Dissolvable Containers for Milk as an Alternative to Pre-Portioned Packaging

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Table of contents

1. Introduction

Coffee is one of the most popular beverages worldwide. In Germany, warmth, love and energy are associated with the consumption of coffee. Over 70 % of Germans consume coffee regularly of which > 67 % add milk, coffee cream or condensed milk [Bra17]. Every year, approximately 500,000 tons of coffee cream, coffee milk and condensed milk are filled in portion sizes [Obe14]. Due to their practical size these pre-portioned plastic jars are applied in a variety of sectors such as gastronomy, transportation services or events. However, inconvenient opening and splashing while opening the lid are some of the disadvantages. Concerning the matter of unclean handling, recent inventions focused on optimizing pre-portioned milk packaging to create a cleaner opening process that avoids splashing. Further solutions do not exist. The major disadvantage of this type of packaging is the significant environmental impact due to the production of plastic waste.

The production of plastic waste is an increasing global problem. Since 1950, global plastic production has increased drastically from annually 1.5 million tons up to 300 million tons nowadays. In total, 8.3 billion tons of plastic have been produced since 1950. According to Geyer et al. [Gey17], only a small proportion has been recycled or incinerated and 79 % of plastic waste accumulated in landfills and the environment. This development not only damages the world's oceans and nature in general, but also the health of the population through bioaccumulation in the food chain.

National governments are trying to face these problems in different ways. In 2015, for example, the European Parliament adopted an anti-plastic bag directive to reduce the consumption of plastic bags within the EU [EU15]. Currently the EU Commission is discussing a general ban on disposable plastic products and a plastic tax. Among the general population sustainability is gaining more and more attention – and consequently, companies face an increasing demand of sustainable products and packaging.

Therefore, the development of alternative materials to plastic based packaging and single-use articles becomes a significant economic factor, hence, the research on alternative materials has been growing for years. These materials are often based on components of renewable raw materials such as seaweed.

This work is focusing on the development of an alternative, sustainable and convenient packaging method to conventional single-portion packaging for milk or coffee cream. The aim is to avoid the disadvantages of unclean handling of conventional plastic containers and to contribute to plastic waste reduction. In this context, the product idea is first formulated and the exact product claims are defined. A suitable manufacturing process should then be selected and suitable materials identified. Furthermore, product properties regarding quality and applicability are investigated.

2. State of the art

Current research focuses on the development of new and, in particular, sustainable packaging options and food contact materials. In the following chapter general requirements for food packaging will be presented. Furthermore, alternative and innovative materials for use in the food sector and their production will be explained. Conventional methods of encapsulation in the field of foods and pharmaceuticals will be presented. Additionally, the unit operation 'crystallization' and its application for coating processes as well as the essential basics of crystallization will be discussed.

2.1 Requirements for food packaging

General legal requirements for food packaging and food contact materials are specified in the European Regulation *EU 1935/2004* [EU04]. In this context food packaging has three main functions:

- protection
- transport and storage function
- carrier of important information

Furthermore, there are numerous regulations regarding durability and hygiene. Food contact materials and articles must behave inert. Manufacturing according to the GMP (good manufacturing practice) principle is mandatory, i.e. they must be manufactured within the framework of documented quality assurance systems. Individual regulations apply to individual materials.

In addition to the legal requirements, the expectations and demands of customers also affect the development of new packaging. In this context the focus is on two major aspects:

- convenience
- sustainability

The focus is on innovative design, intuitive handling and easy-to-open packaging. However, the processing of renewable raw materials in production to reduce plastic waste is also playing an increasingly important role.

2.2 Alternative materials applied in food industry

In the past few years, many alternative materials have been developed for use in food packaging and other food contact materials. In the following, only a few will be mentioned and briefly presented.

Hydrocolloids are frequently used and well-suited natural substances in the manufacturing of alternative packaging and food contact materials.

For example, pectin is used in the production of edible and biodegradable straws (Fig. 2.2-1). These are stable in form in liquids for about 60 minutes before they slowly begin to dissolve [Lei16].

Figure 2.2-2 shows an edible and biodegradable alternative to common disposable cups made from plastics. The material is made from liquids, sucrose and hydrocolloids such as agar, carrageenan and pectin. Coloring agents are applied to produce colored products.

Figure 2.2-1: Straws made from pectin [Wis18]

During the manufacturing process, all components are heated, dissolved and then poured into molds to harden [Bri14]. Since these edible containers are manufactured on the basis of hydrocolloids, it can be assumed that the surfaces soften or even dissolve after certain holding times of liquids.

Figure 2.2-2: Edible cups made from hydrocolloids [Lol18]

Through the process of spherification, e.g. alginate can be used for the production of small 'edible water bottles' [Ski16]. Through the interaction of calcium ions and sodium alginate, a soft and insoluble shell of calcium alginate is formed around the water. This degradable packaging for water was created by Skipping Rocks Lab (Fig. 2.2-3).

Figure 2.2-3: Small edible water bottle made by alginate [Ooh17]

Proteins can be used for the production of edible and biodegradable films. Films based on casein, peas or soy proteins can be produced by casting or extrusion [Fro10].

2.3 Encapsulation and coating processes

Encapsulation and coating are of great importance in both the pharmaceutical and food industries. Encapsulation is described as a process to entrap one substance (active agent) within another substance (wall material). In comparison, coating is described as covering, which is applied to the solid surface of an object.
The main objectives for application of these techniques are summarized in Table 2.3-1.

Table 2.3-1: Aims of encapsulation and coating processes in the field of food and pharmaceutical industries [Ned11, Gib99, Inp01, Rie01]

food industry	pharmaceutical industry
protection against environmental influences	
dosability	
easy handling	
taste masking	
barrier for gas and water exchange	
stabilization during processing	
protection of actives	
controlled release	

The most common process for encapsulation in the food industry is spray drying. It is a flexible, continuous and economical technique. Further methods are freeze drying, melt extrusion, fluidized bed coating or spray cooling [Ned11]. However, by the application of these mentioned techniques products limited in size are obtained. Therefore, these processes can be classified in the field of microencapsulation.

A further technology, which is frequently used in the pharmaceutical industry, is the filling of hard or soft gelatin capsules. These are produced in several process steps. Hard gelatin capsules are used to enclose powders, granules or pellets. Soft gelatin capsules are suitable for encapsulating pasty or liquid material [Cad96].

2.4 Coating and encapsulation by crystallization

The process of crystallization can be applied as a tool for product development, e.g. in the field of pharmaceutical and food industries. Stelzer et al. [Ste10] give a good overview of the potential applications. Crystallization can be used, for example, to produce fast-dissolving tablets [Fro16], hollow crystalline needles [Sei17] or for the coating of tablets [Kim03, Mam17].

The *in situ* coating process presented by Römbach et al. [Röm07] allows a reduction of the process steps by direct self-coating. Figure 2.4-1 compares the process steps between the classic production of coated tablets and in-situ coating. Due to its few process steps the in situ process is a highly effective and economical coating process. A self-controlled coating process from a binary melt is initiated by cooling (Fig.2.4-2).

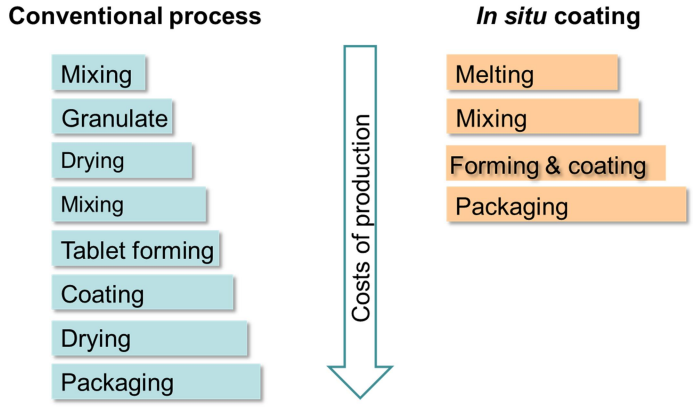


Figure 2.4-1: Process steps of classic coating process compared to *in situ* coating [Röm10]

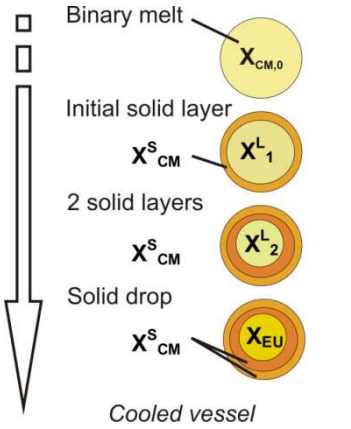


Figure 2.4-2:Schematic illustration of the soldification process during *in situ* coating [Röm10]

In further work on *in situ* coating, Wendt et al. [Wen14] identified the need for controlled nucleation in order to achieve a uniform coating of the pastilles. Both ultrasound and seeding with intrinsic seeds were used as nucleation techniques.
Hartwig [Har16] applied the *in situ* technique in combination with a pastillation process for the production of pastilles with a liquid filling. In this case xylitol has been used as encapsulant. However, Hartwig [Har16] only determined the conditions for the production of the pastilles experimentally.

Crystallization is also used in the production of sugar crust chocolates [Hof04a] and other encrusted products [Her17, Sel16]. In this context, supersaturated solutions are filled into starch beds used for shaping. The containing starch particles initiate the nucleation of the solution from the outside. The supersaturation of the solution is reduced by a cooling process and the growth of the crystalline shell is continued until equilibrium is reached [Hof04a].

2.5 Crystallization

In this chapter, the basics of crystallization that are necessary for the understanding of the present work are briefly outlined. Further information on the process of crystallization is presented in detail in a variety of literature (e.g. Hofmann [Hof04], Mersmann [Mer05], Mullin [Mul01] or Myerson [Mye02]).
Fundamentally, crystallization is a unit operation of thermal separation from supersaturated phases. One or more substances are transferred from an amorphous, liquid or gaseous state into a solid and ordered phase (crystalline state) [Hof04].

Supersaturation zones

Supersaturation is the driving force for crystallization. In order to separate a substance from a liquid or gaseous state by crystallization, it must be present in a supersaturated concentration, a thermodynamically non-equilibrium state. The supersaturation can be generated by various processes such as cooling, evaporation, by a vacuum, a chemical reaction or an addition of a further substance. The supersaturation factor (y) indicates the respective state of supersaturation [Hof04a]. It results from the ratio of the present supersaturation of a solution (q) to the saturation value (qL).

In a phase diagram three zones can be defined (see Fig. 2.5-1):

- Stable zone (SZ)
- Metastable zone (MSZ)
- Unstable zone (USZ)

Nucleation defines the border between USZ and MSZ -a kinetic border. In the metastable zone, however, only secondary nucleation can occur, i.e. if crystals are already present, but no classical crystal nuclei can form. Already existing crystals, however, will grow.

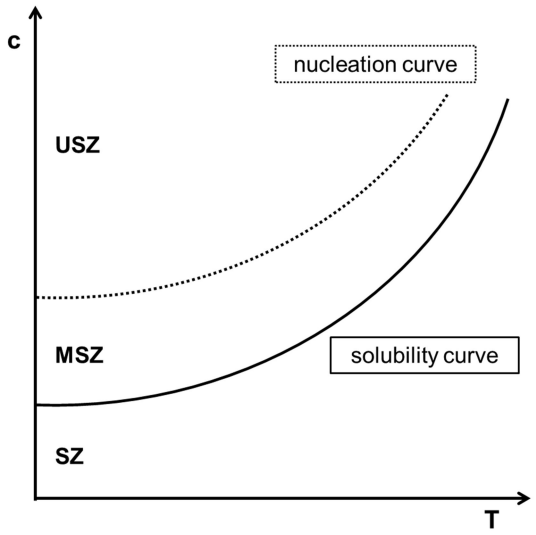


Figure 2.5-1: Schematic illustration of a phase diagram (drawing according to Hof04])

Nucleation

Nucleation takes place at the very beginning of each crystallization process. For example, Mullin [Mul01] differentiates between primary and secondary nucleation. The primary nucleation is divided into homogeneous and heterogeneous. According to Hofmann [Hof04], homogeneous nucleation occurs when nucleation is generated only by supersaturation and without influence by other components. If this is triggered by external material (e.g. impurities), this is called heterogeneous nucleation. The process of secondary nucleation is initiated based on already existing crystals or crystal fragments due to energy input (e.g. stirring or pumping) in supersaturated solutions [Mul01]. If the nucleation is stimulated by the addition of seed crystals, it is also a secondary nucleation. The rate of nucleation depends on the degree supersaturation.

Crystal growth

The nucleation is followed by the growth of the nuclei. Crystal growth is usually described in the literature as a 3-step process. In the first step, molecules or ions from the solution are first transported to the crystal surface by convective and diffusive mass transport, in order to be absorbed. In the second step the growth units are incorporated into the existing crystal lattice [Hof04]. The growth rate increases with increasing supersaturation (e.g. [Gni93]). The third step concerns the heat of fusion which is always present at phase changes and needs to be transported [Kru93].

3. Aims of the work

The development of new packaging methods is a fundamental part of product development, especially in the food industry. On the one hand, this is intended to meet customers' needs for innovative and sustainable products, and on the other hand to ensure a cost-effective production of the end product. In particular with regard to the steadily growing concepts of sustainability, various alternative materials for food packaging and food contact materials have been developed. So far, no stable material is known that can hold liquids for a longer time, but dissolving concurrently in other liquids.

Therefore, the aim of this work is the development of a dissolvable packaging option for liquids, explained on the example of milk as an alternative to conventional pre-portioned plastic jars (Fig. 3-1). This packaging should be part of the consumable product in order to avoid the disadvantages of common single-use plastic packaging.

Figure 3-1: Pre-portioned plastic jars for milk and condensed milk

In previous studies crystallization techniques have already been successfully applied in the area of product development for coating and encapsulation processes [Röm10, Wen15, Har16]. Following those works, a crystallization technique is chosen to encapsulate larger volumes of milk and condensed milk in a solid coat.

The defined **claims of the future product** are summarized in Figure 3-2.

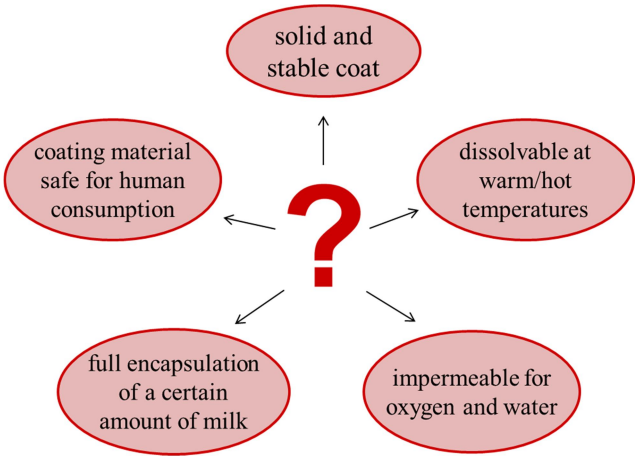


Figure 3-2: Defined claims of the future product

Based on these claims, 4 fundamental research questions are derived, which have to be dealt with in this thesis:

1. Can the so far known **crystallization technique** also be applied or adopted for the encapsulation of larger volumes of milk and condensed milk?
2. Which **substances are suitable** for the encapsulation of milk or condensed milk in order to fulfil all defined properties and which requirements must they fulfill?
3. Which suitable methods can be recommended for the **quality analysis** of the resulting products?
4. Is it possible to establish a **general process description** for the production of crystalline containers with liquid filling?

If the defined claims can be achieved, an innovative, convenient and sustainable product with special focus on food and beverage sector can be produced.

4. Materials and methods

4.1 Materials

In the following chapter, all relevant substances that have been used for the encapsulation process are introduced. Table 4.1-1 shows all substances used and their intended application.

Table 4.1-1. Used materials and their intended application

intended application	substance	supplier
encapsulation material	Sucrose	Local food retailer
	Erythritol Mannitol Isomalt	Cargill Krefeld, Germany
	Cellobiose	N/A
	Xylitol	Sigma Aldrich
encapsulated liquid	Milk (3.5 % fat)	Local food retailer
	Condensed milk (10 % fat)	Local food retailer
	Coconut milk (powder)	N/A
seeding material	Corn starch	N/A
	Xylitol (milled)	Sigma-Aldrich Chemie GmbH, D-32839, Steinheim
additive	Flavor (toffee caramel)	N/A
	Food coloring (blue)	Dr. Oetker GmbH Bielefeld, Germany

4.1.1 Encapsulation material

Within the framework of this work, different encapsulation materials are tested for the encapsulation of the desired liquids by means of crystallization. These crystalline substances are applied to form the future coat of the final product.

Disaccharides

The disaccharide sucrose has been chosen as it is a well investigated substance. Due to its excellent properties, it has a large variety of applications in the field of food technology [Hof04a].
Due to negative effects on human health (influence on insulin level, cariogenicity), an increased sugar intake is not recommended [WHO15].
Cellobiose is used in the food industry because of its low sweetening intense and neutral taste to produce low-calorie products such as fruit spreads, sweets, beverages and meat products [Pfe16a]. In the context of this work it has been chosen to produce sugar-free products with a low intensity of sweetness.
Relevant properties of the used disaccharides are shown in Table 4.1-2.

Table 4.1-2: Relevant properties of used disaccharides [Hof04a]

property	sucrose	cellobiose
sweetness	100 %	20 %
calories	400 kcal/100 g	N/A
solubility in water (20 °C)	68 g/100 g solution	N/A
density	1.59 g/cm^3	1.46 g/cm^3

Polyols

In order to be capable of producing sugar-free and less sweet products, various polyols have been selected as an alternative to sucrose. Sugar alcohols are found in nature, especially, in fruits, and are produced by reducing carbohydrates. Compared to sucrose, polyols have a lower caloric value. They are suitable for diabetics due to their low glycemic index [Ros07]. Furthermore, polyols are not cariogenic compared to sucrose [Mäk10]. However, polyols belong to the group of hard digestible carbohydrates, which stimulate the intestinal activity and have a laxative effect [Car14]. Foods containing more than 10 % polyols must therefore be labelled with a warning. Relevant properties of the used polyols are summarized in Table 4.1-3.

Table 4.1-3: Relevant properties of used polyols [Bel01, Bon06, Car13, Car14a, Fre10]

property	erythritol	mannitol	isomalt	xylitol
E-number	E968	E421	E953	E967
sweetness	60 %	60 – 69 %	45 – 50 %	98 %
calories	20 kcal/100 g	240 kcal/100 g	200 kcal/100 g	240 kcal/100 g
solubility in water (20 °C)	32 g/100 g solution	18 g/100 g solution	25 g/100 g solution	62.5 g/100g solution
density	1.45 g/cm^3	1.36 g/cm^3	1.3 g/cm^3	1.52 g/cm^3

4.1.2 Solvents

Milk and condensed milk have primarily been used for the encapsulation experiments. The aim was to encapsulate these solvents in a solid and stable coat during the manufacturing process.

Milk

Milk is defined as a product obtained by milking from the mammary glands of female mammals without any addition or removal. Consequently, milk may only be treated by means of heating, homogenization and fat content adjustment [Glo15]. From a physical point of view, milk is a white, turbid emulsion or colloidal dispersion of 4 % milk fat, proteins and milk sugar in water. The fat is emulsified in the form of droplets in the milk serum, which are surrounded by a membrane. The white coloring of the milk is caused by the scattering and absorption of light by the fat droplets and protein micelles.
Due to the special composition and properties of milk, the application of this liquid in a crystallization process is a special challenge.
For all experiments UHT milk with a fat content of 3.5 % has been used.

Condensed milk

Condensed milk is a product produced from milk. Therefore, the water is removed by evaporation at 40-80 °C. Approx. 60 % of the water is removed, which increases the dry mass of the milk to a thick, pasty consistency. The homogenization of the condensed milk, which prevents fat separation, significantly increases the whitening power in the coffee. To achieve the desired shelf-life, the condensed milk heat-treated at ultra-high temperature a sterilized after filling. Due to the Maillard reaction during the heating, the condensed milk obtains a slightly dark color and caramel flavor [Glo15].
Within the experimental process of encapsulation condensed milk in a solid coat, heat-treated condensed milk with a fat content of 10 % has been used. It has been applied to proof whether encapsulation of liquids with a higher fat content is possible or not.

Coconut milk

Coconut milk is the liquid derived from the grated flesh of a ripe coconut [Seo97]. This plant-derived milk is one of the most popular vegan and lactose-free alternatives to conventional cow's milk in Germany [Sta16]. Coconut milk has been chosen to produce crystalline containers with vegan fillings.
In this work coconut milk powder has been used. By adding distilled water, coconut milk with a fat content of 7 % was produced. It has been applied to produce vegan products.

4.1.3 Seeding material

In the course of the encapsulation process seeding material is necessary to initiate the crystallization process of the future container coat. Native corn starch with a narrow monomodular particle size of ~ 10 µm has been applied.

4.2 Methods

In the following chapter the preliminary experiments necessary for the preparation of the product samples and their preparation in general will be explained. Furthermore, methods for quality analyses of the samples produced will be described. In addition, the necessary methods for the investigation of the physical properties of the sample solutions will be presented. All devices and evaluation programs are listed in the appendix.

4.2.1 Determination of solubility and nucleation

The solubility and nucleation of the investigated systems has been determined by isothermal and polythermal measurements.

Isothermal measurement

The solubility of the crystalline substances in different solvents with respect to temperature has been determined by means of an isothermal measurement via index of refraction. For this purpose, the required solvent has been heated to the respective temperature in a temperature-controlled double-walled vessel. The corresponding crystalline substance has then been added in excess and homogenized for 1 hour (S=0.6 m/s). Then the stirring process has been stopped so that the undissolved and excess crystals could settle at the bottom of the vessel. After 1 h the concentration of the saturated supernatants has been determined via index of refraction (see Chapter 4.2.2). All measurements have been carried out in triple determination.

Polythermal measurement

Furthermore, an ultrasound measurement technique has been applied to investigate the metastable zone width (MSZW) of all solutions used. Solubility and nucleation temperatures have been determined as a function of concentration. Further backgrounds and functionality of this measuring technique are described in detail by Omar et al. [Oma99]. The experimental setup is shown in Figure 4.2-1. First, the respective crystalline substances have been dissolved in the solvents under stirring (S=0.6 m/s) in a temperature-controlled double-walled vessel. After the adjustment of the ultrasonic probe inside the solution (liquid sample), the solution has been cooled and heated up with a rate of 10 K/h. These polythermal measurements have been carried out in threefold.

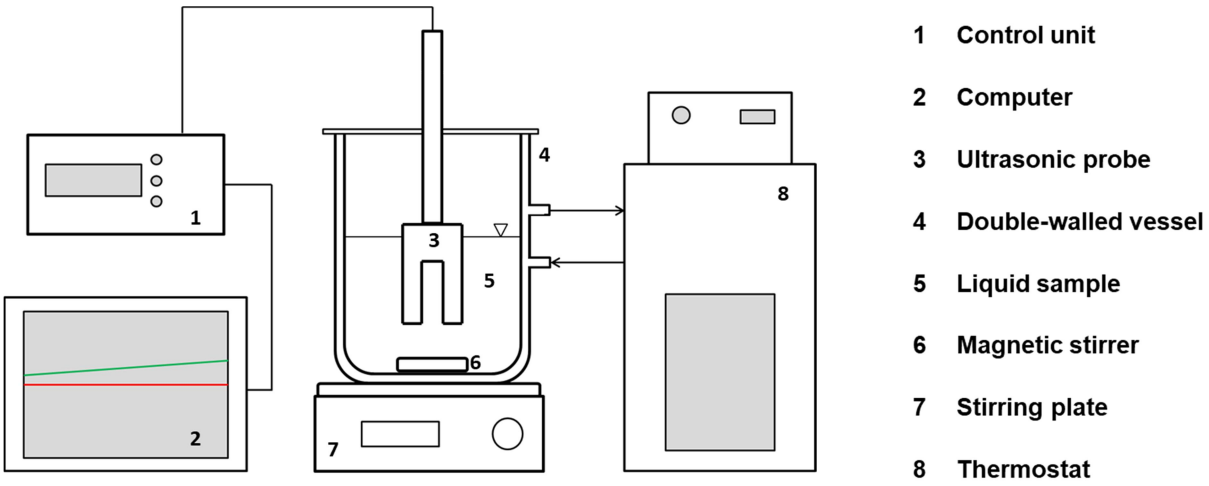


Figure 4.2-1: Schematic setup of ultrasonic measurement device for the polythermal determination of MSZW

During the cooling or heating process, the ultrasonic velocity within the solution has been measured by means of the ultrasonic probe and recorded by a control unit. This ultrasonic velocity results from the time it takes for sound to travel a defined distance [Köh01]. It depends on the temperature, pressure, density and adiabatic compressibility of the material through which the signal passes.

4.2.2 Determination of concentration via refractive index

The concentrations of the sample solutions to be investigated have been determined by a refractometer using the refractive index. The refractometer is based on the principle of refraction, which is influenced by the type and concentration of a dissolved substance.
First, a calibration curve for each sample solution has been generated. For this purpose, solutions of the respective crystalline substances and the desired solvents in different defined concentrations have been prepared. The refractive index of each sample has been determined at 60 °C in fivefold. Depending on the defined concentration and using linear regression, the averaged values have resulted in a calibration curve on which the further solubility calculations are based.
For the determination of the concentration, the refractive index of the solution to be examined has been measured and the respective concentration has been calculated on the basis of the corresponding calibration curve.

4.2.3 Determination of densities

Knowledge of the density of the respective solvents is necessary to calculate the optimum starting concentration of the casting solutions. The densities of the solvents used have been determined in threefold using an oscillating U-tube density meter.

4.2.4 Definition of sample parameters

For all experiments the shape of the product samples has been defined to be hemispheres with a diameter of 30 mm and a height of 15 mm (Fig. 4.2-2). The thickness of the container coat has been set to be 1.5 mm. The desired product storage temperature has been set to be 25 °C.

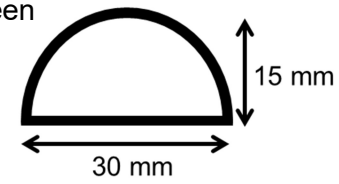


Figure 4.2-2: Defined shape and size of product sample

4.2.5 Calculation of optimum start concentration

In order to determine the optimum starting concentration (corresponding to the amount of solids used), following equations have been defined:

$$m_{solid} = \left(\frac{V_T - V_C}{100} \cdot c_{storage} + V_C\right) \cdot \rho_{solid} \qquad \textbf{Equation 4.2-1}$$

$$m_{solvent} = \left((V_T - V_C) - \left(\frac{V_T - V_C}{100}\right) \cdot c_{storage}\right) \cdot \rho_{solvent} \qquad \textbf{Equation 4.2-2}$$

The equations contain all parameters described in the preceding chapters.

4.2.6 Process of sample production

All samples have been produced by using the technique of crystallization. For the process following essentials are required:

- SOLVENT (liquid to be encapsulated)
- CRYSTALLINE SUBSTANCE (solid to form the future coat)
- MOLDS (shaping of the final product)
- SEEDING MATERIAL (initiation of crystallization)

The starting point for the encapsulation process is an unsaturated solution prepared from the desired components. The crystalline substance is dissolved in a tempered double-walled vessel for 1 h in the solvent and homogenized with S=0.6 m/s. The solution temperature ($T_{solution}$) is selected > 10 K above the saturation temperature ($T_{saturated}$) to ensure complete dissolution. Then this unsaturated solution is cooled down until a certain supersaturation is reached and the metastable zone is attained. This supersaturated solution (casting solution) is then filled into the molds and the top side of the future container is covered with seeding material. The molds are then cooled from the casting temperature ($T_{casting}$) to the previously defined storage temperature ($T_{storage}$) and stored for 24 hours. The resulting samples are then removed from the molds and remaining seed material is removed with a brush.

