecules (Leal-Calderon et al., 2007), whereby the protein interactions depend besides the chemical structure on the ambient conditions. In the study by Du et al. (2023), an approximation of the isoelectric point of soy protein isolate leads to a reduction in the electrostatic repulsion and emulsifying capacity of the protein. McClements et al. (2019) describe an optimization of emulsification by using two or more emulsifier systems.

The PBMA products are homogenized to increase the stability of the O/W emulsion and to achieve a more homogeneous, narrower droplet size distribution of the disperse phase. Different types of homogenization systems can be used, but the high-pressure homogenizer is most commonly applied in PBMA production from a variety of plant-based ingredients (McClements et al., 2019; McClements & Grossmann, 2021). During high-pressure homogenization, the lipid droplets and aggregates are ruptured as a result of the tensile and shear stresses as well as cavitation (Leal-Calderon et al., 2007). The forces result from the transport of the liquid product through a radial gap, which increases the flow velocity, and the prevailing pressure difference in the homogenization zones (Kivelä et al., 2010). In addition to homogenization, the emulsion quality also depends on the used formulation ingredients and forms the basis for further process steps. The final product properties and thus the consumer application as well as long-term storage stability can already be controlled through targeted adjustments during emulsion production (Kramm et al., 2024).

1.2 Powder production by spray drying

The homogenized O/W emulsions are dried to generate a powdered product from the liquid PBMA emulsions. Often spray drying is used for the production of numerous food products and thermosensitive materials, in which the liquid product to be dried is first atomized by a nozzle (Singh et al., 2022). The droplets formed from atomization result in a higher partial pressure of the solvent at the droplet surface to the solvent in the drying gas. Due to the partial pressure difference, the solvent evaporates and the viscosity of the PBMA liquid droplets increases. The particle characteristics in the process can be specifically controlled by selecting the atomization conditions, drying temperature and inlet feed properties (Palzer et al., 2012). In the study by Singh et al. (2022) on the production of soy milk powder, a maximum product yield, minimum water activity and wetting time were determined at higher inlet air temperature of 140 - 160°C. In addition, a direct relation between the evaporation and feed rate could be identified. Bhandari (2013) also described the correlation between the feed viscosity and the moisture content of the powder produced.

Spray drying is commonly used due to easy scalability, high process control and implementation for the encapsulation of oil and bioactive compounds (Sánchez-Osorno et al., 2023). In the investigation by Roccia et al. (2014), a higher solids content of the feed had a positive effect on the encapsulation of sunflower oil, as the rapid crust formation impeded oil diffusion to the particle surface. In particular, the carbohydrates such as maltodextrins used as carrier material for matrix formation improved the yield and efficiency of oil encapsulation, whereby a ratio of wall material to core between 2:1 and 4:1 (w/w) should be maintained. The authors described that the operating conditions during the spray drying process can strongly influence the encapsulation efficiency, capsule stability and shelf life of the oil core from oxidative degradation. Haas et al. (2019) showed high encapsulation efficiency and carotenoid stability during storage at low surface-to-volume ratios using constant drying parameters. The encapsulation was also significantly influenced by the particle geometry and the lipophilic phase. When a highly porous system was generated, particle porosity proved to be a stronger impact parameter than particle diameter (Haas et al., 2019). To achieve the desired product properties, the adjustment of optimal spray drying parameters depending on the PBMA formulations is thus relevant.

1.3 Properties of food powders

To control the technological behavior such as the reconstitution properties or the affinity for the formation of agglomerates, extensive knowledge of the product system is required. Particularly PBMA powders result in different surface characteristics of the particles depending on the used ingredients, affecting the properties of the heterogeneous food in addition to the chemical raw material composition and the ambient conditions (Cuq et al., 2011). In the subsequent sections, the pertinent characteristics of the model product examined in this study are delineated.

