Coating of gel materials by crystallization

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1. Introduction

The crystallization of sugar is a widely investigated topic. Important knowledge on the production and crystallization of sugar is reported e.g. in the books of Hoffmann et al. [Hof04a] or Asadi [Asa07]. Sugar is often used as one component in a complex recipe for products in the food industry. These components of a multicomponent system (recipes) interact in different ways with each other. Therefore, sometimes changes in the production process are necessary or undesired changes of end products occur. It is therefore essential, to observe the influence of minor components (also called additives or impurities) on the main components to estimate products and process changes. Especially, during the development of new products with different composition or new ingredients the changes in product properties and processes must be investigated and subsequently adjusted.

The food market demands constantly new developed products that have new features and which should attract consumers. Well known sweets in Germany are, e.g. filled with liquid (alcohol/flavored sugar solutions) having a sugar crust, which is coated with chocolate. Replacing this liquid core by a gel core leads to new challenges in production and development. An understanding of the problems involved can lead to an important widening of the range of product diversities. There is only little literature on the crystallization of sugar for coating purposes in combination with the process of gelation.

Coated food products are commonly produced, especially, in confectionary industry e.g. smarties® or different crust pralines are prominent examples. To realize a coating of gels with crystallized sugar in one production step, it is important to combine two different processes. These two fundamental processes are gelation of hydrocolloids and crystallization of highly viscous solutions (sucrose). A crystalline coat can be realized by the use of starch molds (mogul technique) to enforce the nucleation and thermo-reversible gels were chosen to get desired gel textures. Interaction from gels (macromolecules) with the crystallization of sugar is a very interesting issue. There are only very few publications on the topic. It is already known that the growth of sugar crystals can be inhibited by the use of hydrocolloids (macromolecules) [Har91] and the crystallization process is slowed down strongly in highly viscous supersaturated solutions due to a slow mass transport (diffusion controlled growth) [Har91]. These highly viscous supersaturated solutions lead to changes in crystallization e.g. crystal appearances. Kinetic and thermodynamic changes have to be considered during the production process of e.g. crystalline sweets [Ben06]. The crystalline material can change its purity and that results in different product properties, qualities and storage stabilities. A crunchy crystalline layer can change to soft and even the thickness of the layers can be changed. Therefore, the production process under the application of

hydrocolloids should be adjusted and optimized considering the changes of the sugar crystallization process triggered by the presents of macromolecules (hydrocolloids).

To achieve crystalline coated gels, the initiation of nucleation is necessary. The application of materials (seed material) to enforce nucleation of a high viscous supersaturated solution was examined to gather facts, which have to be considered during a production process. These external seed materials are commonly used to produce shaped candies and gums [Sch07]. This technique, called starch mogul technique, is well described by Hoffman et al. [Hof04a]. There are only very few literature quotes on the performance of seed materials (different powders) concerning the shaping and crystallizing of sweets. It is important to search for alternative seed materials to optimize the production process (crystallization of sugar) and to lower costs. There is no clear understanding of the seed materials and their properties, which are able to enforce the nucleation. Therefore, theory should be combined with experimental results to develop a model including the key properties of seed materials (e.g. particle size, moisture and surface appearance) for enforced nucleation, especially, in production of crystalline sweets.

2. Fundamentals

Frequently focused themes in different literature are on the one hand, the crystallization of sucrose [Hof04a] and on the other hand, the gelation of different hydrocolloids [Phi09]. These two different processes have to be coordinated to enable the production of crystalline coated gels in one production step. The basic requirement to produce a crystalline coat is the knowledge on the principles of crystallization, the understanding of the mechanism of gelling, as well as the combination of the two processes, which will be explained in the following Chapter.

2.1 Crystallization

Fundamentals on the process of crystallization are summarized in many books. A good overview on the topic of crystallization are given by Mullin [Mul01], Mersmann [Mer01], Beckmann [Bec13], Hofmann [Hof04], Ulrich [Ulr02], Ulrich et al. [Ulr06] and Myerson [Mye02]. The crystallization and properties of sugars are explained, especially, by literature from Hoffmann et al. [Hof04a], Asadi [Asa07], Wohryzek [Woh14] or Rosenplenter et al. [Ros07].

Crystals consist of spatially ordered unit cells as the smallest unit in a crystal lattice [Mat69]. Crystals of a material have similar physical properties but vary in their directions also called anisotropy [Mul01]. It can be distinguished between seven crystal systems, which differ in their structure (see Figure 2.1-1) [Mer05]. Sucrose can be classified as a monocline crystal system (see Figure 2.1-1, red bordered) [Hof04a]. The sucrose molecule builds a molecular lattice connected by hydrogen bonds (mostly hydroxyl-groups are liked with oxygen atoms [Pan10]) [Hof04a].

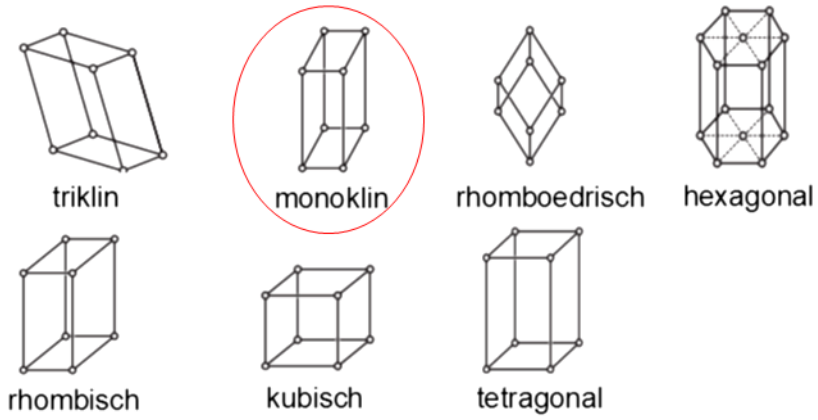

Figure 2.1-1: Crystal systems [Mer05]

Crystallization is a thermal process to separate a mixture of a multicomponent system by forming crystals [Gni93]. Crystals can be built out of a liquid phase, solid phase as well as gaseous phase depending on its environment [Hof04]. A system no matter if it is liquid, solid or gaseous strives to reach equilibrium. The equilibrium state of a thermal system does not change with time anymore [Hof04].

To reach supersaturation (non equilibrium) in a system of a liquid mixture different processes can be applied. Changing pressure in a system or changing the temperature as well as a removal of solvents can lead to a supersaturation [Sch11]. This supersaturation (more molecules are dissolved as in equilibrium state) is the driving force to recover the equilibrium state. Recovering of the equilibrium can be reached by nucleation (formation of new particles) on the one hand and crystal growth (increase of the particle size) on the other hand [Hof04]. An optimal supersaturation concerning the crystal growth is reached in the middle of the metastable zone [Hof04]. The metastable zone is surrounded by the solubility line and the supersaturation line (see Figure 2.1-2, black line and dashed line). The metastable zone width (MZW) is the operating zone for crystal growth. At the solubility line the thermodynamic equilibrium of the solid in the liquid is reached. By e.g. increasing the temperature the solubility of the solid becomes higher and the solution is undersaturated (stable). In an undersaturated solution no crystallization takes place and existing particles dissolve.

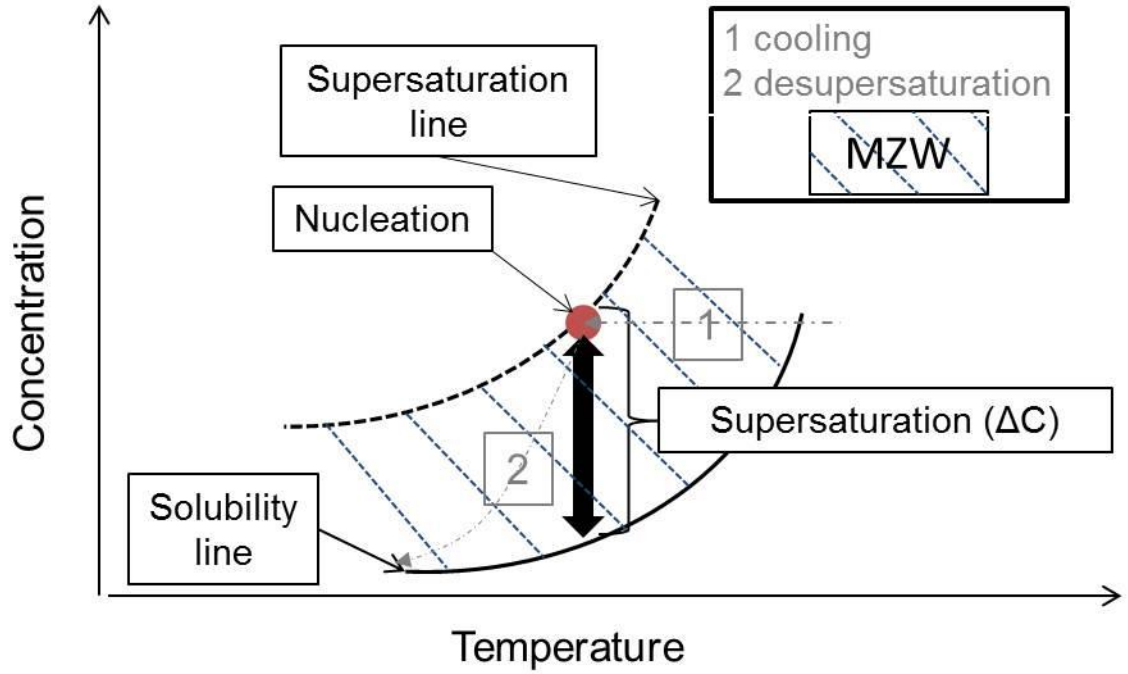

Figure 2.1-2: Metastable Zone (drawing according to [Met16])

By decreasing the temperature (see Figure 2.1-2, cooling) the solution becomes super-saturated. In a critical supersaturated state (on the supersaturation line) nucleation happens

(see Figure 2.1-2, red point). This nucleation depends on process conditions so the width of the metastable zone is thermodynamically not fixed and is influenced by kinetical factors and process conditions [Hof04]. The formation of nuclei can be divided in primary and secondary nucleation [Mul01]. If nucleation happens at the upper limit of the metastable zone the nucleation process is called primary homogeneous nucleation [Hof04]. Here, a very clean solution without foreign particles must be present but this is almost never the case [Mer05]. If nucleation happens with the help of foreign particles, impurities or mechanical influences the upper limit of the metastable zone is more close to the solubility line. The process is then called primary heterogeneous nucleation [Cla40]. The supersaturation for nucleation is lower due to less necessary nucleation energy, which must be provided e.g. by the surfaces of external materials (e.g. impurities) [Hof04]. Secondary nucleation happens in solutions with already existing crystals (e.g. fragments from collisions). Due to nucleation, no matter of which kind of nucleation, the supersaturation decreases (see Figure 2.1-2, desuper-saturation) and crystal growth starts. The concentration within the solution decreases till the equilibrium is reached again. During growth the molecules are transported to the surface of the nuclei by convection and diffusion [Hof04]. This process is enhanced by higher temperatures and concentrations [Cla40]. Further, the molecules must be absorbed and incorporated into the crystal lattice [Hof04]. Crystals grown industrially from solutions of many materials (mainly smaller molecules) are often grown with growth rates in the range of 10^{-7} to 10^{-9} ms^{-1} [Hof04].

A crystallization process can be influenced by the use of different additives. Additives are widely used in food industry e.g. in confectionary industry to modify properties like taste or texture. Generally, nucleation, solubility and growths rates of crystals can be affected by additives [Hof04]. Therefore, size, size distribution, shape and morphology of crystals can be influenced [Hof04]. Due to viscosity alternating substances (e.g. hydrocolloids) the crystallization process concerning kinetic aspects can be limited [Gni93]. The diffusion of the molecules is slowed down due to a high viscosity [Gni93]. As described in literature e.g. by Hartel et al. [Har91], Panda [Pan10] , Babel [Bab96] or Milani et al. [Mil12] the crystallization of sugar (e.g. nucleation or mass transport of the molecules) can be suppressed systematically by the use of different additives, especially macromolecules (e.g. hydrocolloids). This suppression can e.g. prevent undesired product quality changes during e.g. storage of end products. These suppressing effects are summarized in literature [Har91; Pan10] and are widely understood. Generally, the crystallization process should lead to the formation of as pure as possible products, e.g. crystalline layers. Pure means, that the crystalline product consists of no other materials than the substance which should be crystallized, e.g. sugar.

2.2 Fundamentals on sugar and hydrocolloids

Sucrose is a disaccharide consisting of monosaccharides α-D-glucose and β-D-fructose connected by α,β-1,2-glycosidic bonds [Bud03; Hof04a]. This non reducing sugar (as crystal) is temperature stable till 140 °C [Hof04a] exceeding (160 - 190 °C) leads to fast caramelize-ation [Hof04a]. High temperatures and acidic conditions over a longer time lead to inversion [Arm06, Asa07]. Inversion is the decomposition of the disaccharide into its monosaccharides (fructose and glucose) [Wie87; Hof04a].

Fundamentals on hydrocolloids and gelation can be found in different books. Phillips et al. [Phi09], Nishinari et al. [Nis94], Laaman [Laa10], Ottenbrite et al. [Ott10] and Nussinovitch [Nus97] give a good summary and overview on hydrogels or hydrocolloids.

The worldwide dominant used food hydrocolloids in 2009 are starches (70 - 75 %) followed by gelatin (9 - 10 %) [Wue15]. Carrageenans are with 2 - 3 % less important than starches and gelatin [Wue15].

Hydrocolloids have an affinity to water (hydrophilic, with many hydroxyl groups) and can form colloidal solutions (homogenous mixtures) [Wue15] (see Figure 2.2-1).

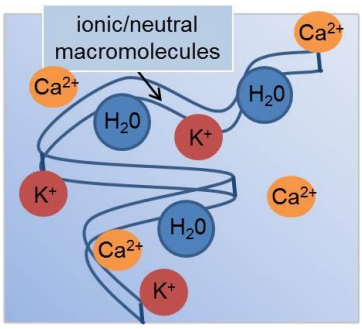

Figure 2.2-1: Simplified structure of hydrocolloids

These macromolecular substances build two separate phases [Phi09; Pan10]. A gel e.g. has got a dispersed phase consisting of liquid and a continuous phase consisting of solid [Pan10; Phi09; Nis00]. As a structural definition the linking of these macromolecular chains by e.g. hydrogen bonds or ionic bonds, lead to a gelation process (sol-gel transition) [Gul11; Phi09; Nis09]. The homogeneous mixture of soluble branched polymers can be called the sol state [Gul11]. The sol state is a colloidal solution with moveable molecules and the gel state is a gelatinous mass, which is connected to a network [Kol01]. To define a gel rheological it can be described as a system that is not able to flow [Nis09].

Hydrocolloids have a wide application field. They can be used in the pharmaceutical industry, in photography, cosmetics or for technical applications but they play the most important role in food industry, especially, in confectionary industry [Sch07]. Hydrocolloids can act as gelling agents and influence therefore, the texture of a product [Mil12]. All the tested

hydrocolloids are thermo-reversible [Phi09]. Thermo-reversible gels form gels by temperature changes and therefore, molecular forces like hydrogen bonds or hydrophobic interactions changes [Bor98; Nis00]. That means they are gel when being cooled and “melt” again when warmed up [Phi09]. These gel types can be classified as weak physical gels characterized by hydrogen bonds, ionic and hydrophobic associations with only temporary links between the macromolecules (reversible gels) [Gul11; Ros99]]. Whereas chemical gels form strong gels with covalent bonds and include a condensation, vulcanization and polymerization step (permanent gel) [Gul11].

Agar as well as carrageenans are galactose polymers, which can be obtained from cell walls of seaweed (red algae*; Rhodophyceae*) [Sch07; Phi09]. Agar is a mixture of two main components [Bel08]. The neutral linear polysaccharide agarose (70 %) as gelling agent and a heterogeneous mixture of smaller molecules called agaropectin consisting of sulfate ester, glucuronic and pyruvic acid groups (30 %) as the non-gelling agent [Phi09, Bel08]. In contrast to carrageenans, the gelation process of agar is independent from cations (neutral hydrocolloid). κ-carrageen forms the strongest gels with potassium and ι-carrageen with calcium (anionic hydrocolloids) [Wue15; Sta87]. The sulfate content of agar is with < 4.5 % (mostly 1.5 - 2.5 %) lower compared to carrageeans with 18 - 40 % [Wue15].
For all hydrocolloids (agar, carrageen and gelatin) it is important to add acid (if necessary) at the last possible moment in the production process to avoid a polymer breakdown [Phi09]. Further information on basic building blocks, producing countries and other characteristics of agar, carrageen and gelatin can be seen in Table 2.2-1.

Table 2.2-1: Characteristics of hydrocolloids [Wue15; Sch07]

Hydro-colloid	Basic units	Producing countries	pH stability	Dosage level [%]	Hysteresis [°C]
agar	D-galactose and (3-6)-anhydro-L-galactose α(1-3) and β(1-4) linked	Japan, USA, Chile, Spain	Hydrolysis by cooking in acidic (pH <4) systems, but e.g. carrageen gels are acid stable (pH: 5.5 – 9.0)	0.5 - 2.0	50 - 60
carra-geenan	D-galactans: (1-3) linked β-D-galactose-4-sulfate and (1-4) linked anhydro-α-D-galactose with sulfate ester groups	Coasts of North Atlantic and Pacific Ocean		0.02 - 3.0	5 - 30
gelatin	amino acids (e.g. Glycine, Hydroxyprolin, Proline)	Western Europe, Asia		3.0 - 10.0	2 - 5

The polymer molecular mass is crucial for the viscosity of the polymer solutions [Mil12]. Functional properties are determined by the molecular mass and structure of the basic macromolecules [Dre99]. Table 2.2-2 compares the different molecular weights of hydrocolloids like agar, carrageen and gelatin based on the literature [Phi09].

Table 2.2-2: Molecular weights of hydrocolloids [Phi09]

Hydrocolloid		Molecular weights
agar	Agaroses: Agaropectin:	> 100 - 150 kDa < 20 kDa
carrageen		200 - 800 kDa
gelatin	Typ A (acid pre-treatment) Typ B (alkaline pre- treatment)	94 kDa 171 kDa

The gelling process of agar can be described in two steps. First, the molecular chains (polymers) associate into double helices (also described as microcrystalline junctions zones [Sch97]) during cooling with immobilizing of water and afterwards the macromolecular network is formed by aggregation with formation of hydrogen bonds (see Figure 2.2-2) [Ime09]. The helix formed by agar is more compact compared to helixes formed by carrageen due to lower sulfate content in agar [Mil12].