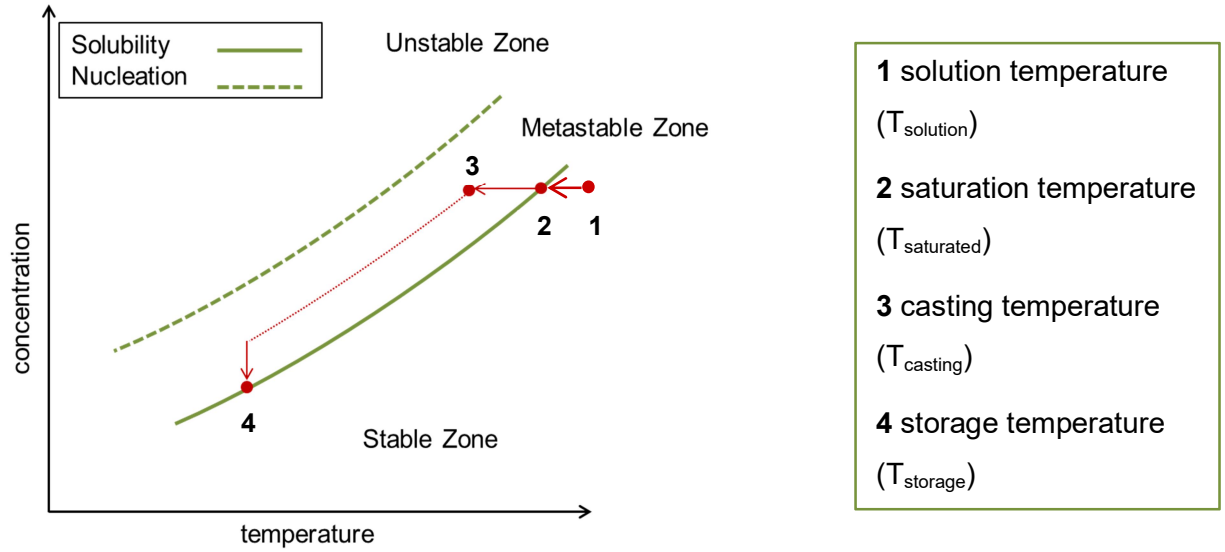


Figure 4.2-3: Schematic illustration of sample preparation based on phase diagram

Powder trays are used as shaping technique. Therefore, starch is sieved into trays and dried. Molds are prepared by using a stamp (Fig. 4.2-4).

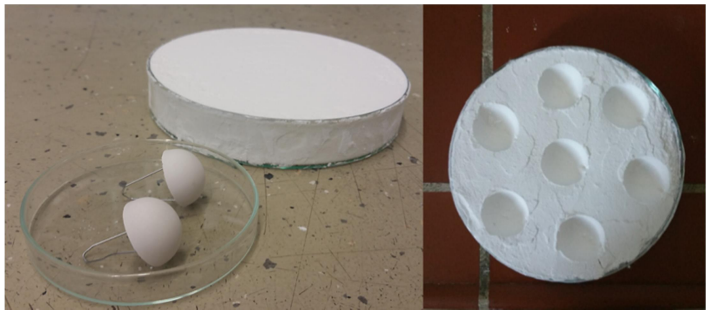


Figure 4.2-4: Shaping technique (left:Stamps and powder tray, right: Molds)

4.2.7 Verification of the equations to determine the optimum start concentration by means of microscopic layer thickness analysis

The equations for calculating the optimum application quantity of crystalline solids and solvents (optimum starting concentration of the casting solutions) have been verified experimentally. For this purpose, the expected layer thicknesses have been calculated for four different previously defined solid fractions and then compared with the actually determined layer thicknesses.

To evaluate the layer thickness, the milk containers have been examined as a function of the solid content. The cross-section of the resulting crystalline coat of ten samples each has been investigated microscopically.

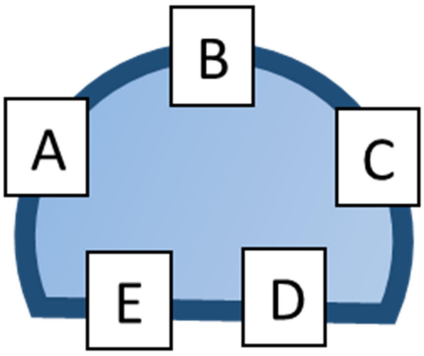


Figure 4.2-5: 5 microscopic sections (A-E) of a capsule cross-section

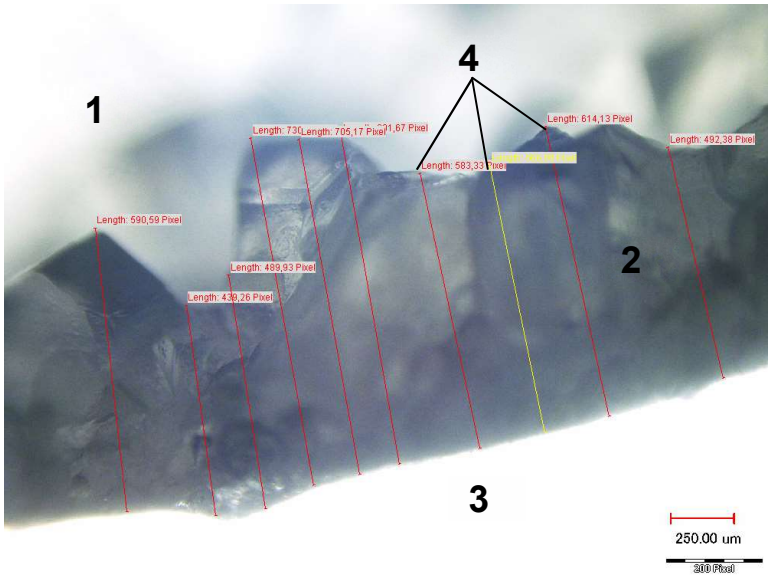


Figure 4.2-6: Exemplary evaluation of a sample cross-section using AnalySIS (1.sample interior, 2.crystalline coat, 3.outside, 4.measuring lines for thickness determination)

As shown in Figure 4.2-5, five images (A-E) of the cross-section of each container have been taken at 100x magnification. The microscopic images have been evaluated graphically with the “AnalySIS” software. Ten measurement lines have been inserted into each image (Figure 4.2-6). The length of these measurement lines has been converted to millimeters based on the number of pixels from which the layer thickness results.

4.2.8 Maturation time

The determination of the maturation time of crystalline containers has been carried out exemplarily using the system 'sucrose-milk'. To determine the maturation time of the containers after manufacturing the concentration of the solids inside the containers has been measured over time. The concentration has been determined by a refractometer (see Chapter 4.2.2). For this purpose, five samples have been taken from each of ten containers.
The reduction of the concentration of dissolved solids in the encapsulated liquid provides information about the progress of the encapsulation process. The degradation should correlate with the growth of the crystalline capsule coat. When the “temporary thermodynamic equilibrium” of the container is reached at the previously defined storage temperature, the reduction of the concentration is ended -the concentration should remain constant.

4.2.9 Mechanical stability

Sufficient mechanical stability of the containers is essential for safe handling, transport and storage of the end product.
To determine the mechanical stability (p_{max}) of the containers a stability measurement device described by Hartwig et al. [Har17] has been used. This method is based on the crushing force applied, which is required to break a single container in relation to the surface of the examined samples (Eq. 4.2-3).

$$p_{max}\left[\frac{N}{cm2}\right] = \frac{\mathrm{m}_{\max}\,[g]\cdot \mathrm{g}\left[\frac{m}{s^2}\right]}{A_{sample}\,[cm^2]} \qquad \textbf{Equation 4.2-3}$$

The stability has been determined at different points of time after the production. At any point 10 containers out of two production batches have been examined.
The mechanical stability over time should provide information on the point of time after manufacturing at which the products are already safe for possible packaging, even if the maturation process has not yet been completed. The mechanical stability at the end of the maturing period should allow comparison between different types of samples, which are either produced in a different process or contain different ingredients.

4.2.10 Mass loss

The mass loss of the produced containers over time is intended to provide information about the impermeability of the resulting crystalline coats of the containers. In this experiment three different container systems (see Table 4.2-1) have been compared with each other. For the determination 20 samples have been stored in a climatic chamber at 25 °C and 50 RH% for a period of three weeks. During this time the samples have been weighed at frequent intervals.

Table 4.2-1: Experimental setup for the investigation of the storage behavior of different container types

sample type	solid content [wt%]	sample number [-]	storage time [d]
sucrose-milk	73.6	20	21
sucrose-condensed-milk	64.9		
erythritol-condensed-milk	49.1		

4.2.11 Shelf-life

The shelf-life is one of the most important properties of a product in the food sector as it is a compulsory label element and spoiled products can cause health hazards to consumers. The shelf-life has been investigated in two different test sections with two different methods.

pH value

In the first test section, the shelf-life of containers stored at 25 °C has been investigated over a period of three weeks by determining the pH value of the encapsulated liquids as the pH value is an indicator for the perishability of milk. Therefore, pH test strips were used. The experiment has been carried out in fivefold. This test method is intended to give initial indications of the shelf-life of the products.

Microbiological investigation

In order to make more precise statements regarding the shelf-life of the containers, microbiological tests have been carried out in a second test section. The analyses have exemplarily been performed using sucrose- and xylitol-based samples. All samples investigated are summarized in Table 4.2-2.

Table 4.2-2: Samples used for microbiological investigations

sample type	sample age	sample number
sucrose-milk	4 days	3
	4 weeks	
	6 weeks	
	6 months	
sucrose-coconut milk	4 days	
	6 weeks	
	3 months	
xylitol-milk	4 days	
	4 weeks	
xylitol-coconut milk	4 days	
	4 weeks	

Resazurine assay

A first microbiological rapid test has been carried out using a resazurine assay. This method is based on the change of the resazurine coloring by metabolic processes of microorganisms. With an increased cell count, the color changes from pastel blue (<0.5 x 10^5 cell/mL) to reddish violet (4-20 x 10^5 cells/mL) to pink red and colorless (>20 x 10^5 cells/mL).
For the experiments, encapsulated liquid has been removed from the crystalline containers by using a sterile syringe. Then 100 µL of each sample solution have been placed in a microwell plate and 10 µL of 0.01 % resazurine solution have been added. Mixing has been achieved by slightly tilting the well plate. Then the samples were incubated for 1 h at 37 °C. During incubation, the samples have been protected from light exposure. The evaluation has been carried out through optical color comparison.

Determination of total bacteria count china-blue lactose agar

The total bacteria count (TBC) of the encapsulated liquid of the different product samples has been determined by using china-blue lactose agar plates. This culture medium is recommended in Germany for the determination of TBC of milk and milk products by the Food and Feed Code (LFGB).
For the experiment, encapsulated liquid has been removed from each product sample by using a sterile syringe. Then a dilution series from 10^{-1}–10^{-6} has been prepared. 1 mL of each dilution has then been pipetted on a prepared sterile agar plate. After the following incubation for 48 h at 30 °C the colonies have been counted. A TBC up to 10^5/mL is considered to be tolerable.

4.2.12 Release behavior of encapsulated liquid

The release behavior plays a significant role for the product developed in this work. The milk container should be able to be placed in hot or warm drinks. There, the crystalline layer serving as packaging should dissolve as fast as possible and release the encapsulated liquid into the beverage. For this purpose, the release behavior of the encapsulated liquid at different temperatures has been investigated.
UV/Vis photometry has been applied to determine the release time of the encapsulated liquid out of the container into a liquid (Figure 4.2-7).

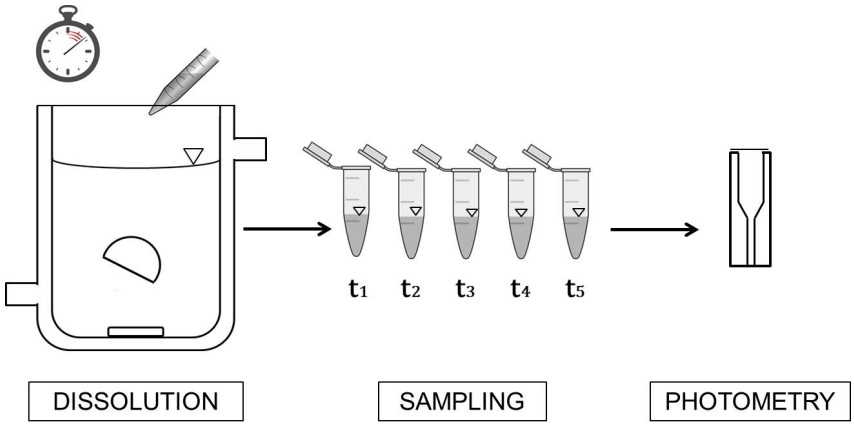


Figure 4.2-7: Determination of release time via UV/Vis photometry [Wel18a]

Therefore, a single container has been dissolved in a stirred vessel (S=0.6 m/s) with 110 mL water at different temperatures. In the course of the dissolution the sampling has been executed in 5 to 10 s intervals. The absorbance of the samples taken, has then been determined via UV/Vis photometry at 500 nm. The absorbance correlating with the released liquid should allow conclusions concerning the release time and furthermore, with the dissolution time of the coating. The experiments have been carried out in fivefold. All containers have been investigated four days after the production.
The dissolution behavior of sugar cubes at different temperatures has been investigated as a reference. The measurements have been carried out under the same conditions, but by means of concentration measurements (see Chapter 4.2.2) instead of UV/Vis photometry.

4.2.13 Product properties under different storage conditions

During transport and storage of a product after production, it is not always possible to guarantee constant environmental conditions. Due to this, it is necessary to determine the limits of the storage conditions in order to guarantee the optimum properties of the end product.
In this context, the influence of different storage temperatures and air humidity on the product quality has been investigated exemplarily on the system sucrose-milk. For this purpose, ten samples each from two different production batches have been stored for 24 h under the specified conditions. The storage conditions are shown in Table 4.2-3. The mechanical stability (see Chapter 4.2.9) of the samples has then been examined as it has been identified as a suitable comparison parameter with regard to safe handling and transport.

Table 4.2-3: Experimental setup for the investigation of the influence of temperature and air humidity on sucrose milk capsules

sample type	sample number [-]	storage time [h]	storage temperature [°C]	storage air humidity [RH%]
sucrose-milk	10	24	5	50
			15	
			25	
			40	
			50	
			60	
	10		25	10
				30
				50
				70

4.2.14 Investigation of physical properties of sample solutions

Physical properties, e.g. viscosity, surface tension and contact angle of the sample solutions used for the encapsulation process, have been investigated. The concentrations of the investigated supersaturated solutions are summarized in Table 4.2-4. The compositions correspond to the casting solutions.

Table 4.2-4: Concentration of different sample solutions used for investigation of physical properties

sample solution	concentration [wt%]
sucrose-milk	73.6
sucrose-condensed milk	69.1
erythritol-milk	54.4
erythritol-condensed milk	49.1
isomalt-milk	61.8
isomalt- condensed milk	44.6
mannitol-milk	35.3
mannitol- condensed milk	28.7
cellobiose-milk	20.2
cellobiose- condensed milk	16.7

Dynamic viscosity (η)

The dynamic viscosity (η) can be described as the inner friction of a liquid or the tendency of a liquid to resist flowing. The measurements have been performed using a rotational viscometer (searle-type). The measuring unit of the rotational viscometer consists of two coaxial cylinders, with the inner measuring body rotating at a constant rotational speed (n). This results in the formation of a shear flow within the viscous measuring solution in the annular gap. Rotational speed (n) and torque (M) are recorded by software as measuring signals. The measured variables correlate with the rheometric variables shear rate (γ) and shear stress (τ). The dynamic viscosity is then given in millipascal seconds.

For the experiments, 70 mL of each sample solution have been examined. Each measurement has been carried out over a period of 5 minutes with n=200 1/s. The dynamic viscosity has been investigated as a function of temperature. All measurements have been carried out in triple-determination.

Surface tension (σ)

The surface tension of the respective sample solutions has been determined by means of a plate-tensiometer as a function of time. For this purpose, 15 mL of the sample solution to be investigated have been filled into a tempered vessel. Subsequently, a vertically suspended platinum plate has been immersed in the sample solution. The surface tension is calculated based on the force (F) acting on this plate when it touches the surface of the liquid. The surface tensions of pure milk and condensed milk have been determined as reference values. All measurements have been carried out in threefold.

Infiltration factor (I)

From the results of the viscosity and surface tension determinations, an infiltration factor (I) has been determined based on Equation 4.2-4 [Pas94].

$$I \sim \left(\frac{\sigma}{\eta}\right)^{0.5}$$ **Equation 4.2-4**

Contact angle (θ)

For further investigation of the infiltration behavior of the casting solutions, the change in the contact angle of a drop of the respective solution on a starch bed over time has been determined. The contact angle has been obtained by a drop shape analysis.

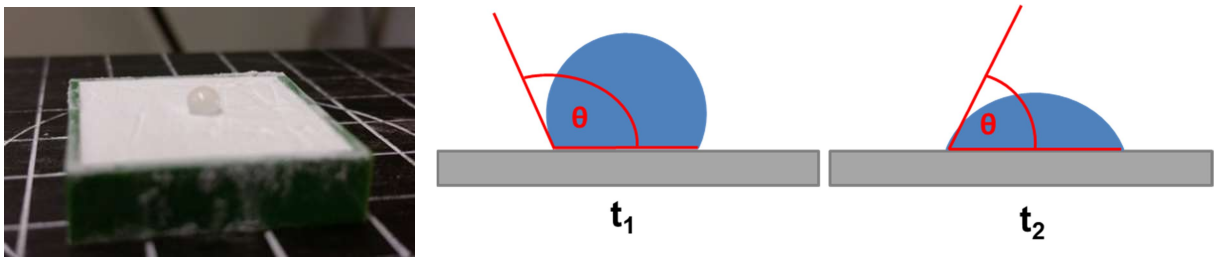


Figure 4.2-8: Schematic contact angle measurement of a drop (left: supersaturated drop on starch bed; right: contact angle determination)

As shown in Figure 4.2-8 (left) 20 µL of the supersaturated casting solution have been placed as a drop on a small starch bed (filling density 0.5 g/cm³). The drops have then been photographed and its shape analyzed. To evaluate the contact angle, a tangential method has been used which adapts the entire profile of the horizontal drop to a general conic section equation. The base line of the drop is used to determine the slope at the three-phase contact point and therefore calculate the contact angle. The contact angle has been determined directly after placement of the drop (t_1) until no further deformation has been detected (t_2) as shown in Figure 4.2-7 (right).
The change of the contact angle has been calculated by Equation 4.2-5.

$$\Delta\theta = \frac{\theta(t_2) - \theta(t_1)}{t_2}$$ **Equation 4.2-5**

Quick test for the investigation of infiltration behavior

In order to investigate the infiltration behavior of casting solutions in a fast procedure, a tube test has been performed as a quick test. For this, 2 mL of the respective solution to be investigated have been filled into a plastic tube filled with starch (ρ_{bulk} ~0.5 g/cm³) (Fig. 4.2-9). Subsequently, the infiltration behavior of the solution into the starch has been observed over time. Pure water and a sucrose-milk solution served as reference values.

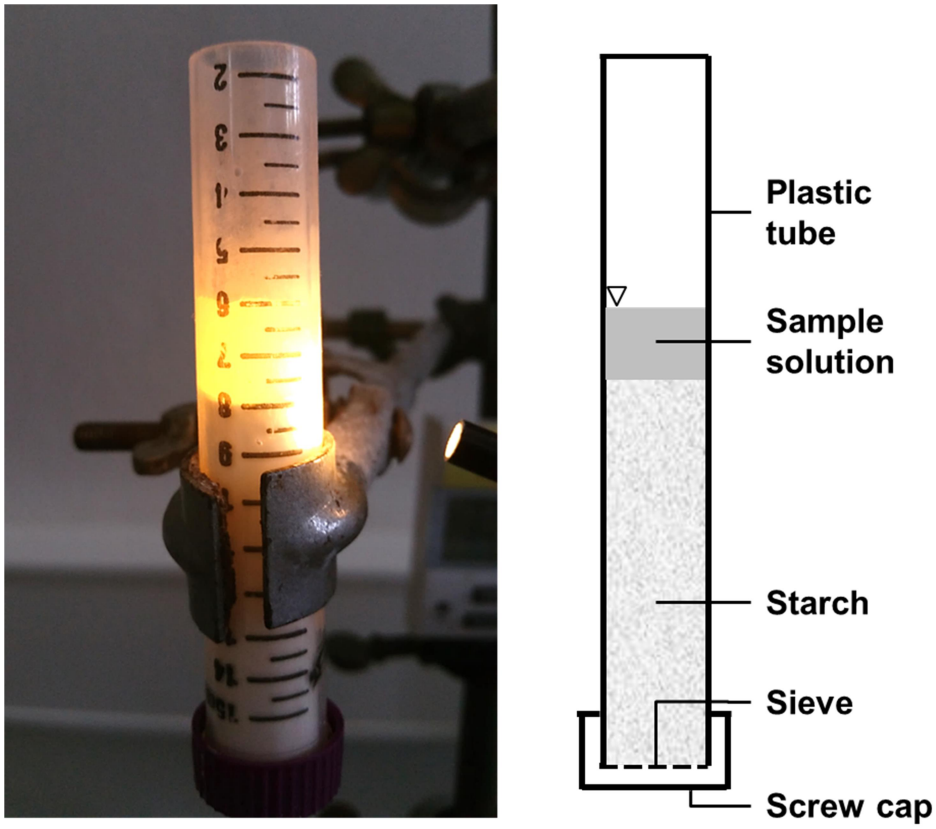


Figure 4.2-9: Schematic setup for tube test for infiltration behavior

5. Results

5.1 Encapsulation process using sucrose and erythritol

Encapsulation of milk and condensed milk

In the following, the results of the necessary preliminary experiments are presented and the determination of the required parameters for the encapsulation process explained. The results of the encapsulation of milk and condensed milk using sucrose and erythritol as encapsulation material are then presented.

In a first step, the **densities** of the used encapsulation materials (solids) and the liquids to be encapsulated (solvents) have been determined. The results are shown in Table 5.1-1.

Table 5.1-1: Densities of used solids and solvents

solid/solvent	density [g/cm^3]
sucrose	1.59
erythritol	1.45
milk (3.5 %)	1.028
condensed milk (10 %)	1.08

In a second step, the **solubility curves** of the selected systems have been determined by isothermal measurements. Figure 5.1-1 shows the solubility curves of sucrose and erythritol in milk and condensed milk. For all systems the solubility increases with increasing temperatures. If condensed milk is applied as solvent, the points of solubility are shifted towards higher temperatures. Compared to sucrose, erythritol generally has a lower solubility and a steeper increase in the solubility curve.

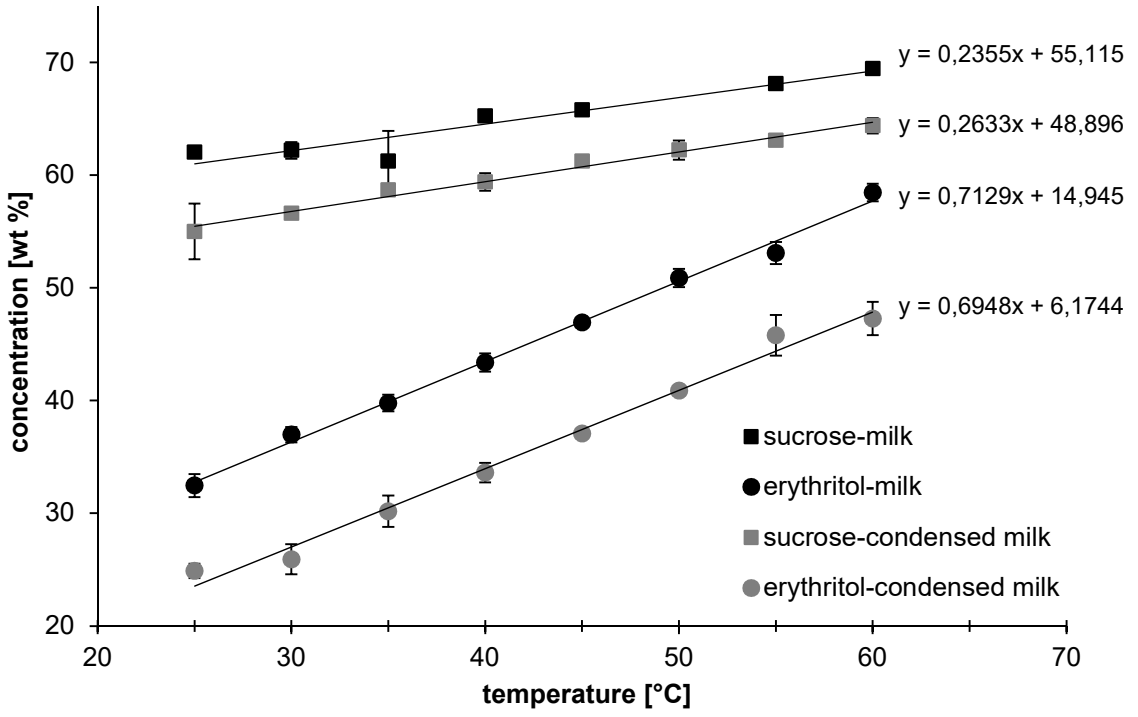


Figure 5.1-1: Solubility of sucrose and erythritol in milk and condensed milk determined by isothermal measurements [Wel17]

The concentrations of each solution at 25 °C (defined storage temperature of future containers) are summarized in Table 5.1-2.

Table 5.1-2: Solid concentrations of different solutions at 25 °C

casting solution	concentration at 25 °C [wt%]
sucrose-milk	62.0
sucrose-condensed milk	55.0
erythritol-milk	32.5
erythritol-condensed milk	24.9

Based on the defined product shape, size, storage temperature as well as on the results of the density and solubility measurements the **optimum start concentrations** (contents of solids and solvents) of the future casting solutions have been calculated by Equations 4.2-1 and 4.2-2 (see Chapter 4.2.5). The results are shown in Table 5.1-3.

Table 5.1-3: Calculated optimum start concentrations (solid and solvent) of different solutions

casting solution	content of solid [wt%]	content of solvent [wt%]
coat thickness = 1 mm (25 °C storage temperature)		
sucrose-milk	69.4	30.6
sucrose-condensed milk	64.8	35.2
erythritol-milk	47.9	52.1
erythritol-condensed milk	41.7	58.3
coat thickness = 1.5 mm (25 °C storage temperature)		
sucrose-milk	73.6	26.4
sucrose-condensed milk	69.0	31.0
erythritol-milk	54.4	45.6
erythritol-condensed milk	48.8	51.2

In a next step the **MSZW** of each system has been determined by polythermal measurements. The results shown in Figures 5.1-2 (sucrose) and 5.1-3 (erythritol) correlate with the results of the isothermal solubility measurements. However, the polythermal measurement shows higher standard deviations.
Sucrose-milk solutions reveal a MSZW of 10-22 K. The application of erythritol instead of sucrose results in a MSZW of 8-20 K.