1.3.1 Supramolecular structure

Food powders are complex systems with structure-dependent material properties that determine the behavior during drying, agglomeration and storage (Palzer, 2010). The supramolecular structure of the powder systems can be generally differentiated between the amorphous and crystalline molecular structure, whereby the PBMA model used in these investigations has predominantly amorphous components. Amorphous molecules are characterized by a disordered, open and porous structure, which enables water molecules to be easily absorbed (Bhandari, 2013). The amorphous matrix is highly entropic, so the dissolution of the product systems proceeds exothermically (Palzer, 2010). The material properties of products with amorphous components alter based on the moisture content of the environment and the temperature, therefore the glass transition temperature is to be determined as a reference value. The glass transition temperature decreases with increasing moisture content (see Eq. 1.4) and, if the product temperature falls below the glass transition temperature, the product system is in a glassy state. In contrast, the product reaches a rubbery state above the glass transition temperature, where undesirable effects such as sintering and caking can be observed. In the glassy state, the auto diffusion of the matrix-forming molecules is inhibited and the system is thermodynamically more stable despite the imbalance. Conversely, the auto diffusion of the matrix molecules is accelerated in the rubbery state and the system is thermodynamically unstable. The state transition also affects the material viscosity. Palzer et al. (2012) describe the viscosity of amorphous materials in the glassy state at $10^{12} – 10^{13}$ Pa·s, whereas the viscosity drops below 10^6 Pa·s when the product-specific glass transition temperature is exceeded.

1.3.2 Hygroscopicity and hygrosensitivity

For the identification of the material characteristics and structuring of the particles through the formation of agglomerates, the hygroscopicity and hygrosensitivity have to be investigated. Hygroscopicity describes the tendency of a material to adsorb water from the atmosphere (Palzer, 2006). The water adsorption rate depends on the material composition of the bulk, particle surface, particle size, porosity and molecular structure (Bhandari, 2013). The sorption isotherm enables the correlation between the equilibrium water quantity w' contained in the material and the water activity a_w at a defined temperature. According to Guggenheim, Anderson and de Boer (GAB), the sorption behavior of food powders can be described considering the amount of water w'_m required for the formation of a monomolecular water layer on the solid surface and the material-specific, temperature-dependent constants C and K in Eq. 1.1 (Anderson, 1946; de Boer, 1953; Guggenheim, 1966):

$$\frac{w'}{w'_m} = \frac{C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 + (C - 1) \cdot K \cdot a_w)}, \qquad (1.1)$$

with

$$a_w = \frac{p_v}{p_S}. \tag{1.2}$$

The water activity a_w indiciates the availability of free water in the powder material and is defined by the water vapor pressure in the immediate environment of the food p_v and the saturation pressure of pure water p_S at the same temperature. The parameter can attain values between 0, which reflects absolute dryness of the product, and 1, which represents condensing moisture. After the product system has reached equilibrium, the relative humidity of the environment corresponds to the water activity of the material. Palzer (2010) defines the chemical product composition, temperature, supramolecular structure and microstructure as influencing parameters of the water activity. The GAB isotherm in Eq. 1.1 can be transformed with K=1 into the Brunauer, Emmett and Teller (BET) sorption isotherm in Eq. 1.3 (Brunauer et al., 1938):

$$\frac{w'}{w'_m} = \frac{C \cdot a_w}{(1 - a_w) \cdot (1 + (C - 1) \cdot a_w)}. \tag{1.3}$$

In contrast, hygrosensitivity describes the change in the physico-chemical properties of food due to the moisture content. Amorphous materials adsorb moisture from the environment and thus alter the free volume of the molecular matrix, which reduces the material-specific glass transition temperature. The correlation between the glass transition temperature T_g of a moist material in relation to the moisture-related water content w can be expressed with the Gordon-Taylor equation (1.4), considering the Gordon-Taylor constant k, the glass transition temperature of the anhydrous material $T_{g,s}$ and of pure water $T_{g,w}$ (Gordon & Taylor, 1952):

$$T_g = \frac{(1 - w) \cdot T_{g,s} + k \cdot w \cdot T_{g,w}}{(1 - w) + k \cdot w}. \tag{1.4}$$

In the literature, the glass transition temperature of pure water is reported to be -135°C (Hartmann & Palzer, 2011; Palzer, 2006).