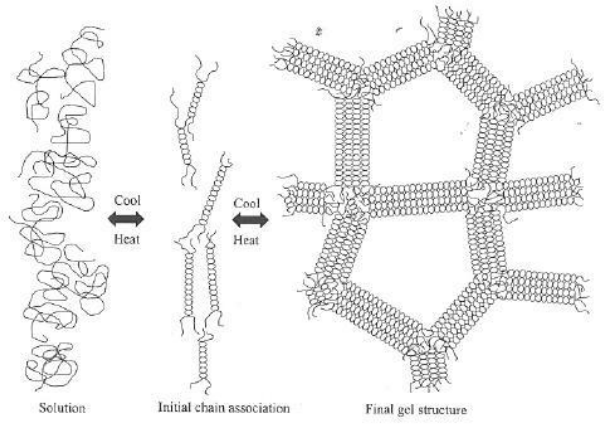

Figure 2.2-2: Sol-gel transition of agar [Ime09]

Carrageenans differ in their functional groups (see Table 2.2-3). Functional groups have an influence on the texture, gel strength, solubility, melting- and setting point of the formed gels [Phi09]. The gelation process of carrageenans is caused by a high content of hydrophobic anhydrogalactose with low-medium content of sulfate ester groups [Wue15]. The more regular sequences (anhydrogalactose) appear the more double helices can be formed [Bel08]. Sulfate ester (e.g. galactose-6-sulfate) lead to interruptions within the sequence

[Bel08]. A high amount of anhydrogalactose leads to firmly, more brittle gels [Bel08]. As in the case of agar the gelation process can be described in two steps. First of all, the formation of single helices by ionic interaction and spiral-like association occur and second single helices form double or triple helical structures by hydrogen bonds formation [Wue15]. During aging e.g. an agar gel increases the formation of double helices and the space for intestinal water decreases [Ste06]. That leads to a shrinking of the gel (syneresis) but the structure of the gel remains [Ste06]. κ-carrageen forms firm and brittle gels with strong syneresis (loss of water during aging) and ι-carrageen a soft elastic texture with no syneresis [Wue15; Sch07; Whi93]. The ability for syneresis decreases with a higher degree of sulfation (see Table 2.2-3) [Mil12].

Table 2.2-3: Functional groups of carrageenans [Phi09]

Carrageen	Sulfate ester [%]	3,6-anhydro-galactose [%]
κ	22	33
ι	32	26

Different values for the gelling temperature can be found in literature (see Table 2.2-4). This values show for all hydrocolloids a very wide range, because the gelling temperature depends on many factors. These factors are e.g. the hydrocolloid concentration, existence of other co-solutes or cation concentration [Phi09]. Remelting temperatures of the gels are different. The difference between gelation temperature and melting temperature is called hysteresis (see Table 2.2-1).

Table 2.2-4: Temperatures of gel formation [Phi09; Rin08; Sch07]

Hydrocolloid	Gel formation temperature [°C]
agar	30 - 40
carrageenan	40 - 70
gelatin	20 - 29

The animal product gelatin can be obtained from collagen of scleros-proteins in the bodies of animals [Sch07]. Collagen of animal by-products e.g. skin and bones is able to form triple helix structures [Sch07; Bab96]. Depending on the production process of gelatin (Typ A= acidic pretreated; Typ B= basic pretreated) the molecular weight profile can be very different [Mil12]. The amino acid structure in gelatin, which plays an important role in triple helix formation can be seen in Figure 2.2-3. The formation of a gelatin gel can be described in three steps [Bab96]. Aggregation of polypeptide chains with hydrophobic structures (see Figure 2.2-3) to ordered structures [Bab96], association of two or three segments and

stabilization of the structure by hydrogen bonds between and inside the helices [Bab96]. The gel strength is influenced by many factors e.g. the gel strength of the starting material, pH, and temperature profile during gelation [Bab96; Sch76]. Many other interesting facts and properties of the raw material gelatin are given at the homepage of GELITA [Gel16]. Applications fields and physical properties are given [Gel16].

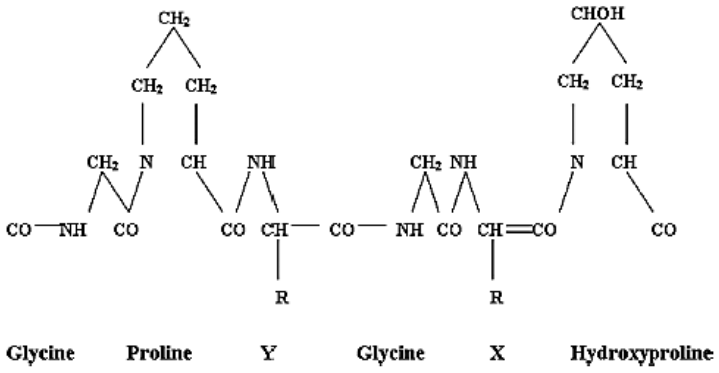

Figure 2.2-3: Amino acid structure for triple helix formation [Bur08]

The gels of gelatin are clear, elastic and syneresis free [Mil12]. There are different products of gelatin obtainable. Granulated gelatin obtained from pig skin with 300 Blooms (Bloom-grams= the firmness of a gel with a defined concentration after 17 h storage at 10°C) leads to texturized, gelled products.

2.3 Influence of co-solutes (sugar) on the gelation process of hydrocolloids

To understand the influence of sugars on the gelation process, it is necessary to know the changeable zones inside the three-dimensional network of a gel. Generally, the types of cross linking [Pan10] can be classified in:

1. Hydrogen bonds (e.g. non-ionized carboxyl groups)
2. Linkage between electrovalent groups (e.g. carboxyl groups or bivalent cations like calcium)
3. Covalent linkages

Figure 2.3-1 shows the important cross linking and the formation of junction zones in a gel network as the basis requirement for the formation of a three-dimensional network [Nis00]. The gelation process can be enhanced by e.g. ions as explained before or by temperature changes (thermo-reversible gels).

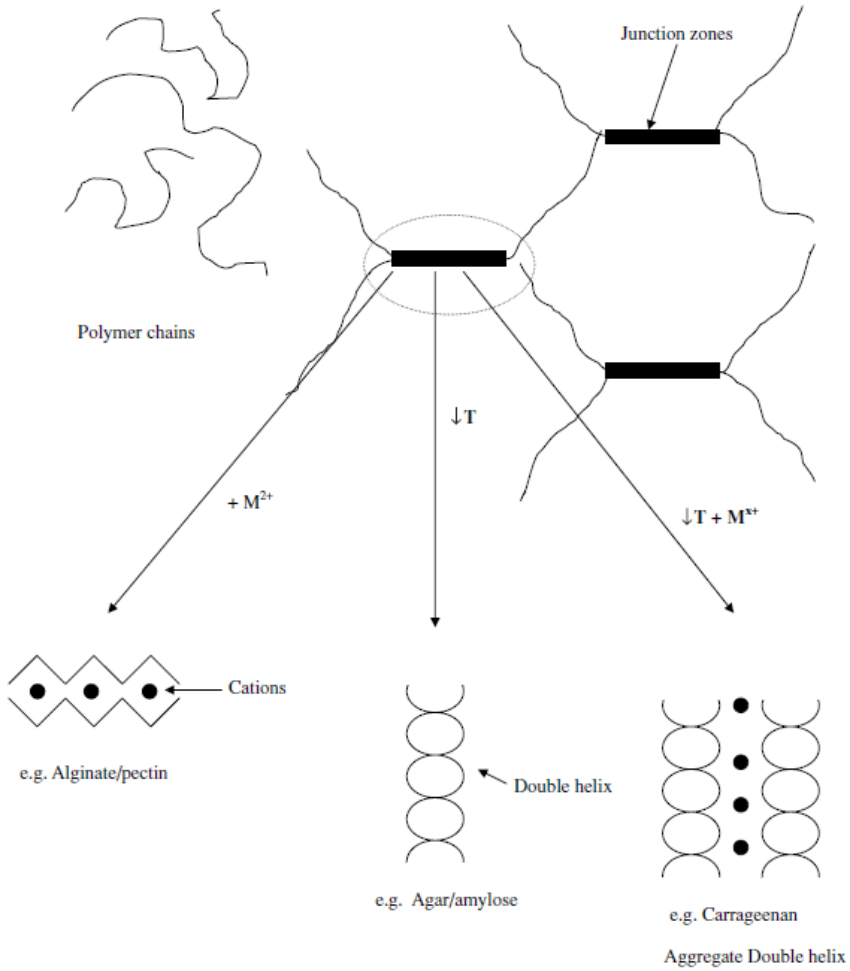

Figure 2.3-1: Cross-linking in hydrocolloid gels [Bur08]

Shuman [Shu60] summarized three effects of hydrocolloids on crystallization.
The hydrocolloid can be attached on the surface of the crystal (hydrogen bonds of hydroxyl groups in the polymer match to oxygen atoms of the crystal) so that the growth can be influenced [Shu60]. Here the compatibility plays an important role [Shu60]. Another effect is the competition for building block units e.g. for water molecules [Shu60]. The third effect of hydrocolloids on crystallization is the combination of polymers with impurities e.g. calcium so that calcium does not affect the crystallization of e.g. sugar anymore [Shu60].

Many sources of literatures focus on the influence of sugars (different polyols like e.g. sucrose, corn syrup, glucose syrup) on the gel formation of hydrocolloids. All of them, no matter which kind of hydrocolloid (gelatin, agar, carrageenan) was observed, show the formation of hydrogen bonds and therefore, the formation of junction zones is enhanced by the use of sugars. These results in different intramolecular effects and therefore, the properties of a gel are influenced, as can be seen in Figure 2.3-2. Gekko et al. [Gek92], Oakenfull et al. [Oak86; Oak00], Schrieber et al. [Sch07] and Nishinari et al. [Nis92]

summarize the effects of sugars on a gelatin gel. Nishinari et al. [Nis90; Nis92a] and Al-Amri et al. [Ala05] focuses on the effect of sugars on κ-carrageenan gels. Effects of sugar on agar respectively agarose gels were investigated by e.g. Watase et al. [Wat90], Normand et al. [Nor03] and Al-Amri et al. [Ala05].

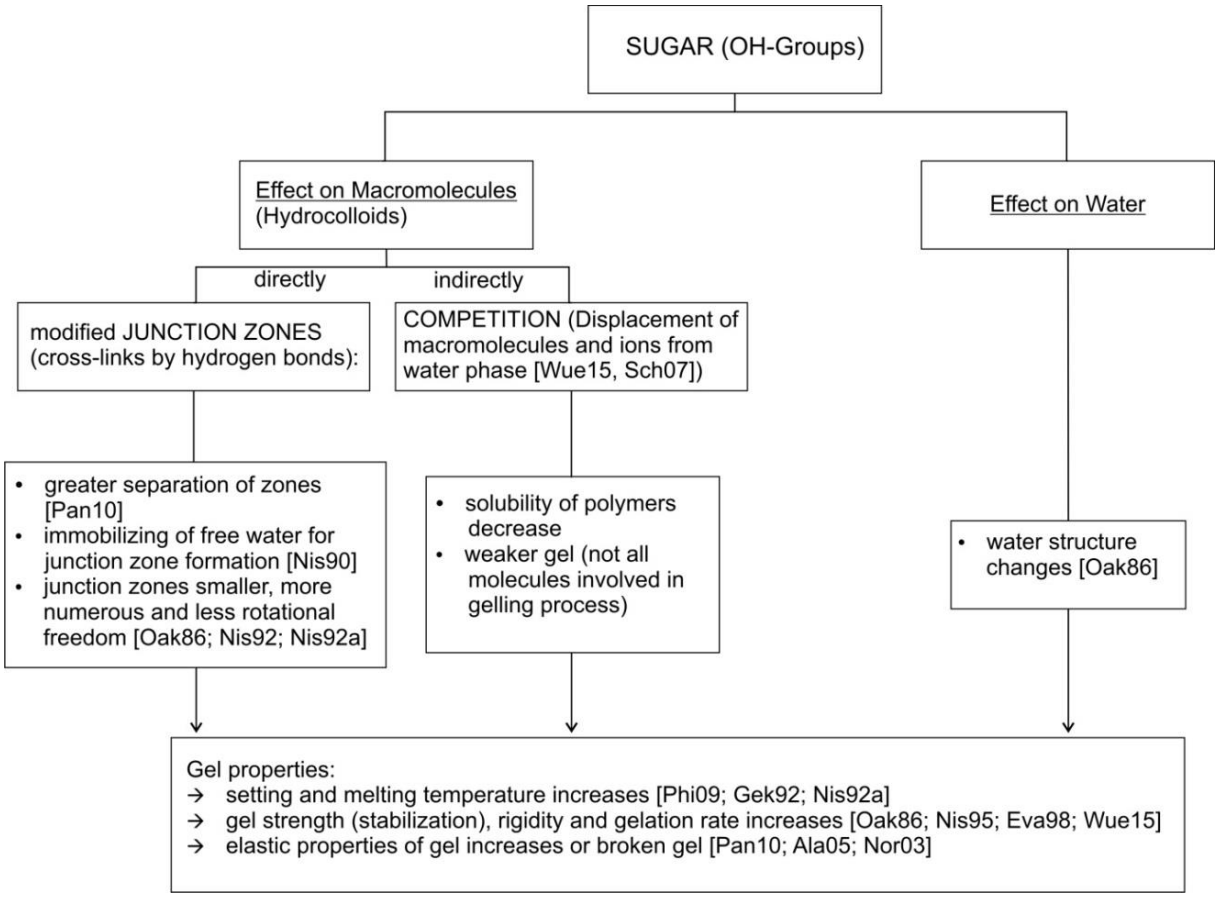

Figure 2.3-2: Scheme on the influence of sugar molecules on gel formation

Wüstenberg [Wue15] summarized that the concentration of κ-carrageen and ions in the aqueous phase due to high solid contents can shift the gelation temperature to 80 - 85 °C or higher. Loret et al. [Lor09] described an additional step in gelation mechanisms of κ-carrageen gels (three step mechanism). The transition of coil-helix depends on co-solutes e.g. sugar and builds a previous step followed by formation of double helices and helix aggregation.

The junction zones in a gel network can be influenced in different ways (see Figure 2.3-2). They can be stabilized due to an enhanced hydrogen bond formation and the disordering shifts to higher temperatures [Nis95]. The formation of junction zones can be reduced because of a lack of free water molecules for mobilizing the chains [Nis90].

Agar builds rather a discontinuous network with gel islands at very high sugar concentrations (80 %) rather than in lower sugar concentrations [Des03].

Normand et al. [Nor03] stated that it should be distinguished between effects on an agarose gel with sucrose concentrations up to 60 % and above 60 %. Sucrose amounts up to 60 % lead to a decrease in gelation temperature and increase in gel formation rate so the sucrose can boost the gelation process [Nor03]. Sucrose contents up to 60 % in agarose gels lead to an increasing elasticity [Mau12]. Sucrose concentrations above 60 % lead to an apparent decrease in gelation temperature because the gelation process is slowed down due to higher viscosities and a reduction in polymer chain mobility [Nor03]. Higher amounts (60 %) of sucrose decrease the elastic modulus (G´) significantly [Mau12]. Normand et al. [Nor03], Al-Amri [Ala05] and Maurer et al. [Mau12] described agarose gels and κ-carrageen gels without sugar as turbid. With a higher amount of sugar the gel becomes clear due to a change in refractive indices. The microstructure is more homogeneous for agarose and κ-carrageen gels (visible in transmission electron micrographs) with 75 and 80 % glucose syrup [Ala05]. Brittle gels are more deformable and elastic with sugar [Nor03; Ala05] to a certain degree. Too much sugar leads to a too high formation of cross links and the gel structure can change into a broken one [Pan10; Nor03].

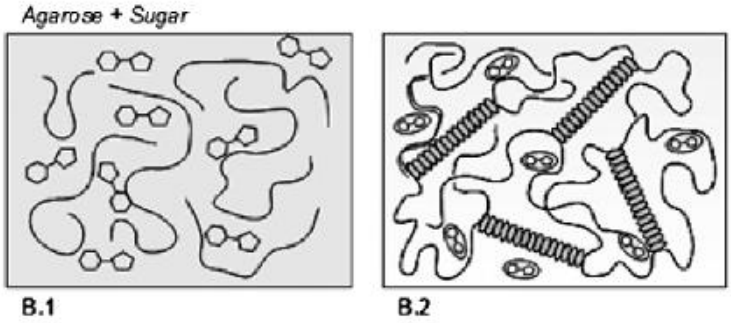

Figure 2.3-3: Interaction of agarose with sugar molecules [Mau12]

High sugar amounts (60 %) in a water-agarose system react preferably with the water. Sucrose molecules have many OH-groups that interact with water molecules [Mau12]. Sucrose builds a hydration shell (see Figure 2.3-3, B.2.). As shown in Figure 2.3-3, B. 1 from Maurer et al. [Mau12] a lack of water as solvent can lead to a destabilization of the helices and a lower helix formation. Maurer et al. [Mau12] concluded that a lack of water molecules influences the gelation in a negative way because for the aggregation of helices water is necessary. Therefore, the gel network is due to water shortage weaker [Mau12]. If the lack of water concerns the solvation of sugar, a crystallization of sugar occurs [Mau12].

3. Aim of the work

Nowadays, the consumer's wishes and expectations are not easy to be satisfied. Therefore, the development of new products or advancements of already existing products is necessary. As a consequence, the knowledge on the influence of new additives to change e.g. the texture (hydrocolloids) or other ingredients e.g. sugar in the production is essential.

Gelled products with a sugar coat are already known products in confectionary industry. Today, two steps in the production are necessary to coat the sweets with a sugar layer. The **first aim** was therefore the **production of coated gels in one production step**. Based on a product in confectionary industry a liquid core was replaced successfully by a gel core while maintaining an outer crystallized sugar layer. The advanced products should change the texture inside the core but the sugar layer outside should be retained with the same stability and characteristics. The **process of crystallization and gelation** should be enabled **simultaneously**.

In Chapter 2.3, literature is summarized [Lor09; Wat90; Nis90; Let03; Nis92; Nor03], which focuses on the rheological behavior of texturizing materials (hydrocolloids). That literature describes how viscoelastic properties and the gel-sol transition of gels were affected due to sucrose and other sugars. Therefore, the **second aim of this work** is to describe and summarize the changes during the **crystallization process of sugar** (especially, for a coating purpose) in the **presents of hydrocolloids** (agar, gelatin and carrageenans). Furthermore, there is a lack of knowledge on the influence of hydrocolloids on the crystallization behavior of sucrose to get coated gels. Hydrocolloids can affect the **liquid phase** by changes of the **diffusion process** (slower molecule transportation) and the **solid phase** by kinetical changes **in the formation of crystals** (purity of the layer). The resulting product changes (e.g. appearance of crystals and the end product, process ability, storage stability and layer thickness) in sweets due to texture altering substances is an important topic for the confectionary industry. Processing parameters like nucleation and solubility of supersaturated hydrocolloid-sugar solutions as well as the crystal growth or other parameters (e.g. gelation temperature and viscosity) should be observed and controlled in industrial processes. Only with the knowledge of these effects of hydrocolloids on the sugar crystallization the production process can be controlled and reproducible products with respect to quality are achievable.

In literature [Har91; Pan10; Mil12] it is described that the crystallization of sugar (e.g. nucleation or mass transport of the molecules) can be suppressed systematically by the use of different macromolecules (e.g. hydrocolloids). A typical application for gelatin in confectionary industry is to act as a tool to control sugar crystallization by avoiding undesired

product changes during storage [Phi09]. The suppressing effect of the crystallization mechanisms can prevent undesired product quality changes during storage of supersaturated end products. These suppressing effects are summarized in literature [Har91; Pan10] and are widely understood. Not completely understood and with few literature descriptions, however, is how the crystallization of high viscous supersaturated sugar solutions in combination with a gelling process of different hydrocolloids works. The suppression of crystallization due to macromolecules (hydrocolloids) should be overcome to achieve a uniform and desired formation of a crystallized sugar layer.

The use of powder molds to shape candies or gelled products are commonly known. This technique is called mogul technique [Sch07]. Information and descriptions of the applicability of different powders are also described in literature [Hof04a]. Not to be found, however, and therefore an important **third aim of this work**, are information on the **ability of seed materials to enforce the nucleation of high viscous supersaturated sugar solutions**. Nucleation enforced by suitable foreign seeds is an important tool to control the production of defined crystalline products. The quality of a surface provided by seed materials represents an important variable in the production of crystallizing layers that means for the nucleation process. Parameters like shape and surface structure, size and size distribution of the seed particles as well as the ability to hold up the moisture (the solvent), can have an influence on the nucleation process of different viscous supersaturated solutions. The effect of seed materials is not clearly described up to now, therefore different seed materials (potato, rice, tapioca and wheat starch) need to be tested to find alternatives for corn starch in the production of sweets in confectionary industry. An overview needs to be given for typical properties of seed materials and the resulting effects on the nucleation of a sugar solution in order to select properly the “right” seed material for the desired application.