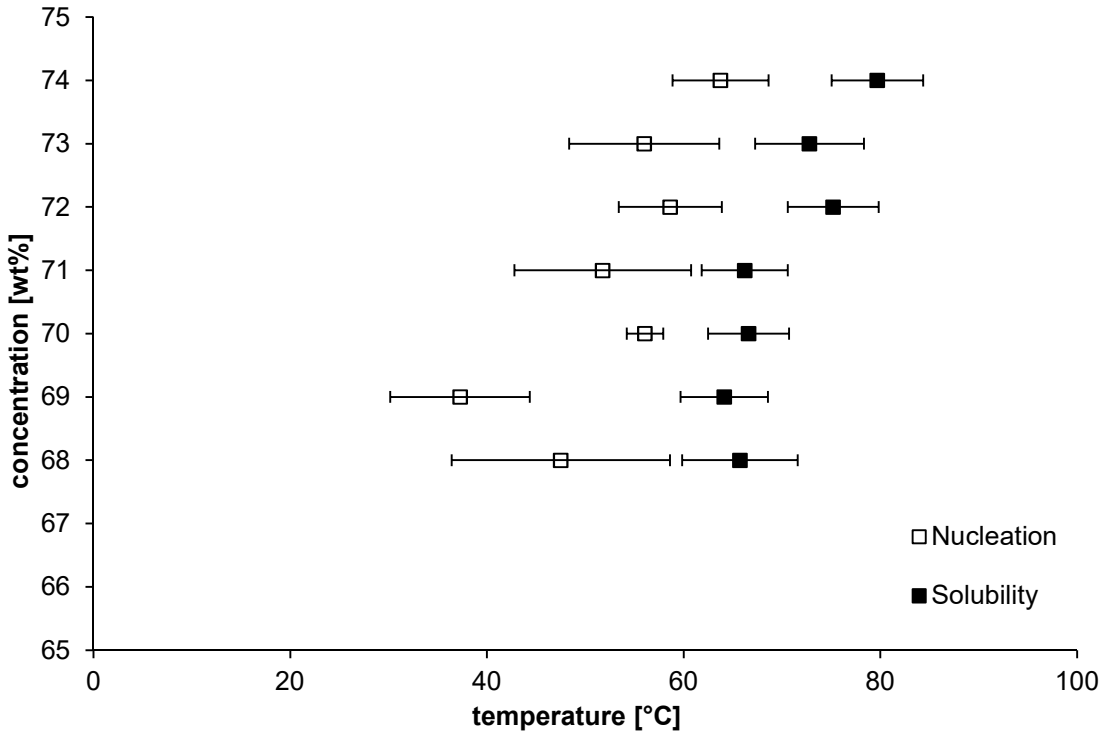


Figure 5.1-2: Nucleation and solubility of sucrose in milk determined by polythermal measurements

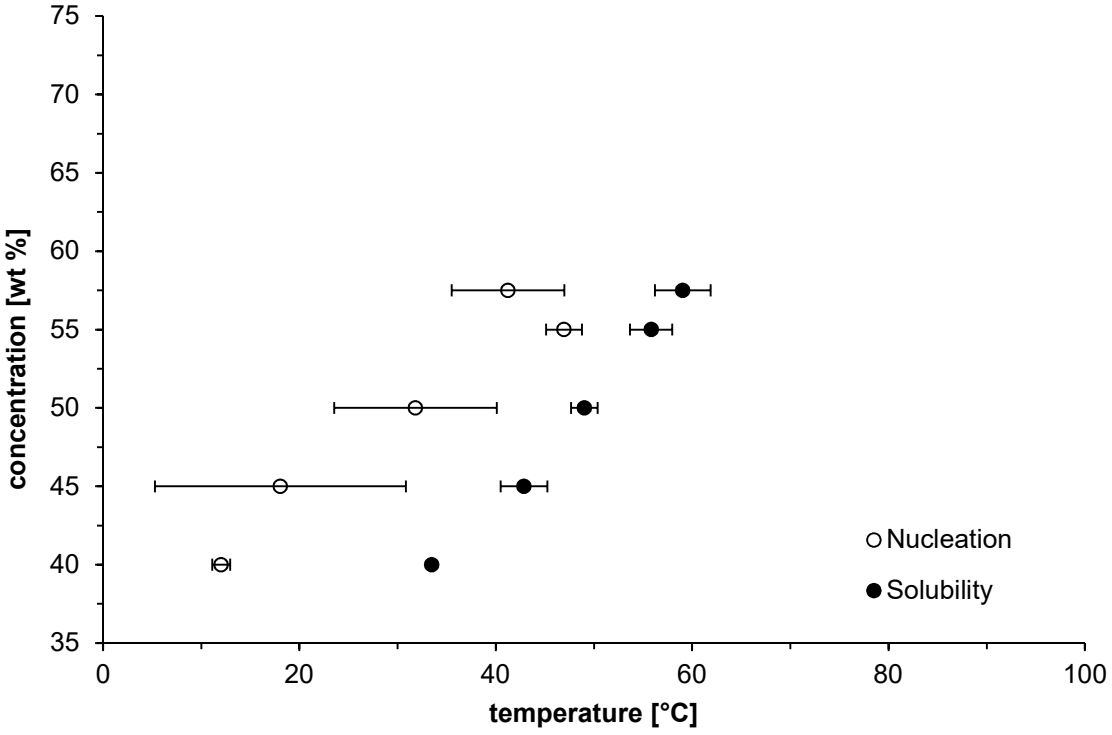


Figure 5.1-3: Nucleation and solubility of erythritol in milk determined by polythermal measurements

Based on the solubility curves the **saturation temperature** ($T_{saturated}$) for each casting solution has been determined. Then a **solution temperature** ($T_{solution}$) of 10 K above the saturation temperature has been selected to ensure complete dissolution of the encapsulation material. After the dissolution process, the casting solutions have been cooled down to the **casting temperature** ($T_{casting}$). $T_{casting}$ has been defined to be approx. in the middle of the MSZW.

Table 5.1-4 shows the results for each casting solution based on a crystalline container with a coat thickness of 1.5 mm.

Table 5.1-4: Process parameters for the production of crystalline containers based on different casting solutions (coat thickness=1.5 mm)

sample system	$c_{optimum}$ [wt%]	$T_{saturated}$ [°C]	$T_{solution}$ [°C]	$T_{casting}$ [°C]
sucrose-milk	73.6	78	88	68
sucrose-condensed milk	69.1	77	87	67
erythritol-milk	54.4	55	65	47
erythritol-condensed milk	49.1	61	71	53

In the following the results of the **encapsulation processes** are presented. Using sucrose as encapsulation material, crystalline containers with a hard coat and a liquid filling could be produced. All samples revealed a smooth and an intact surface. Milk (Fig. 5.1-4) and condensed milk (Fig. 5.1-5) have successfully been encapsulated.

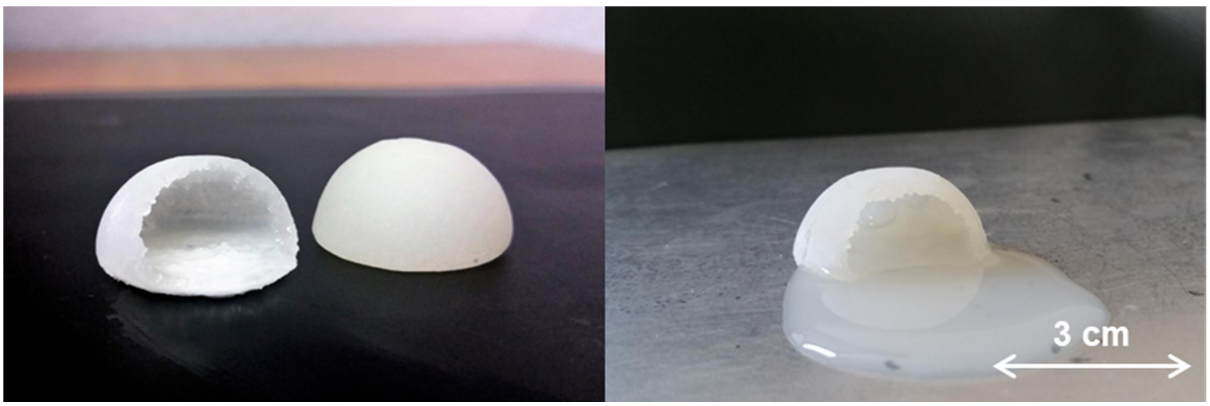


Figure 5.1-4: Crystalline containers (sucrose-milk)

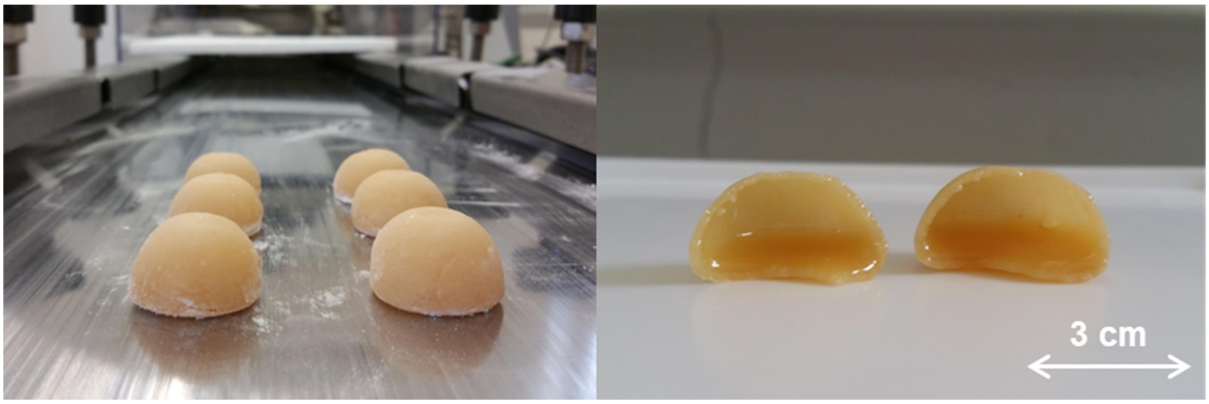


Figure 5.1-5: Crystalline containers (sucrose-condensed milk)

The use of erythritol for the encapsulation of milk has not led to a positive encapsulation result. Although hemispheres have been produced, they have had no liquid content. All samples have completely been crystallized.
Condensed milk has successfully been encapsulated by erythritol. As shown in Figure 5.1-6 all samples have had a completely closed crystalline coat and a liquid filling. The surface of the shell formed by erythritol did not appear smooth, but very uneven and rough.

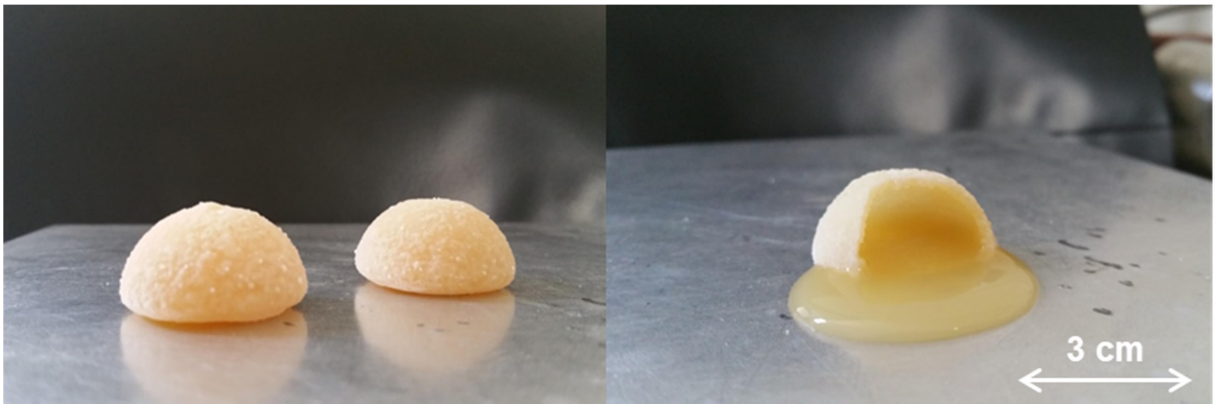


Figure 5.1-6: Crystalline containers (erythritol-condensed milk)

Encapsulation of coconut milk

In the following the encapsulation process of coconut milk (7 % fast content) is summarized and explained exemplarily by using sucrose as encapsulation material.

Figure 5.1-7 shows the solubility curve of sucrose in coconut milk determined by isothermal measurements as well as the points of solubility and nucleation determined by polythermal measurements.

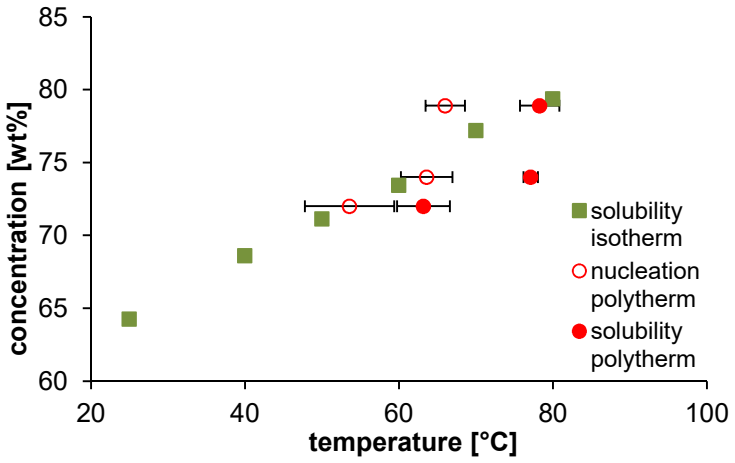


Figure 5.1-7: Solubility and nucleation curve of sucrose in coconut milk determined by isothermal and polythermal measurements

The solubility increases with increasing temperatures, with a saturation concentration of 64.3 wt% at 25 °C. Compared to sucrose-milk and sucrose-condensed milk solutions, sucrose-coconut milk solutions reveal higher solubilities. The MSZW has been determined to be 9-13 K.

The process parameters shown in Table 5.1-5 have then been calculated based on the defined product parameters (see Chapter 4.2-4) and the results of the solubility measurements.

Table 5.1-5: Process parameters for the production of crystalline containers containing coconut milk (7 % fat content)

sample system	ρ_{solid} [g/cm^3]	$\rho_{solvent}$ [g/cm^3]	$c_{storage25}$ [wt%]	$c_{optimum}$ [wt%]	MSZW [K]	$T_{saturated}$ [°C]	$T_{solution}$ [°C]	$T_{casting}$ [°C]
sucrose-coconut milk	1.59	1.022	64.3	74	9-13	68	78	60

The results of the following encapsulation process are shown in Figure 5.1-8. Coconut milk has successfully been encapsulated by using sucrose as encapsulation material.

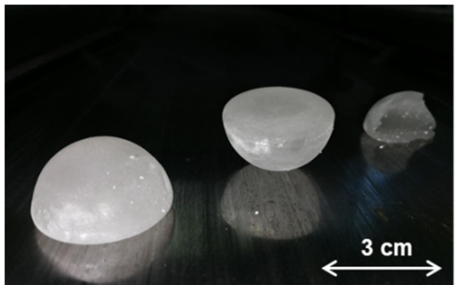


Figure 5.1-8: Sucrose-containers containing coconut milk (7 % fat content)

5.2 Encapsulation process using sugar substitutes

Figure 5.2-1 shows the **solubility curves** of different sugar substitutes in milk and condensed milk determined by isothermal measurements.

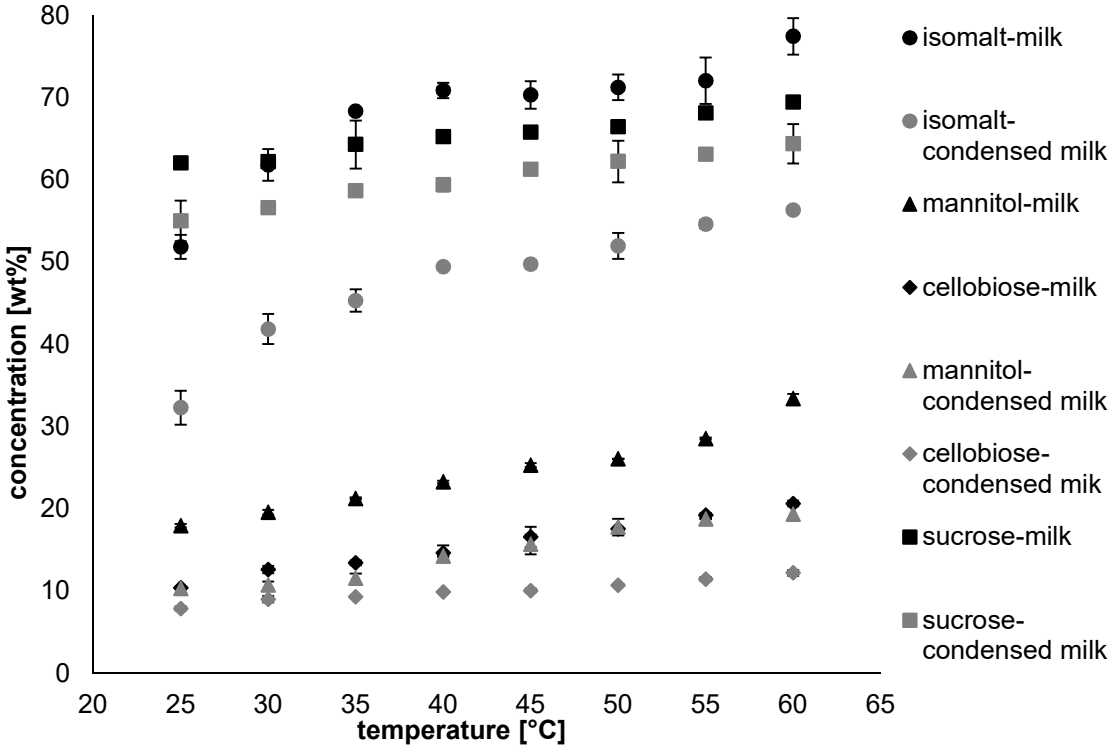


Figure 5.2-1: Solubility curves for different polyols in milk and condensed milk

Compared to sucrose all sugar substitutes used reveal lower saturation concentrations. As the temperature increases, the solubility of all sugar substitutes increases. If condensed milk is used as a solvent, the points of solubility are shifted to higher temperatures. Considering all sugar substitutes, isomalt reveals the highest solubilities, cellobiose the lowest.
Table 5.2-1 summarizes the saturation concentrations of the respective solutions at 25 °C.

Table 5.2-1: Saturation concentration of different solutions at 25 °C

initial solution	$c_{25\,°C}$ [wt%]
sucrose-milk	62.0
sucrose-condensed milk	55.0
isomalt-milk	51.8
isomalt-condensed milk	32.3
mannitol-milk	17.9
mannitol-condensed milk	10.3
cellobiose-milk	10.4
cellobiose-condensed milk	7.9

The points of nucleation and solubility (**MSZW**) determined by polythermal measurements are shown in Table 5.2-2.

Table 5.2-2: Results of MSZW determination for different solutions determined by polythermal measurements

initial solution	c [wt%]	nucleation [°C]	solubility [°C]	MSZW [K]
cellobiose-milk	20	22,48 ± 1,66	53,43 ± 1,22	30,96
	25	38,57 ± 0,45	64,96 ± 1,22	26,40
	30	48,16 ± 0,21	63,92 ± 4,09	15,76
cellobiose-condensed milk	10	30,60 ± 0,06	61,86 ± 2,14	31,26
	12,5	30,33 ± 0,18	64,49 ± 0,69	34,17
	15	30,20 ± 0,13	66,30 ± 1,46	36,10
mannitol-milk	25	20,31 ± 0,68	32,57 ± 2,04	12,26
	30	35,78 ± 0,66	42,30 ± 0,03	6,52
	35	45,99 ± 1,28	51,08 ± 0,21	5,10
mannitol- condensed milk	15	26,75 ± 0,57	38,26 ± 0,27	11,51
	20	27,25 ± 1,51	35,79 ± 1,05	8,54
	25	30,27 ± 0,53	47,95 ± 2,49	17,69
isomalt-milk	55	29,19 ± 3,06	62,11 ± 0,75	32,93
	60	35,73 ± 1,62	68,35 ± 0,64	32,63
	65	38,67 ± 2,71	67,65 ± 0,74	28,99
isomalt-condensed milk	45	26,64 ± 0,87	62,65 ± 0,86	36,01
	50	36,72 ± 4,50	66,65 ± 0,69	29,93
	55	39,28 ± 1,86	71,29 ± 0,48	32,02

The results of the polythermal measurements by means of an ultrasonic measurement technique deviate from the results of the isothermal measurements. The points of solubility are shifted to higher temperatures.

Based on the defined product size and coat thickness as well as on the results of the MSZW measurements, the **optimum start concentrations** have been calculated and the corresponding process parameters determined. The results are summarized in Table 5.2-3.

Table 5.2-3: Process parameters for the production of crystalline containers using sugar substitutes

sample system	ρ_{solid} [g/cm^3]	$\rho_{solvent}$ [g/cm^3]	$c_{storage25}$ [wt%]	$c_{optimum}$ [wt%]	MSZW [K]	$T_{saturated}$ [°C]	$T_{solution}$ [°C]	$T_{casting}$ [°C]
isomalt-milk	1.51	1.028	51.8	66.9	~30	35	45	25
isomalt-condensed milk		1.08	32.3	44.6	~30	35	45	25
mannitol-milk	1.47	1.028	17.9	35.3	5-10	65	75	65-60
mannitol-condensed milk		1.08	10.3	28.7	8-15	70	80	70-65
cellobiose-milk	1.44	1.028	10.4	20.2	15-30	60	70	50
cellobiose-condensed milk		1.08	7.9	16.7	~30	70	80	60

The following **encapsulation process** has been carried out on the basis of the previously determined parameters. None of the substances used for the encapsulation of milk or condensed milk could be identified as suitable encapsulation material.
Both mannitol-milk solutions and mannitol-condensed milk solutions have started to sink into the molds directly after the casting process. An exemplary result of an encapsulation test is shown in Figure 5.2-2. In the course of the experiments, lump-like samples with a powdery consistency have been produced. An encapsulation of liquid has not been achieved.

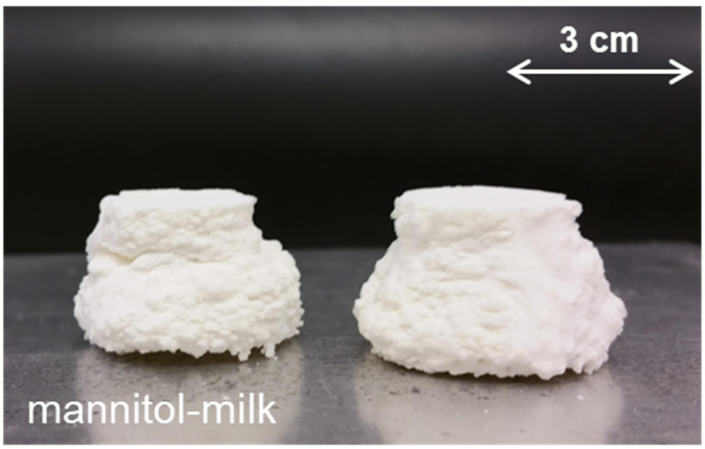


Figure 5.2-2: Result of encapsulation experiment of milk using mannitol

Also, the use of isomalt as encapsulation material has not led to a positive result. Figure 5.2-3 shows a result of the encapsulation experiment of condensed milk. The use of isomalt has enabled the production of samples in the desired shape, but they have not revealed any liquid interior. The entire sample has contained crystalline structures.

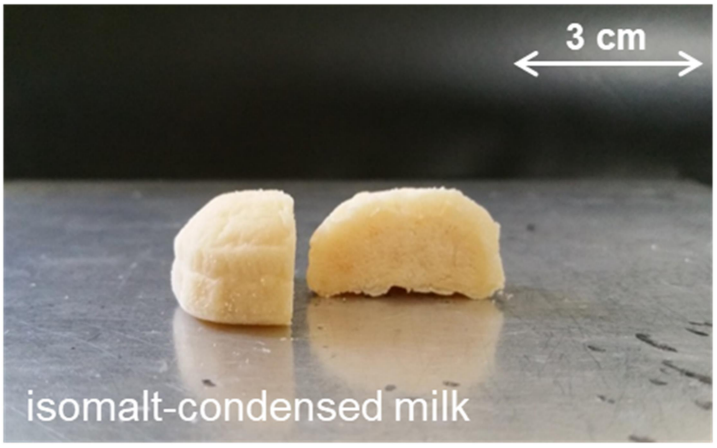


Figure 5.2-3: Result of encapsulation experiment of condensed milk using isomalt

The encapsulation experiments of milk and condensed milk by the application of cellobiose also has not led to the desired results. Lump-like samples without liquid filling have been produced (Fig. 5.2-4).

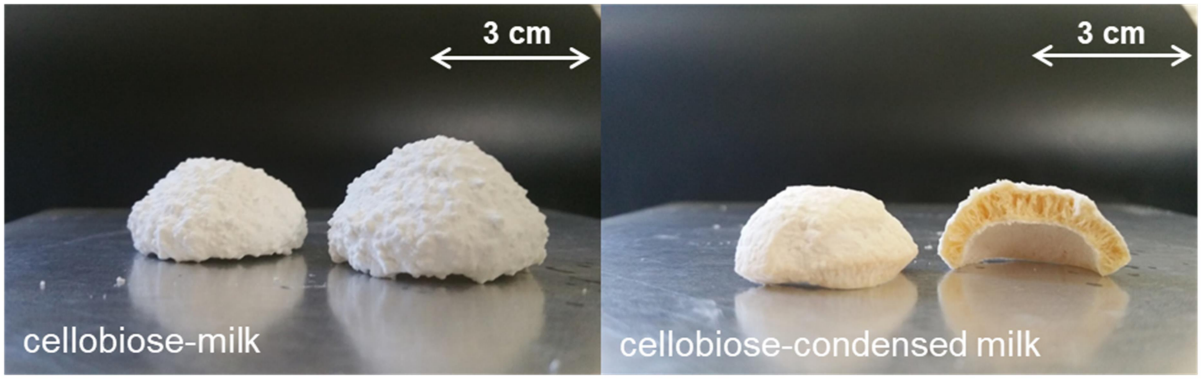


Figure 5.2-4: Results of encapsulation experiments of milk and condensed milk using cellobiose

5.3 Verification of usability of the equations to determine the optimum start concentration by means of microscopic layer thickness analysis

The applicability and accuracy of the equations to determine the optimum application quantities have been verified by means of a microscopic layer thickness analysis. The expected layer thicknesses for containers with different solid contents has been calculated and compared to the microscopically determined values. The results are summarized in Table 5.3-1.

Table 5.3-1: Results of layer thickness determination by microscopic analyses compared to calculated layer thicknesses

sample type	solid content [wt%]	calculated layer thickness [mm]	determined layer thickness [mm]	standard deviation [mm]
sucrose-milk	70	1.0	1.12	0.208
	72	1.27	1.67	0.315
	74	1.56	1.48	0.237
	78	2.2	1.9	0.303

Figure 5.3-1 shows the results of the comparison of both values graphically. As the quantity of the applied crystalline solids increases, the layer thickness (calculated and determined) of the container coat also grows. Slight deviations can be detected between the calculated and actually determined values.