1.4 Fluidized bed agglomeration

Fluidized bed agglomeration is used for targeted product design by binding fine primary particles into agglomerates (Palzer, 2005) and is characterized by high heat and mass transfer rates, which allow short operating times and lower process temperatures (Smith, 2007; Schmidt, 2018). The performance of the fluidized bed depends on the operating parameters and the plant geometry (Fries, 2012). The process is based on the fluidization of powder particles by introducing gas into the solid particle bed via a distributor plate and exceeding the minimum fluidization velocity of the particles (Schmidt, 2018). Above the minimum fluidization velocity, the drag force of the fluid on the particles is equal to the particle weight, so that the particles are homogeneously suspended in the gas and exhibit fluid behavior (Smith, 2007). Depending on the fluid velocity, uniform fluidization behavior can transform to bubble formation, turbulent fluidization or pneumatic transport (Schmidt, 2018). For the formation of agglomerates, a binding agent is sprayed onto the fluidized particles via a nozzle, generally in top- or bottom-spray position. In the top-spray process, the atomized liquid is applied to the particles in counterflow, whereas in the bottom-spray process, the binding agent is sprayed in the movement direction of the particles and thus in a co-current flow. The top-spray nozzle configuration is typically used for size enlargement of culinary and beverage powders, whereas the bottom-spray installation is preferably applied for dairy powder agglomeration (Fries, 2012). In the study by Palzer (2006), the quantity of binder added and the spray rate of the liquid have been identified as the key parameters influencing the agglomerate formation. Once the particles in the fluidized bed are sufficiently wetted with the binding liquid and collide with another particle, a liquid bridge can form. Thereby, the strength and range of the adhesive forces have to be greater than the constantly acting separation forces. In addition to bridge formation, liquid penetrates into the particle matrix by diffusion or capillary pressure and, depending on the surface composition of the particles, the solids concentration in the liquid bridge increases due to material dissolution (Schubert, 1974). Depending on the sprayed liquid, evaporation occurs due to the warm gas flow and the liquid turns into a solid bridge (see Fig. 1). In the case of inefficient wetting, cohesive failure occurs in which the liquid bridge between two particles is unstable or droplets coalesce instead of forming the desired agglomerate structure (Palzer, 2006).

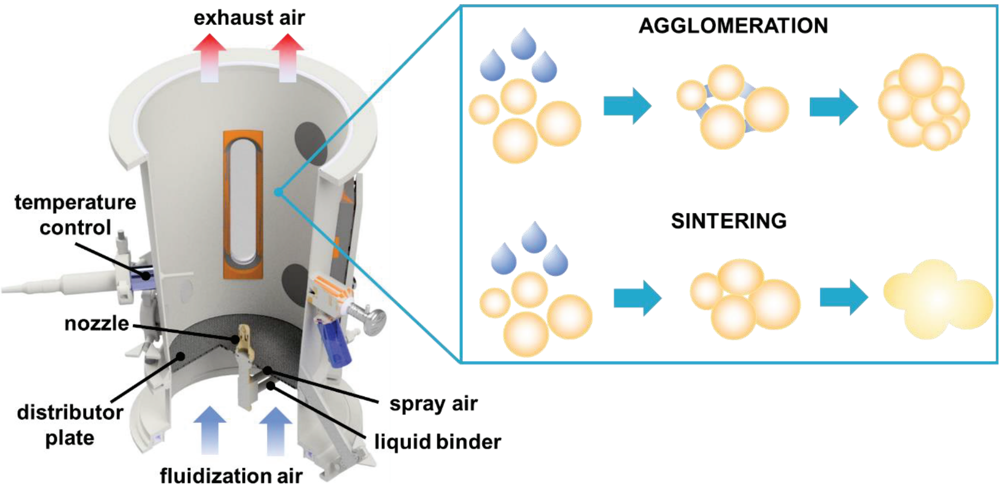

Figure 1: Setup of the fluidized bed process chamber (courtesy of Glatt GmbH, Germany) with a two-fluid nozzle in bottom-spray position and simplified illustration of the particle binding mechanisms agglomeration and sintering for structuring the PBMA powders.

Amorphous powder components continuously change their physical state due to the water adsorption of the particles in the fluidized bed process. Bhandari (2013) describes an increase in adhesion forces because of surface stickiness occurring with primary particles containing particularly carbohydrates, whereby the stickiness temperature is between 10 – 20°C above the glass transition temperature. During the drying process, high temperatures above the glass transition temperature can cause the powder to clump. Dopfer et al. (2013) postulated that exceeding the glass transition temperature between 20 – 35°C leads to a collapse of the particle collective and formation of a single large agglomerate. Depending on the moisture content and temperature, the material viscosity also decreases and sintering processes can appear between the powder particles. For amorphous, water-soluble powders, the sintering mechanism is assumed to be the major adhesion force between the particles (Hartmann & Palzer, 2011). During sintering, a bridge is formed between neighboring particles due to volume diffusion from the particle interior and surface diffusion, reducing the surface energy and porosity of the system (Palzer, 2006). The growth of the sintered bridge is accelerated by low dynamic viscosities, high surface tensions, increasing contact force and time. By drying the agglomerates through the fluidizing air in the process chamber, the initially formed liquid bridges or sinter necks in amorphous powders are transformed into a solid bridge (Schmidt, 2018). If the sintering is extensive, the solid material has no open but only closed pores (Palzer, 2006). The quality of the agglomerate produced is directly related to its physical and chemical properties. Particle size, density, reconstitution behavior and the morphological properties like porosity and surface structure are very important aspects of the product quality. In addition, the moisture content of the agglomerates produced is crucial in terms of shelf-life and mass gain. From an economic point of view, the product should contain a sufficient amount of water without negatively affecting the quality, since the water contained in the product is also a saleable mass. For some food products, the colour and mechanical strength of the agglomerates are also additional quality aspects (Schmidt, 2018).