Optimal conditions must be found regarding the concentration of all components, process temperatures as well as the shape, the layer thicknesses and the stability of the crystalline coated gels (end products). General guidelines from the experimental results can be given, which help to pay attention to important process and product changes during the combination of crystallization and gelation.

4. Materials and Methods

Most studies on hydrocolloids and sugars use sucrose and distilled water for their rheological experiments. The produced solutions here, however, consist of a constant amount of white sugar and tap water (pH 7.37) and a varying amount of different additives, especially, hydrocolloids. These additives are thermo-reversible gelling agents, which can be classified in animal products and products obtained from plants.

Different methods to observe the material properties of the sugar-hydrocolloid solutions were used to define an optimal handling and production process. Other techniques to observe on the one hand a steady nucleation process of a sugar solution by determining the seed material properties and on the other hand by looking at the crystal growth from a sugar-hydrocolloid solution were developed. Another part focusses on the characterization of seed material properties, which are used to enforce the nucleation of a sugar solution.

4.1 Materials and manufacturing methods of the solutions and coated gels

Preliminary experiments showed the applicability of four different hydrocolloids during production of coated gels (see Figure 4.1-1). Important during these investigations was to get a sugar layer outside and an inner gelled core (see Figure 4.1-1). By visual evaluation of the appearance of the achieved gel core hydrocolloids like agar, gelatin, κ-carrageen from two different producers (Roth and Cargill) and ι-carrageen were chosen. The producers Cargill and Roth will be named as (C) and (R) in the following work.

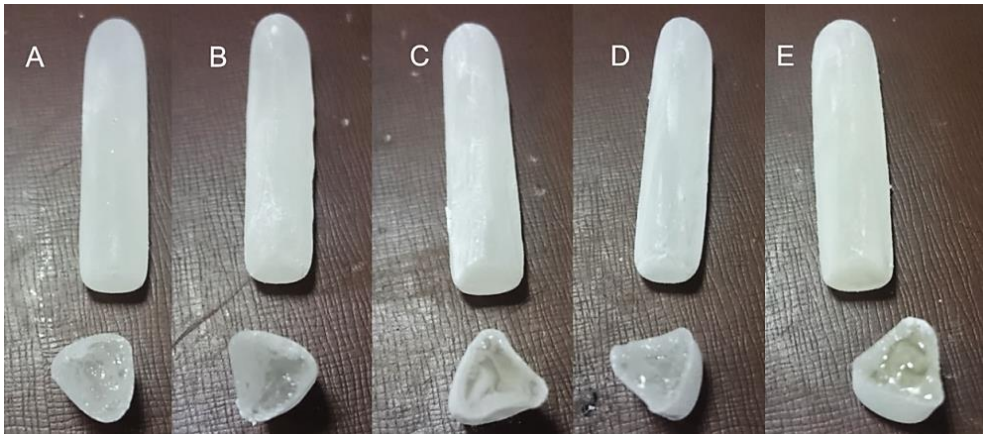

Figure 4.1-1: Coated gels A: 1.5 wt% agar; B: 2.4 wt% gelatin; C: 0.7 wt% κ-carrageen (C); D: 0.5 wt% κ-carrageen (R); E: 1.7 wt% ι-carrageen

Data sheets of the producers (Cargill, Roth and GELITA®) give information on the hydrocolloids as can be seen in Table 4.1-1.

Table 4.1-1: Information on the used hydrocolloids

Hydrocolloid (Producer)	Specification / Charge (MFG Date)	Properties
agar (Cargill)	Flanogen™ P /20142770 (11.2014)	pH: 6 - 8 decomposition from 200 °C, 5 % dextrose, density: 0.6 - 0.7 g/cm³ dissolution from 90 °C
κ-carrageen (Roth)	Carrageen, kappa nach FAO/WHO, EEC, FCC, hochrein /484151924	pH: 7 - 11 gel strength: (1.5 %, aqueous) 1200 - 1800 g/cm² particle size (99 %) < 0,25 mm H_20 content < 1 2 % arsenic < 3 ppm; lead < 5 ppm; cadmium < 2 ppm; mercury < 1 ppm; heavy metals < 20 ppm
κ-carrageen (Cargill)	Satiagel PG 500 /20141807 (07.2014)	pH: 6 - 11 decomposition from 200 °C H_20 content < 12 % dissolution from 80 °C sugar: 29 %; dietary fiber: 40 % Na: 4960 mg; K: 3170 mg; Ca: 25 mg; Mg: 15 mg; H_20: 6 g; ash: 25 g
ι-carrageen (Cargill)	Satiagel PG 300 /20140023 (01.2014)	pH: 8 - 11 dissolution from 80 °C sugar: 13 %; dietary fiber: 55 % Na: 2610 mg; K: 6280 mg Ca: 620 mg; Mg: 45 mg; H_20: 7 g; ash: 25 g
gelatin (GELITA)	GELITA® 300 PS Edible Gelatine /634390 (29.10.2013)	pH: 4.7 - 5.7 (6.67 %; 60 °C) gel strength: 290 - 310 g (300 Bloom) Pig Skin Viscosity: 3.5 - 4.7 mPa*s (6.67 %; 60 °C) Particle size: 20 mesh (0.8 mm) H_20 content: 9.0 - 13.0 % Peroxides < 10 mg/kg; arsenic < 1.0 mg/kg; cadmium < 0.5 mg/kg; chromium < 10 mg/kg; copper < 30 mg/kg; mercury < 0.15 mg/kg; lead < 5mg/kg; zinc < 50 mg/kg; sulfur dioxide < 10 mg/kg

The used gelatin (GELITA® 300PS) was an acid processed gelatin extracted from pig skin. This acid processed gelatin shows lower (30 - 50 %) viscosities at hot conditions compared to alkaline-conditioned gelatin despite the same gelling power properties [SCH07]. This is important for the crystallization process. Lower viscosities enable the mass transport of sugar molecules to build up a crystallized layer on the outside of the gel core. Beside the low hot viscosity the use of 20 mesh (standard particle size of 0.8 mm) is beneficial for the production. Small particles can swell more easily and dissolve well without agglomeration in a hot sugar solution and without too much foaming during stirring.

Table 4.1-2 shows the typical compositions of the hydrocolloid-sugar solutions. Different concentrations of hydrocolloids were tested in an approx. 78.50 wt% sugar solution.

Table 4.1-2: Composition of the investigated sugar solutions with weight percentage in brackets

Hydrocolloid solutions	Sugar [g] and weight percent [wt%]	Water [g] and weight percent [wt%]	Hydrocolloid [g] and weight percent [wt%]	Water for swelling [g] and weight percent [wt%]
pure sugar solution	78.50 (78.50)	21.50 (21.50)	-	-
0.5 wt% agar	78.50 (78.11)	21.50 (21.39)	0.50 (0.50)	-
1.0 wt% agar	78.50 (77.72)	21.50 (21.29)	1.00 (0.99)	-
1.5 wt% agar	78.50 (77.34)	21.50 (21.18)	1.50 (1.48)	-
0.2 wt% κ-carrageen (R)	78.50 (78.31)	21.50 (21.45)	0.24 (0.24)	-
0.5 wt% κ-carrageen (R)	78.50 (78.11)	21.50 (21.39)	0.50 (0.50)	-
0.5 wt% κ-carrageen (C)	78.50 (78.11)	21.50 (21.39)	0.50 (0.50)	-
0.7 wt% κ-carrageen (C)	78.50 (77.95)	21.50 (21.35)	0.70 (0.70)	-
1.0 wt% ι-carageen	78.50 (77.72)	21.50 (21.29)	1.00 (0.99)	-
1.7 wt% ι-carrageen	78.50 (77.19)	21.50 (21.15)	1.70 (1.67)	-
1.5 wt% gelatin	78.50 (75.85)	19.50 (18.84)	1.50 (1.45)	4.00 (3.87)
2.4 wt% gelatin	78.50 (73.71)	19.50 (18.31)	2.50 (2.35)	6.00 (5.63)

All hydrocolloids except for gelatin were boiled together with sugar and water to dissolve the solid and to enable a gel formation. During the boiling a loss of water should be prevented by a cover.

Agar was mixed together with white sugar, further tap water was added. Afterwards the mixture of hydrocolloid, sugar and water has been heated to dissolve the dry matter while

stirring till all compounds were distributed homogeneously. Stirring was important otherwise the sugar caramelized and the dissolution was not homogeneous.
A similar procedure was applied for the carrageenans (κ and ι-carrageen). The dry matter that means carrageen and sugar was mixed together and added to boiling water to ensure the dissolving of all components.
For gelatin a modified process was used. The production with gelatin needs an additionally step in processing. Gelatin needs to swell before being added to the solution. The sugar and water mixture (see Table 4.1-2) were boiled to dissolve the sugar and cooled down to 90 °C. Afterwards the swollen gelatin was added to the solution under gentle stirring. If stirring is too high gelatin tends increasingly to foam [Sch07]. Gelatin is not heat resistant so very hot solutions (> 90 °C) would lead to destroyed material and result in a reduced gelling behavior of the material [Sch07; Gor76]. Keeping a gelatin solution, e.g. for 1 hour at 100 °C, leads to a decrease in gel strength from 100 % to < 80 % [Sch07].
Solutions with agar and carrageenans must be poured into the powder mold (see Figure 4.1-3) directly after cooking (at 100 °C) otherwise the viscosity becomes too high to produce uniform products. Tailing (formation of jelly strings which connects the end products undesirable together) is an intensified occurring problem. Gelatin and pure sugar solutions were poured at lower temperatures (80 - 90 °C and 60 °C) but during cooling the solution must be swiveled to ensure a homogenous heat distribution and to avoid nucleation on the surface of the solution. Afterwards the sidewalls of the bottle were cleaned to avoid crystallization at the bottles wall.

To produce coated gels in a specific shape (see Figure 4.1-1), dried powder molds (see Figure 4.1-3) were used. After creating a smooth surface of the filled starch molds, these molds were dried for 24 hours at 50 °C to enforce comparable moisture contents in the powder beds. Thereafter, imprints were made with special shaped stamps to create cavities in the starch molds. The supersaturated sugar solutions (with or without hydrocolloid) were poured into the imprints in the starch molds. The imprints can have any desired shape but here sticks were shaped with a triangular basic shape (dimensions: 1.0 cm x 4.2 cm x 1.0 cm) (see Figure 4.1-2). The sugar solution was enclosed by the external seed material at all sides of the product (see Figure 4.1-2). Selbmann [Sel16] gives a precise instruction for the production steps of crystallized sugar bodies. The use of external seed materials to enforce the nucleation of a sugar solution is very important. A typically mold to shape the products and to induce the nucleation can be seen in Figure 4.1-3. The powders are sprinkled on top to induce the nucleation homogeneously at all sides of the product.

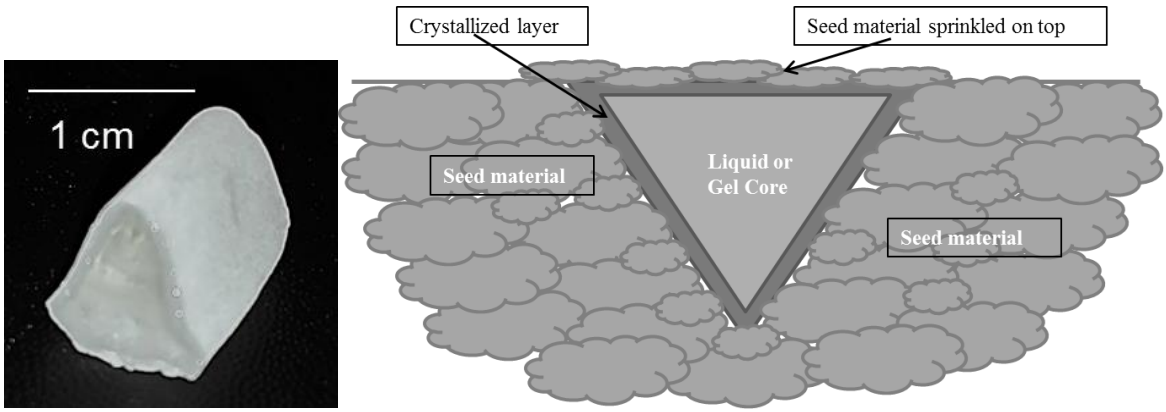

Figure 4.1-2: Left: Bisected end product with a crystallized layer and triangular shape and right: Cross section of a crystallized product in a seed powder bed [Her16a]

This technique is based on the commonly used starch mogul technique in the confectionary industry [Hof04a; Sch07]. It includes the following process steps: First of all, the starch powder beds were prepared, followed by imprints with stamps to shape the end products. Afterwards, the solution is poured into the imprints and sprinkled on top with starch to initiate the nucleation of the solution. Furthermore, the starch trays were stored in a ripening room and after a specific time the products can be removed from the starch trays. The starch trays are sieved after product recovery, to allow the circulation mode.

Figure 4.1-3: Corn starch mold with imprints filled with sugar solution [Her16]

To enforce the nucleation of sugar solutions, different powders were used to replace the commonly used corn starch in production of gums and confectionaries. In order to assess the applicability of the tested seed materials, production-relevant parameters such as particle size and size distribution, ability to hold up moisture and shape as well as the texture of the materials were observed. Different flours like wheat flour type 405 and wheat flour instant produced by the Kathi Rainer Thiele GmbH were used. Potato flour (Frießinger Mühle GmbH), wheat powder (Unilever Germany), tapioca starch (Cargill), rice starch (Naturkornmühle Werz) and icing sugar (Pfeifer & Langen and Sweet Family Nordzucker)

were used to initiate the nucleation. All used materials were pure starches without any other declared ingredients. To induce the nucleation, the production of sugar bodies (see Figure 4.1-1) based on the already explained starch mogul technique was used. The provided surface area of the products was approx. 13.7 cm^2 (4 - 5 g solution per mold). All products were turned upside down after three hours to facilitate a uniform crystallization on all sides.

4.2 Description of produced solutions (texture, pH value)

Optical (habitus and color) and textural (homogeneity, tailing, haptic properties) evaluations of the produced solutions were carried out. The properties of the crystallized layer and the gel texture of the end products were described. These are important factors, which influence the mouth feeling of the gel and the taste of the end product.

The pH value of these hydrocolloid containing solutions were determined. The hot solutions were filled into a small glass bottle. The pH value was measured with a glass electrode. The sample bottle was closed and measured for 24 hours (till the value stays almost constant).

4.3 Viscosity determination

A rotary viscometer called Viscotester 550 by HAAKE was used to determine the viscosity of the solutions at different temperatures. This device works in a Searle System that means the cylinder inside rotates and a cylinder outside is static. Details on the measuring principle are given by Wittenberger [Wit73] and the manual of HAAKE [Haa96]. Almost all solutions showed at high temperatures (> 60 °C) Newtonian behavior that means the viscosity was independent of the shear rate [Bab96]. Non-Newtonian fluids are e.g. ketchup or blood. Several low concentrations of some high molecular weight polymers show Newtonian behavior [Pan10]. The applied rotation speed was 60 s^{-1}. The applied stress should be as low as possible to minimize the disturbance of the sucrose solution [Qui06]. Not only the supersaturated solutions were sensitive to shearing [Qui06] but also the hydrocolloids must be measured carefully. All experiments were performed in a triplicate determination with a measuring time of 240 seconds. The measuring temperatures had to be adapted individually depending on the viscosity of different hydrocolloid-sugar solutions at different temperatures. Measurements at high temperatures decrease the driving force for nucleation during shearing and prohibit the gelation of the thermo-reversible gels. Highly concentrated sucrose solutions tend to nucleate and further crystal growth appears during shearing [Qui06]. It was therefore the aim to determine the viscosity of all solutions at 70, 80, 90 and 100 °C. The temperature had to be varied for κ-carrageen (Roth) and ι-carrageen (Cargill) in order to enable measurements. In general, a processing of the hot solutions (> 80 °C) is necessary and the viscosity values give important information for the processing parameters.

Beside the variation of the concentration of hydrocolloids according to the composition shown in Table 4.1-2 also the sugar amount was varied (see Table 4.3-1).

Table 4.3-1: Variation of sugar during viscosity measurement

Hydrocolloid solutions	Sugar [g] and weight percent [wt%]	Water [g] and weight percent [wt%]	Hydrocolloid [g] and weight percent [wt%]	Water for swelling [g] and weight percent [wt%]
1.5 wt% agar	78.50 (77.34)	21.50 (21.18)	1.50 (1.48)	-
3.5 wt% agar	20.00 (46.50)	21.50 (50.00)	1.50 (3.50)	-
6.5 wt% agar	-	21.50 (93.48)	1.50 (6.52)	-
0.5 wt% κ-carrageen (R)	78.50 (78.11)	21.50 (21.39)	0.50 (0.50)	-
1.2 wt% κ-carrageen (R)	20.00 (47.60)	21.50 (51.20)	0.50 (1.20)	-
2.3 wt% κ-carrageen (R)	-	21.50 (97.73)	0.50 (2.27)	-
0.7 wt% κ-carrageen (C)	78.50 (77.95)	21.50 (21.35)	0.70 (0.70)	-
1.7 wt% κ-carrageen (C)	20.00 (47.40)	21.50 (50.90)	0.70 (1.70)	-
3.2 wt% κ-carrageen (C)	-	21.50 (96.85)	0.70 (3.15)	-
1.7 wt% ι-carrageen	78.50 (77.19)	21.50 (21.15)	1.70 (1.67)	-
3.9 wt% ι-carrageen	20.00 (46.30)	21.50 (49.80)	1.70 (3.90)	
7.3 wt% ι-carrageen	-	21.50 (92.67)	1.70 (7.33)	
2.4 wt% gelatin	78.50 (73.71)	19.50 (18.31)	2.50 (2.35)	6.00 (5.63)
5.2 wt% gelatin	20.00 (41.66)	19.50 (40.63)	2.50 (5.21)	6.00 (12.50)
8.9 wt% gelatin	-	19.50 (69.64)	2.50 (8.93)	6.00 (21.43)

4.4 Sugar content determination

The sugar content can be specified in Brix% and shows the sucrose content in weight percent of a sucrose-water solution. The principle of the Brix% determination is based on the refraction of light. The light is refracted differently depending on the concentration of sucrose in the sample (see e.g. [Met99]).

The refractometer RE 40 by Mettler Toledo shows values for the initial solution and the sugar contents in gels over time. Measuring temperature was 25 °C. Brix% measurements in dependency of the sugar content, hydrocolloid content, time and different storage conditions (e.g. ambient temperature (22 °C) and 50 °C) were taken.

4.5 Metastable zone determination

The determination of kinetic and thermodynamic properties of different hydrocolloid-sugar solution is necessary to handle and adapt the production, especially, in developments of new products and product conditions. Determination of fundamental crystallization parameters, like nucleation and solubility were important while creating a crystalline coated gel. Two different methods were used to get information on the metastable zone width of solutions with different amounts of hydrocolloids.

4.5.1 Turbidity measurement

To determine the nucleation and solubility temperatures of the hydrocolloid-sugar solutions, the turbidity of the solution was measured. An IR (infrared) -probe determines the turbidity of solutions during changes in supersaturation. During cooling of a solution, crystallization starts and the solutions became turbid (IR-Signal decreases) so the nucleation temperature was detectable. During heating of a solution containing crystals, the crystals dissolve and the turbidity disappears (IR-signal increases) so the solubility temperature of the solution was determined. After graphical analysis of the results, the metastable zone width of the solution as one of the key parameters in production was determined. The measuring principle and the evaluation of the data in more detail are explained by Selbmann [Sel16] or Maosoongnern et al. [Mao12].