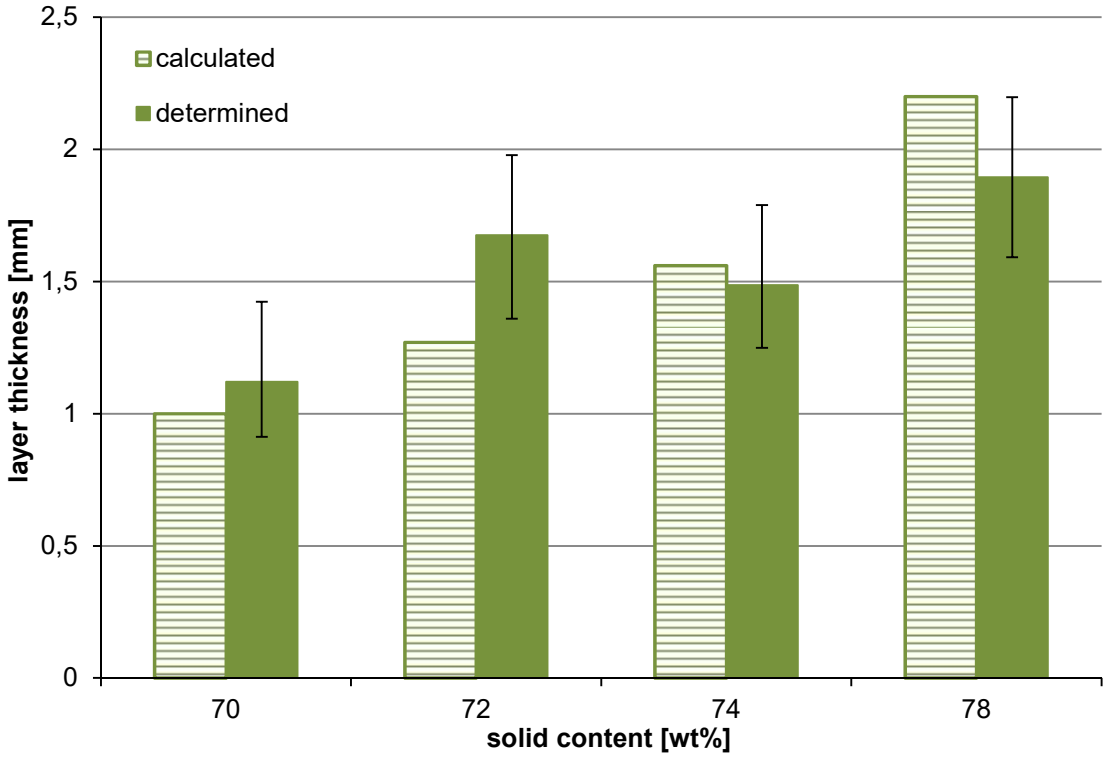


Figure 5.3-1: Results of layer thickness determination via microscopic analysis compared to calculated layer thickness of milk containers with different sucrose contents

5.4 Physical properties of solutions used for encapsulation

The **dynamic viscosity (η)** of the respective casting solutions used for the production of the crystalline containers has been investigated as a function of temperature. The results are shown in Figures 5.4-1 and 5.4-2.

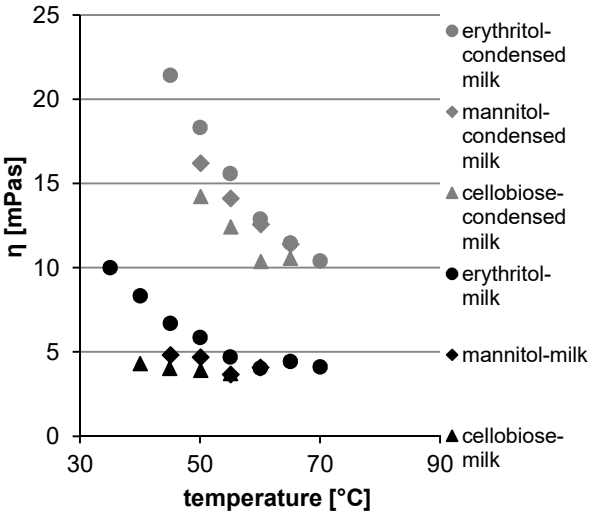


Figure 5.4-1: Dynamic viscosity of low viscosity solutions as a function of temperature

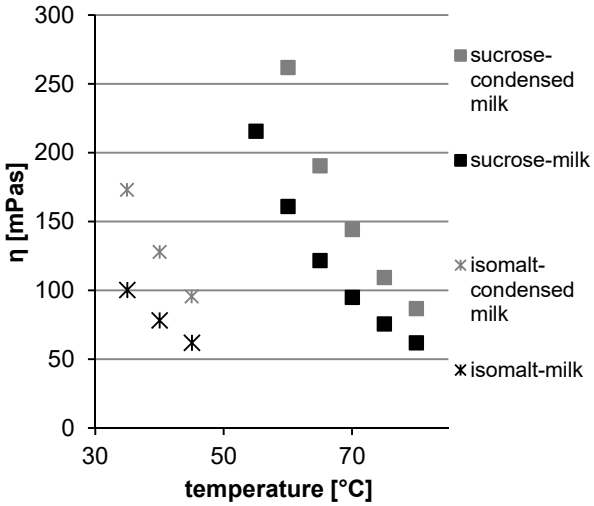


Figure 5.4-2: Dynamic viscosity of high viscosity solutions as a function of temperature

The viscosity of all sample solutions tested decreases with increasing temperature. It could also be observed that the use of condensed milk generally leads to an increase in viscosity compared to milk. Solutions based on erythritol, mannitol and cellobiose reveal relatively low viscosities as shown in Figure 5.4-1. All values vary between 21.4 mPas (erythritol-condensed milk, 45 °C) and 3.7 mPas (cellobiose-milk, 55 °C). Sucrose and isomalt based solutions reveal significantly higher viscosity values (Fig. 5.4-2). Here, all results range between 262 mPas (sucrose-condensed milk, 60 °C) and 62 mPas (isomalt-milk, 45 °C).

The **surface tension (σ)** of respective sample solutions at different temperatures is shown in Figure 5.4-3.

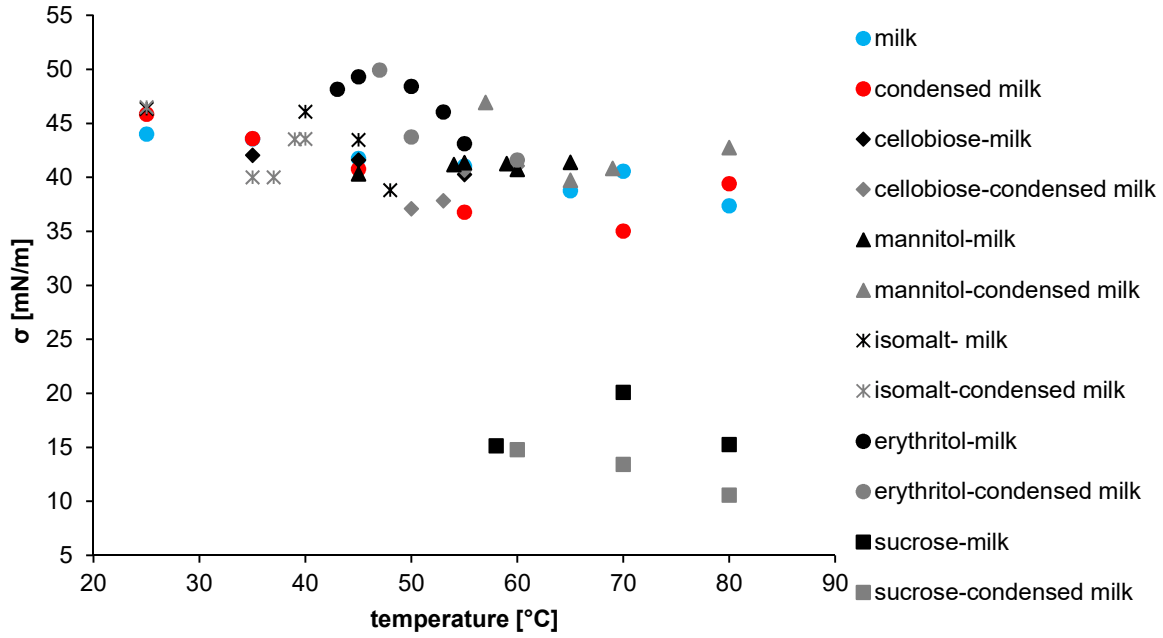


Figure 5.4-3: Surface tension of different solutions as a function of temperature

The surface tension of milk at different temperatures has been determined to be between 36.7 and 43.9 mN/m. Values of σ between 35 and 45.8 mN/m have been determined for condensed milk. A decrease of the surface tension has been determined for sucrose-based solutions. Values between 15.1 and 20.0 mN/m (sucrose-milk) and 10.6-14.7 mN/m (sucrose-condensed milk) have been determined. The application of sugar substitutes indicates no effect on the surface tension of milk and condensed milk.

Based on Equation 4.2-4 (see Chapter 4.2.14) the **infiltration behavior (I)** of respective sample solutions has been determined as a function of surface tension and viscosity. The results are shown in Table 5.4-1.

Table 5.4-1: Infiltration behavior of different sample solutions based on surface tension and dynamic viscosity

sample solution	σ [mN/m]	η [mPas]	I $[\sqrt{\frac{m}{s}}]$
water	72.7	0.9	9
sucrose-water	14	100.3	0.37
sucrose-milk	46.9	144.2	0.57
sucrose-condensed milk	42.2	160.9	0.51
erythritol-water	48.9	5.1	3.1
erythritol-milk	48	6.7	2.7
erythritol-condensed milk	42.9	15.6	1.6
cellobiose-milk	42.1	3.7	3.4
cellobiose-condensed milk	40.8	15.6	1.9
mannitol-milk	32.4	3.7	2.9
mannitol-condensed milk	36.5	11.4	1.8
isomalt-milk	39.8	127.9	0.56
isomalt-condensed milk	42.2	62.0	0.82

The **contact angle (θ)** of respective sample solutions on a powder tray has been investigated as a function of time. Figure 5.4-4 exemplary shows the contact angle change (Δθ) of an erythritol-condensed milk solution at 55°C. Immediately after placing the drop, the contact angle has been determined to be 99 °. The contact angle decreases to 77.5 ° over time. The contact angle change totals 21.5 ° or 2.4 °/min.

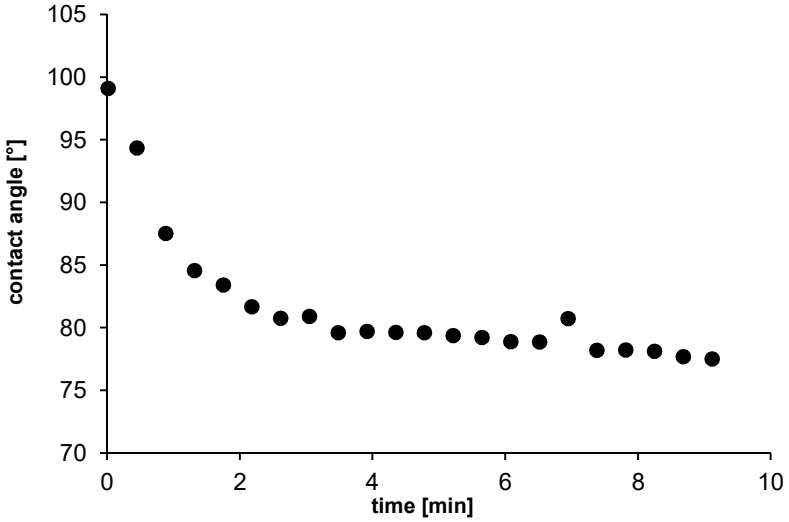


Figure 5.4-4: Contact angle of erythritol-condensed milk drop (20µL) over time

Figure 5.4-5 shows the changes in the drop shape over time (t_1=0 min to t_2=9 min) using the example of a sugar-milk solution and a erythritol-condensed milk solution.

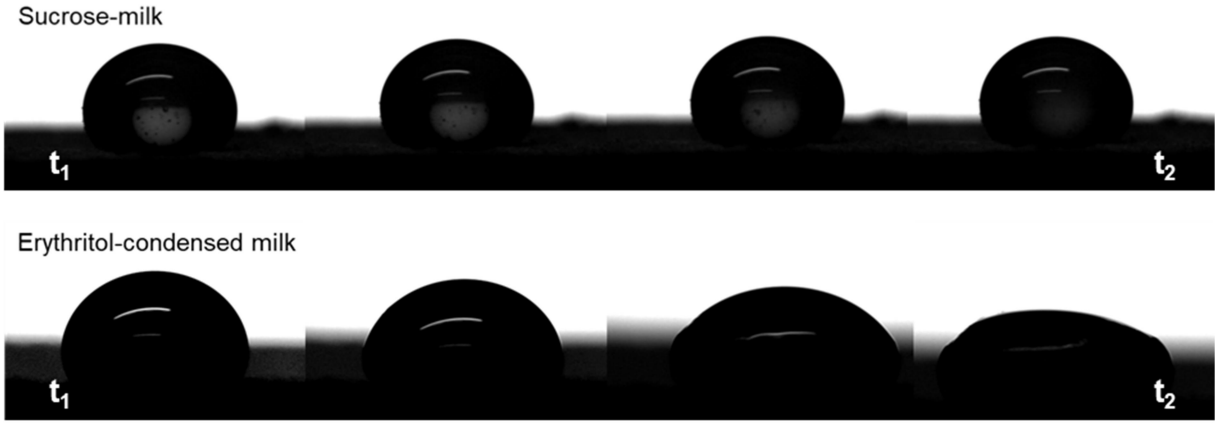


Figure 5.4-5: Drop shape of sucrose-milk and erythritol-condensed milk solutions over time

The drop shape of a sucrose-milk solution reveals no changes in the course of 9 minutes. However, the drop of erythritol-condensed milk solution reveals a strong modification of shape over time.

The **contact angle changes (Δθ)** over time of all sample solutions are summarized in Table 5.4-2.

Table 5.4-2: Contact angle changes of different sample solutions

sample solution	Δθ [°/min]
sucrose-milk	0.49
sucrose-condensed milk	0.11
erythritol-milk	5,8
erythritol-condensed milk	2.4
ceollobiose-milk	6.3
cellobiose-condensed milk	3.1
mannitol-milk	7
mannitol-condensed milk	1.88
isomalt-milk	0.46
isomalt-condensed milk	0.22

Figure 5.4-6 shows the **infiltration rates** of different erythritol-based solutions over time determined by a 'tube test'. Pure water and a sucrose-milk solution have served as reference values.

It can be seen that the sucrose-milk solution does not show any infiltration. The solution remains on the surface of the starch over the entire period of time. Water, on the other hand, begins to infiltrate into the starch immediately after filling. After 35 s, 25% of the water has already infiltrated into the starch, the entire volume has infiltrated after 5.5 minutes. Erythritol-based solutions also begin to infiltrate into the starch after filling, but at different rates: 25 % of the erythritol-water solution were infiltrated after 4.5 minutes, 25 % of the erythritol-milk solution after 14 minutes.

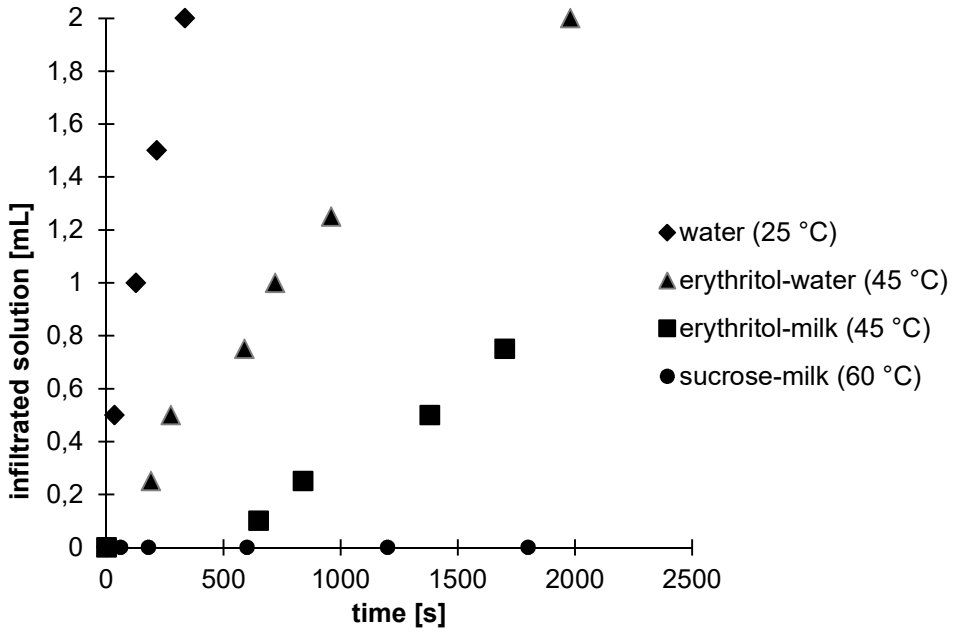


Figure 5.4-6: Infiltration behavior of different casting-solutions compared to water over time investigated by a tube test

5.5 Physical properties of containers produced by crystallization

5.5.1 Maturation time

The maturation time of sucrose-milk containers has been determined by investigating the sucrose degradation within the containers over a period of 14 days. All samples have been stored at 25 °C.

Figure 5.5-1 shows the sucrose concentration within sucrose-milk containers (72 wt%) over time after the manufacturing process. Within the first 48 h the concentration decreases significantly. A slight change in concentration follows after 48 h. From the fourth day after production, the sucrose concentration within the containers remains constant.

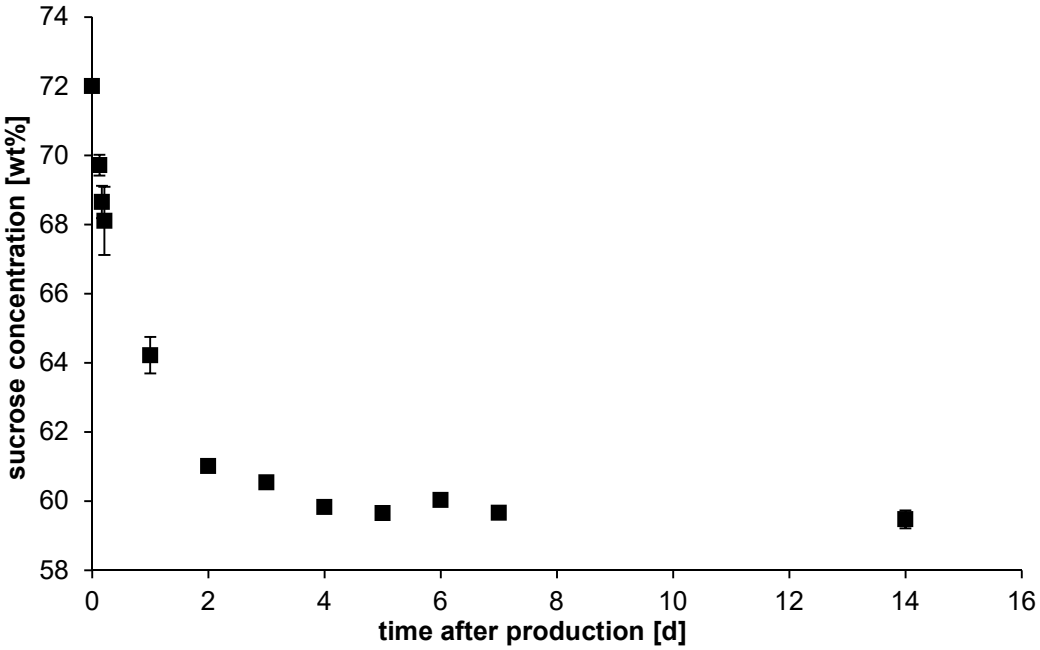


Figure 5.5-1: Sucrose concentration [wt%] inside milk containers as a function of time

5.5.2 Mechanical stability

Figure 5.5-2 shows the mechanical stability of three different crystalline container systems over time. The mechanical stability of all container systems increases continuously from the time of production and stagnates from a certain point in time. Sucrose-milk containers show the highest mechanical stability. Already 1 day after production, the mechanical stability is 1.5 N/cm². The maximum of 2.25 N/cm² is reached after 4 days.

If condensed milk is used as a solvent, the increase in mechanical stability is slower. After 1 day the mechanical stability is 0.3 N/cm². The maximum of 1.4 N/cm² is reached after 4 days. All sucrose-based samples have shown a stable and unbreakable characteristic during handling.

Erythritol-condensed milk containers have the lowest mechanical stability of 0.15 N/cm² maximum. Compared to sucrose-based containers, these containers have been difficult to handle. Even a careful handling has led to breakage or damage of the samples.

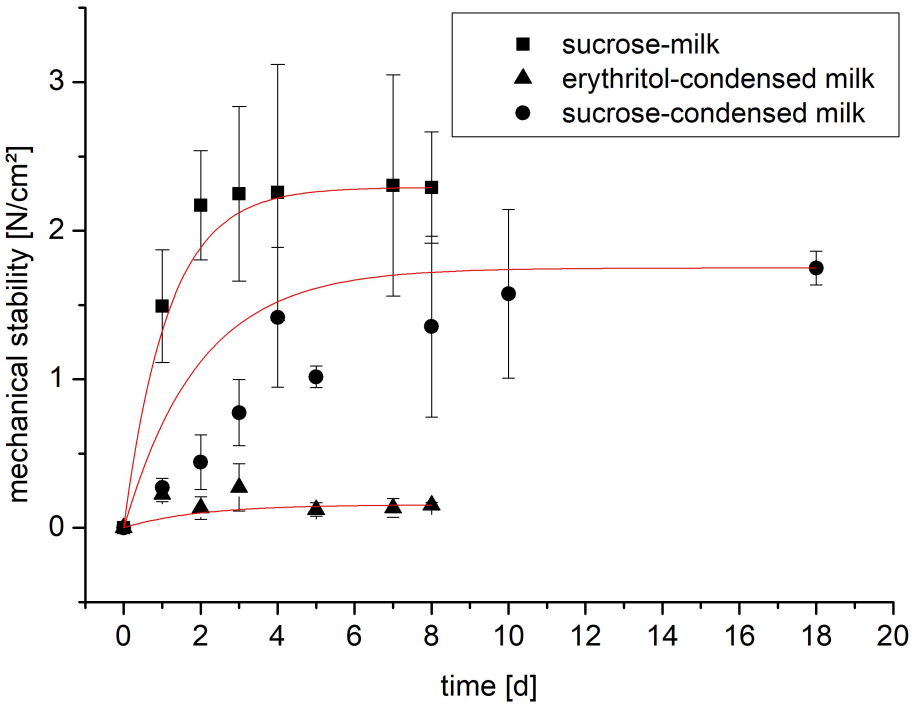


Figure 5.5-2: Mechanical stability of different products over time [Wel18a]

5.5.3 Mass loss

The results of the investigation concerning the storage stability are shown in Figure 5.5-3. The change of the container mass has been determined over time during storage under defined conditions. All containers reveal a decreasing mass during storage. The mass of sucrose-milk containers is reduced by 0.5 % within 20 days. A decrease of mass of 1 % within 18 days has been determined for containers based on sucrose and condensed milk. Erythritol-condensed milk containers reveal the highest mass loss of 4.8 % within 18 days.

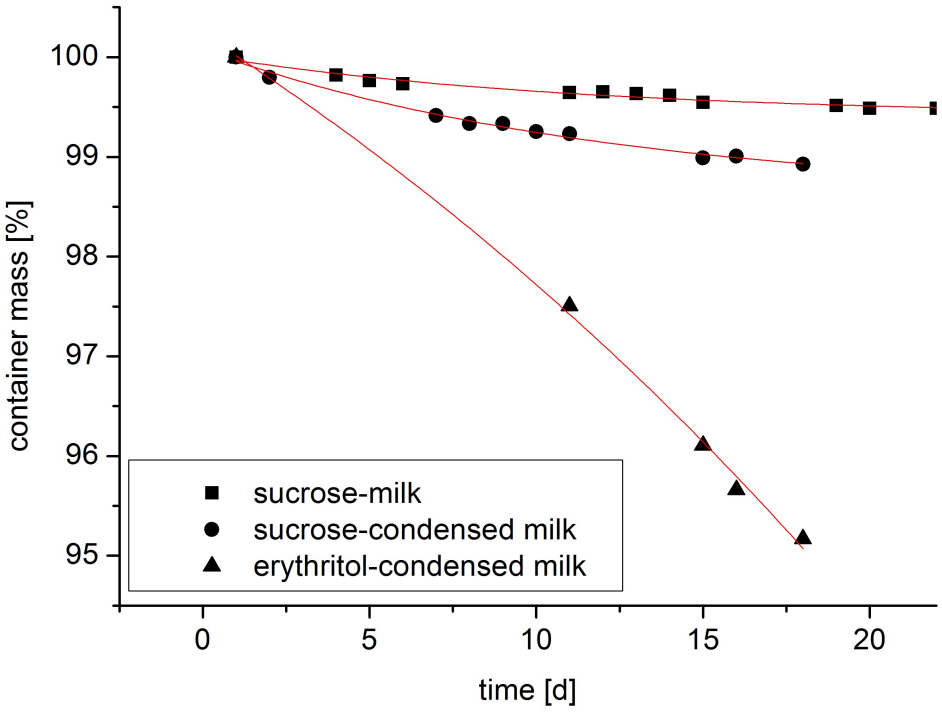


Figure 5.5-3: Container mass of different products over time [Wel18a]

Sucrose-based containers have not shown any changes in appearance over time. However, containers with an erythritol based coat revealed major deformations (Fig. 5.5-4).

Figure 5.5-4: Erythritol-condensed milk containers after storage of 20 days

5.5.4 Shelf-life

Investigation of pH

Figure 5.5-5 shows the pH value of pure milk and condensed milk over a period of 20 days. In comparison, the pH value of milk or condensed milk encapsulated by sucrose and erythritol over the same period is shown in Figure 5.5-6. All samples have been stored at 25 °C.

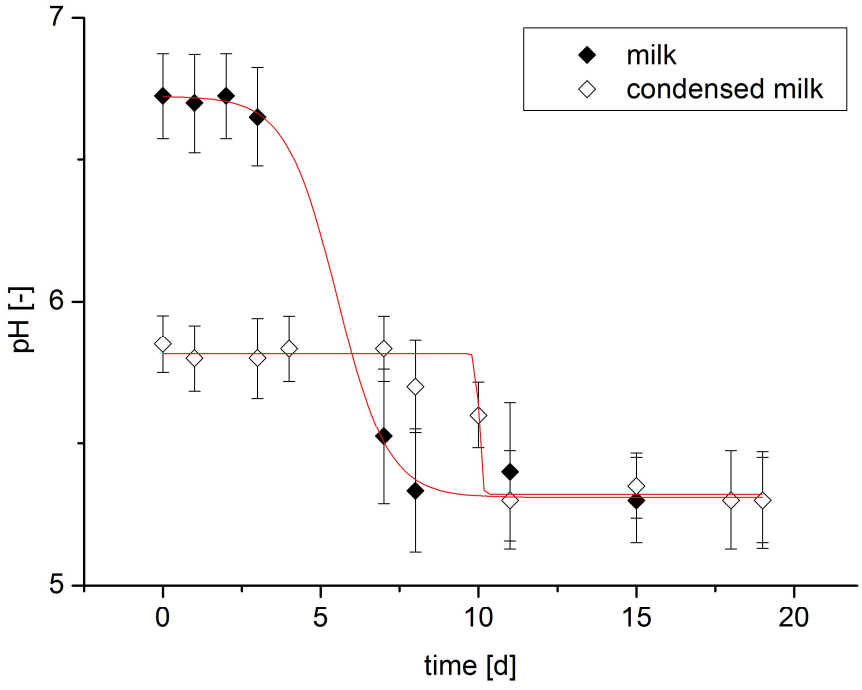


Figure 5.5-5: pH value of milk and condensed milk over time (storage at 25 °C) [Wel18a]

During storage pure milk and condensed milk reveal a sharp decrease of the pH value: Milk between 3.6 days, condensed milk between 8-10 days.