1.5 Reconstitution

The reconstitution properties of powdered food products are of great importance, as the product systems often require a redispersion step for preparation (Schuchmann & Schuchmann, 2005). Reconstitution can be subdivided into wetting, sinking, dispersion and dissolution (see Fig. 2).

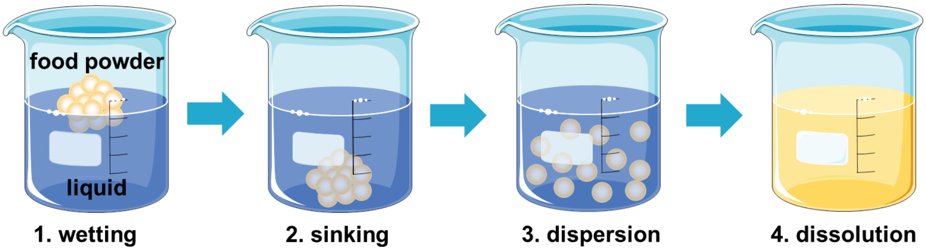

Figure 2: Overview of the wetting, sinking, dispersion and dissolution step during reconstitution.

During wetting, liquid penetrates into the pore system of the powder particles due to capillarity. The Washburn equation (1.5) describes this process assuming an infinite volume of liquid (Washburn, 1921):

$$l^2 = \frac{\sigma \cdot r \cdot cos\theta}{2 \cdot \eta} \cdot t\,. \tag{1.5}$$

The penetration distance of the liquid into the capillary l depends on the surface tension σ and the dynamic viscosity η of the penetrating liquid, the capillary radius r, the contact angle θ and the time t. The contact angle describes the spreading of a liquid droplet on the powder surface (see Fig. 3), whereby the adhesion forces between the powder and the liquid are stronger than the internal cohesion of the liquid and the adhesion forces between the powder and the vapor. The contact angle formed at the three-phase contact line is influenced by the surface roughness and porosity of the solid as well as the physical and chemical properties of the liquid (Wangler, 2019).

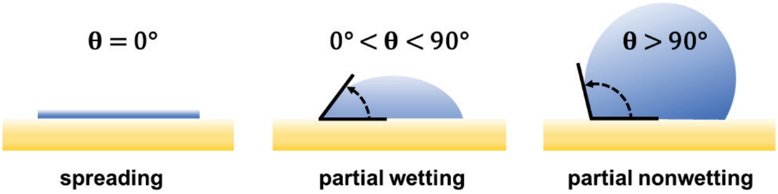

Figure 3: Wetting of a liquid droplet on a flat solid surface for the three cases spreading, partial wetting and partial nonwetting.

The wetting properties can be evaluated using Young's equation (1.6), wherein the interfacial tension γ_{sv} is pronounced between the solid and the gaseous phase, γ_{ls} between the liquid and solid phase and γ_{lv} between the liquid and the gas (Young, 1805):

$$cos\ \theta = \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}}. \tag{1.6}$$

For heterogeneous systems, the Cassi-Baxter equation (1.7) is used to calculate the contact angle of two components θ^*, which is defined by the surface fraction f and the contact angle θ of the respective component (Cassie & Baxter, 1944):

$$\cos \theta^* = f_1 \cdot cos\ \theta_1 + f_2 \cdot cos\ \theta_2\ . \tag{1.7}$$

In porous particle structures, the contact angle θ_2 increases to 180° due to the entrapment of air in the pores, leading to a more hydrophobic character and a higher apparent contact angle of the heterogeneous system. Carman (1956) and Kozeny (1927) introduce the hydraulic pore diameter d_h to describe porous systems in terms of wetting kinetics:

$$d_h = \frac{4 \cdot \varepsilon}{(1-\varepsilon) \cdot S_v} = \frac{2 \cdot \varepsilon \cdot d_p}{3 \cdot (1-\varepsilon)}. \tag{1.8}$$

Thereby ε corresponds to the bulk material porosity, d_p to the particle diameter and S_v is the specific surface area of the porous system.