The kinetic and thermodynamic properties of a gelatin-sugar and agar-sugar solution were measured by using a linear temperature profile. The determination was carried out in a triple measurement. 10 mL of the solutions (0.5, 1.0 and 1.5 wt% agar and 1.5 wt% gelatin) were cooled from 100 to 25 °C with a rate of 9 K/h followed by a heating up to 120 °C. For 2.4 wt% gelatin and 0.24 wt% κ-carrageen (R) the slowest possible heating rate of the device that means 6 K/h was used. All solutions (10 mL) were stirred with 350 rpm during the measurements to enable a homogenous heat distribution.

Not all metastable zones of the hydrocolloid-sugar solutions could be measured by the IR-probe (carrageenans). Due to a limited heating and cooling rate mainly gelatin- and agar-sugar solutions were observed. The metastable zone of carrageenans was alternatively measured by ultrasound velocity determination (see Chapter 4.5.2).

4.5.2 Ultrasound velocity measurement

To determine the metastable zone of ι- and κ-carrageen, a non-optical method was used. The velocity probe determines the ultrasound between a transmitter and receiver. This signal depends on the density and adiabatic compressibility of a sample. These two parameters can be influenced by pressure, concentration and temperature of a solution. Starting

temperature during the measurements was 110 °C. The solutions were cooled with a rate of 9 K/h to 60 °C, followed by heating till 110 °C. The solutions were stirred homogeneously and measured always three times. The following concentrations were measured: 0.50 wt% ι-carrageen, 0.24 wt% κ-carrageen (R) and 0.30 wt% κ-carrageen (C). By changing the temperature profile to a heating and a cooling rate of 6 K/h and starting from 110 °C to 50 °C and 110 °C again the metastable zone of a 0.5 wt% κ-carrageen (C) sugar solution was detectable.

Higher concentrations of hydrocolloid-sugar solutions were not detectable with these methods, because the metastable zone is influenced in such a way, that the nucleation is inhibited completely (without external seeding). The hydrocolloid network of high concentrated hydrocolloid sugar solutions is too strong to enable the formation of clusters as basics for nucleation. The extremely wide range in metastable zone (MZW) was difficult to detect and very low cooling and heating rates are necessary as well as very hot temperatures (> 110 °C) due to the sluggish system and hysteresis of hydrocolloid-sugar solutions.

4.6 Characterizations of external seed materials in crystallization terms

The nucleation behavior of a supersaturated (β ≈ 1.16 at 20 °C) sugar solution enforced by different external seed materials (e.g. flours like wheat flour (type 405 and instant), potato starch, wheat powder, tapioca starch, rice starch and icing sugar) was tested. These external seed materials were commercial powders, which can be purchased in many supermarkets. All materials were used several times and were each time sieved before reuse. The powders were dried at 50 °C for 24 hours to avoid agglomeration of the particles.

In order to assess the applicability of the tested seed materials, parameters such as particle size and size distribution, ability to hold up moisture and shape of the particles as well as the texture of these seed materials were observed.

4.6.1 Determination of moisture content, particle sizes and external appearance of seed materials

The moisture of the seed materials was measured by a Moisture Analyzer MA 50 (Sartorius) [Sar50] after storage of the samples at ambient temperature (22 °C) and 50 °C for different times (24 hours or longer). If possible, the moisture of new materials and also already used (recycled) materials were measured. The principle of the Moisture Analyzer was a detection of the material weight during heating (till 150 °C) with an infrared lamp. The water evaporates

till a constant level is reached and the measurement stops. The moisture values were determined by a triple measurement and a sample amount of 3 - 5 g per measurement.
To estimate the influence of a drying process, also the humidity of the air was determined.

The particle size and size distribution were measured with a Mastersizer 2000 (Malvern). This device makes use of laser diffraction. The helium-neon laser beam is scattered by particles in different ways. Small particles show a big deflection angle and bigger particles show a small deflection angle [Mal00]. The Fraunhofer- and Mie-Theory is the principle assumption to get exact values. Particles sizes from 0.02 to 2000 µm are detectable (see e.g. [Mal00]). The samples were measured in dry state (dry dispersing unit: Scirocco 2000) with an air pressure of two bar. Feed rates to achieve an optimal sample supply were 47 % for corn, 63 % for potato, 50 % for rice, 52 % for tapioca and 53 % for wheat starch. The dried (24 hours at 50 °C) materials were measured three times for eight seconds. The used refractive index was 1.538 for icing sugar and 1.53 for the starch materials as well as fort the different flours. Measuring principle is a formation of a characteristic light scattering pattern of the particles. The measurement is based on an assumption that all particles were spherical.

Using two different microscope devices, the surface of the particles was observed and illustrated. The light microscope (VHX-500F) provides images with a polarizing filter to illustrate the behavior of the materials in polarized light. These images are shown in the Appendix in Figures 11-1, 11-2, 11-3, 11-4, 11-5, 11-6, 11-7 and 11-8. Scanning Electron Microscope images of different seed materials were taken to observe the surface properties as well as the shape of the particles. The materials were not modified for these measurements and a low accelerating voltage of 2 kV was used. Tegge [Teg04] showed similar microscopic images from different starches (e.g. corn and tapioca) so that it can be assumed that the used materials were undamaged and in a good state.

4.7 Determination of layer thicknesses

To evaluate the process of crystallization, the thicknesses of coated gels were determined. Therefore, microscope (VH X-500F from KEYENCE) images were observed. An example is shown in Figure 4.7-1. At least six samples from minimum three different sugar bodies were used. Two images from every side were taken that means six images per sample (see also Selbmann [Sel16]). The images were evaluated by drawing 7 - 12 measuring lines (see Figure 4.7-1) inside the image by using the program “AnalySIS”.
The layer thicknesses from coated gels produced with different hydrocolloids in different concentrations were observed. Further, this evaluation was made at different times and under different storage conditions (temperature changes). Results are shown in Chapter 5.7.

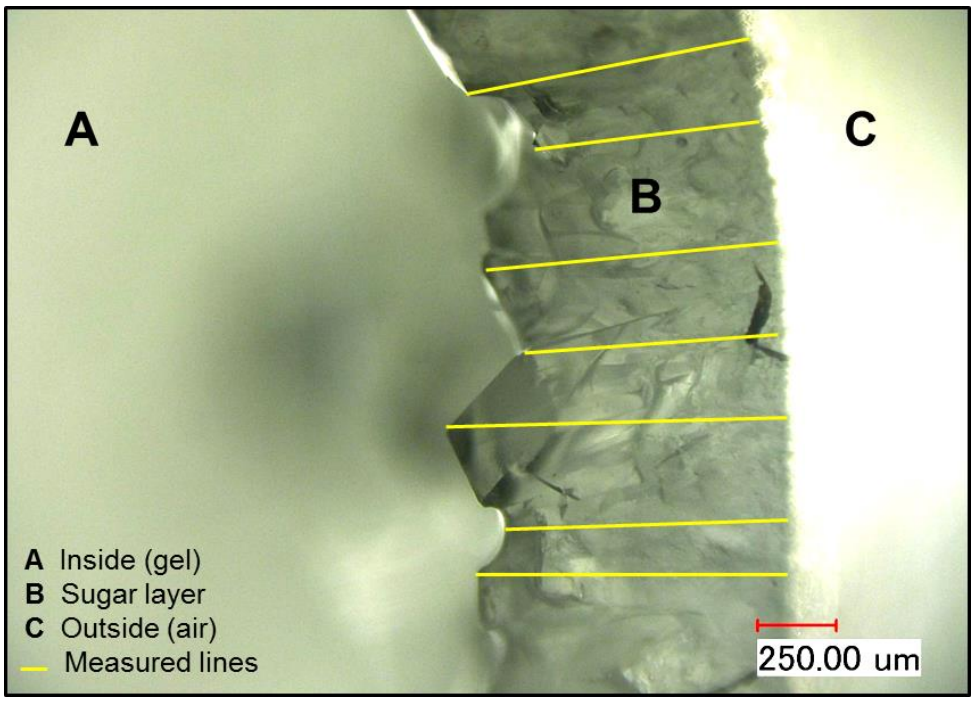

Figure 4.7-1: Microscope image with crystallized layer [Her16]

4.8 Detection reaction of hydrocolloids in layers

Due to a much higher loss of water of sugar bodies produced with hydrocolloids during storage (see Results of Chapter 5.9) the purity of the crystallized layers was observed.
To determine the hydrocolloids inside the sugar layer, the layer was separated from the gel core. Two different methods were used (an overview is given in Table 4.8-1). On the on hand, the sugar layer was dissolved with hot water and on the other hand, the layer was sliced partially off, to obtain the material for the detection reactions [Her17].

Table 4.8-1: Overview of the used detection methods for hydrocolloids [Kat16]

Hydrocolloids	Proof	Coloring
gelatin	saturated ammonium sulfate solution	-
agar		41 mM methylene blue
κ- and ι-carrageen	photometric detection with methylene blue	

4.8.1 Precipitation

The proof of presents of gelatin is possible by a salting out method [Her17]. Therefore, the precipitate of a gelatin-ammonium sulfate (AS) complex was observed by microscope images.

Agar and κ- and ι-carrageen were precipitated with AS. Addition of saturated ammonium sulfate (MERCK) leads to a flocculent precipitate [Ewa52]. Additionally, the hydrocolloids were colored with the coloring agent methylene blue from Roth with a concentration of 41 mM. Due to sulfated groups in agar and carrageen molecules, these structures are negatively charged. Therefore, the coloring with the cationic dye was possible. Starch must be removed completely before starting the experiments with AS because that leads to false positive results. The use of the dye helps to distinguish between agar and starch.

4.8.2 Coloring reaction (Photometer)

Proofing the hydrocolloids ι- and κ-carrageen was easier due to higher sulfate contents in the molecules compared to agar. The cationic dye methylene blue interacts reversible with these sulfate groups (anionic hydrocolloids) [Soe94]. Therefore, the absorption maxima were shifted from 610 nm and 664 nm (blue) to 559 nm (purple) [Her17]. Sugar and starch have no influences on the measurements. The color result was verified by the single beam photometer SPECORD 40 UV/VIS from Analytic Jena (version: 3.2.3.0; no.: 232E158). 50 µL of a 0.02 wt% hydrocolloid solution was measured and show the different colors of the solutions [Soe94]. Ten drops of water and 0.5 mL methylene blue were added to the crystalline material. The scan mode was in the range of 450 to 700 nm using the program WinAspect. For the absorption measurements the Lambert-Beer law must be fulfilled (see Equation 4.8-1).

$$\boldsymbol{A = \log\left(\frac{I_0}{I}\right) = \varepsilon * c * d} \qquad \text{(Eq. 4.8-1)}$$

A is the extinction [L mol^{-1} cm^{-1}], I_0 is the intensity of incoming light [Wm^{-2}], I is the intensity of transmitted light [Wm^{-2}], ε is molar absorption coefficient [m^2 mol^{-1}], c is the concentration of the solution [mol/L] and l is the length of solution the light passes through [cm].

4.9 Identification of storage stability of coated gels

Data obtained from a company showed, that the storage conditions during ripening time in the production process of sweets are not completely constant. Figure 4.9-1 illustrates the

temperature changes. Depending on the time and place where the products are stored the temperature varies (23 - 38 °C).

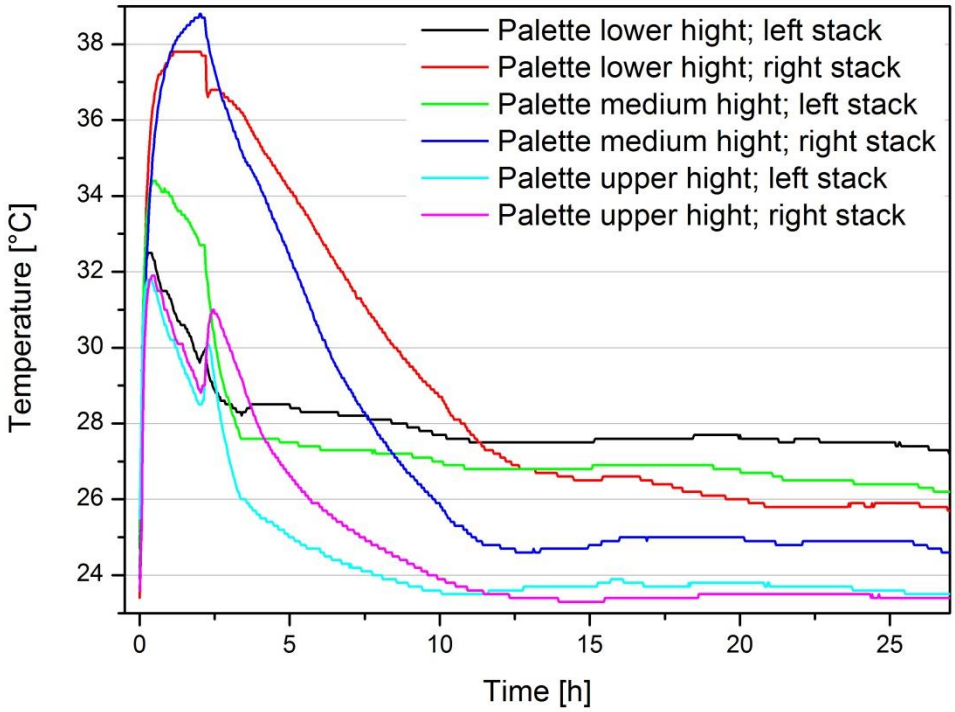

Figure 4.9-1: Temperature profile in production processes of sweets

Different temperatures during storage can change the layer thicknesses, purity of crystalline material and water content of the end product. The influence of the storage temperature was recorded. Also the loss of water during storage after different times was measured by weight determination (weight after 3 or 24 hours after production as starting value and weights after different times as end values).

Additionally, different storage conditions for agar-sugar products were tested. The processes of gelation and crystallization were separately enhanced. The processes were controlled by temperature. First, the process of gelation takes place at low temperatures (13 °C) and afterwards (3 hours later) the crystallization process was enabled by higher temperatures (50 or 70 °C). The measured layer thicknesses, loss of water of the coated products and Brix% values helped to explain the production relevant process conditions (especially, temperature conditions) that have to be controlled. The variation of the temperature during a production of crystalline coated gels is a beneficial tool to get desired, stable and reproducible end products.

4.10 Determination of the stability of coated gels

An already used method established by Selbmann [Sel16] was used to determine the stability. The setup was described by Selbmann [Sel16] in detail. Basically this method makes use of weight detection during an applied pressure. The pressure is produced by a height-adjustable (moveable) plate.

The equation 4.10-1 was used to calculate the stability:

$$\text{stability}\ \left[\frac{N}{cm^2}\right] = \frac{\text{strain on test body [kg]} \times \text{constant of gravitation } [\frac{m}{s^2}]}{\text{base of test body } [cm^2]} \qquad \text{(Eq. 4.10-1)}$$

The used base of the test body was 5.4 cm². Every stability measurement consists of at least 30 measured sugar bodies. The stability of different hydrocolloid-sugar products at different times was observed. The point where the bodies (end products) brake was detected either visually due to a crack within the layer or acoustically by listening to a noise (crack).

5. Results

Many factors can influence the process of crystallization in combination with the gelation process. The following Chapter will show results obtained by the examination of the crystallizing material containing hydrocolloids. Product properties of the coated gel will be emphasized and the variation of the conditions during the production process (e.g. usage of different external seed materials or temperature variations) will give new insights in producing crystalline coated gels.

5.1 Properties of crystallizing material

During the production of sugar solutions containing hydrocolloids, the dissolution of all materials is an important process. The starting material (completely dissolved sugar and hydrocolloids in water) is a basic requirement to achieve desired end products. All solutions containing agar or carrageen have to be heated up till all compounds are dissolved. An exception is gelatin. Here, the sugar solution can be heated up first and after cooling to 90 °C the swollen gelatin can be added.

The determination of the pH value of the hydrocolloid-sugar solution is important to estimate the influence of inversion of sugar as well as a degradation of the macromolecules of hydrocolloids. Inversion includes the splitting of sucrose into fructose and glucose [Wie87]. The supersaturation can be changed due to this process and the gel strength can be decreased. Table 5.1-1 shows the results for pH values within the hydrocolloid-sugar solutions. All solutions show with a pH-value range of 6 to nearly 9 neutral conditions.

Table 5.1-1: pH values of the hydrocolloid sugar solutions

Solution	**pH value**
agar (1.48 wt%)	6.3
gelatin (2.35 wt%)	5.8
κ-carrageen Roth (0.50 wt%)	8.0
κ-carrageen Cargill (0.70 wt%)	8.2
ι-carrageen (1.67 wt%)	8.5

While pouring of the solutions into the starch molds it could be noticed that all produced solutions show tailing (tailing means the formation of jelly strings and connecting of end products) during production. Due to a fast gelling process the solution should be poured directly after the heating step, at around 100 °C for agar and carrageenans or approx. 85 °C for gelatin.

Looking at the prepared solutions and resulting end products (coated gels, see Chapter 4.1, Figure 4.1-1) all products show different product properties. The appearance (shape like a stick) is similar for all tested solutions. The desired products of the coated gels can be seen in Figure 5.1-1. Different hydrocolloids lead to different textures within the sugar shells.

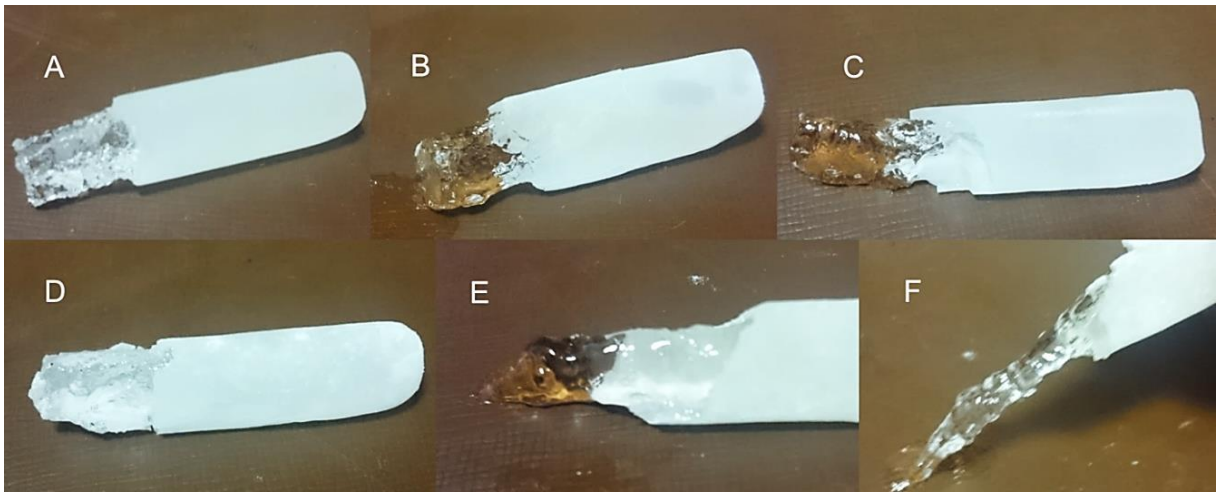

Figure 5.1-1: Gel core with sugar coat A: 1.48 wt% agar; B: 2.35 wt% gelatin; C: 0.7 wt% κ-carrageen (C); D: 0.5 wt% κ-carrageen (R); E and F: 1.7 wt% ι-carrageen

Table 5.1-2 summarizes the obtained properties of the different crystalline coated gels. Gelatin and ι-carrageen show a soft texture whereas agar and κ-carrageen lead to a more firm and brittle texture.