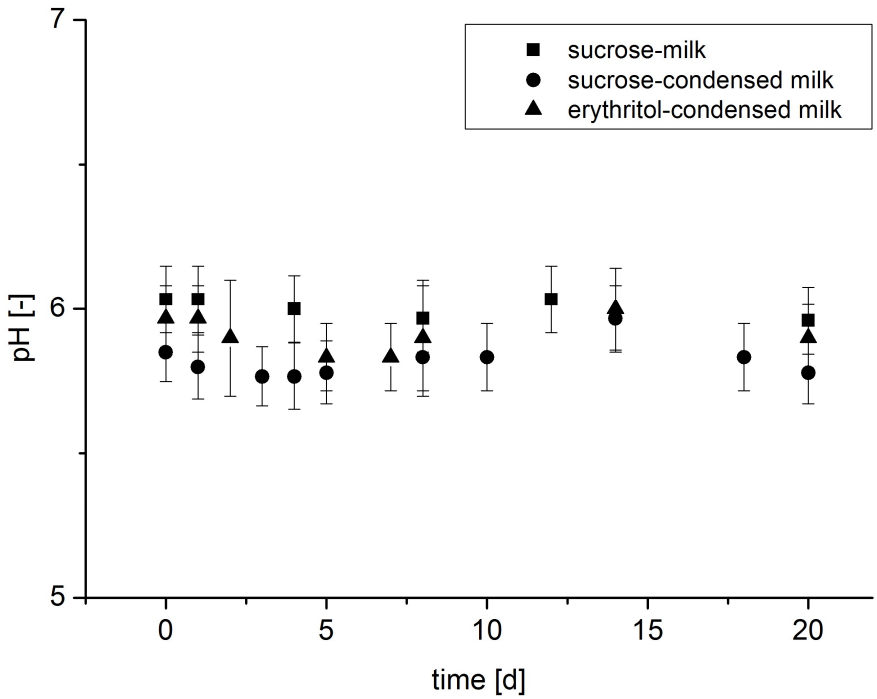


Figure 5.5-6: pH value of encapsulated milk and condensed milk over time (storage at 25 °C) [Wel18a]

The examination of the pH value of milk and condensed milk encapsulated by sucrose or erythritol shows no change over time. The pH value of all encapsulated solutions remains constant over a period of 20 days. Furthermore, the product samples have shown no changes in color, smell or taste after a period of 20 days.

Microbiological investigations

Microbiological investigations have been carried out for sucrose and xylitol-based containers with a filling of milk and coconut milk. Samples with an age of 4 days to 6 months have been investigated.

Figure 5.5-7 shows results of the resazurine assay (quick test). None of the sample shows a color change depending on sample type and sample age.

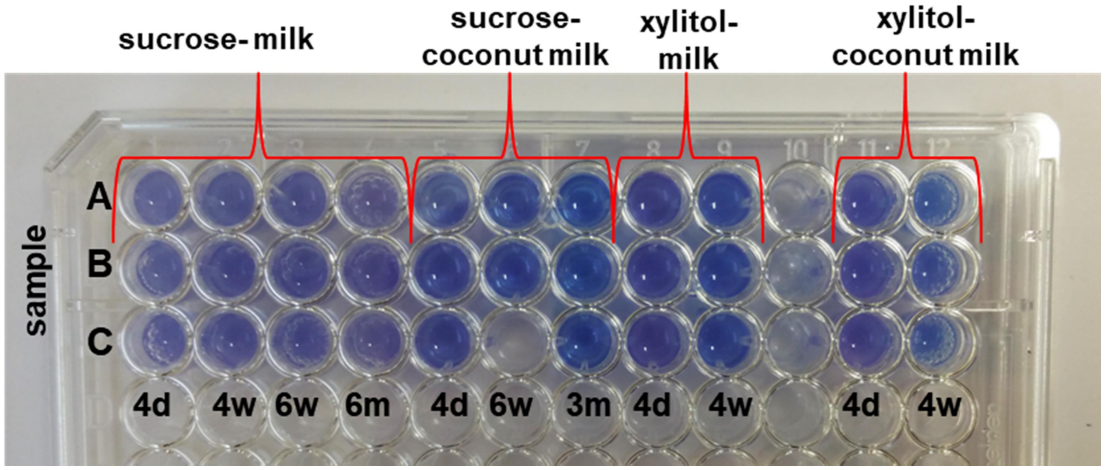


Figure 5.5-7: Results of resazurine assay (shelf-life of encapsulated liquid depending on sample type and sample age)

The total bacteria count (TBC) of the investigated samples depending on type and age is summarized in Table 5.5-1.

Table 5.5-1: Determined TBC of samples depending on container type and age

sample age	sucrose-milk	sucrose-coconut milk	xylitol-milk	xylitol-coconut milk
4 days	$17.3 * 10^1$ $22.3 * 10^2$	$18.3 * 10^4$ $1 * 10^5$	$5.5 * 10^4$ $3.5 * 10^5$	$3.3 * 10^4$ $1 * 10^5$
4 weeks	$0.6 * 10^1$ $23.3 * 10^2$	N/D	$6.3 * 10^2$ $2 * 10^3$	$19 * 10^2$ $1 * 10^3$
6 weeks	$2 * 10^4$ $2.5 * 10^5$	$2.5 * 10^1$		
3 months	N/D	$18 * 10^1$ $7 * 10^2$	N/D	N/D
6 months	$10.5 * 10^2$ $5 * 10^3$	N/D		

5.5.5 Release behavior

The following Figures 5.5-8-12 show the release behavior of sucrose-milk containers (72 wt%) compared to the dissolution behavior of sugar cubes in distilled water over time at different temperatures.

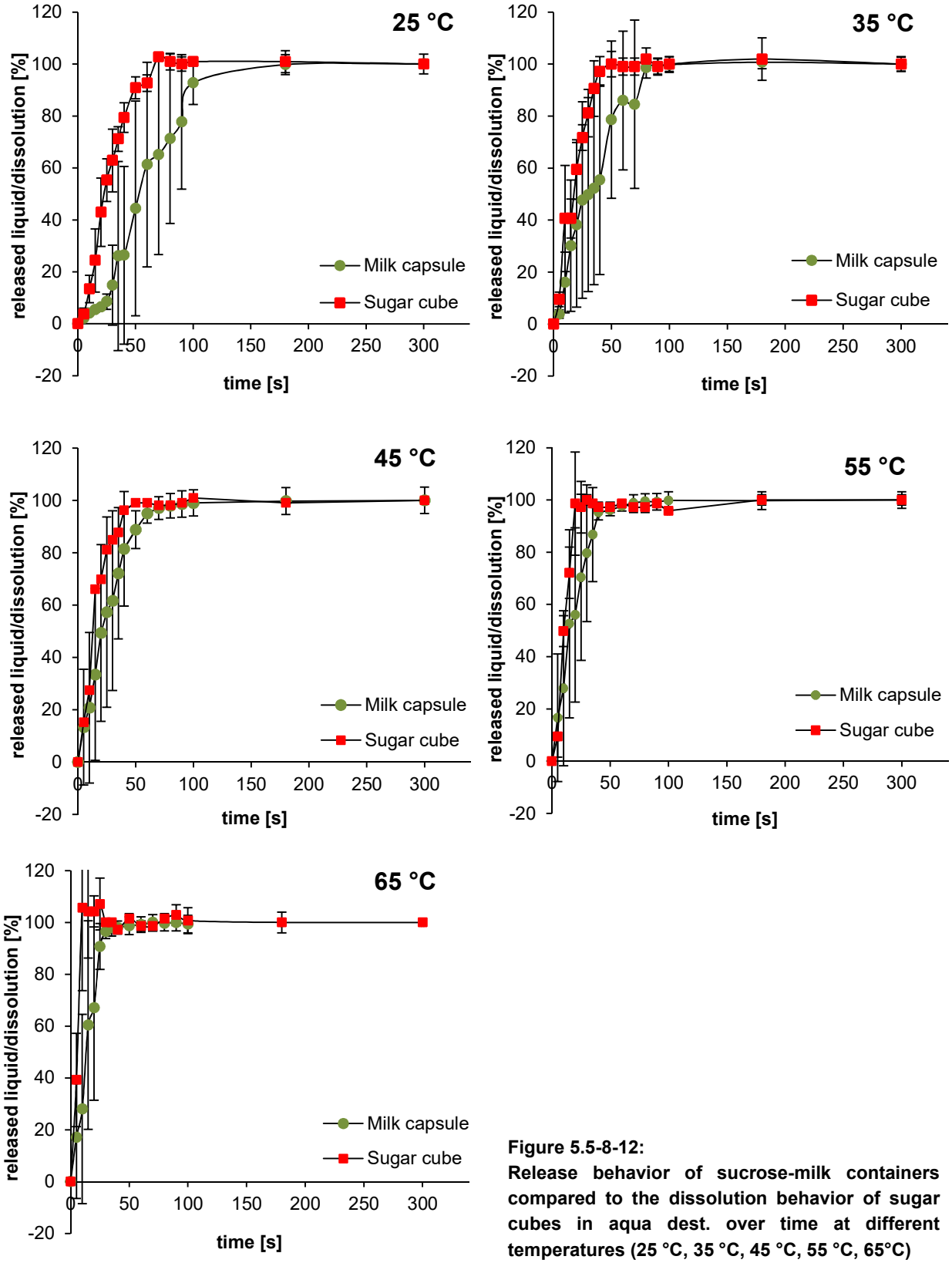


Figure 5.5-8-12:
Release behavior of sucrose-milk containers compared to the dissolution behavior of sugar cubes in aqua dest. over time at different temperatures (25 °C, 35 °C, 45 °C, 55 °C, 65°C)

With increasing water temperature, both the time to complete release of the encapsulated milk from the crystalline containers into the medium and the dissolution time of the sugar cubes are reduced. The release behavior of milk containers is slower than the dissolution behavior of sugar cubes. At a medium temperature of 65 °C, the entire liquid content of the milk capsules is released within approx. 30 s, whereas a sugar cube dissolves completely within 10 s at this temperature.

5.5.6 Influence of different storage conditions on the product properties

Figure 5.5-13 shows the effect of different air humidities (RH%) on the mechanical stability of sucrose-milk containers. At a humidity of 10-50 % a mechanical stability of 0.98-1.37 N/cm² (±0.39-0.2 N/cm²) has been determined. At 70 RH% a reduced stability has been detected (0.75 N/cm²).

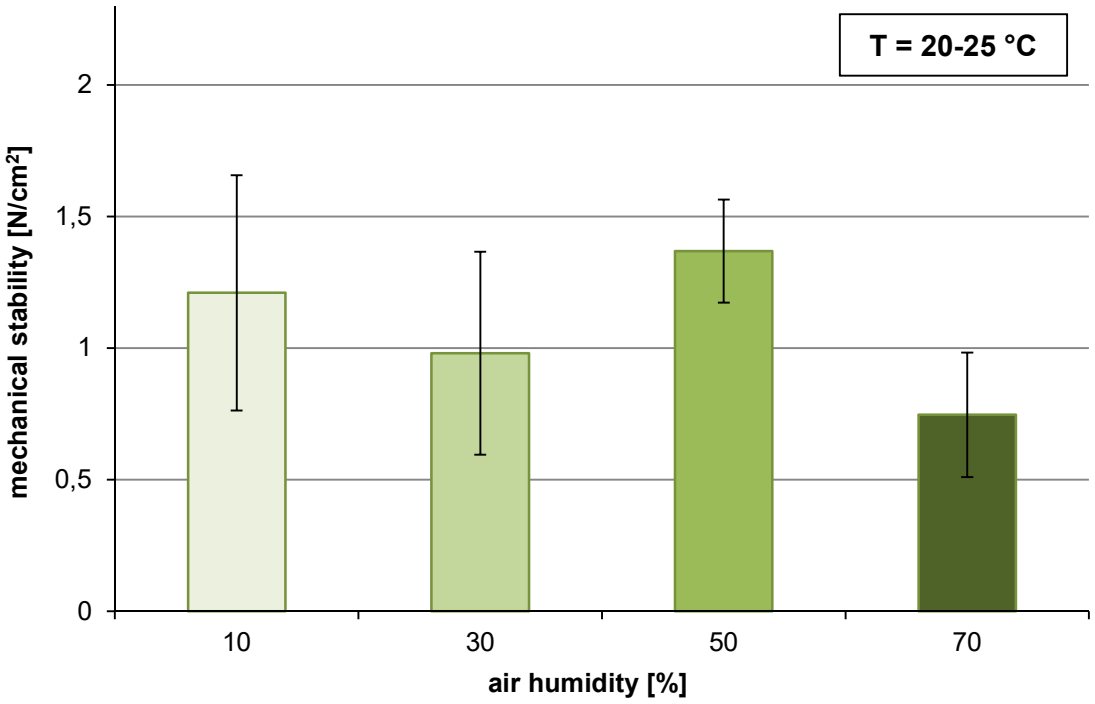


Figure 5.5-13: Mechanical stability of sucrose-milk containers after storage at different air humidities for 24 h

The effects of different storage temperatures (5 to 50 °C) on the mechanical stability of sucrose-milk containers are shown in Figure 5.5-14. At storage temperatures between 5 and 25 °C mechanical stabilities between 1.69 and 1.46 N/cm² (±0.53-0.72 N/cm²) have been determined. At 40 °C a marked reduction in mechanical stability of 0.46 N/cm² (±0.29 N/cm²) has been observed. No external changes of the containers have been detected. At a temperature of 50 °C, the original shape of the containers is retained and no defects are visible. However, the mechanical stability is significantly reduced (0.008 N/cm² ±0.003 N/cm²). No measurements have been possible at storage temperatures > 50 °C. Figure 5.5-14 also shows an increasing concentration of dissolved solids within the containers as the temperature increases.

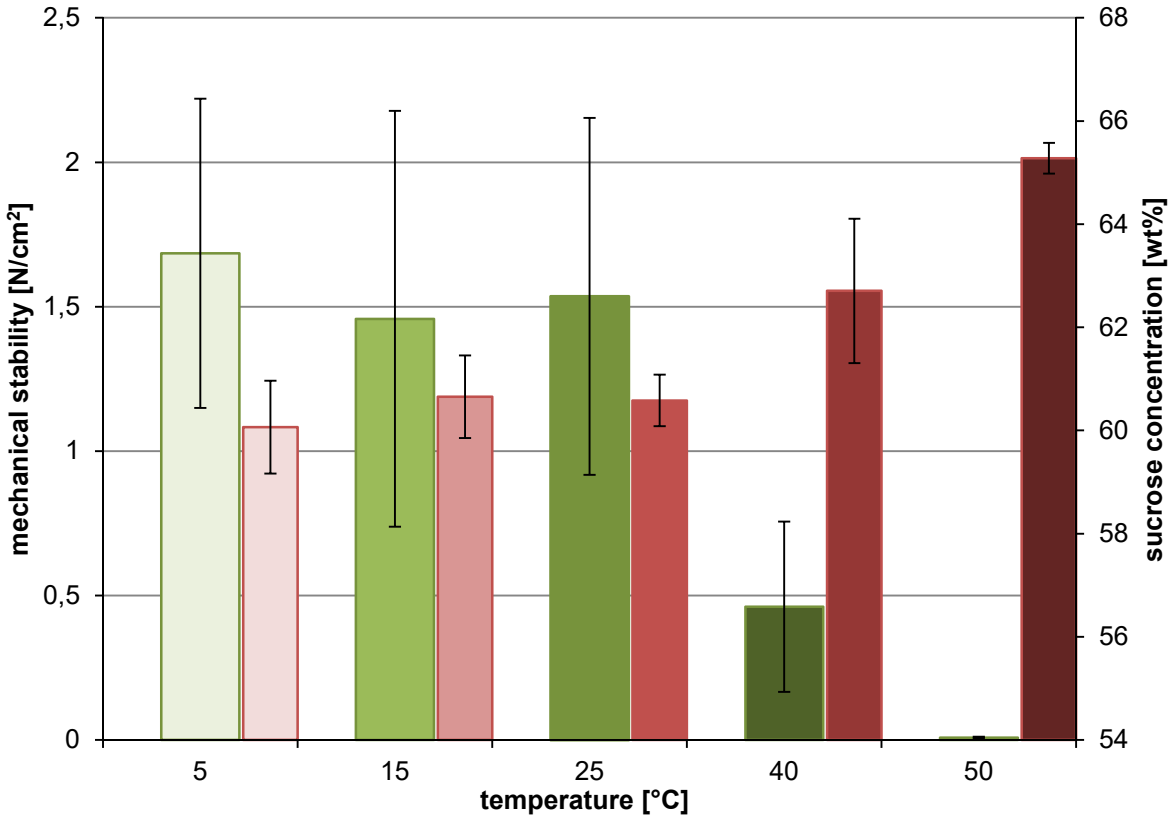


Figure 5.5-14: Mechanical stability (left bar) of sucrose-milk containers and concentration inside containers (right bar) after storage at different temperatures for 24 h

5.5.7 Influence of temperature fluctuations on container properties

The influence of temperature fluctuations on certain container properties has been investigated. The results are shown in Figures 5.5-15 and 5.5-16.

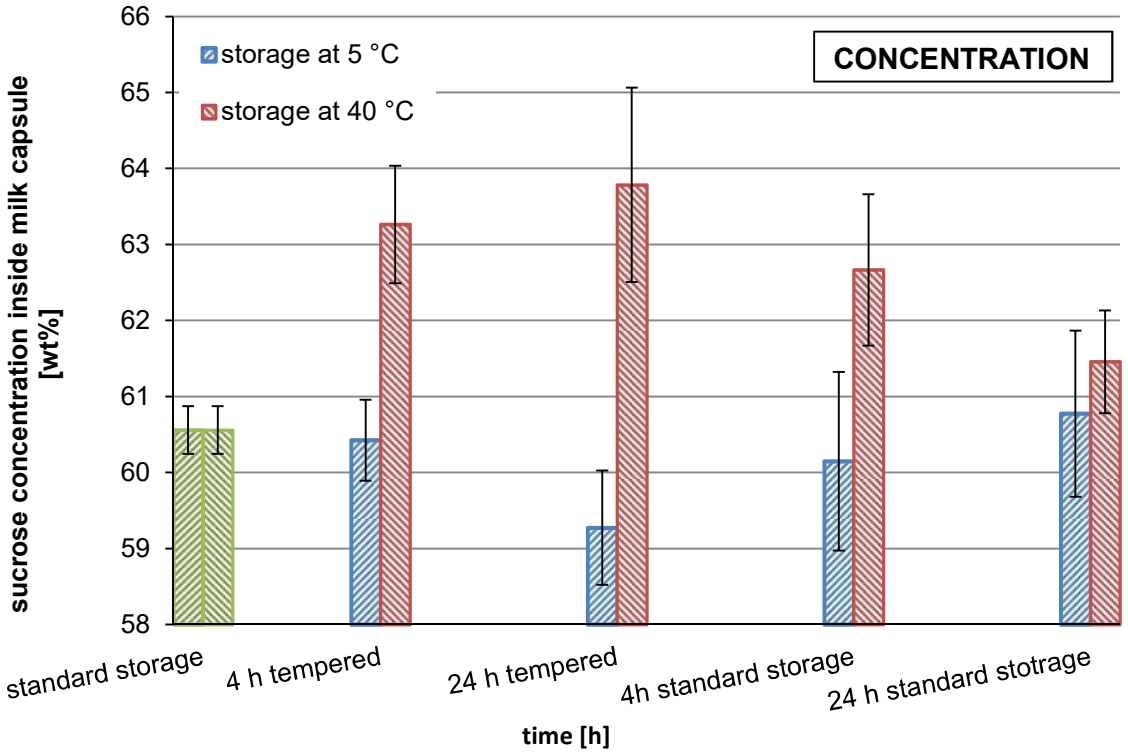


Figure 5.5-15: Sucrose concentration inside crystalline container over time under temperature fluctuations

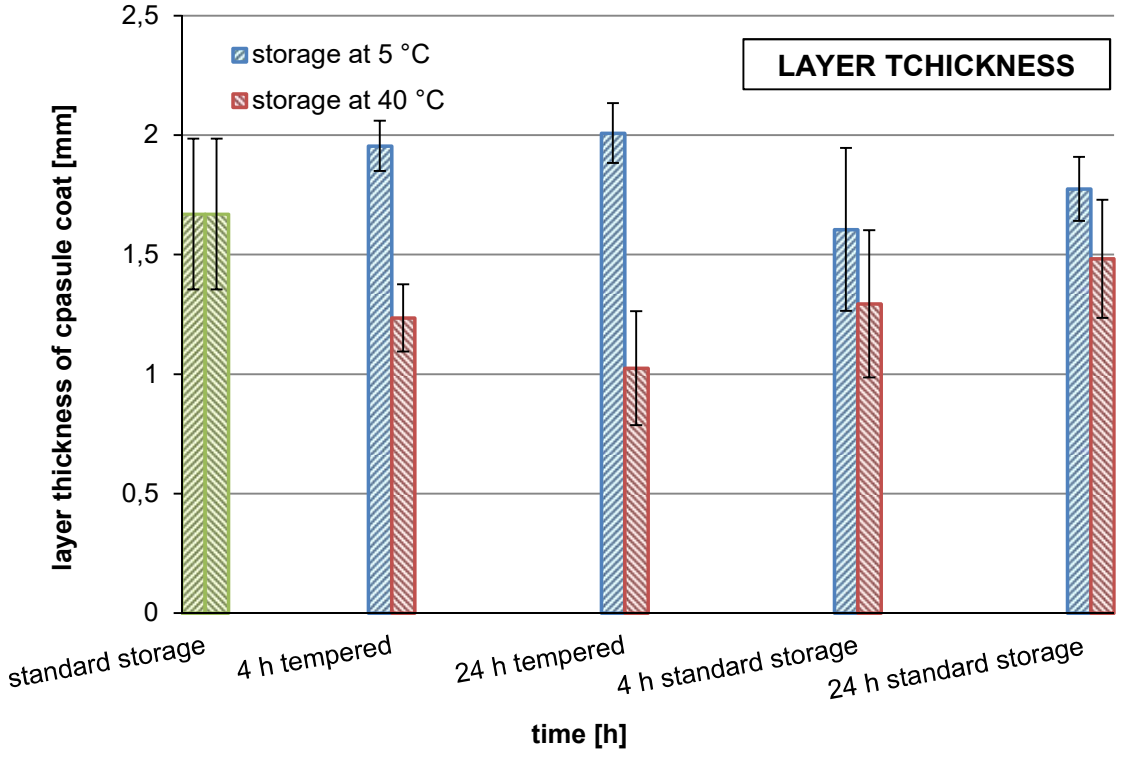


Figure 5.5-16: Layer thickness of crystalline coat over time under temperature fluctuations

As shown in Figure 5.5-15, the sucrose concentration of the encapsulated liquid changes with decreasing or increasing temperature. If the samples are exposed to a higher storage temperature of 40 °C, the concentration increases by 4.5 % within the first 4 h and by 5.3 % after 24 h. If the temperature is then reset to the defined optimum storage temperature (25 °C), the concentration decreases again. However, the change in concentration is slower – after 24 h the initial concentration of the encapsulated liquid is not yet reached again. If the samples are stored, however, at a lower temperature of 5 °C, the concentration decreases by 0.2 % (4 h) and 0.78 % (24 h). The increase in concentration when the samples are returned to the optimum storage temperature is also slower.

The change in storage temperature also has an effect on the layer thickness of the container coat (Fig. 5.5-16). If the storage temperature is increased to 40 °C, the layer thickness decreases by 26 % after 4 h and by 38.6 % after 24 h. The layer thickness increases again, after the storage temperature is reset to the defined optimum conditions. After 24 h, however, the initial layer thickness is still reduced by 11.2 %. At decreased storage temperature of 5 °C the layer thickness increases by 19.5 % (after 4 h) or 20.3 % (after 24 h) and decreases. Figure 5.5-17 illustrates the decrease and increase of the layer thickness after storage for 4 h at 40 °C and 5 °C.

Comparing Figures 5.5-15 and 5.5-16 the change in the concentration of dissolved solids within the container correlates with an increase or decrease in the layer thickness of the crystalline coat.

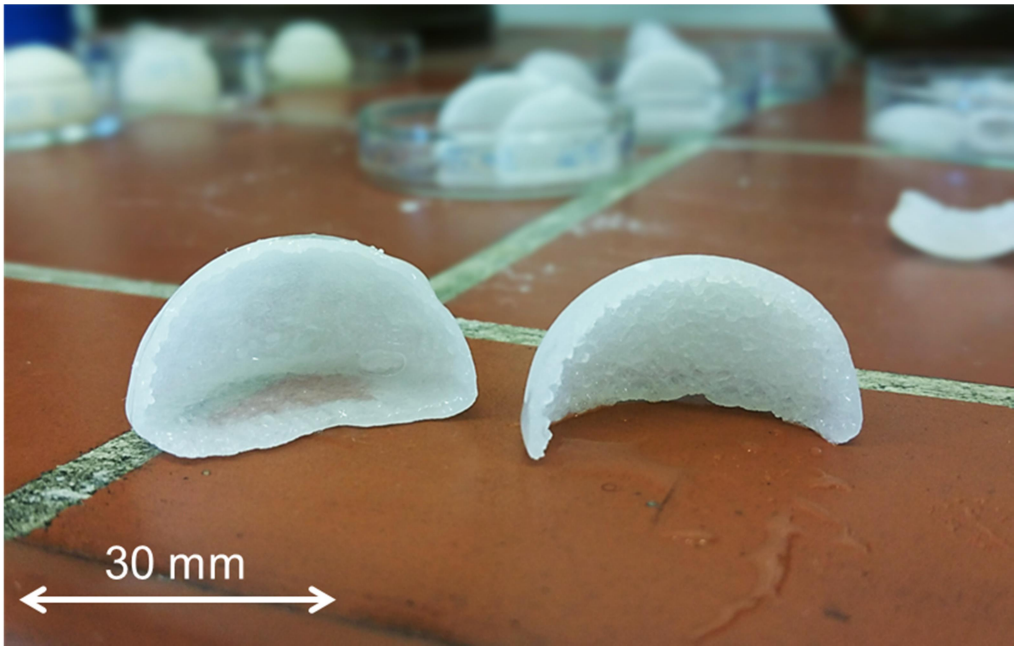


Figure 5.5-17: Crystalline coat of sucrose-milk container: Decrease in layer thickness after storage for 4 h at 40 °C (left), increase in layer thickness after storage for 4 h at 5 °C (right)

5.6 Influence of powder tray properties on container quality

The moisture content of the corn starch used in powder trays depending on type and storage is shown in Table 5.6-1. Corn starch, which has already been used multiple times and dried for 24 h at 50 °C, reveals a moisture content of 5.13 %. First-used starch, which has not been exposed to a drying process, has a moisture content of 12.62 %.

Table 5.6-1: Influence of type and storage on the moisture content of corn starch used in powder trays

sample		moisture content [%]	SD
type	storage conditions		
first-used	24 h, room temperature	12.62	0.24
	24 h, 50 °C	7.14	1.84
multiple-used	24 h, room temperature	9.8	0.39
	24 h, 50 °C	5.13	0.53
	24 h, 50 °C → 10 min, room temperature	5.63	0.11

Figure 5.6-1 shows the effect of type and storage of the starch used on the probability of sample defects. No defects, as well as smaller (holes < 1 mm) and larger defects (holes > 1 mm) in the coat of the container have been considered.