After wetting, the powder product sinks into the liquid and the particles begin to disperse and dissolve (Schubert, 1989; Fitzpatrick et al., 2016). Agglomerates and aggregates are first broken down into their primary particles before being dissolved to produce a solution (Fitzpatrick et al., 2016). The dissolution rate depends on the diffusive supply of the solvent to the surface, the transition from the solid to the dissolved state of the surface component and the diffusive as well as convective transport of the dissolved matter into the solvent (Forny et al., 2011). The process occurring during dissolution proceed sequentially and with temporal overlap (Hogekamp & Schubert, 2003). The swelling and viscosity developments slow down the moistening process by changing the physical properties of the powder-liquid system (see Fig. 4). Furthermore, the mass transfer coefficient is reduced over time due to the swelling and viscosifying properties (Fitzpatrick et al., 2016). Hogekamp et al. (2003) postulated that product ingredients such as proteins and starch tend to have different swelling behavior in water. In addition, a highly viscous layer can form on the surface of the powder particles, which acts as a diffusion barrier for the solvent (Haas et al., 2020). Nnaedozie et al. (2019) demonstrated in studies with maltodextrin and lactose-maltodextrin mixtures that powder clumping occurs within the first 20 seconds and that a lower proportion of maltodextrin in the powder formulations reduces the overall hydration time compared to the pure raw material. Schubert (1989) recommends the formation of agglomerates with a diameter ≥ 0.2 mm for swellable powder products to optimize the instant properties. Since agglomerates have large voids between the particles, the solvent can easily penetrate and increase the total mass, so the product sinks faster than with finer powder systems (Pfalzer et al., 1973). Besides the particle size, rehydration and lump formation are influenced by the product composition and physical properties, the particle surface, particle structure, moisture content, wetting process and solubilization method (Fitzpatrick et al., 2016; Wangler, 2019).

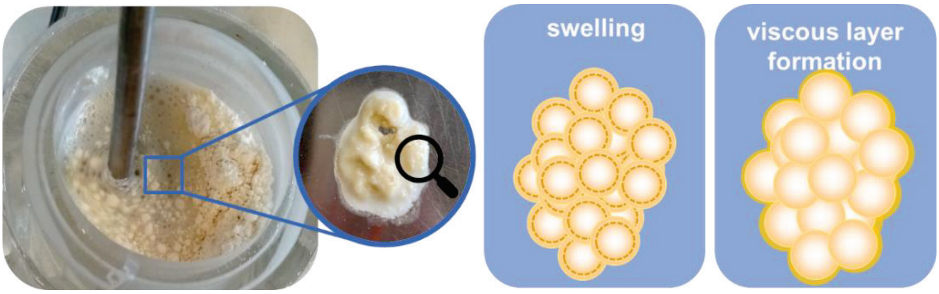

Figure 4: The processes of particle swelling and viscous layer formation around the particles that occur in PBMA powders during wetting, which negatively influence reconstitution and result in lump formation.

1.6 Objectives and strategy

To improve the reconstitution process by reducing lump formation, a targeted particle design through formation of agglomerates during spray drying or in the fluidized bed has to be conducted. But the structuration of plant-based products differs from the classic amorphous food materials due to the ingredients, which require the generation of fundamental expertise in agglomerate formation and consumer application. The investigation is performed on a model system of plant-based milk alternatives of relevance for the cooperation partner Nestlé S.A.. To identify the component influences in the complex product compositions, various formulations in particular regarding the protein and fiber source are developed and the differences are to be detected during the process steps of homogenization, spray drying and agglomeration in the fluidized bed. The combination of material systems and their effects on the overall physical as well as chemical properties reflected in the manufacturing process have not been researched to date. The project topic thus closes a gap in previous research, requiring the identification of the influence between material properties, manufacturing process and product quality. By generating knowledge, the research project provides a significant benefit in the product and process development of plant-based milk alternatives, which enables a transfer to more complex product compositions and production systems. To achieve an optimization of the reconstitution with the targeted particle design, the following aspects are investigated:

- Identification of the material properties of plant-based milk alternatives in liquid and powder form to regulate product quality.
- Investigation of agglomeration depending on the process parameters and formulation compositions to control the product properties.
- Implementation of targeted structuring to determine the optimal particle size and structure to improve reconstitution depending on the product compositions.
- Detection of the main impact factors on the reconstitution process.