Table 5.1-2: Optical description of typical properties of gel core and sugar crust

Hydrocolloid	**Gel properties**	**Crust appearance**
gelatin	soft, elastic, very clear and sticky	thin (after 24 h) and soft (not crunchy), unstable
ι-carrageen	soft, elastic, sticky and more creamy gel, small lumps (undesired mouthfeel)	hard and crunchy
κ-carrageen	brittle and clear, cut resistant (firmly)	hard and crunchy
agar	brittle, cut resistant (firmly)	hard and crunchy (easy removable from gel core)

5.2 Sugar content of initial sugar solutions

The measured sugar content within the gel core can vary. In dependency of the water evaporation during the production process the values can be different (see Table 5.2-1).

Table 5.2-1: Measured Brix% = $\frac{x\ g_{sucrose}}{100\ g_{solution}}$ values with standard deviation compared with calculated values in wt%

Solutions		Brix% at 25 °C	Sugar [g] and [wt%]
pure sugar solution		79.4 ± 0.60	78.50 (78.50)
0.5 wt% agar		80.0 ± 0.57	78.50 (78.11)
1.0 wt% agar		80.3 ± 0.72	78.50 (77.72)
1.5 wt% agar		80.2 ± 0.59	78.50 (77.34)
	5 % more sugar	84.6 ± 0.40	82.43 (78.19)
	5 % less sugar	77.4 ± 0.68	74.58 (76.43)
0.2 wt% κ-carrageen (R)		81.8 ± 0.67	78.50 (78.31)
0.5 wt% κ-carrageen (R)		81.4 ± 0.75	78.50 (78.11)
0.5 wt% κ-carrageen (C)		80.8 ± 0.60	78.50 (78.11)
0.7 wt% κ-carrageen (C)		80.8 ± 0.61	78.50 (77.95)
1.0 wt% ι-carageen		81.5 ± 1.14	78.50 (77.72)
1.7 wt% ι-carrageen		81.8 ± 0.72	78.50 (77.19)
1.5 wt% gelatine		78.6 ± 0.55	78.50 (75.85)
2.4 wt% gelatine		78.0 ± 0.76	78.50 (73.71)

5.3 Viscosity

Characterizing the physical structure that means flow behavior of the hot hydrocolloid-sugar solutions (temperatures > 70 °C, above the gelling temperature) with the rotational viscometer was possible. Determination of the flow behavior is important for the production process of gelled bodies. Filling the solutions into powder molds should be possible before the gelling process starts. Figure 5.3-1 shows the viscosity of the sugar solutions containing the highest amounts of hydrocolloids. For all hydrocolloid-sugar solutions the viscosity increases with decreasing temperature. ι-carrageen shows the highest viscosity values with 1300 mPas at 100 °C (see Figure 5.3-1, orange quare). κ-carrageen (R) and (C) and agar

show high viscosities (600 and 350 mPas). Gelatin containing solutions and pure sugar solutions have lower viscosity values (< 100 mPas) at 100 °C (Figure 5.3-1, black and blue symbols) compared to the other measured hydrocolloid solutions at 100 °C.

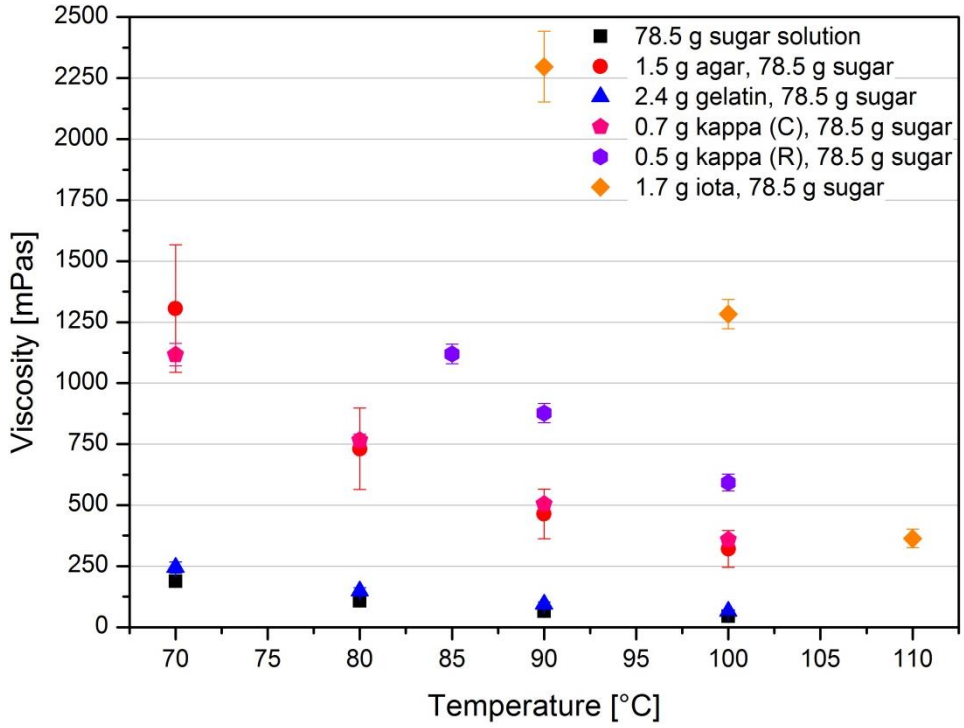

Figure 5.3-1: Temperature dependent viscosity of different hydrocolloid solutions

Results shown in Figures 5.3-2 and 5.3-3 illustrate the dependency of the used concentration of hydrocolloids. Agar and the carrageenans show a high dependency of the concentration of hydrocolloid on the measured viscosity of the tested solutions. Adding different amounts of hydrocolloids e.g. agar can vary the viscosity at 70 °C from 200 mPas without agar to 1300 mPas with 1.5 wt% agar (Figure 5.3-2, red circles). An even higher effect can be seen by adding ι-carrageen into a sugar solution (Figure 5.3-3, orange squares). Viscosities at 70 °C are not measureable for ι-carrageen but values at 90 °C show a difference of nearly 2200 mPas between solutions with ι-carrageen (1.7 wt%) and without ι-carrageen. These thickening effects do not appear for gelatin. Here, the concentration of gelatin does not changes the viscosity values (50 mPas difference at 70 °C between high gelatin amount and without gelatin) and results in similar viscosity values like for a pure sugar solution (200 mPas at 70 °C) (see Figure 5.3-2). The standard deviation increases with decreasing temperature. High values in standard deviation can be seen for agar (1.48 wt%) (see Figure 5.3-2, red circles) and ι-carrageen (1.67 wt%) (see Figure 5.3-3, orange squares).

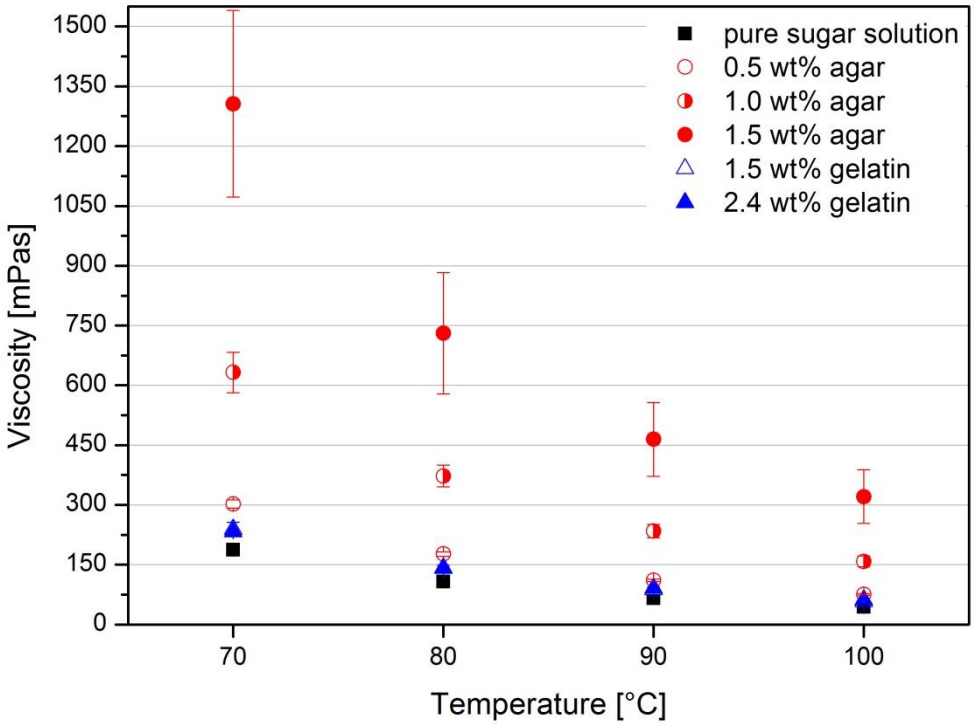

Figure 5.3-2: Temperature dependent viscosity of different agar and gelatin concentrations [Her16]

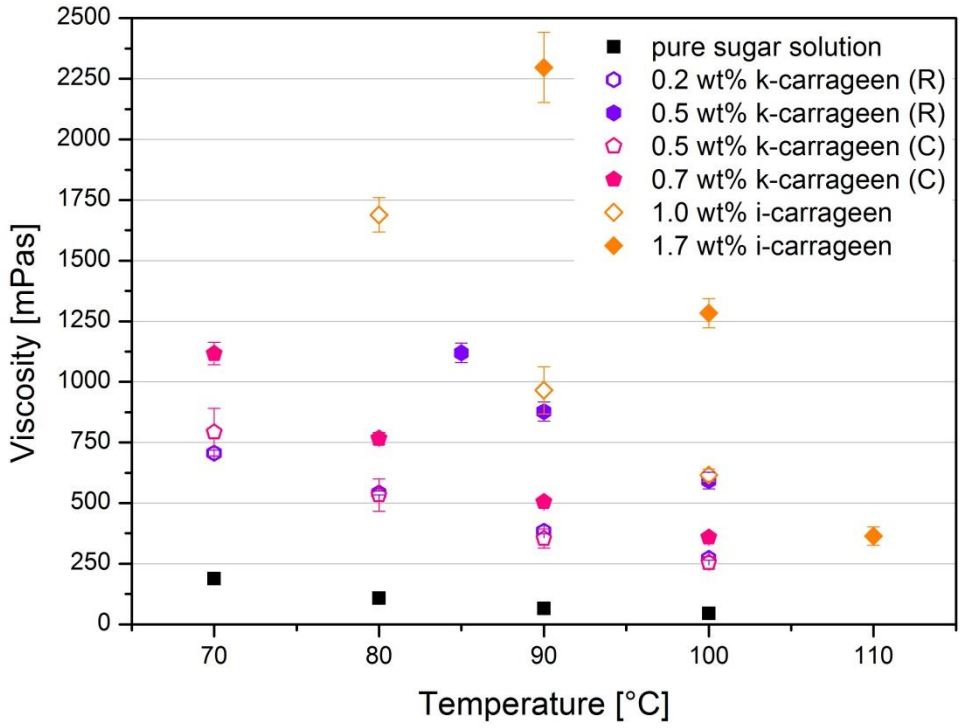

Figure 5.3-3: Temperature dependent viscosity of different carrageen concentrations

Variation of the sugar amount shows different effects on the viscosity of the hydrocolloid-sugar solutions. The amount of sugar added to the hydrocolloid solution is very important for the measured viscosity at hot temperatures (> 70 °C). The addition of sugar (78.5 g)

increases the viscosity of gelatin, κ- and ι-carrageen-sugar solutions (see Figures 5.3-4, 5.3-5, 5.3-6 and 5.3-7) compared to hydrocolloid solutions without sugar. Gelatin solutions without sugar or a low amount of sugar (20 g) show very low viscosities (< 20 mPas) compared to solutions with higher sugar amounts (78.5 g) (see Figure 5.3-4). The lower the measuring temperature is the higher the standard deviation becomes (see Figure 5.3-4, triangles and squares).

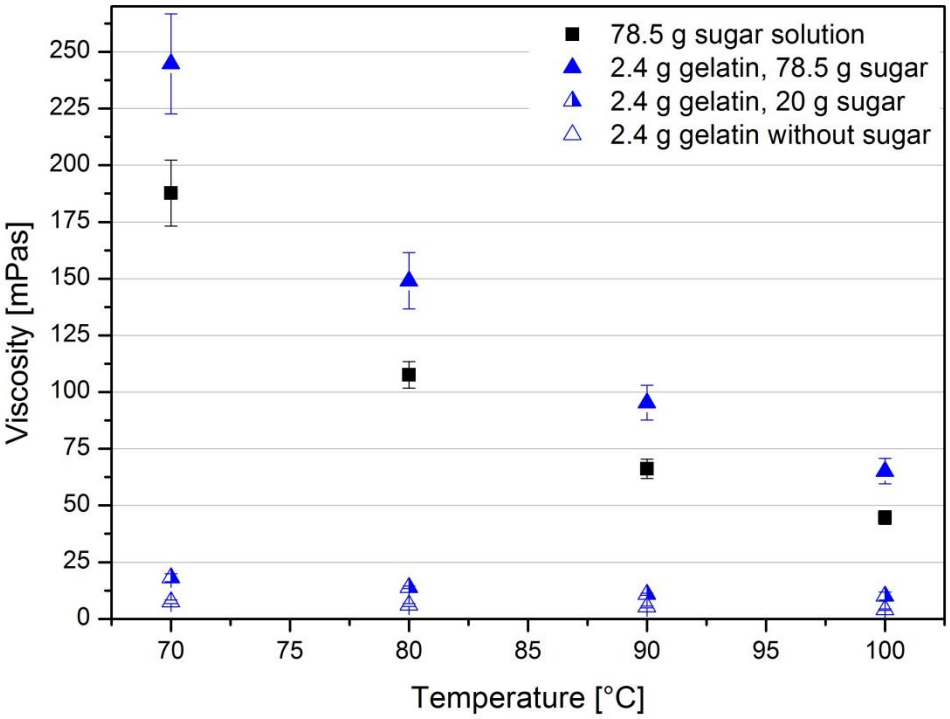

Figure 5.3-4: Temperature dependent viscosity of gelatin solutions with varying sugar amount

κ-carrageen solutions from Cargill (C) and Roth (R) without sugar, show similar viscosity values to the pure sugar solution (see Figures 5.3-5 and 5.3-6). Comparison between the κ-carrageen of different producers (Cargill and Roth) shows that the viscosities at medium sugar concentrations (20 g) are similar (with 180 mPas (C) and 170 mPas (R) at 80 °C) and the solutions show no big differences (see Figures 5.3-5 and 5.3-6).

But at the highest sugar amount (78.5 g) the viscosity of κ-carrageen from Roth (90 °C: 900 mPas) increases more than the viscosity of κ-carrageen of Cargill (90 °C: 500 mPas) (see Figure 5.3-5, pink symbols and Figure 5.3-6, purple symbols). Measurements with the solution from Roth can be made at 85 °C. Lower temperatures block the rotational viscometer (see Figure 5.3-6).

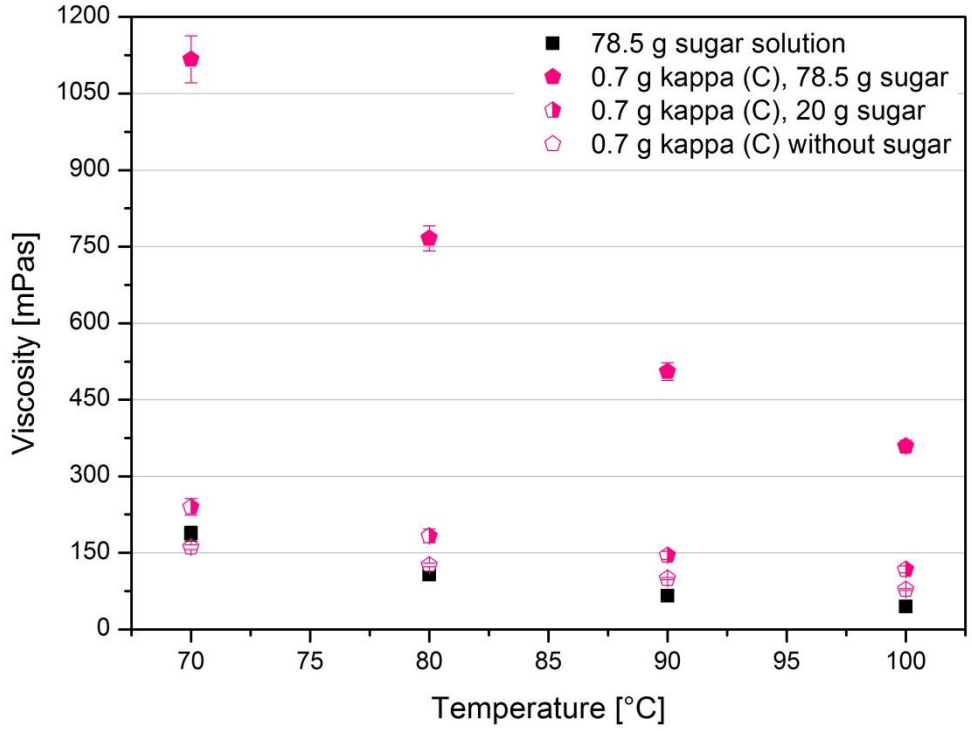

Figure 5.3-5: Temperature dependent viscosity of κ-carrageen solutions (Cargill) with varying sugar amount

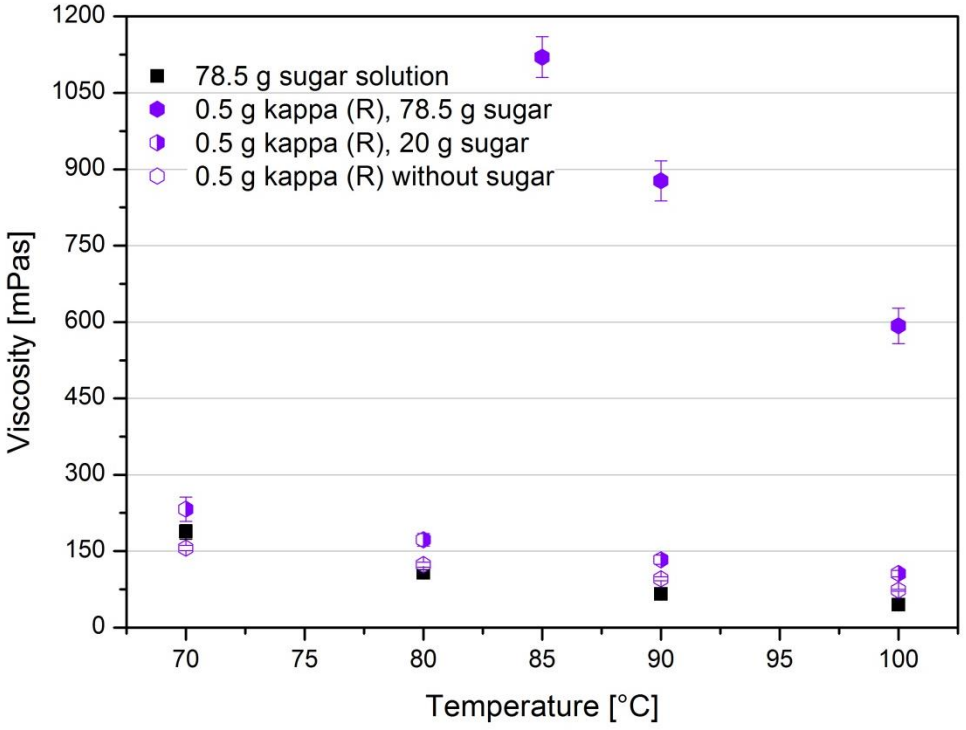

Figure 5.3-6: Temperature dependent viscosity of κ-carrageen solutions (Roth) with varying sugar amount

By far, the largest values of viscosities were obtained by ι-carrageen. In general, the amount of hydrocolloid (1.7 wt%) increases the viscosity a lot compared to sugar solutions without hydrocolloid (see Figure 5.3-7, black squares). Values increase from 200 mPas without ι-carrageen at 80 °C to > 1250 mPas with ι-carrageen (1.7 wt%) at 80 °C. Viscosity values of ι-carrageen solutions without sugar are higher compared to ι-carrageen sugar solutions with 20 g sugar. A really noticeable increase in viscosity for ι-carrageen solutions can be seen at high sugar amounts (78.5 g) (see Figure 5.3-7, orange filled symbols).