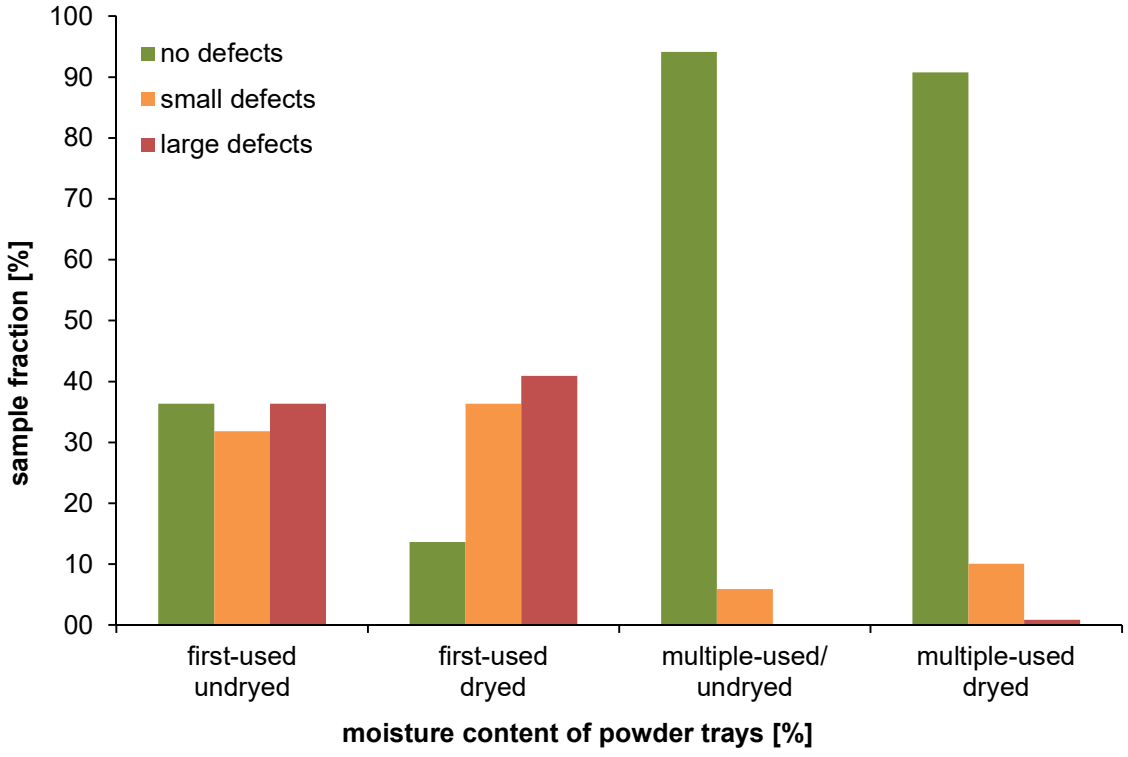


Figure 5.6-1: Effect of type and storage of corn starch on the probability of product defects

If multiple-used starch (5.63-9.8 % moisture content) is applied for the preparation of the samples, over 90 % of the sample are free of defects. When first-used starch (7.14-12.62 % moisture content) is used, 68 – 77 % of the samples show smaller to larger defects. Variation of the moisture content (5.13-12.62 %) of the starch has no effect on the formation of defects.

Furthermore, the influence of the bulk density of the powder trays on the probability of sample defects has been investigated. Figure 5.6-2 shows the sample fractions of products with and without defects depending of bulk densities of 0.5 g/cm^3 and 0.6-0.65 g/cm^3.

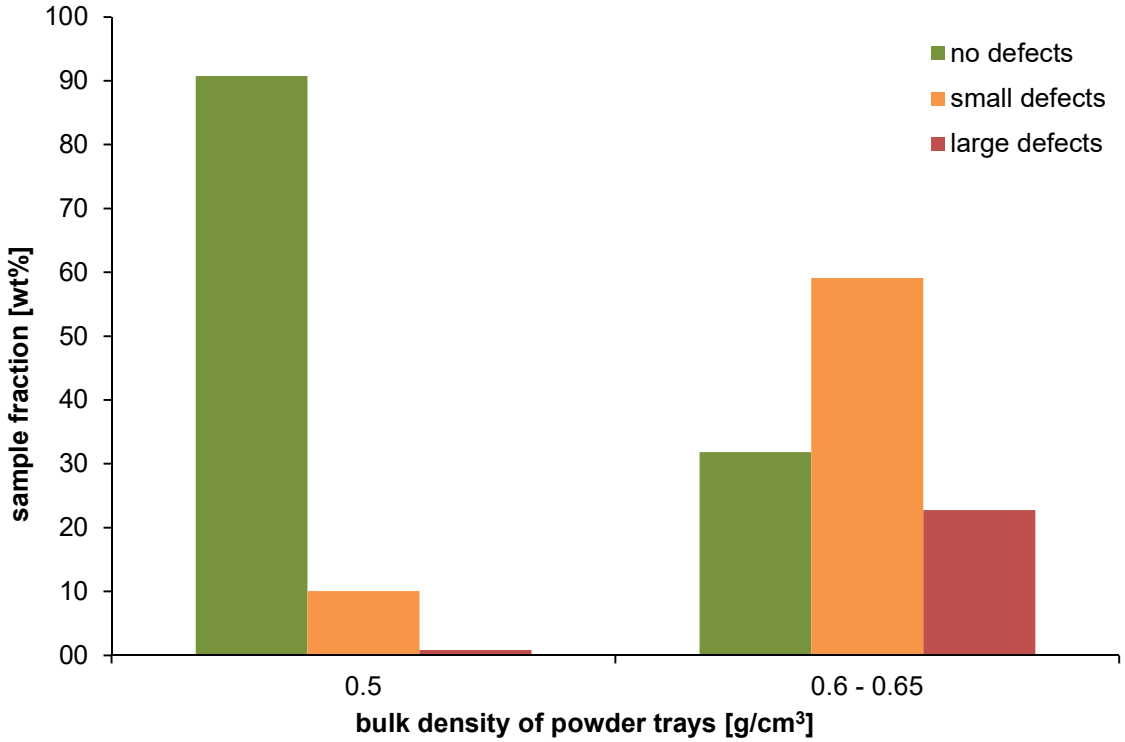


Figure 5.6-2: Effect of bulk density of powder trays on the probability of product defects

A low bulk density of 0.5 g/cm^3 results in a proportion of > 90 % samples without defects. 82 % of the samples produced in a powder tray with a higher bulk density of 0.6-0.65 g/cm^3 revealed small and large defects on the container coat.

5.7 Alternative shaping technique

In the further course of the work, the shaping technique has been transferred from powder trays to silicone molds (Fig. 5.7-1). Shape and size of the molds have been retained.

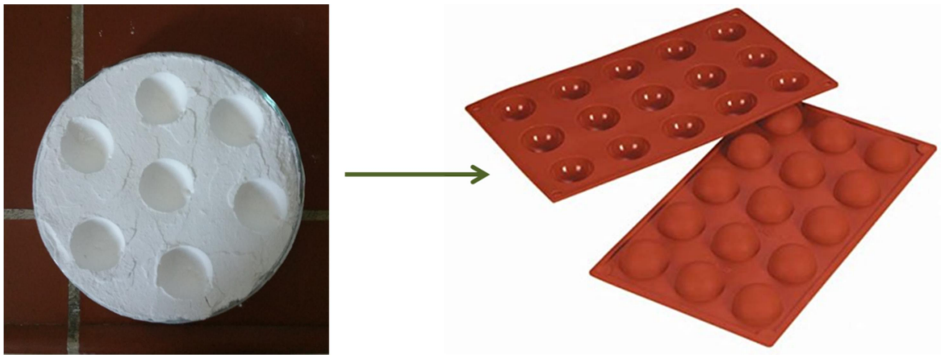


Figure 5.7-1: Different shaping techniques for the production of crystalline container (left: Powder tray, right: Silicone molds)

The optimum amount of seeding material necessary for the formation of the crystalline coat has been determined. Therefore, 1-24 mg/cm² of seeding material have been added to the silicone molds. The results are shown in Figure 5.7-2.

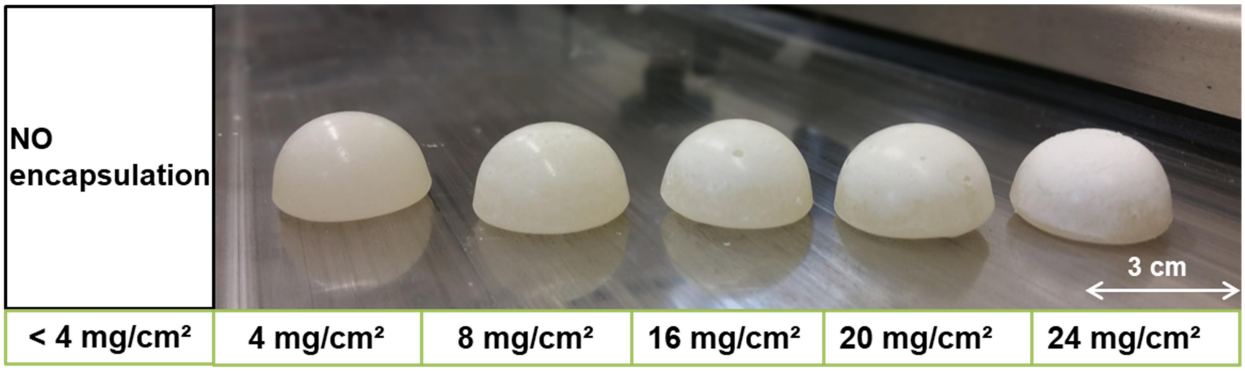


Figure 5.7-2: Effects of different amounts of seeding material added to the molds on the formation of the container coat

If less than 4 mg/cm² are added to the silicone molds, no encapsulation occurs. Either no complete crystalline coat is formed or the coat reveals severe defects. As the amount of seeding materials increases, more material is built into the coat. The optimum amount of seeding material is determined to be 4 mg/cm².

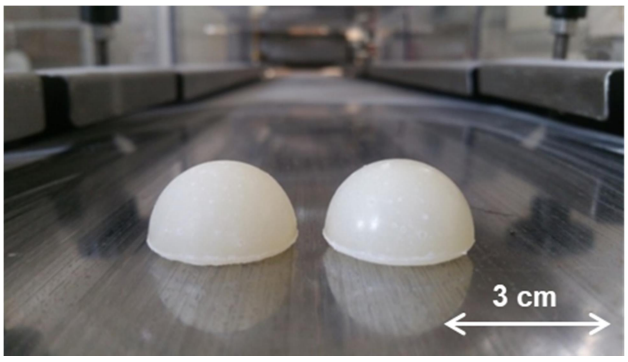


Figure 5.7-3: Sucrose-milk containers (72wt%) produced in powder tray (left) and silicone mold (right)

Figure 5.7-3 presents two crystalline milk containers as a comparison. The left container has been produced in a powder tray, the right one in a silicone mold. The applied shaping technique does not seem to have a great effect on the sensory properties. However, containers produced in silicone molds reveal a smoother surface.

The mechanical stability of sucrose-milk containers (72wt%) depending on the applied shaping technique (silicone molds and powder trays) is presented in Figure 5.7-4. All containers reveal a similar mechanical stability of ~1.5 N/cm².

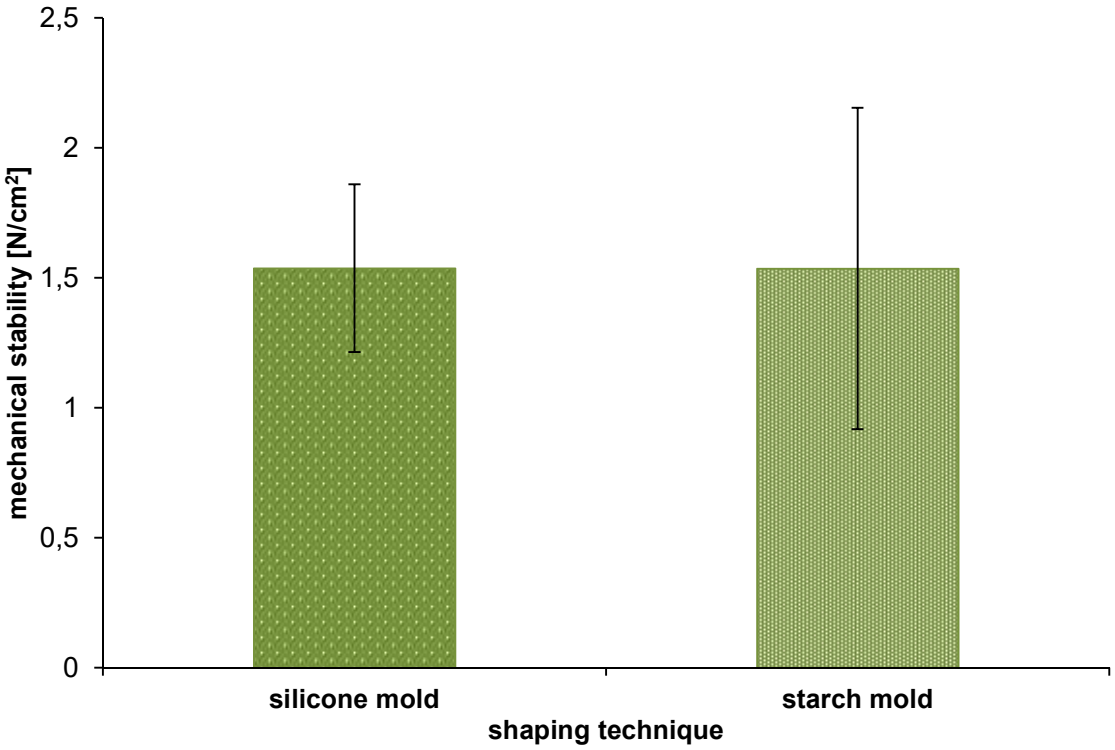


Figure 5.7-4: Mechanical stability of sucrose-milk containers (72wt%) depending on applied shaping technique

5.8 Encapsulation process using xylitol

In the first step, the **phase diagrams** for xylitol and the respective solvent have been determined.

The results of the isothermal and polythermal solubility measurements of xylitol in milk (3.5 %) and of the nucleation temperatures are shown in Figure 5.8-1.

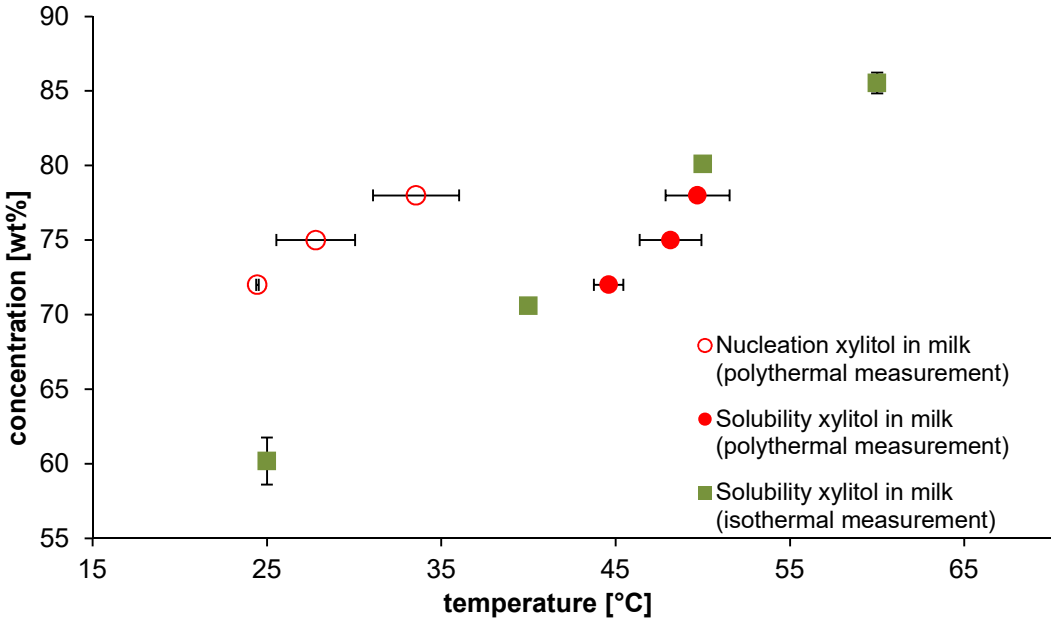


Figure 5.8-1: Solubility and nucleation of xylitol in milk determined by isothermal and polythermal measurements

As the concentration of xylitol in milk is increasing, the temperatures of solubility and nucleation increase. The different measurement techniques (isothermal and polythermal) provide consistent results. The MSZW is determined to be ~16-20 K.

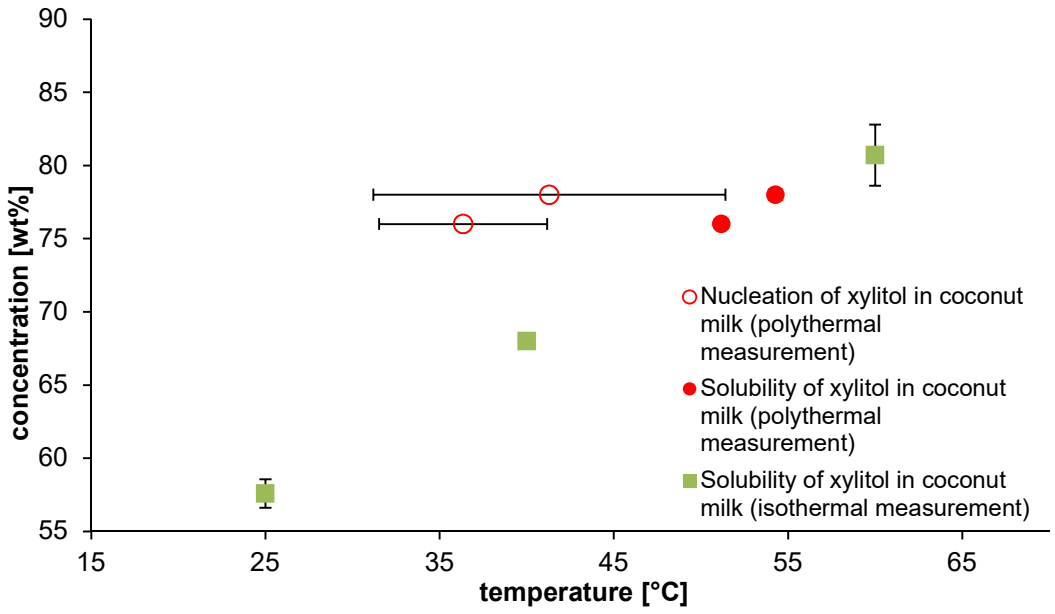


Figure 5.8-2: Solubility and nucleation of xylitol in coconut milk determined by isothermal and polythermal measurements

Figure 5.8-2 shows the temperatures of nucleation and solubility of xylitol in coconut milk (7 % fat) determined by isothermal and polythermal measurements.
The solubility of xylitol in coconut milk also increases with increasing temperature, with similar results obtained by the different measurement techniques. Compared to milk the points of solubility are shifted to higher temperatures. The MSZW is 12-15 K.

Based on the defined product size (see Chapter 4.2.3) and coat thickness (1.5 mm) as well as on the results of the phase diagrams, the **optimum application quantities** have been calculated by using Equations 4.2-1 and 4.2-2 and the corresponding **process parameters** determined. The results are summarized in Table 5.8-1.

Table 5.8-1: Process parameters for the production of crystalline containers (xylitol-milk, xylitol-coconut milk) with a layer thickness of 1.5 mm

sample system	ρ_{solid} [g/cm^3]	$\rho_{solvent}$ [g/cm^3]	$c_{storage25}$ [wt%]	$c_{optimum}$ [wt%]	MSZW [K]	$T_{saturated}$ [°C]	$T_{solution}$ [°C]	$T_{casting}$ [°C]
xylitol-milk	1.52	1.028	60.2	72.4	16-20	42	52	35
xylitol-coconut milk		1.022	57.6	71.0	12-15	46	56	40

Figure 5.8-3 shows the effects of the application of different seeding materials on the final product. If pure corn starch is added to the silicone molds to initiate the crystallization process, the resulting crystalline coat reveals major defects. If the corn starch is completely substituted by milled xylitol, an intact crystalline coat with a smooth appearance is formed.

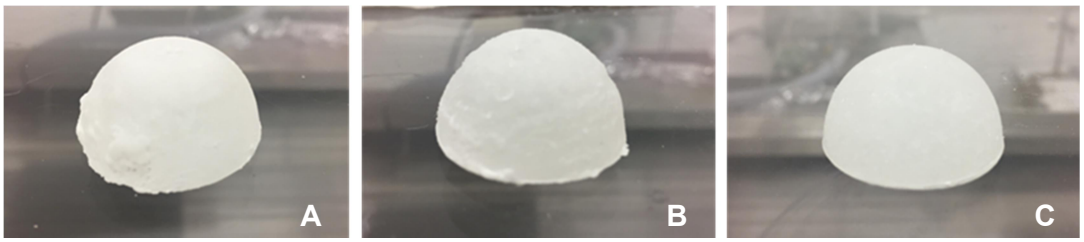


Figure 5.8-3: Effects of different seeding materials on the quality of the capsule shell (A: Corn starch, B: Xylitol/corn starch 50:50, C: Milled xylitol)

Using the process parameters listed in Table 5.8-1 and the application of ground xylitol as seeding material, crystalline containers with an intact crystalline coat filled with liquid milk (Fig. 5.8-4) and coconut milk have been produced.

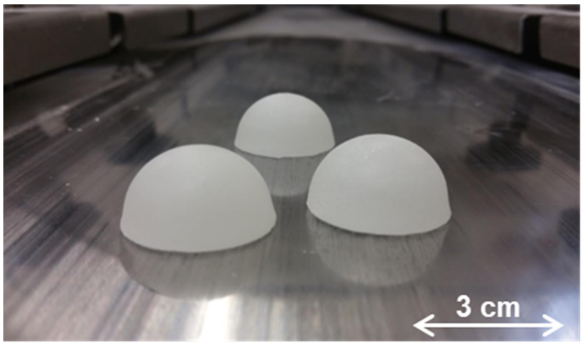


Figure 5.8-4: Crystalline containers (xylitol-milk)

The mechanical stability of xylitol-milk containers (72.4 wt%) has been determined. The results are shown in Figure 5.8-5 and compared to the mechanical stability of sucrose-milk containers. Containers with a xylitol-based coat reveal a lower mechanical stability (0.95 N/cm^2) than sucrose-based containers (1.54 N/cm^2).

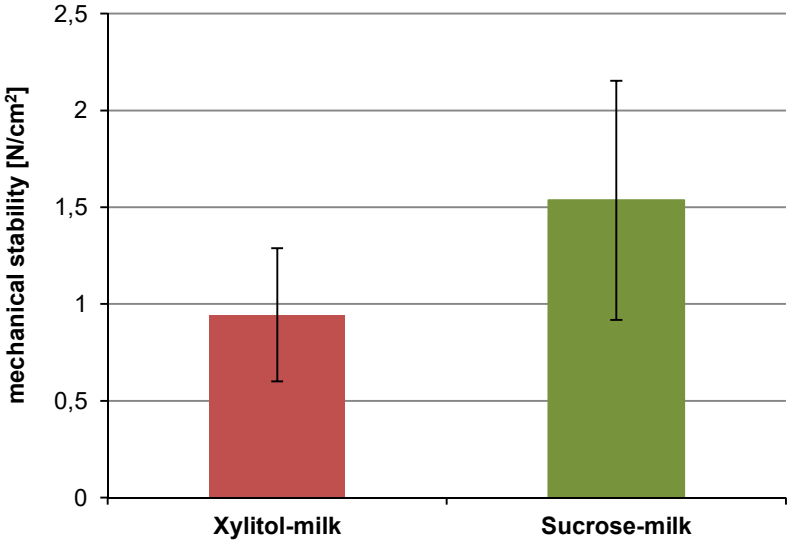


Figure 5.8-5: Mechanical stability of xylitol-milk containers compared to sucrose-milk containers

5.9 Product variation

Figure 5.9-1 shows crystalline containers with liquid fillings revealing different shapes and sizes.

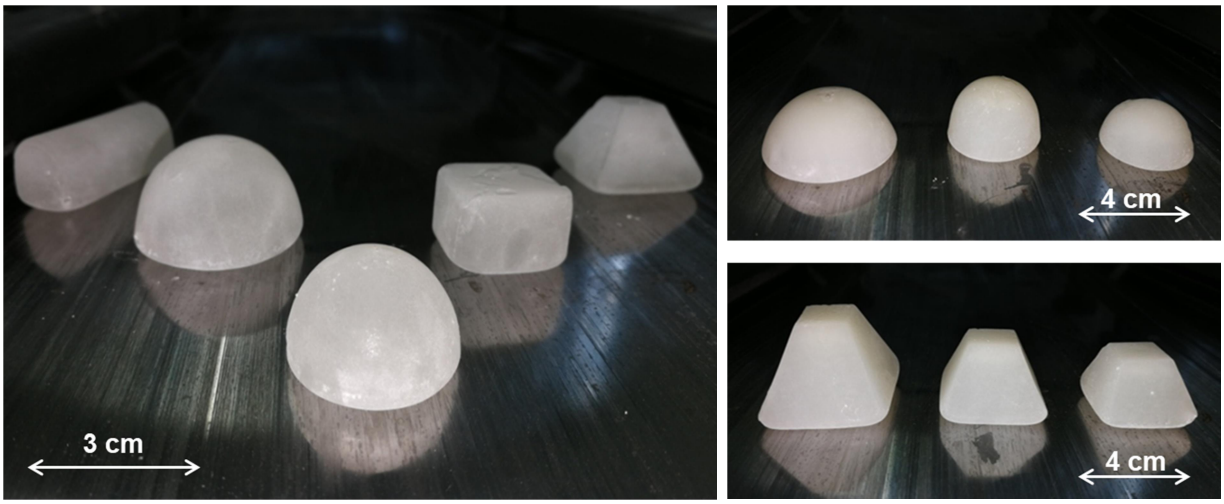


Figure 5.9-1: Different product shapes and sizes of crystalline containers with liquid filling [Wel18c]

Figure 5.9-2 shows the effect of different flavor concentrations on the nucleation and solubility temperatures of sucrose-milk solutions (72 wt%). No significant influence on nucleation and solubility could have been determined.

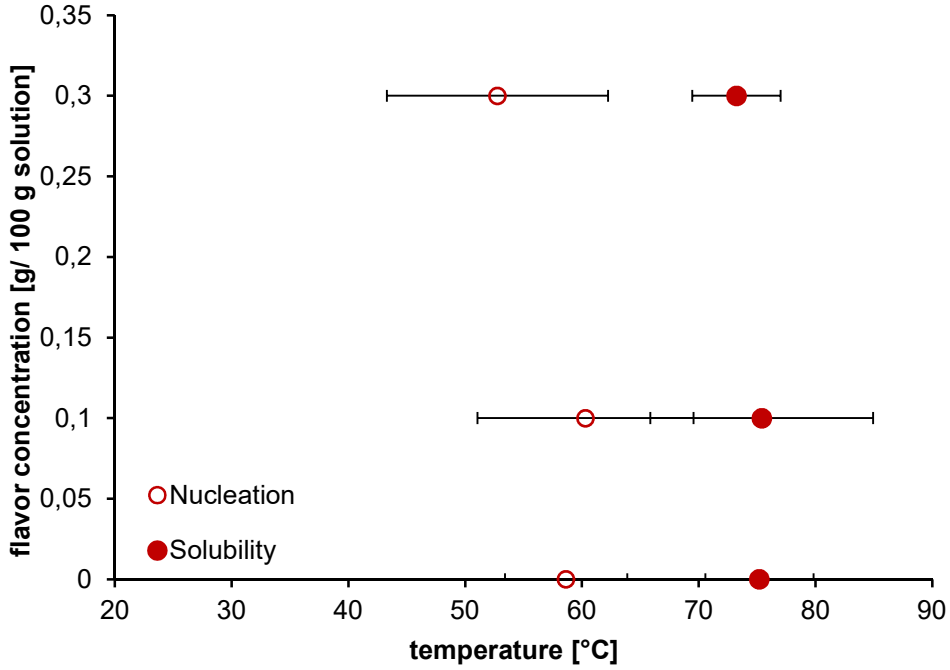


Figure 5.9-2: Nucleation and solubility temperatures of sucrose-milk solutions (72 wt%) as a function of flavor concentration [Wel18c]

The nucleation and solubility temperatures of sucrose-milk solutions (72 wt%) with added coloring are shown in Figure 5.9-3. Again, no effect on the MSZW can be detected.

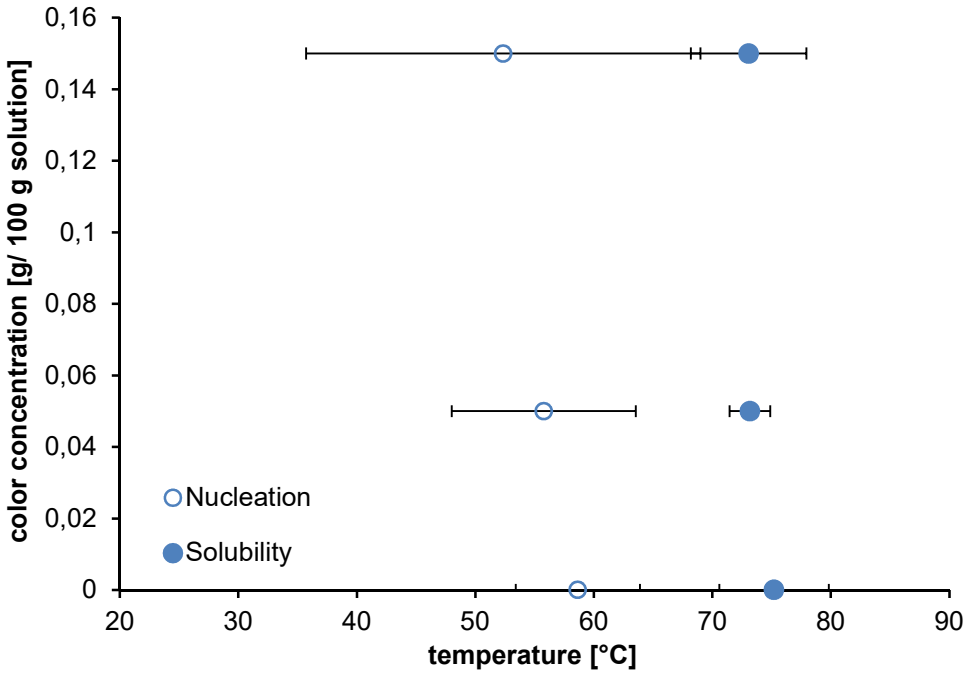


Figure 5.9-3: Nucleation and solubility temperatures of sucrose-milk solutions (72 wt%) as a function of color concentration [Wel18c]

Products with different color and flavor intensities have been produced. Despite the addition of additives, the crystalline coats did not reveal any defects (Fig. 5.9-4).

Figure 5.9-4: Crystalline containers with addition of color (left) and flavor (right) [Wel18c]

The influence of different concentrations of colors and flavors on the mechanical stability of the final products is shown in Figure 5.9-5.

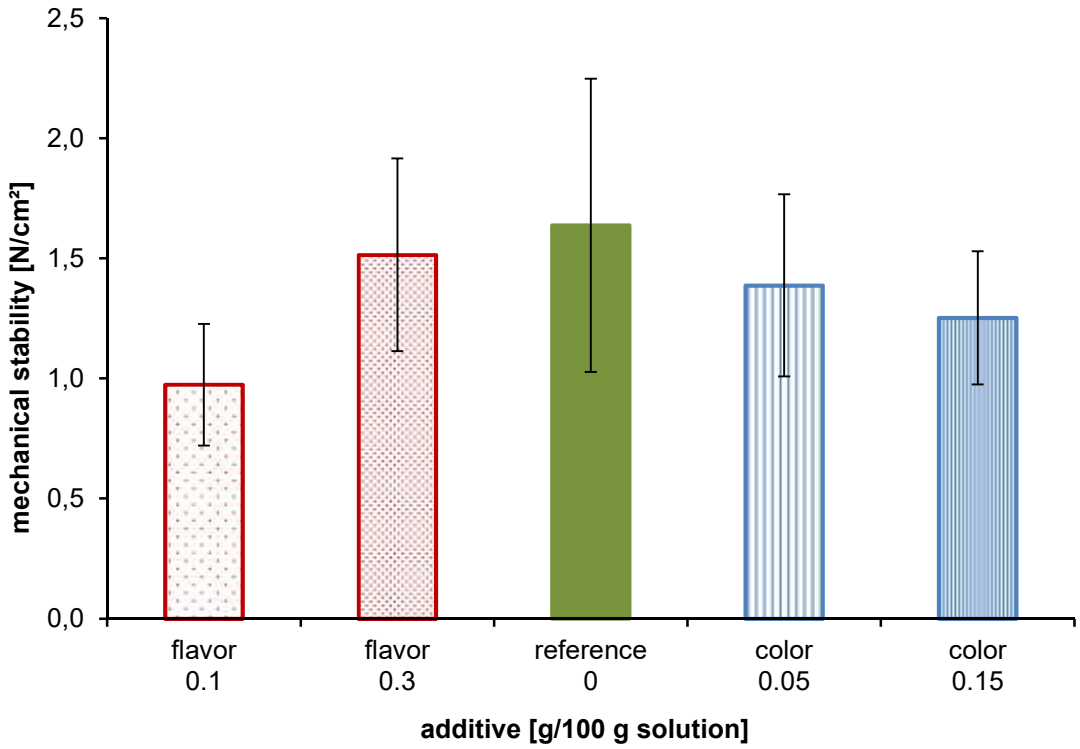


Figure 5.9-5: Effect of different concentrations of flavor and color on the mechanical stability of liquid filled crystalline containers (sucrose-milk 72 wt%) [Wel18c]

In additional experiments, the application of further liquids for the encapsulation process by means of crystallization has been tested. Figure 5.9-6 shows the results of the encapsulation of fruit juice and fruit juice concentrate. The tested liquids have been completely enclosed in a solid crystalline coat.

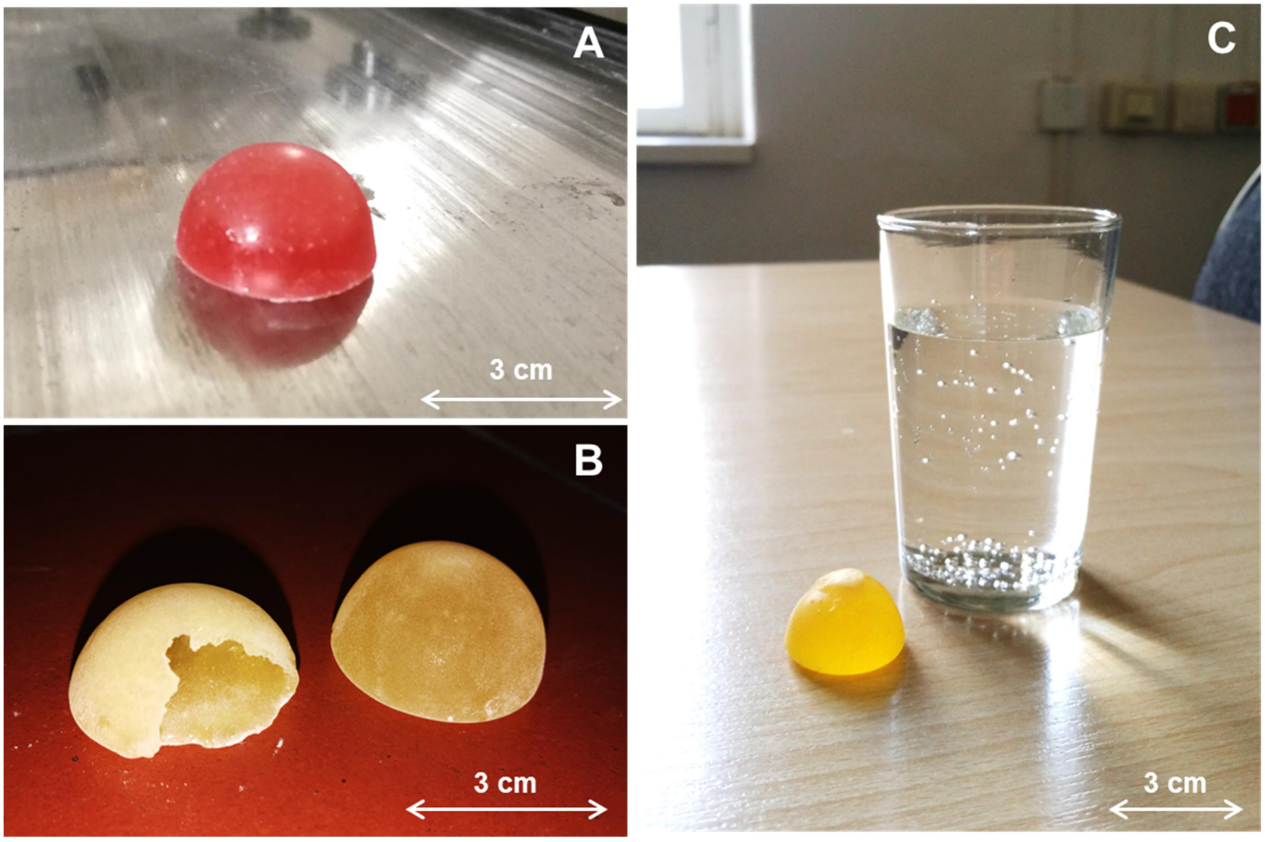


Figure 5.9-6: Results of the encapsulation test of fruit juice (A) and fruit juice concentrate (B) for the application in beverages (C)

In addition, the encapsulation of alcoholic beverages has also been successfully applied, as shown in Figure 5.9-7.

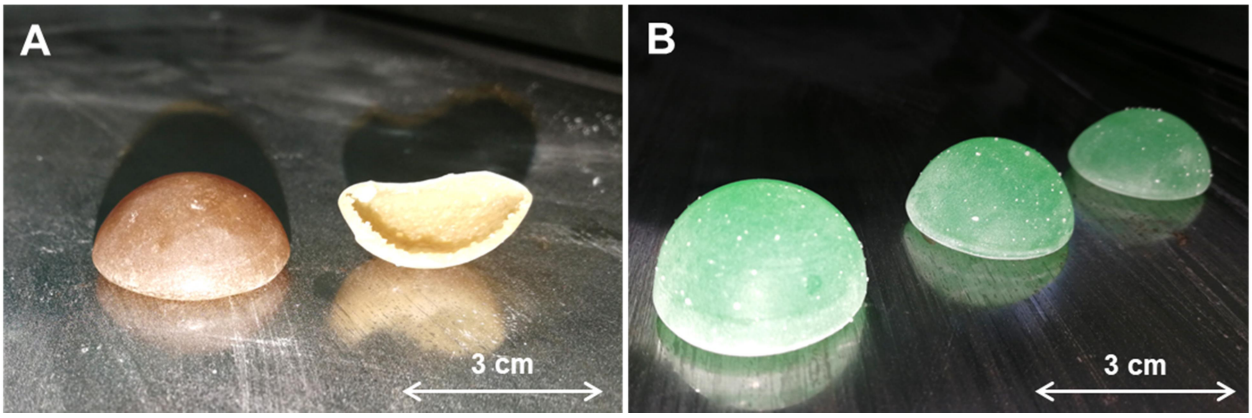


Figure 5.9-7: Results of the encapsulation tests of cream liqueur (A) and peppermint liqueur (B)

6. Discussion

6.1 General discussion

6.1.1 Encapsulation process

In the course of this work the process of crystallization has been chosen for the production of crystalline containers with liquid fillings. Within this process, a crystalline coat is formed around the liquid from a supersaturated solution by specific initiation of the crystallization on the outside and the resulting degradation of the concentration within the created containers (Fig. 6.1-1). Required for this process are:

- Crystalline substance (encapsulation material to form the future coat)
- Solvent (desired liquid to be encapsulated)
- Molds (to achieve the desired shape)
- Seed material (to initiate the crystallization of the coat)

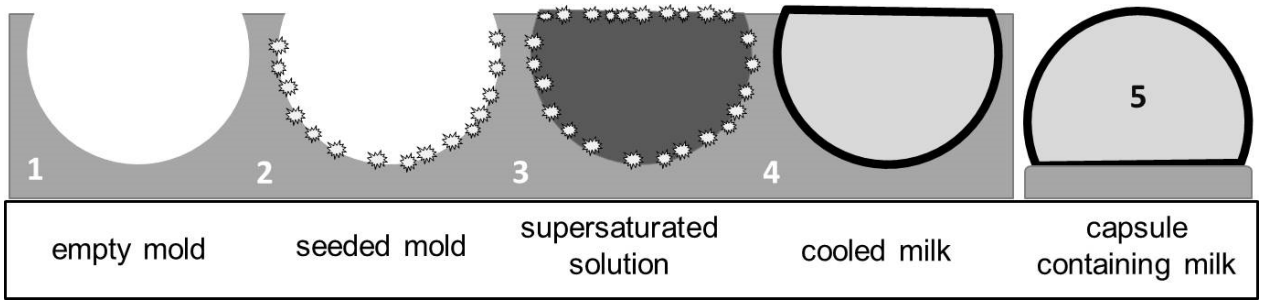


Figure 6.1-1: Production of crystalline containers with liquid filling [Wel16]

In a first step, an unsaturated solution is prepared by dissolving the crystalline substance in the desired solvent at $T_{solution}$ and subsequently cooling to $T_{casting}$. In a second step, this supersaturated casting solution revealing a certain concentration ($c_{optimum}$) is filled in previously prepared molds. The crystallization is then initiated from the outside by seed particles added prior to these molds.
Powder trays, prepared by sieving starch and subsequent drying, are used for shaping. The molds are created by inserting stamps into the powder trays. Using this shaping technique, the starch particles serve as seed material.

Figure 6.1.2 illustrates the process of formation and growth of the crystalline coat. As the casting solution is filled into the molds, the solution reveals $c_{optimum}$ ($=c_{start}$). As soon as this supersaturated solution gets in contact with the seed particles, crystallization and therefore the formation of the crystalline coat from the outside is initiated. Specific cooling then leads to a degradation of the concentration inside the future container – the crystalline layer around the solution is growing towards the inside. The cooling stops at the previously defined storage temperature ($T_{storage}$). The resulting crystalline container is then in thermodynamic equilibrium and the final concentration is reached (c_{end}). The degraded concentration (Δc) of dissolved solids correlates to the mass of the grown container coat.

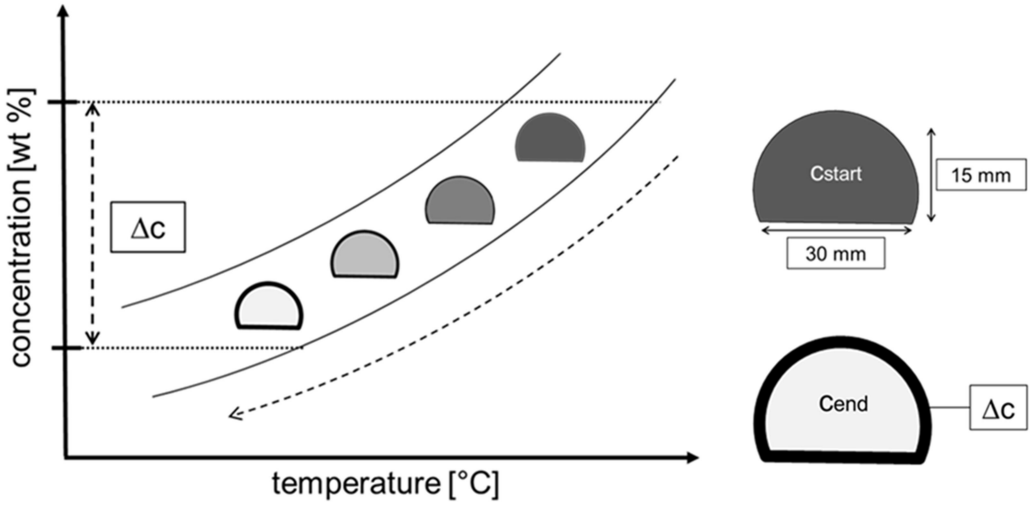


Figure 6.1-2: Formation and growth of crystalline layer as a function of concentration and temperature [Wel17]

6.1.2 Preliminary experiments

In order to use this encapsulation technique for a specific substance system, various parameters must first be determined within the framework of preliminary experiments.

Prior to the encapsulation process it is necessary to **define certain product properties** in order to produce uniform and therefore comparable samples. In the course of this thesis the **shape** has been set to be hemispheres as it has been considered to be a handy and visually appealing shape. On the one hand, the **size** should be big enough to encapsulate a suitable amount of liquid and, on the other hand, small enough for an application in beverages. In this context, the diameter of the hemispheres has been set to be 3 cm, the height to be 1.5 cm.
A suitable **thickness of the container coat** is essential for the generation of stable products. The thickness has been defined to be 1.5 mm. A sufficient mechanical stability in relation to the size can then be assumed.
The **storage temperature** of the future products has been defined to be 25 °C, since this corresponds to the approximate room temperature. This temperature has been chosen on the one hand, to provide an easy handling while conducting the experiments and, on the other hand, to ensure storage of the final product at room temperature. In food retail, product placement in the cooling area is considerably more cost-intensive than in the non-cooling area. Storage at room temperature therefore contributes to a more favorable pricing of the end product.

Furthermore, the **solubility** of the used crystalline substance in the solvent has to be determined – an accurate solubility curve has to be generated and the **MSZW** of the solution system has to be determined**.** Especially, the exact determination of the saturation concentration at the defined storage temperature is important for the following encapsulation process.

The **densities** of the solid (encapsulation material) and the solvent (liquid to be encapsulated) have to be determined. In the course of this work, the density of the used crystalline substances has been taken from literature. The density of the solvents has been determined using an oscillating U-tube density-meter. Low standard deviations indicate accurate results.

6.1.3 Prediction of suitable production parameters

For a successful encapsulation process it is necessary to predict 4 main production parameters: $\mathbf{c_{optimum}}$, $\mathbf{T_{saturation}}$, $\mathbf{T_{solution}}$ and $\mathbf{T_{casting}}$.

Based on the defined product parameters as well as on the results of the preliminary experiments, $\mathbf{c_{optimum}}$ of the casting solution can be calculated. Therefore, equations have been defined.

In order to investigate the accuracy of the equations, the layer thickness of the container coat has been examined as a function of the amount of solids used and compared with the calculated layer thicknesses. The thickness of the crystalline container coat has been determined microscopically. The equation has been proven to be suitable to determine the required application quantity. However, slight deviations have been detected. Both results are afflicted with errors: On the one hand, caused by the application of the formula, since the required values for the calculation have to be determined as accurately as possible. In particular, the inexact determination of the solubility has an effect on the results. On the other hand, the layer thickness measurement by microscopically analyses can be improved, to be statistically more accurate.

However, the accuracy of the formula is sufficient to provide guidelines and is therefore a sound foundation for the development process of crystalline containers with liquid filling.

The referring $\mathbf{T_{saturation}}$ can be calculated based on the respective determined solubility curve.

The temperature at which the amount of calculated solid and solvent has to be dissolved ($\mathbf{T_{solution}}$) has been defined to be 10 K above $T_{saturation}$ to ensure complete dissolution within 1 h. If the crystalline substance is not completely dissolved, small particles remain within the casting solution. A specific initiation of the crystallization from the outside is then not possible - a layer formation around the liquid cannot occur.

The exact prediction of $\mathbf{T_{casting}}$ is of great importance for the following process of layer formation. It is necessary to cool the initially undersaturated solution until the MSZ is attained. Based on the resulting supersaturation, the crystallization process is initiated as soon as the solution is filled into the molds and getting in contact with the seeding particles. Cooling too far could lead to spontaneous nucleation inside the casting solution. Again, a specific initiation of nucleation only on the outside of the future container is not possible.

In order to avoid spontaneous nucleation inside the solution but to ensure sufficient supersaturation, $T_{casting}$ has been set to be in the middle of the MSZW.

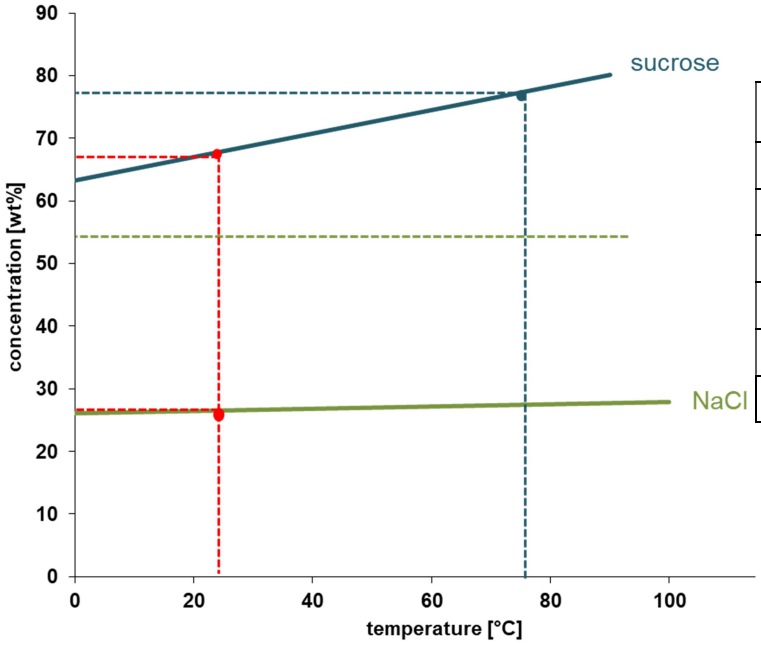
During the encapsulation process, **powder trays** have been used for shaping the future products. For this purpose, starch is sieved in trays with a certain bulk density and then dried. A stamp is used to create negative imprints of the future product shape in the starch. The influence of the **moisture content** of the starch as well as the **bulk density** on the quality of the formed crystalline coat has been investigated. The results suggest that the moisture content in a range of ~5 to 12 % of the starch used has no effect on the formation of defects. However, it has been observed that the application of first-used starch leads to an increased formation of defects in the crystalline coat of the products. If multiple-used starch is applied, less than 10 % of the samples reveal defects. Furthermore, the formation of defects is stimulated by an increased bulk density. An optimal bulk density of 0.5 g/cm^3 has been determined. A higher bulk density and therefore a more compact accumulation of starch particles impair the penetration of the stamps and causes incorrectly shaped molds.

As a result, crystallization is not initiated homogeneously on the entire surface – holes are generated in the forming coat.

6.1.4 Applicability of encapsulation materials

Not all crystalline substances can be applied for the crystallization-based encapsulation process. As a result of the experiments carried out within this work, three parameters have been determined to have an effect on the applicability of a certain crystalline substance.
It has been investigated that a large **MSZW** contributes to a successful encapsulation process. If the applied casting solution reveals a MSZW < 10 K, the encapsulation process based on crystallization cannot be applied.

In addition, the **slope of the solubility curve** has effects on a successful encapsulation process. If the slope is too flat, the required concentration necessary to form a crystalline coat cannot be achieved. Figure 6.1-3 illustrates the solubility curves of sucrose (slope=0.188) and NaCl (slope=0.018) in water as well as the relevant production parameters for an encapsulation process. On the one hand, sucrose can be applied to encapsulate water, on the other hand, NaCl cannot be applied due to the flat slope.



	sucrose	NaCl
slope	0.188	0.018
$c_{storage}$ [wt %]	67.5	26.45
$T_{storage}$	25	
$c_{optimum}$ [wt %]	77.7	56.5
$T_{saturation}$	78	-
result	√	x

Figure 6.1-3: Slope of solubility curve as indicator for the applicability of crystalline substances

Also, a sufficient **crystal growth rate** of the respective crystalline substance is necessary with regard to the growth of the crystalline coat of the future containers. In preliminary experiments the sufficient crystal growth rate has been determined to be between 10^{-7} and 10^{-9} m/s.

6.1.5 Encapsulation results

In the course of this thesis, different crystalline materials have been investigated with regard to their applicability for the encapsulation process (Table 6.1-1).

Table 6.1-1: Applicability of different crystalline substances for the encapsulation process

substance	applicability
sucrose	✓
erythritol	✓
isomalt	x
cellobiose	x
mannitol	x
xylitol	✓

In the first experiments, **sucrose** has been chosen as it is a well investigated substance. Crystalline containers have been produced revealing an intact crystalline coat with liquid fillings of milk, condensed milk and coconut milk. Further properties of the different containers produced will be explained in Chapter 6.1.6.

In order to expand the product range, the focus in the further course of this work has been on the development of a sugar-free alternative to the sucrose containers. For this purpose, further crystalline materials have been investigated with regard to their applicability for an encapsulation process.

The sugar substitute **erythritol** has been applied for the encapsulation of milk and condensed milk. The encapsulation of milk has not been successful. The respective casting solutions have been infiltrated into the powder trays as soon they had been filled into the molds. Therefore, an initiation of crystallization to form a crystalline coat has not been possible. Using condensed milk as a solvent instead, has resulted in a successful encapsulation. However, the crystalline containers enclosing condensed milk have revealed uneven surfaces. Further properties of this container system will be discussed in Chapter 6.1.6.

Mannitol has not been proven to be a suitable encapsulation material as the MSZW of mannitol-based solutions is too small.

Furthermore, **cellobiose** has been investigated. Based on the infiltration behavior of cellobiose-based casting solution, no encapsulation has been possible.

Xylitol has been applied using a different shaping technique. The results will be discussed in Chapter 6.1.9.

6.1.6 Determination of product properties

In the course of a product development process the analysis of quality is an essential step since it is necessary to control and improve the production process regarding the desired quality of the final product. Suitable methods for determining the product properties and their application have been established. Regarding the claims of the final product mechanical, chemical, thermodynamic and kinetic properties have been considered (Figure 6.1-4).

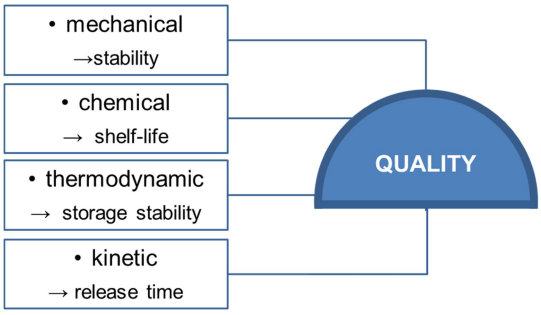


Figure 6.1-4: Methods for quality analysis of liquid filled containers [Wel18a]

The **maturation time** after the production of crystalline containers has been determined exemplarily for the system sucrose-milk (72 wt%). For this purpose, the degradation of the sucrose concentration inside the container has been determined over time. After production, the concentration inside the containers gradually decreases. Based on the continuously decreasing supersaturation, the degradation rate decreases over time. After the fourth day the concentration remains constant. The decrease of the solid concentration correlates with the increase of the crystalline layer. This suggests that at the defined storage temperature of 25 °C the crystalline layer is fully formed after 4 days of maturation – the container is in 'thermodynamic equilibrium'. Depending on the type of the applied solid or the solid concentration, the choice of liquid being encapsulated or the selected storage temperature, the maturation time may be shortened or extended. However, the containers could already reveal a sufficient mechanical stability before the end of the maturation process. Packaging and transport of the products would be possible, even if the maturation process has not yet been completed.
Based on these results, all further experiments (i.e. quality analyses of the containers) have been carried out 4 days after the production, i.e. after completion of the maturation.