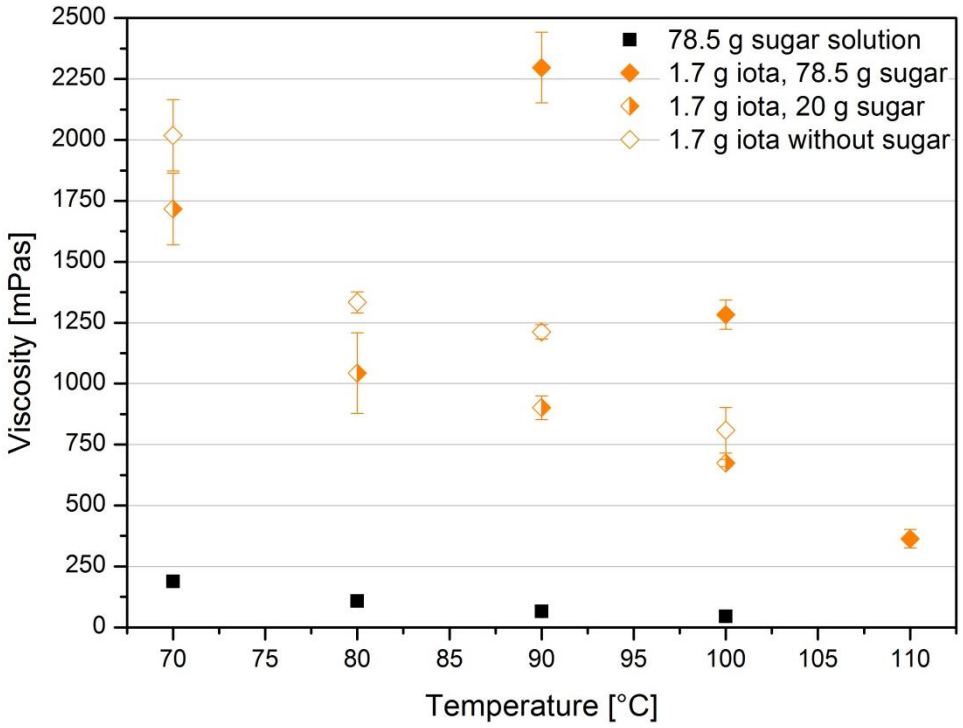

Figure 5.3-7: Temperature dependent viscosity of ι-carrageen solutions with varying sugar amount

Lower sugar amounts (20 g) have only little effects on the viscosity of gelatin and carrageen solutions (see Figures 5.3-4, 5.3-5, 5.3-6 and 5.3-7). An exception can be seen for the hydrocolloid agar. Adding high amounts of sugar in an agar solution leads to a decrease in viscosities (see Figure 5.3-8) compared to viscosities of solutions with other hydrocolloids (gelatin and carrageen). The highest viscosity values were measured for an agar solution without sugar. Sugar amounts of 20 and 78.5 g within an agar solution show no big differences in viscosity values. Lower sugar amounts (20 g) lead to higher viscosity values than higher sugar amounts (78.5 g). All solutions with agar no matter how much sugar was added show clearly higher viscosity values compared to a 78.5 wt% sugar solution.

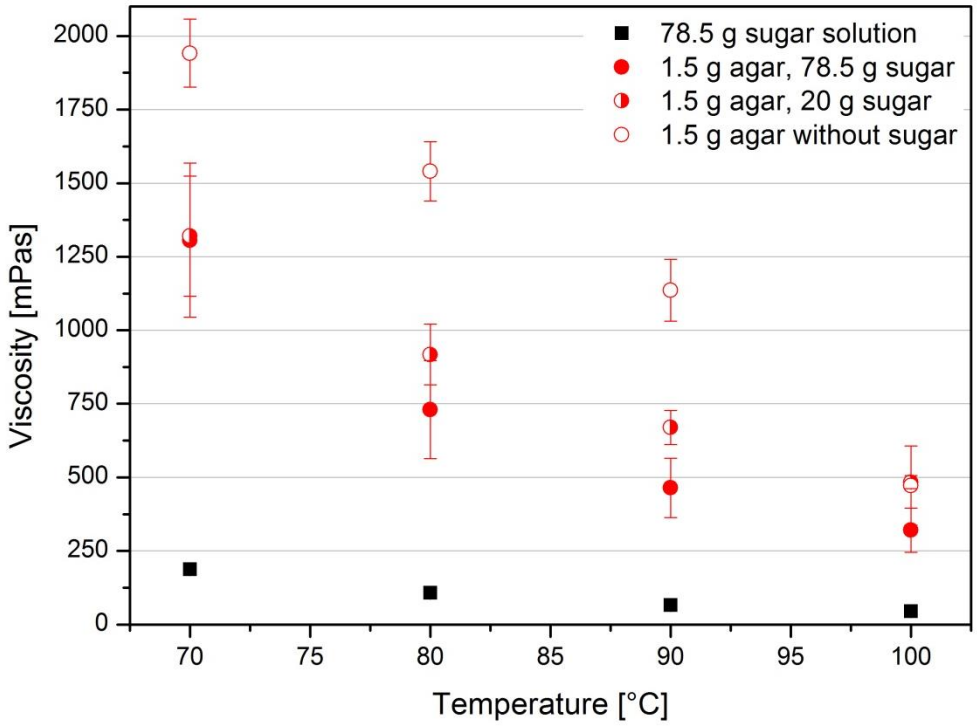

Figure 5.3-8: Temperature dependent viscosity of agar solutions with varying sugar amount

The Appendix shows in Table 11-1 all mean values of the viscosity and their standard deviation.

5.4 Metastable Zone

The metastable zone of agar is shifted due to the addition of agar within a sugar solution. A sugar solution without agar shows a nucleation temperature of 78 °C and a solubility temperature of 88 °C (MZW of 10 K) (see Table 5.4-1).

The average limits of the metastable zone of solutions containing the highest agar amount (1.5 wt%) are shifted with 4 K to lower temperatures compared to solutions without agar. Nucleation happens at 74 °C and solubility at 84 °C. This tendency of a shift to lower temperatures is clear visible (see Figure 5.4-1) but the high standard deviations (with up to 3.6 °C) have to be considered. The MZW of agar-sugar solutions stays with 10 K almost constant.

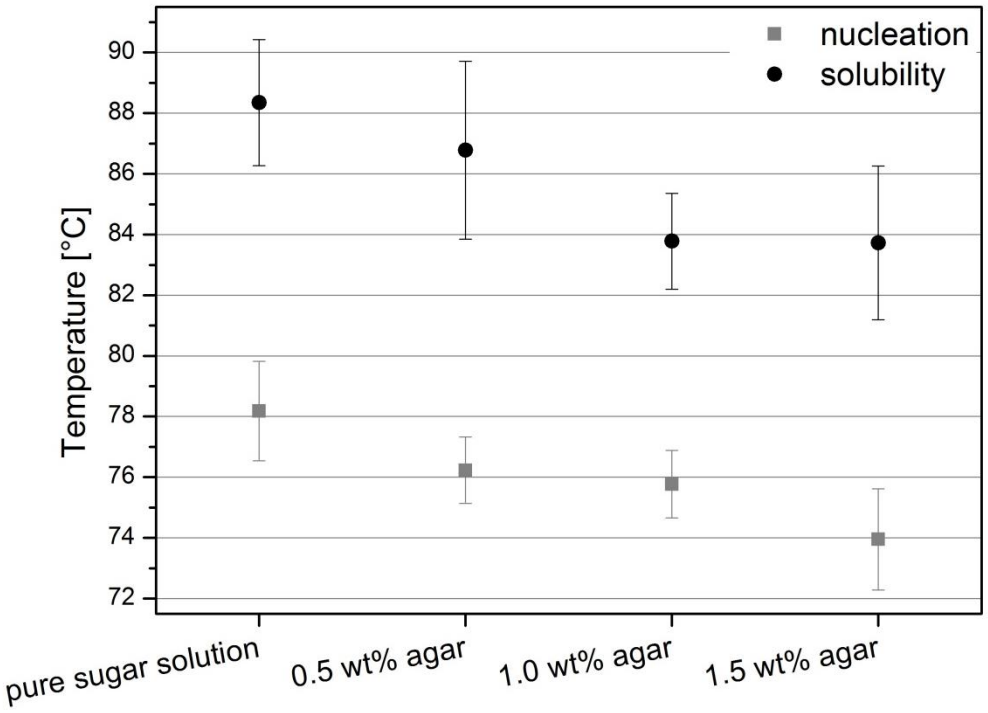

Figure 5.4-1: Metastable zone of sugar solutions with different agar amounts

Solutions containing gelatin show an even more clearly shift of the MZW (see Table 5.4-1) compared to agar-sugar solutions. Other publications dealt already with the influence of different additives on the metastable zone of a supersaturated sugar solution and could show some changes e.g. when citric acid [Sel15] or caffeine [Sel14] as additives were used.

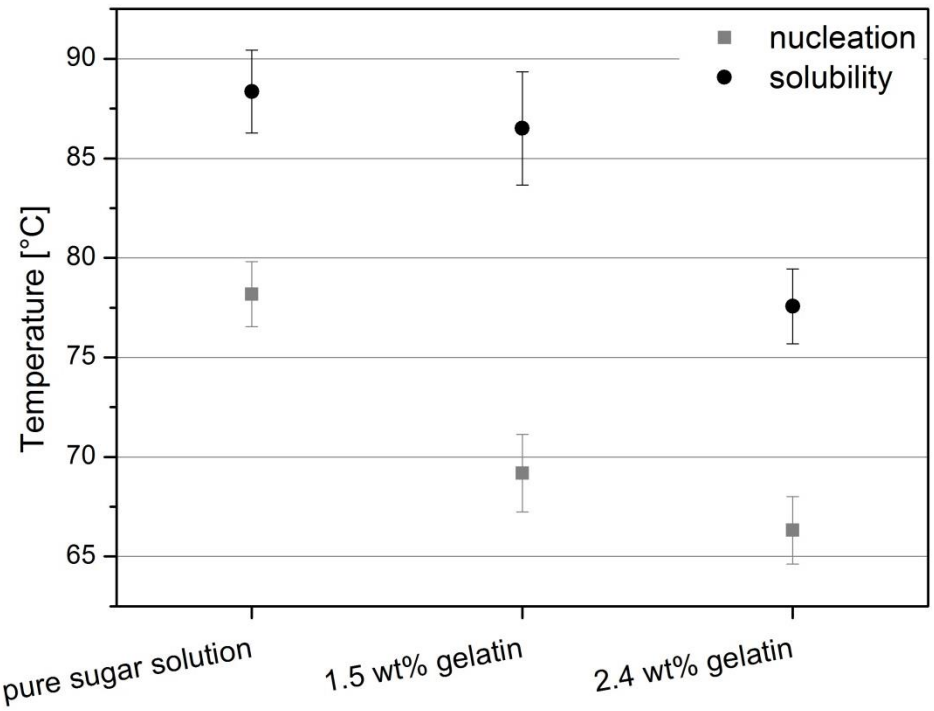

Figure 5.4-2: Metastable zone width of gelatin-sugar solutions [Her16]

The nucleation temperature changes from 78 °C without gelatin to 66 °C with 2.4 wt% gelatin (see Figure 5.4-2). With a higher amount of gelatin the solubility temperature decreases. 1.5 wt% gelatin-sugar solutions have a solubility temperature of approx. 86 °C that is a slightly lower temperature compared to a pure sugar solution with approx. 88 °C. With a 2.4 wt% gelatin-sugar solution the solubility temperature decreases to approx. 77 °C that are more than 10 K difference between 2.4 wt% gelatin-sugar solution and pure sugar solutions.

Table 5.4-1 gives an overview of results measured by the turbidity measurement. Beside gelatin and agar containing sugar solutions also κ-carrageen were measured with a slower heating and cooling rate (6 K/h). Assuming that the solubility is independent of the cooling and heating rate, the measured solubility of a low concentrated κ-carrageen-sugar solution is similar (89 °C) to the solubility of pure sugar solutions (88 °C). Nucleation temperature of 0.2 wt% κ-carrageen is 83 °C (see Table 5.4-1).

Table 5.4-1: Metastable zone of hydrocolloid-sugar solutions with standard deviation measureed by turbidity measurements

Additiv (heating rate)	**Nucleation [°C]**	**Solubility [°C]**	**MZW [K]**
pure sugar solution (9 K/h)	78.18 ± 2.01	88.35 ± 2.55	10.17
1.5 wt% gelatin (9 K/h)	69.18 ± 2.36	86.5 ± 3.49	17.32
2.4 wt% gelatin (6 K/h)	66.32 ± 2.08	77.57 ± 2.31	11.25
0.5 wt% agar (9 K/h)	76.23 ± 1.34	86.78 ± 3.59	10.55
1.0 wt% agar (9 K/h)	75.77 ± 1.36	83.78 ± 1.94	8.01
1.5 wt% agar (9 K/h)	73.95 ± 2.04	83.73 ± 3.10	9.72
0.2 wt% κ-carrageen (R) (6 K/h)	82.59 ± 3.51	88.94 ± 3.50	6.35

Due to limited heating and cooling rates and usable temperatures of the turbidity measurements additionally, the ultrasound technique was used.

Solutions with κ-carrageen (C) show a wider MZW, especially at slower heating and cooling rates compared to pure sugar solutions (see Table 5.4-2). In general, no clear tendency of changes in MZW of the different carrageen solutions can be made.

Table 5.4-2: Metastable zone of hydrocolloid-sugar solutions with standard deviation measured by ultrasound technique

Additiv (heating rate)	Nucleation [°C]	Solubility [°C]	MZW [K]
pure sugar solution (6 K/h)	73.78 ± 0.18	90.83 ± 1.20	17.05
0.5 wt% κ-carrageen (C) (6 K/h)	56.27 ± 1.36	82.88 ± 1.34	26.61
pure sugar solution (9 K/h)	69.22 ± 2.98	84.08 ± 0.77	14.86
0.2 wt% κ-carrageen (R) (9 K/h)	77.03 ± 1.63	87.38 ± 1.04	10.35
0.3 wt% κ-carrageen (C) (9 K/h)	71.09 ± 0.32	88.25 ± 1.59	17.16
0.5 wt% ι-carrageen (9 K/h)	70.94 ± 1.30	81.60 ± 0.84	10.66

For ι-carrageen, the solubility is more than 2 K lower and for κ-carrageen the solubility temperatures are 3 – 4 K higher compared to the measured solubility of pure sugar solutions (see Table 5.4-2). The MZW is for all solutions very different and fluctuates from approx. 10 to 27 K with no clear tendency. The standard deviation for the ultrasound measurements are lower (< 3.0 °C) compared to standard deviations of measurements with the turbidity device (3.6 °C).

A clear difference between the different measuring techniques (turbidity and ultrasound) for pure sugar solutions is detectable (see Table 5.4-3).

Table 5.4-3: Comparison between heating and cooling rates and measuring techniques

Technique (heating rate)	Nucleation [°C]	Solubility [°C]	MZW [K]
pure sugar solution (9 K/h) **Turbidity**	78.18 ± 2.01	88.35 ± 2.55	10.17
pure sugar solution (9 K/h) **Ultrasound**	69.22 ± 2.98	84.08 ± 0.77	14.86
pure sugar solution (6 K/h) **Ultrasound**	73.78 ± 0.18	90.83 ± 1.20	17.05

The MZW of sugar solutions measured with the turbidity technique is smaller compared to the MZW of measurements with the ultrasound technique. The different heating rates for pure sugar solutions show for the same method (ultrasound) clear differences. More than 6 K difference in solubility temperatures for sugar solutions measured with ultrasound and different cooling and heating rates was measured. The used method and the cooling rates have beside the used additive a strong impact on the measured solubility and nucleation temperatures.

5.5 Properties of seed materials to enforce nucleation

It is important to know about the properties of different seed materials, to enforce the crystallization of coated sweets. Depending on the nucleation behavior of a sugar solution a specific nucleation state must be reached to create, e.g. a reproducible crystallized sugar layer. Here, the use of heterogeneous nuclei (different starch types) to provide a surface, where sugar can crystallize, was tested. Without enforcing the nucleation a homogeneous, reproducible crystallized layer is not reachable (see Figure 5.5-1).

Figure 5.5-1: Crystallization in the absence of seed materials in a 1.0 wt% agar-sugar solution [Her16]

Figure 5.5-2 shows the particle size distribution of the tested seed materials. Here, different starches, flours and icing sugar were used. Corn and tapioca starch have similar size distributions (orange line and dotted blue line) from 6 to 30 µm. Rice starch is a little bit smaller than corn and tapioca starch. Rice starch shows a noticeable wide range of the particle sizes (2 - 125 µm) due to agglomeration (see Figure 5.5-2, dotted, light blue line).

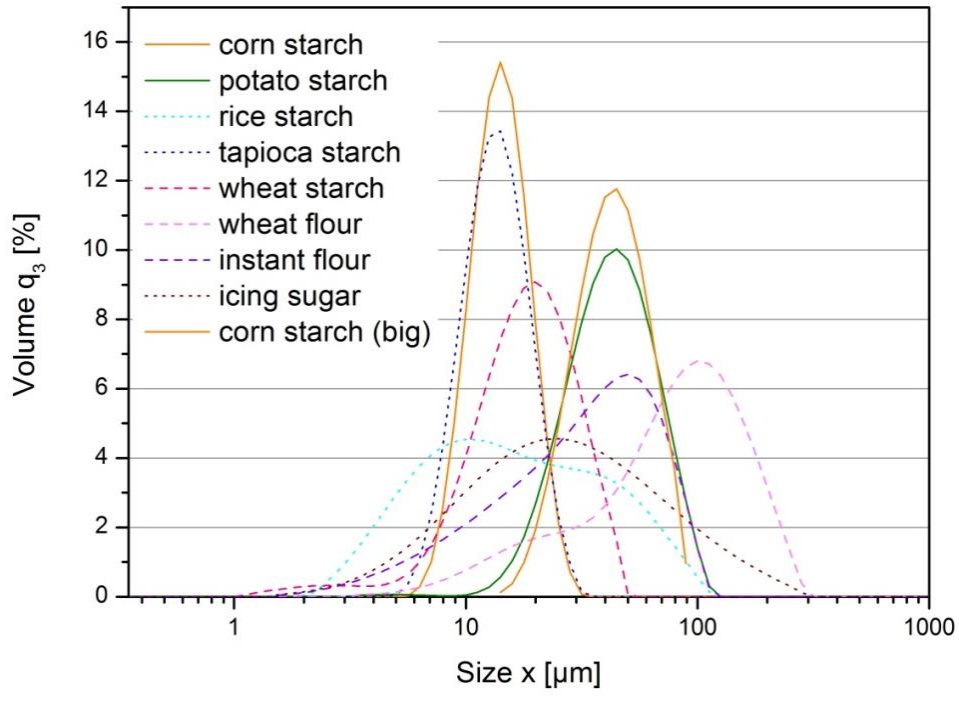

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Figure 5.5-2: Volume-weighted particle size distribution density, $q_{3,}$ of different seed materials [Her16a]

Wheat starch (dashed, pink line), potato starch (green line) and instant flour (purple dotted line) are with an average size of mostly 20, 40 and 50 µm, respectively, a little bit larger compared to the other seed materials (size 10 - 14 µm) (see Figure 5.5-2). The biggest average size shows wheat flour (rose, dotted line). The different flours as well as icing sugar show a wider particle size range and bigger mean sizes (see Figure 5.5-2).

All measured particle sizes show comparable values to the literature (see Table 5.5-1). Only rice starch shows bigger values due to a very wide measured particle size distribution. Figure 5.5-3 (rice starch) confirms the characteristic of forming agglomerates. Therefore, mode, mean size and median values of rice starch differ more than for the other tested starch materials (see Table 5.5-1).

Table 5.5-1: Characteristics of particle size distributions of different seed materials compared to the literature [Teg02]

Materials	x (Q_3= 5 %) [µm]	Mode [µm]	Mean size [µm]	Median [µm]	x (Q_3= 95 %) [µm]	Literature [Teg02] [µm]
corn starch	8.2	14.1	14.6	13.3	21.3	10 - 25
potato starch	18.4	44.7	45.7	40.2	78.4	5 - 100
rice starch	3.8	10.0	23.0	14.4	63.5	2 - 10
tapioca starch	7.3	14.1	14.0	12.6	21.5	5 - 35
wheat starch	6.0	20.0	19.5	17.3	35.1	2 - 15 or 30 - 40
wheat flour	12.4	100.0	90.5	77.4	192.1	-
wheat flour instant	5.5	50.1	37.2	31.5	78.1	-
icing sugar	5.0	25.1	40.2	24.2	121.9	-
corn starch (big)	21.2	44.7	44.6	40.1	70.3	-

Figure 5.5-3 illustrates the surface of the different seed materials. Whereas corn and rice starch appear more edged/polygonal, potato, tapioca and wheat starch show more rounded particles with an even and regular surface. The image (top right) of rice starch illustrates clearly the tendency to form agglomerates. Corn and tapioca starches differ in their surface appearance but have similar sizes. The wheat starch particles seem to be pressed flat and are not as round as potato starch particles. Icing sugar particles have sharp edges and wheat flour show merged big particles as well as very small particles (see Figure 5.5-3).

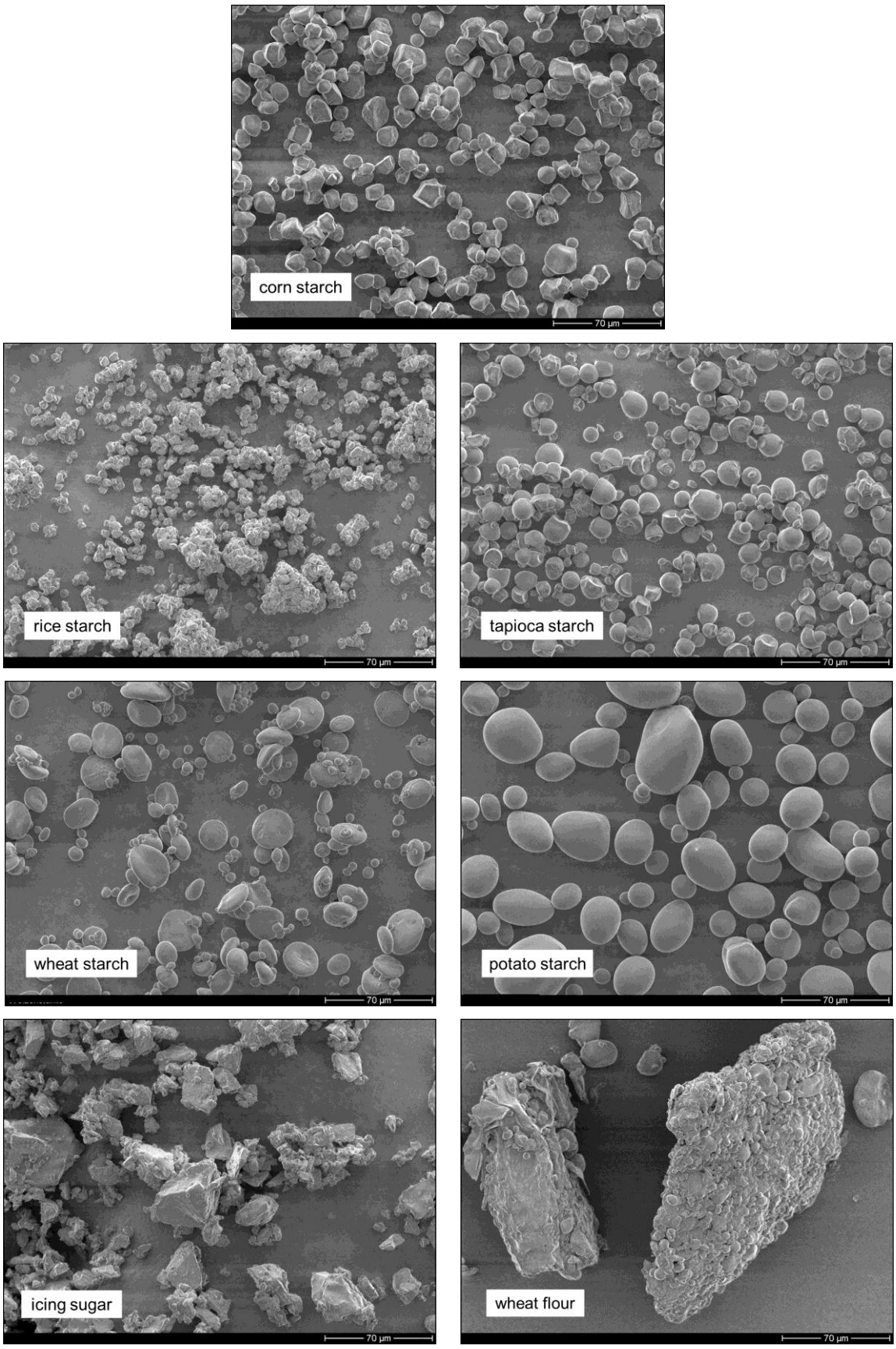

Figure 5.5-3: SEM images of different seed materials (Magnification: 1000) [Her16a]

Beside the particle size and surface of the seed materials, the ability to hold up the moisture (solvent) can have an influence on the nucleation of sugar solutions. Table 5.5-2 shows the moisture values for different seed materials measured after storage at 22 and 50 °C for 24 hours and the standard deviation of three measurements. In general, the moisture content of the different seed materials depends not only on the different physical properties, but also on the ambient conditions (air moisture, air temperature, air circulation) and whether the seed materials are new or frequently used before. Icing sugar has got the lowest moisture content at ambient temperature (0.31 %) and after drying (0.38 %) compared to the other materials. The commonly used corn starch has got together with rice and wheat starch lower moistures after storage at 22 °C whereas potato starch holds the highest moisture content after the first use (see Table 5.5-2, left column). After drying for the first time at 50 °C all powders have the same moisture content (approx. 6.5 %) except for tapioca and potato starch with higher moisture values (> 8 %).

Table 5.5-2: Ability to hold up moisture during first use of seed materials

Seed Materials	Moisture [%] at 22 °C	Moisture [%] at 50 °C
corn starch	11.43 ± 0.11	6.55 ± 0.03
potato starch	19.03 ± 0.67	9.44 ± 0.02
rice starch	10.90 ± 0.03	6.41 ± 0.35
tapioca starch	13.84 ± 0.11	8.33 ± 0.09
wheat starch	11.69 ± 0.10	6.21 ± 0.11
wheat flour	11.78 ± 0.25	6.38 ± 0.08
wheat flour instant	13.95 ± 0.08	6.88 ± 0.10
icing sugar	0.31 ± 0.02	0.38 ± 0.19

During the production of sweets in confectionary industry the seed materials were used frequently and are recycled for reuse. After sieving to remove impurities (e.g. crystallized sugar drops) the seed materials were dried. After a frequent drying at 50 °C all seed materials have moisture contents between 4.7 and 5.5 % (see Table 5.5-3), except for icing sugar with a lower moisture of 0.3 %.

Table 5.5-3: Moisture content of seed materials (reused) after different storage times

	Moisture content [%] after drying and at ambient temperature (22 °C)		
Seed Materials	**24 h drying at 50 °C**	**14 days at ambient temperature**	**28 days at ambient temperature**
corn starch	4.84	8.11	7.58
potato starch	4.77	8.72	7.95
rice starch	5.05	8.54	7.60
tapioca starch	5.50	8.98	8.38
wheat starch	5.10	8.74	8.16
wheat flour	4.81	8.06	7.87
wheat flour instant	4.77	8.50	7.57
icing sugar	0.28	0.36	0.51

In general, the moisture content of the seed materials is easily affected by the daily variability of ambient temperature and humidity (see Table 5.5-3). The moisture content of the seed materials changes up to 1 % depending on the ambient conditions. Relative humidity of the air at 22 °C was 30.4 ± 5.5 %H and at 50 °C 11.4 ± 1.8 %H.

Not all seed materials are able to shape the end products in a desired way. Figure 5.5-4 shows some powder molds filled with bigger corn starch (left image) or potato starch (right image). Both materials have particle sizes larger than 44 µm. The negative imprints are not stable and the side walls slide down (see Figure 5.5-4).

Figure 5.5-4: Molds (left: Bigger corn starch; right: Potato starch)

Both powder molds (filled with corn or potato starch) lead to products with an undesired not controllable shape as can be seen in Figure 5.5-5.

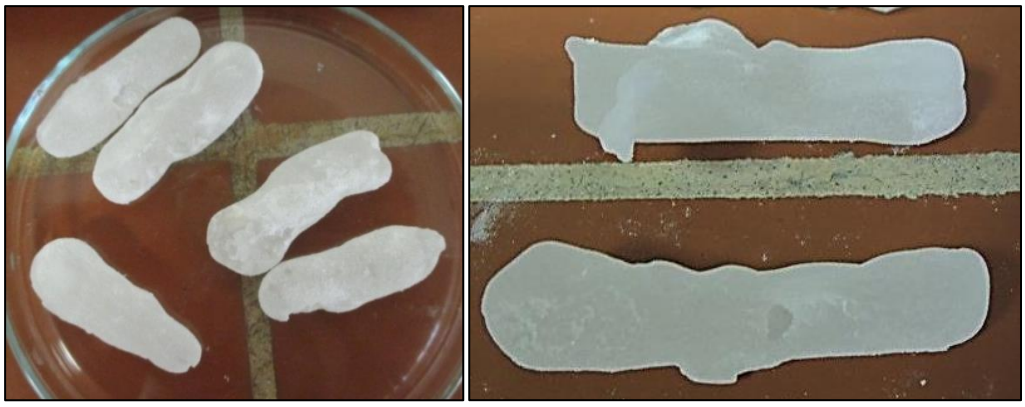

Figure 5.5-5: Crystallized products (left: Bigger corn starch, right: Produced in potato starch)

The moisture content within the seed material has to be controlled to achieve desired end products. Pouring the sugar solution in corn starch molds with different moisture contents lead to different results for the production process. The moisture content should not exceed 6 %, because otherwise, the material is not completly removable. Measurements of the layer thicknesses show with 10 % moisture of the corn starch material an increasing average layer thickness (see Figure 5.5-6).

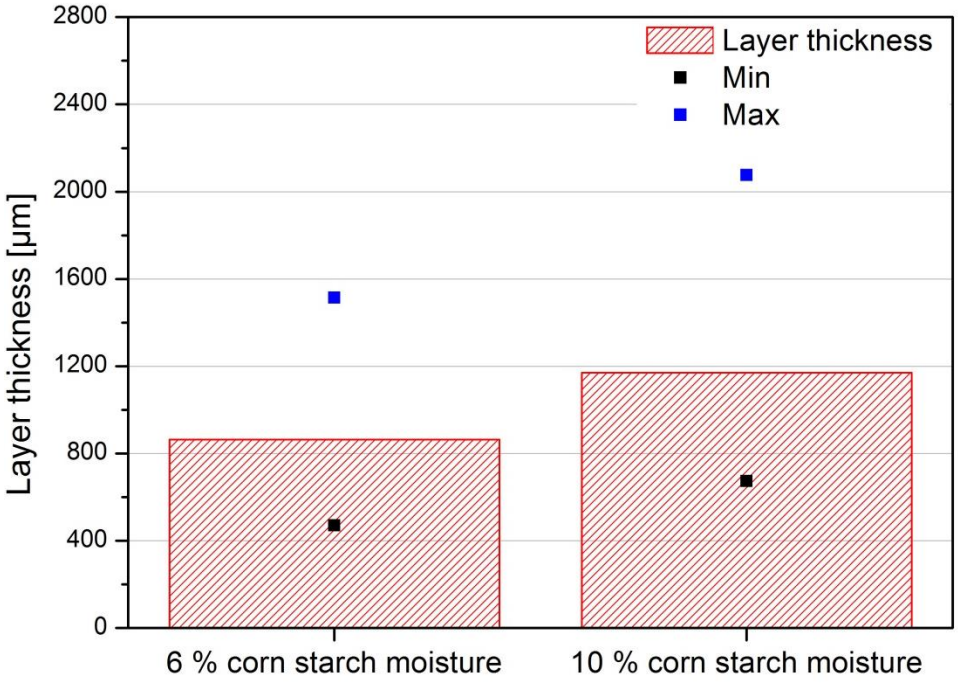

Figure 5.5-6: Layer thicknesses of crystallized products produced in different moisture contents

Often occurring phenomena with 10 % moisture in the corn starch material are holes on the upper side of the product as can be seen in Figure 5.5-7, marked with the red arrow.

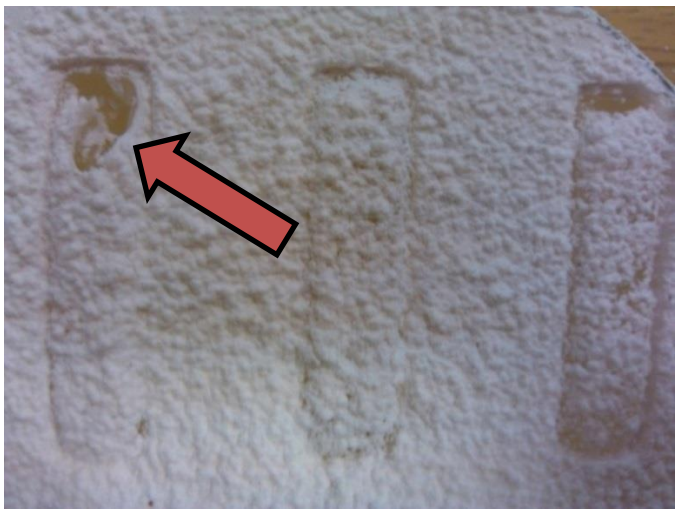

Figure 5.5-7: Defects of crystallized products produced in corn starch with 10 % moisture

These outer conditions of different moistures within a seed material do not lead to changes in the measured sugar content within the liquid core. The sugar content decreases over time in the same extent no matter which moisture the corn starch has (see Figure 5.5-8). The same was also measured for e.g. 1.5 wt% agar products in corn starch or icing sugar powder molds (see Appendix, Table 11-6). Experiments with κ-carrageen (R) products show that the process of depowdering after 24 hours shows the same values for the measured sugar concentration within the gel core over time (see Appendix, Table 11-3).

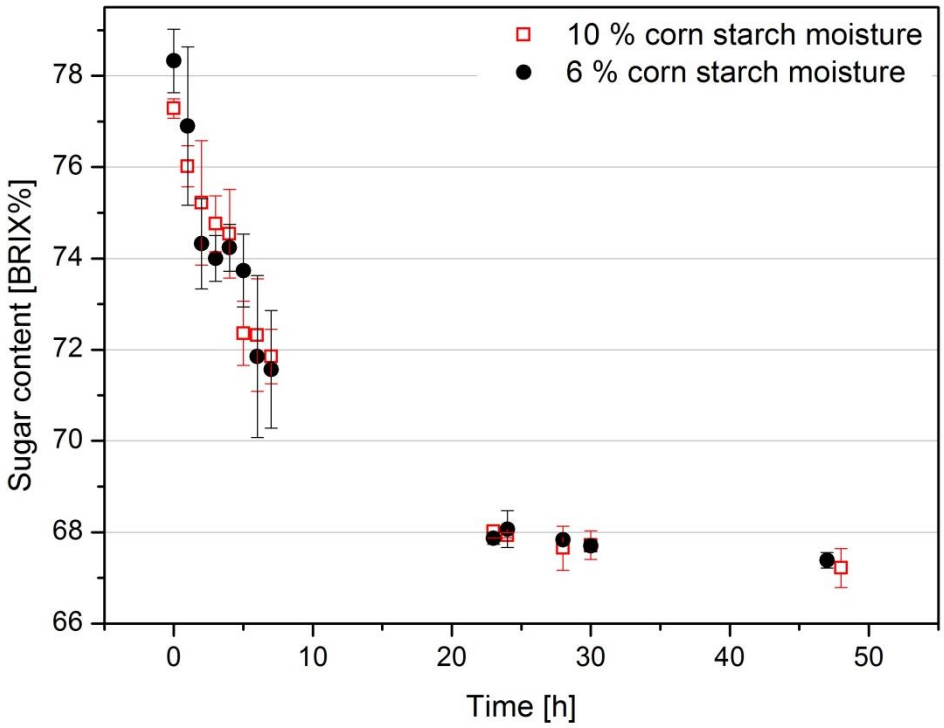

Figure 5.5-8: Sugar content within the liquid core of crystallized products over time with different starch moistures

Even higher moistures (10 %) lead to useless products that means no regularly liquid core enclosed by a crystallized sugar layer is achievable. Figure 5.5-9 shows the results with high moisture contents. This moisture content was reached by storing the corn starch molds in a desiccator filled with water.

The products have a big starch layer, which is not easy removable and the sugar bodies are empty shells without a liquid core (see Figure 5.5-9, right image).

Figure 5.5-9: Crystallized products produced in corn starch with 15 % moisture (left: Starch attachment; right: Powder free)

Figure 5.5-10 illustrates the influence of different seed materials on the measured layer thickness of coated gels. All layers produced in an icing sugar mold no matter which kind of hydrocolloid or amount of hydrocolloid was used, are thicker compared to layers produced in a starch powder mold.