Mechanical stability is an essential property of the crystalline containers produced. Only sufficient mechanical stability can ensure safe packaging, transport and handling of the samples without breaking the product and leaking of the encapsulated liquid. The required minimum stability value for convenient handling was subjectively determined by testing to be 0.8 N/cm². Stability determination is only possible for mechanical values > 0.1 N/cm². The investigation of the mechanical stability by means of a pressure device has been proven to be a suitable method to give good enough indications regarding the possible pressure load limit. Different products can be compared and conclusions concerning the crystalline coat can be drawn. High standard deviations, however, indicate an inaccurate measurement. For more accurate results, it is necessary to examine a larger number of samples.
The mechanical stability has been applied for quality control during product development and as well as for comparison of different products. In this respect, the mechanical stability of sucrose-based containers in comparison to erythritol-containers has been investigated in first place.
The results clearly indicate that erythritol is not a suitable encapsulant. Even if an intact and closed coat is formed during the manufacturing process, it is extremely fragile and sensitive to breakage. Sucrose, however, forms a sufficiently stable and solid coat which ensures safe handling of the samples with liquid contents.

The **mass loss** of the liquid filled containers over time is an indicator for the storage stability. Potential conclusions on the permeability of the formed crystalline coat can be drawn. Only impermeable coats can protect the encapsulated liquid from external influences and ensure a sufficient shelf-life. Therefore, the mass loss of single containers over time has been exemplarily determined using sucrose- and erythritol-based containers. Sucrose based containers show a minimal mass loss stagnating within 20 days. Also, no optical changes of the products could have been observed. This suggests that the use of sucrose as an encapsulant results in the formation of a relatively impermeable coat around the liquid. The application of erythritol as encapsulation material leads to a rapid mass loss of ~5 %. This mass loss can also be detected by visual inspection. The samples reveal major deformations - indicating that the coat formed by erythritol is permeable, causing the product to lose water over time. Erythritol can therefore be excluded as a suitable encapsulation material for liquids. Determining the mass loss of the products over time is a suitable method to investigate the storage stability.

In the field of foods, the **shelf-life** of a product must be determined as it is a compulsory label element. Food packaging is used, among other things, to protect the product from external influences and to ensure an appropriate shelf-life. After the successful encapsulation of milk and condensed milk, it has then been investigated whether an alternative packaging from its crystalline coat can achieve an appropriate shelf-life. It has first been examined based on the pH development of the encapsulated liquids over time. The change of the pH value enables general conclusions concerning the chemical quality (shelf life) of the crystalline containers, as a decrease correlates with the spoilage of these products. The experiments have been based on three different container-systems (sucrose-milk, sucrose-condensed milk, erythritol-condensed mik). In the course of the experiments a pH decrease of encapsulated liquids within 20 days has not been detected for any of the investigated samples. However, non-encapsulated milk and condensed milk revealed a sharp decrease of the pH value in less than 10 days. This method is suitable to receive a rough idea of the shelf-life.
Furthermore, microbiological investigations have been carried out to receive more sufficient information on the shelf-life. These investigations have been based on sucrose and xylitol containers with a filling of milk or coconut milk.
A resazurine assay, which is based on a color change, has been carried out as a quick-test. No color changes have been detected. This indicates no spoilage of the investigated encapsulated liquids.
Furthermore, the total bacteria count (TBC) of the encapsulated liquids has been investigated by using china-blue lactose agar plates. A TBC value >10^5 would indicate a spoilage of the encapsulated liquid. As shown in Table 6.1-2 no critical TBC depending on sample type and sample age has been detected.

Table 6.1-2: Total bacteria count of different encapsulated liquids depending on sample type and sample age

product	storage time	TBC $\leq$ 10^5
sucrose-milk	4 days - 6 months	☑
sucrose-coconut milk	4 days - 3 months	☑
xylitol-milk	4 days - 4 weeks	☑
xylitol-coconut milk	4 days - 4 weeks	☑

The **release behavior** is one of the essential application properties of the product. After the containers have been added to a hot drink, they should dissolve as quickly as possible and release the encapsulated liquid, i.e. the milk, into the drink. The dissolution behavior of sugar cubes under the same conditions has been investigated as a comparative value.
As expected, both the milk containers and the sugar cubes dissolve faster with increasing temperature. In general, the sugar cubes dissolve faster than the milk containers.
The relatively high standard deviations obtained by the experiments can be explained by the small number of samples. For more accurate results, the number of samples should be increased.
Since the optimum coffee drinking temperature is approx. 65 °C, the release behavior of the milk containers at this temperature is particularly relevant. As sown in Table 6.1-3, at 65 °C, the entire encapsulated liquid is released into the beverage after ~ 30 s. Sugar cubes, dissolve after only 10 s. Nevertheless, a release rate of 30 s is still within an acceptable range.

Table 6.1-3: Release time of milk containers compared to dissolution time of cube sugar depending on time

temperature [°C]	release time milk-container [s]	dissolution time sugar cube [s]
25	100	70
35	80	50
45	70	40
55	50	20
65	30	10

As the release behavior has been investigated exclusively in $aqua_{dest}$, this may deviate in other hot beverages as coffee or tea. In addition, the stirring motion of a spoon has been simulated in an experimental set up using a magnetic stirrer. Also, this could have led to different results.

Influence of different storage conditions on product properties

After the production process the crystalline containers remain at defined storage temperature in a temporary thermodynamic equilibrium. Temperature changes result in a shift of this equilibrium. If the temperature increases, the concentration of dissolved solids inside the container increases. Thereby the crystalline coat of the containers is dissolved from the inside – the layer thickness is decreasing. At decreasing temperatures the concentration of dissolved solids decreases – the thickness of the coat increases towards the inside. Changes in the thickness of the coat correspond to changes in the mechanical stability of the products: An increase of the layer thickness leads to an increased stability - a decrease to a reduction of the mechanical stability.
The correlation between the concentration of dissolved solids inside the container and the thickness of the crystalline coat depending on temperature changes is presented graphically in Figure 6.1-5.

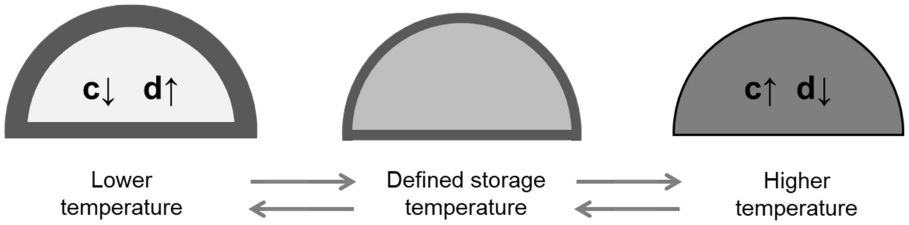


Figure 6.1-5: Correlation between concentrations of dissolved solids inside the container and thickness of the coat depending on the temperature

During transport and storage of products, it is not always possible to maintain constant and optimal ambient conditions. Therefore, the influences of humidity and different temperatures on the product during storage have been investigated. The mechanical stability of the containers has been used as reference parameter. Furthermore, the concentration of dissolved solids within the containers has been examined.
Fluctuations in air humidity of up to 50 RH% do not appear to have any influence on the mechanical stability and therefore the quality of the containers. Whether a higher air humidity (70 RH%) affects the quality of the crystalline shell cannot be determined precisely by taking the standard deviation into account.
Different storage temperatures can have strong effects on the mechanical stability. The mechanical stability of the containers decreases with increasing temperature. If stored at 40 °C, the mechanical stability is already below 0.5 N/cm^2. At this point, the containers are no longer safe for transport. Even small vibrations would lead to breakage. At storage temperatures above 50 °C the container coat starts to melt and the original shape cannot be retained. The decrease of the mechanical stability with increasing temperatures can be explained by the increasing solubility of sucrose. More solid material is dissolved in the liquid filling inside the container as the temperature increases. The concentration of the dissolved solid inside the container increases, causing the crystalline coat to degrade from the inside to the outside – the layer thickness decreases.
In general, storage of the products at higher or lower temperatures is possible. However, the manufacturing process must then be adapted to the desired storage temperature.

In the further course, the effects of temperature fluctuations limited in time, which can occur at short-termed intervals during product transport or storage, have been investigated. In this context, the products have been stored in a first step for 24 h at 40 °C and 5 °C and subsequently in a second step for another 24 h under standard conditions. It has been shown that the effects of short-term temperature changes (up to 24 h) on the concentration of the encapsulated liquid as well as the layer thickness and therefore on the mechanical stability are reversible. However, the recovery of the initial properties is delayed, due to the inertia of the system.

6.1.7 Investigation of infiltration behavior of casting solutions

In the course of this work it has been investigated that a certain infiltration behavior of the applied casting solutions has a negative effect on the encapsulation process. Various casting solutions have been infiltrated into the powder trays as soon they have been filled into the molds. In further experiments, this infiltration behavior has been investigated using three different methods.

An **infiltration factor** (I) has been derived based on the viscosity and the surface tension of the respective casting solutions. The determined infiltration factors correlate with the results of the encapsulation experiments. Based on this, three groups have been derived (Fig. 6.1-6): If I<1, the encapsulation process can be applied successfully. The containers reveal smooth and even crystalline coats. If 1<I<2, the respective solutions infiltrate slowly into the powder tray. Nevertheless, initiation of crystallization occurs – a crystalline coat can be formed. Casting solutions revealing a high infiltration factor (I>2) cannot be applied for the encapsulation process using powder trays for shaping. These solutions infiltrate too fast into the powder tray – crystallization cannot occur.

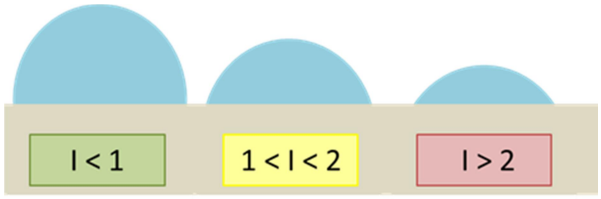


Figure 6.1-6: Different infiltration factors

Furthermore, drop shape analysis has been applied to investigate the change of shape of a drop of the respective solutions. Therefore a drop has been placed on a small powder tray and the change of the **contact angle** of the drop has then been determined over time. It has been investigated that a reduction of the contact angle correlates with the infiltration of the drop into the powder tray.

Furthermore, a **'tube test'** has been established as a quick test. The referring experiments have been carried out exemplarily using erythritol-milk and sucrose-milk solutions. This quick-test is a suitable method to give an indication, whether a casting solution can be applied for the encapsulation process using powder trays.

6.1.8 Application of an alternative shaping technique

In the further course of this work, the encapsulation process has been transferred to an alternative shaping technique. Because of their physical properties, not all crystalline materials can be applied to produce crystalline containers by using powder trays. Viscosity and surface tension affect the infiltration behavior of the initial solution into the powder trays – no crystallization and therefore formation of a crystalline coat can occur. The application of silicone molds has been tested using the system sucrose-milk (72wt%). In a first step, the required amount of seed material has been investigated as it is essential for the initiation of the crystallization of the future coat. The optimum amount has been determined to be 4 mg/cm². The containers produced by means of silicone molds have no impairments with regard to sensory properties or mechanical stability. The application of silicone molds for the encapsulation process offers two significant advantages: on the one hand it is now possible to use low-viscosity materials for encapsulation – the product range can be expanded. On the other hand it leads to enormous reduction of required seed material. Whereas using powder trays 44 g/single product of seeding material is required, only 50 mg/single product is necessary if silicone molds are applied. This results in material saving of over 99 %.

6.1.9 Xylitol

The sugar substitute xylitol has been applied for the encapsulation process based on the new shaping technique. The encapsulation of milk and coconut milk has been investigated.

In a first step, all necessary preliminary experiments have been carried out. The results indicated xylitol to be a suitable encapsulation material. In a second step, the influence of different seeding material on the layer formation has been investigated. It has been shown that an application of intrinsic seeding material (milled xylitol) is required for the production of containers with a uniform and even coat. Furthermore, the mechanical stability of the resulting containers has been investigated and compared to sucrose-based samples. Xylitol-based containers reveal a lower mechanical stability of 0.95 N/cm² than sucrose-milk containers (1.5 N/cm). However, this mechanical stability is sufficient for a safe handling, packaging and transport.
Xylitol has been investigated to be a suitable material for the encapsulation process based on crystallization. Using xylitol, sugar-free products can be produced.

6.1.10 Expanding the product range by product variation

In further experiments liquid-filled containers have been produced in different shapes (e.g. hemispheres, cubes, pyramids, hearts) and sizes (from 1 mL – 10 mL filling). The products can optimally be adapted to the desired application areas. By varying the size, different volumes of liquid can be encapsulated. In the course of the development process, only the concentration of the applied solids and liquids and therefore the process parameters have to be adjusted.
In order to expand the product range, the addition of coloring and flavoring has been investigated. No influence on the MSZW of the solution has been determined in the case of food grade, commercially available food coloring and flavoring. The addition of additives therefore has no influence on the previously defined production parameters. It has been possible to produce products with different degrees of coloring and flavoring. The addition also showed no influence on the mechanical stability of the containers.
Furthermore, the process can be applied for the encapsulation of any other liquid (e.g. fruit juice concentrate). Thereby the product range can significantly be extended and expanded to other areas of application.

6.2 Conclusions

The **technique of crystallization** can be applied for the production of crystalline containers as alternative packaging option for liquids such as milk or condensed milk (Fig. 6.2-1). In this respect, a patent has been applied, which has been granted in 2018 [Ulr18].

Figure 6.2-1: Crystalline containers as alternative packaging for milk (right) and condensed milk (left)

All previously defined **product claims** have successfully been realized:

- ✓ full encapsulation of certain amount of milk
- ✓ solid and stable coat
- ✓ dissolvable in hot drinks
- ✓ coating materials safe for human consumption
- ✓ impermeable for water and oxygen

By using **different encapsulation materials** (crystalline substances) as well as different solvents, several products can be produced:

1. Sucrose has been identified as suitable encapsulation material for the production of sweet containers.
2. Xylitol can be applied for the production of sugar-free alternatives.
3. It is possible to encapsulate milk with different fat contents (3.5 %, 10 %).
4. Plant-based milk substitutes can be applied as a solvent to produce vegan products.

The **applicability** of a certain crystalline substance for the encapsulation process based on crystallization depends on following properties:

- Width of the metastable zone
- Increase of solubility curve
- Crystal growth rate

Suitable **methods** for **quality analysis** determine of relevant quality parameters of the end product have been established as summarized in Table 6.2-1.

Table 6.2-1: Established methods for analyses of relevant product parameters

quality parameter	test method
mechanical stability	crushing force
release behavior	UV/vis photometry
shelf-life	pH changes, microbiological investigation
permeability of coat	mass loss over time

To set up a **general process description**, the following preliminary examinations must be carried out:

- Definition of product parameters (shape and size, layer thickness, storage temperature)
- Measurement of densities of solids and solvents used
- Determination of solubility curve and MSZW

Based on the results of these experiments, equations to calculate the optimum start concentration of the solutions used for encapsulation have been established and verified. Required process parameters ($T_{saturated}$, $T_{solution}$, $T_{casting}$) can then be determined by means of the solubility curve.

Furthermore, the production of samples with different sizes and shapes has also been proven to be possible. Additionally, the product range may be expanded by adding flavors or colors. An influence of these additives on the manufacturing process has not been confirmed.

Additionally, an alternative shaping technique to the commonly used powder trays has been introduced. Using this technique intrinsic seed material is recommended. It enables the application of low-viscosity materials and a considerable material saving (seeding material) of > 99 %.

Figure 6.2-2: Conventional pre-portioned plastic jar (left) and dissolvable container as alternative packaging option for milk (right)

The aim of this work, to develop a process for encapsulating milk in portion sizes based on the technique of crystallization, has fully been achieved. A product has been developed where the packaging is part of the consumable product. It completely dissolves when the product is added to other liquids, releasing the enclosed liquid. The result is a comfortable, convenient and innovative product that also contributes to the avoidance of plastic packaging.

6.3 Future work

Within the scope of this work, it has been possible to develop a product that fulfills all defined requirements. The research questions could be answered and discussed. Further questions and suggestions can be derived from the results:

- In order to make the product producible in large quantities, the next necessary step is a scale up. The technology has to be transferred from laboratory scale to a large-scale (industrial) production.
- For the production of completely unsweetened containers it is necessary to investigate further substances.
- Regarding the shelf-life of the products more detailed investigations depending on the substances used are necessary.
- A transfer of the technology to other application areas (e.g. pharmaceutical industry, cosmetic applications, agricultural products) is recommended. Application areas where clean portioning or dosage is necessary should be considered.
- With regard to national and international food safety, the present product cannot be delivered to the consumer without further packaging. It should be clarified which packaging options can be applied without minimizing the advantages of the product.

7. Summary

Pre-portioned plastic jars containing milk or condensed milk are applied in a variety of sectors due to their convenient size. Disadvantages are the unclean handling, splashing while opening and the production of plastic waste of 1 g per packaging unit. Recent inventions have focused on optimizing the packaging to enable a cleaner opening process. Further solutions do not yet exist.

Figure 7-1: Pre-portioned plastic jars for packaging milk and condensed milk

The production of plastic waste is an increasing global problem [Gey17]. Especially plastic-based packaging, e.g. in the food industry, contributes to this increasing plastic waste production. Therefore, alternative materials for packaging and single-use articles [Bri14, Lea17, Lei16] have been developed and introduced to the market. Furthermore, the development of new packaging opportunities is a fundamental part of product development to meet the customers' needs for innovative and convenient products.

The aim of this thesis has been the development of a plastic-free packaging solution as an alternative to conventional single-portion plastic jars.

First, the **claims of the future product** have been defined. The aim has been to develop containers with a hard and stable coat encapsulating a certain amount of milk and dissolving when being added to a warm/hot drink to release the encapsulated liquid. The packaging should thereby be part of the consumable product. Based on these claims 4 research questions have been formulated.

The results of the performed experiments and their discussion with special focus on the formulated research questions have then been presented.

1. The **process of crystallization** has successfully been applied for the encapsulation of certain amounts of liquids. In this regard a patent has been applied for and granted in 2018 [Ulr18].
   Based on the process of crystallization, a crystalline coat is formed around the liquid from a supersaturated solution (consisting of the desired encapsulation material and the liquid to be encapsulated) by a specific initiation of the nucleation and the resulting degradation of the concentration. Crystallization is initiated specifically by seed particles from the outside. Powder trays have been applied as shaping technique.
2. **Suitable substances** (encapsulation materials) to form the coat of the containers have been investigated and identified.
   - Sucrose can be applied for the production of liquid filled containers, however, with a sweet coat.
   - As an increased sugar intake is not recommended, sugar-free containers with liquid fillings can be produced by applying the sugar substitute xylitol.
   - Erythritol is, in general, suitable to encapsulate liquids. However, instable and impermeable coats are generated.
   - Mannitol, isomalt and cellobiose cannot be applied for the encapsulation of liquids.

In general, all liquids can be encapsulated by using the process of crystallization. In the course of this work milk with different fat contents (milk 3.5 %, condensed milk 10 %) and coconut milk as a plant-based, vegan alternative have exemplarily been encapsulated.

3. Suitable methods for **quality analyses** of the crystalline containers have been established. Special focus has been set on chemical (shelf-life), mechanical (stability), kinetic (release behavior) and thermodynamic (storage stability) properties.

4. A **general process description** for the encapsulation of liquids by applying crystallization has been established.
   Therefore, preliminary experiments are essential, to determine the exact process parameters:
   - Definition of product shape and size
   - Definition of required thickness of the coat
   - Definition of storage temperature
   - Determination of solubility and MSZW
   - Determination of densities of solids and solvents used

   Equations have been established to calculate the optimum concentrations of solids and solvents necessary for the encapsulation process based on the preliminary experiments. Using the determined phase diagram relevant process parameters can be calculated. The exact determination of the process parameters depends on the accuracy of the determination of the parameters used.

In addition, an **alternative shaping technique** has been established. The shaping has been transferred from commonly used powder trays to silicone molds. This enables the application of further encapsulation materials and results in an enormous material saving (seeding material) of 99 %.
Furthermore the product range can be expanded by **varying the product shape and size** as well as by **adding colors or flavors**. The encapsulation process has successfully been applied to **encapsulate further liquids** such as juice, fruit juice concentrate, liqueur or coffee concentrate.

All crystalline containers produced in the course of this work fulfill all defined requirements. At the defined storage temperature, the products reveal sufficient mechanical stability. The mechanical stability decreases with increasing storage temperature. When being added to warm/hot liquids the crystalline coats of the containers dissolve and the encapsulated milk is released into this liquid. The release behavior depends on temperature and stirring. Investigations regarding the shelf-life have given no indication of spoilage of the encapsulated liquid within 4 weeks (xylitol-based containers) or 6 months (sucrose-based containers).

With the dissolving crystalline containers with liquid filling a novel innovative and sustainable product has been developed as alternative to conventional pre-portioned plastic packaging. This, on the one hand, contributes to plastic waste reduction and, on the other hand, provides a more convenient product.

Future work is recommended to focus e.g. on scale up, further quality analyses, the production of non-sweet containers and especially on packaging options of the end product as it must not be delivered to the consumers without packaging.

8. Symbols and abbreviations

Symbols

Greek

γ	[1/s]	shear rate
$\Delta\theta$	[°/min]	contact angle change
η	[mPas]	dynamic viscosity
θ	[°]	contact angle
π	[-]	circle number pi
ρ_{bulk}	[g/cm^3]	bulk density of powder trays
ρ_{solid}	[g/cm^3]	density of solid (encapsulation material)
$\rho_{solvent}$	[g/cm³]	density of solvent (encapsulated material)
σ	[mN/m]	surface tension
τ	[N/m²]	shear stress

Latin

A_{sample}	[cm²]	surface area of product sample
Δc	[wt%]	degradation of concentration
c_{end}	[wt%]	corresponds to $c_{storage}$
$c_{optimum}$	[wt%]	calculated optimum starting concentration of solution
c_{start}	[wt%]	corresponds $c_{optimum}$
$c_{storage}$	[wt%]	saturation concentration at storage temperature
$d_{capsule}$	[mm]	diameter of capsules
d_{shell}	[mm]	thickness of the capsule shell
f	[N/cm^2]	mechanical stability
g	[m/s²]	gravitational force
$h_{capsule}$	[mm]	height of the capsule
I	[$\sqrt{m/s}$]	infiltration factor
M	[Nm]	torque
m_{max}	[g]	maximum mass required to break product samples
m_{solid}	[g]	mass of solid
$m_{solvnet}$	[g]	mass of solvent
n	[1/s]	rotational speed
p_{max}	[N/cm^2]	mechanical stability
S	[m/s]	tip speed of magnetic stirrer
t	[s, min, h, d]	time
T	[°C]	temperature
$T_{casting}$	[°C]	casting temperature of supersaturated solution
$T_{saturated}$	[°C]	calculated saturation temperature of casting solution
$T_{solution}$	[°C]	defined dissolution temperature of sample solution
$T_{storage}$	[°C]	defined storage temperature of the final product
V_T	[cm^3]	total volume of capsule
V_C	[cm^3]	volume of capsule coat

Abbreviations

$aqua_{dest}$	distilled water
GMP	good manufacturing practice
IMZ	intermediate zone
MSZ	metastable zone
MSZW	metastable zone width
N/A	not available
N/D	no data
SD	standard deviation
SZ	stable zone
TBC	total bacteria count
UHT	ultra-high temperature
USZ	unstable zone

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10. Appendix

Table III-1: Summary of devices used

device	name	producer
Climatic chamber	ICH 110	Mammert GmbH & Co. KG, D-91126 Schwabach
Contact angle meter	Tropfenkonturanalyse-System DSA10	Krüss GmbH, D-22291 Hamburg
Density meter	DE40 density Meter	Mettler Toledo, US-Columbus, OH
Heating chambers	Binder; Sanyo Drying Oven	Kleinfeld Labortechnik, D-30989, Gehrden
Microscope	Digital microscope VHX-500F	Keyence International, B-2800 Mechelen
Refractometer	RE40 Refractometer	Mettler Toledo, US-Columbus, OH
Suface tension meter	DCAT Serie 11	Data Physicy, D-70794 Filderstadt
Thermostates	Julabo MH F32; Julabo FP50; Julabo F32/F25	Julabo Labortechnik GmbH, D-77960, Seelbach
	Haake F8	Haake GmbH, D-76227, Karlsruhe
Ultrasound probe	Liqui Sonic 30	SensoTech GmbH, D-39179, Magdeburg
Viscosimeter	Haake VT550	Thermo Haake GmbH, D-76227, Karlsruhe

Table III-2: Summary of software used

software	application	producer
analySIS	microscopy analysis	Olympus, D-20097, Hamburg
Atmo Control	climatic chamber adjustment	Memmert GmbH & Co. KG, D-91126, Schwabach
Drop Shape Analysis DSA 1.0	contact angle evaluation	Krüss GmbH, D-22291, Hamburg
RheoWin Job Manager	viscosity measurement	SensoTech GmbH, D-39179, Magdeburg
RheoWin Data Manager	viscosity measurement	SensoTech GmbH, D-39179, Magdeburg
Scat	surface tension evaluation	Krüsee GmbH, D-2221, Hamburg
Sonic Work 4.1	ultrasonic recording	SensoTech GmbH, D-39179, Magdeburg

Statement of authorship

I declare under oath that this is my own work entirely and has been written without any help from other people. I used only sources mentioned and included all citations correctly both in word and content.

This thesis has not been used previously at this or any other university in order to achieve an academic degree.

Halle (Saale), 19/12/2018

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List of publications

Journals (peer reviewed) and patent

02/2018	Wellner, M., Ulrich, J.: *Quality Analysis of Liquid Filled Crystalline Containers*, Chemical Engineering & Technology, 41 (2018), 1118 - 1121, DOI: 10.1002/ceat.201700618.
03/2018	Ulrich, J., Wellner, M.: *Verpackung von Milch in auflösbaren Portionskapseln und Verfahren zu deren Herstellung durch Kristallisation*, DE 10 2016 004 463, Deutsches Patentamt, 08/03/2018, Munich, Germany.
04/2017	Wellner, M., Ulrich, J.: *Design of Dissolvable Milk Containers for Convenient Handling*, Chemical Engineering & Technology, 40 (2017), 1247 - 1251, DOI: 10.1002/ceat.201600714.

Conference contributions

Conference proceedings (light reviewed)

09/2018	Wellner, M., Träger, V. Ulrich, J.: *Influence of Product Variation on the Production of Liquid Filled Crystalline Containers*, in Proceedings BIWIC 2018: 25th International Workshop on Industrial Crystallization, September 5th-7th, 2018, eds. Cartigny, Y, Couvrat, N., Rouen, France, 251-255.
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	Oral presentations
06/2018	Wellner, M., Träger, V., Ulrich, J.: *Encapsulation of Liquids by Crystallization -Product and Process Optimization-*, Asian Crystallization Technology Symposium 2018, June 20th-22th, 2018, Singapur.
04/2017	Wellner, M., Ulrich, J.: *Required Physical Properties of Materials for Crystalline Coatings*, 25th Croatian Meeting of Chemists and Chemical Engineers, April 19th-22nd, 2017, Poreč, Croatia.
09/2016	Wellner, M., Ulrich, J.: *Design of Dissolvable Milk Containers for Convenient Handling*, 23rd International Workshop on Industrial Crystallization, September 6th-8th, 2016, Magdeburg, Germany.
05/2016	Wellner, M., Ulrich, J.: *Development of a Dissolvable Capsule Containing Milk*, Asian Crystallization Technology Symposium 2016, May 25th- 27th, 2016, Tianjin, China.
	Poster presentations
09/2018	Wellner, M., Träger, V., Ulrich, J.: *Influence of Product Variation on the Production of Liquid Filled Crystalline Containers*, 25th International Workshop on Industrial Crystallization, September 5th-7th, 2018, Rouen, France.
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