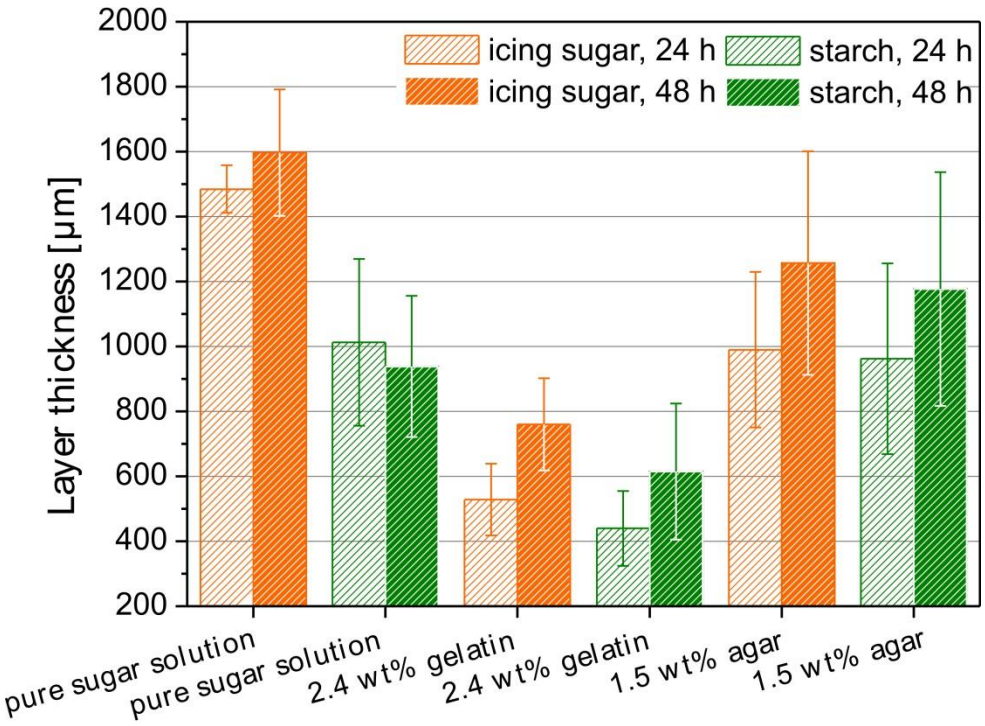

Figure 5.5-10: Comparison of layers produced in icing sugar or in corn starch [Her16]

Figure 5.5-11 shows layer thicknesses of gelatin products. These products were removed from the powder molds after different times. Commonly, the products were removed after 24 hours. Here, the results with storage without depowdering were shown.

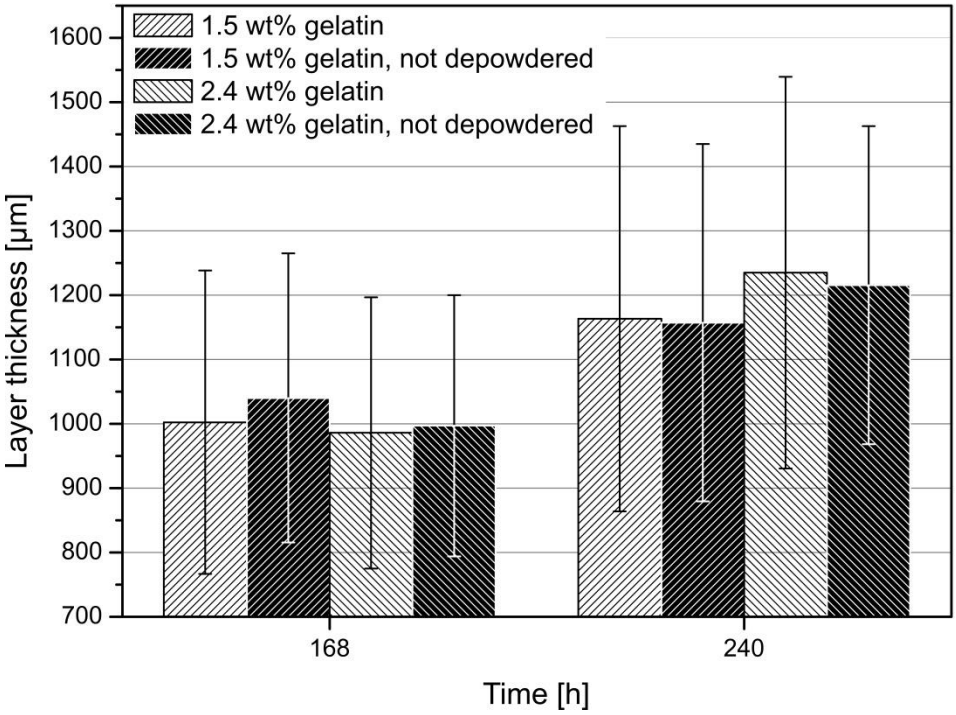

Figure 5.5-11: Differences of layer thicknesses with and without depowdering of the end products after 24 hours

No matter if the products were depowdered after 24 hours, that means removed from the powder molds or not, no big differences in layer thicknesses were measured (see Figure 5.5-11).

All used seed materials (rice, tapioca, potato, wheat starch, wheat flour and instant flour and icing sugar) except for corn starch are not able to initiate the nucleation at the surface of a supersaturated sugar solution in the same extent as corn starch. After 2 and even 5 hours only a thin not crystallized surface layer appears at ambient temperature (22 °C), especially, at the upper side of the products where the seed material is sprinkled on top (see Figure 5.5-12). Even the surface of the different particles can affect the production of crystallized products concerning the product shape (see Figure 5.5-12, left image).

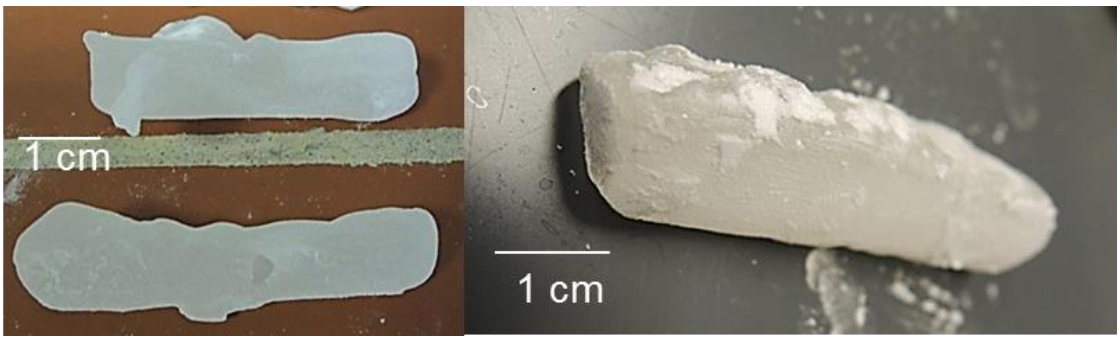

Figure 5.5-12: Products produced with potato starch (left image) and tapioca starch (right image) as seed material [Her16a]

Crystallizing at 50 °C (not at 22 °C) leads to different results than crystallization at ambient conditions. Figure 5.5-13 shows petri dishes filled with a supersaturated sugar solution and sprinkled on top with different seed materials. After 24 hours the seed materials were removed, resulting in different surfaces (see Figure 5.5-13). At these “hot” conditions (50 °C), crystallization on the surface of a sugar solution with e.g. rice, tapioca wheat, potato starch as well as for the flours (wheat type 405 and instant) and icing sugar as alternatives to corn starch is possible. However, differences in crystallization results enforced by different materials can be seen. Corn starch, rice starch and icing sugar lead to a smoother surface compared to the other materials (wheat starch, tapioca, not dried potato starch and the flours). Not all materials are fully removable. Tapioca starch, wheat flour and instant flour sticks on the surface partially due to holes and leaking solution (see Figure 5.5-13).

Figure 5.5-13: Crystallization in petri dishes (d ≈ 11.0 - 11.5 cm) with different seeds, at 50 °C [Kat16]

To evaluate the effect of particle sizes of the seed materials, fractions were separated by sieving. Smaller particle sizes (< 63 µm) were separated from fractions with larger sizes (> 80 µm). Results from, e.g. potato and rice starch at high temperatures (50 °C) and air moisture contents of 11.4 ± 1.8 %H show that larger particles do not influence the nucleation step more positively than the smaller ones.

The surface quality, however, is affected by the particle size (see Figures 5.5-13 and 5.5-14). Larger particles of the used external seed materials create rougher and less smooth surfaces of the crystalline material compared to smaller particles (corn or rice starch).

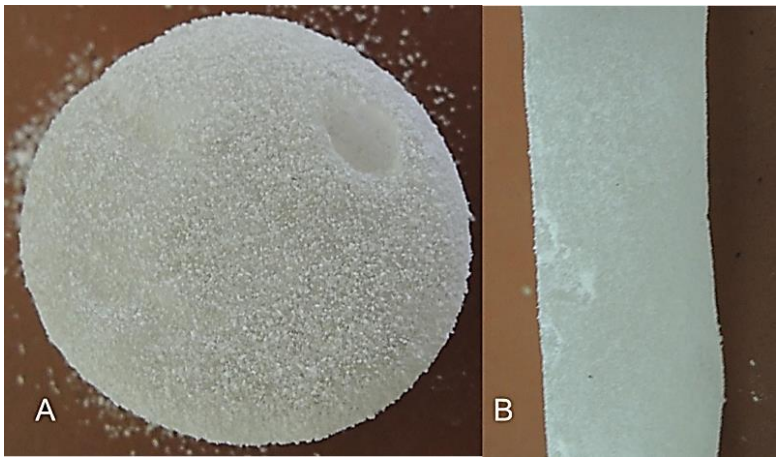

Figure 5.5-14: Surface quality of crystallized products, A: Seed material instant flour, B: Seed material wheat flour [Kat16]

5.6 Sugar content in gel during crystal layer growth

Figure 5.6-1 shows the sugar content within the gels over time and should illustrate the slow decrease in supersaturation. Generally, a higher amount of sugar in gel leads to the conclusion that less sugar is mobilized to the layer.

The decrease of supersaturation for a 1.5 wt% agar containing sugar solution (see Figure 5.6-1, red circles) is significantly slower compared to pure sugar solution (see Figure 5.6-1, black squares). The slowest decrease in supersaturation takes place in a sugar solution containing 2.4 wt% gelatin (see Figure 5.6-1, blue triangles). The shown standard deviation of the sugar contents is for pure sugar smaller than for the measured gel cores (agar and gelatin).

All measured sugar concentrations (Brix%) over longer storage times (0 - 672 hours) of all hydrocolloid-sugar solutions can be seen in the Appendix, Table 11-8.

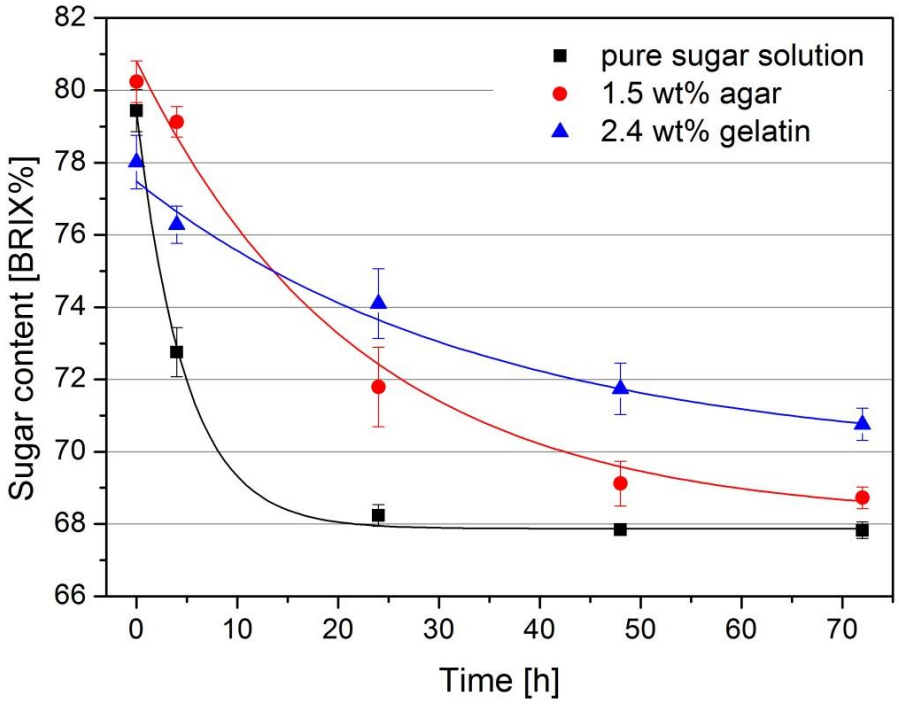

Figure 5.6-1: Decrease of sugar in gel core over time of agar, gelatin and pure sugar [Her16]

The decrease of sugar content within the gel of carrageen products is shown in Figure 5.6-2. The highest difference in sugar content decrease is shown between the cases for pure sugar and carrageen after 24 hours. Carrageen gels have after 24 hours higher sugar content than the products of pure sugar solution. The decrease of sugar within the gel core is the slowest with ι-carrageen (see Figure 5.6-2, orange squares) compared to the other carrageenans and pure sugar solution.

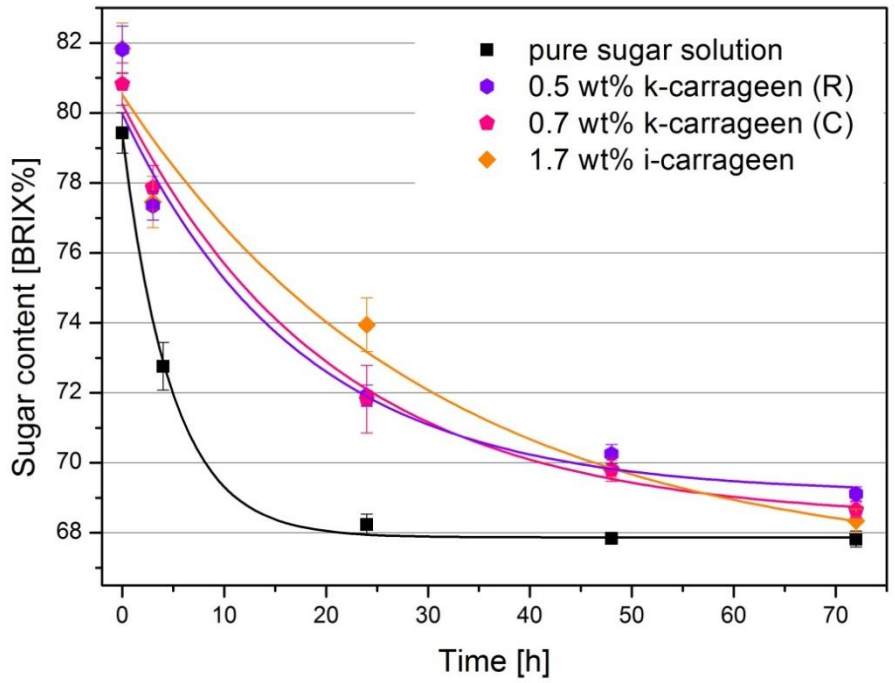

Figure 5.6-2: Decrease of sugar in gel core over time of carrageenans and sugar

5.7 Influence of hydrocolloids on sugar layers

Figure 5.7-1 shows the layer thicknesses of the products produced with a pure sugar solution. After 24 hours the crystalline layer stays constant (approx. 980 µm). Little differences (< 100 µm) occur in average values and standard deviation. The standard deviation for the layer thicknesses are high (200 µm) and show the roughness of the layers.

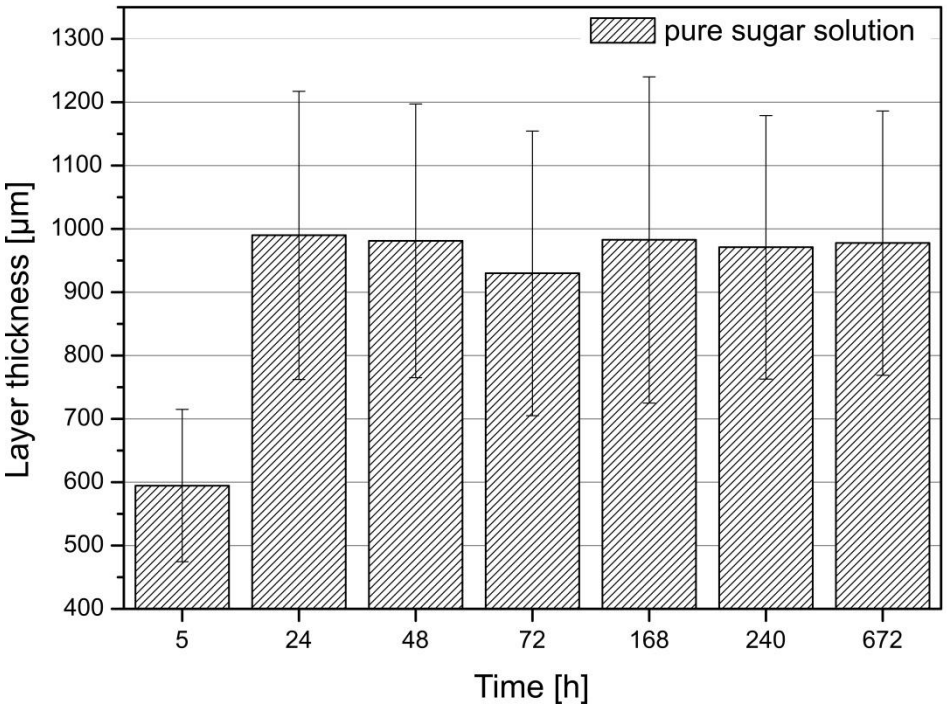

Figure 5.7-1: Layer thicknesses of sugar bodies without hydrocolloids over time with standard deviation

The use of hydrocolloids during the production of crystalline coated gels lead to differences in measured layer thicknesses. Depending on the type, amount of hydrocolloid and storage time the layer thicknesses can vary.

The used amount of agar changes the measured layer thicknesses as shown in Figure 5.7-2, measured after 24 and 48 hours. The more agar was used the higher the measured layer thickness is. The layer thicknesses increase by time (from 24 to 48 hours).

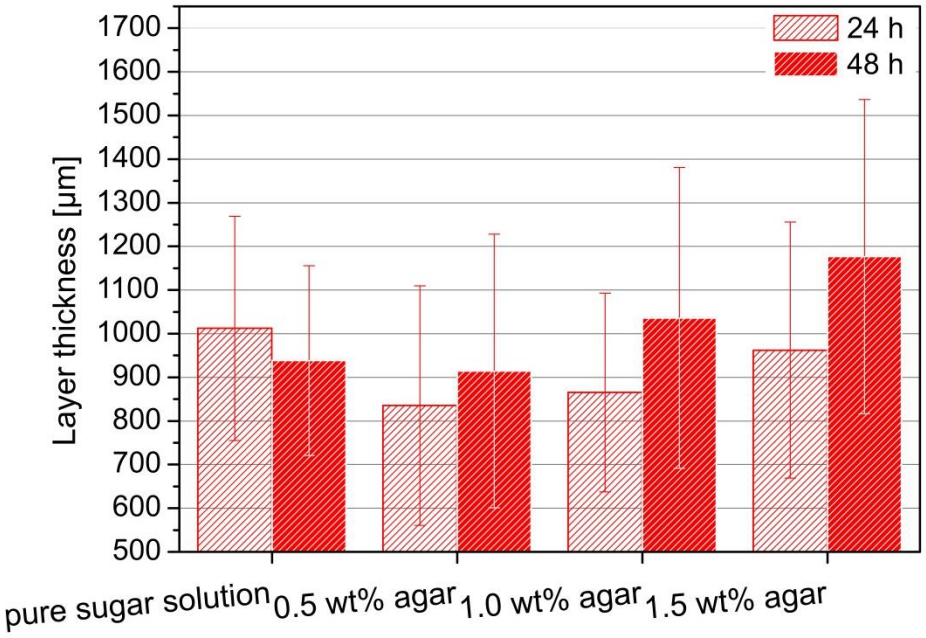

Figure 5.7-2: Layer thicknesses after 24 and 48 hours with different agar concentrations in a starch powder bed [Her16]

A contrary effect can be seen by using gelatin. Figure 5.7-3 shows the effect of different amounts of gelatin (1.5 and 2.4 wt% gelatin) on the layer thicknesses after 24 and 48 hours. The more gelatin was used the thinner the measured layer thicknesses were. The thickness increases for 1.5 wt% gelatin around 200 µm comparing 24 and 48 hours. The increase in layer thickness for the application of 2.4 wt% gelatin is a little bit smaller with 150 µm within 24 hours compared to products containing 1.5 wt% gelatin.

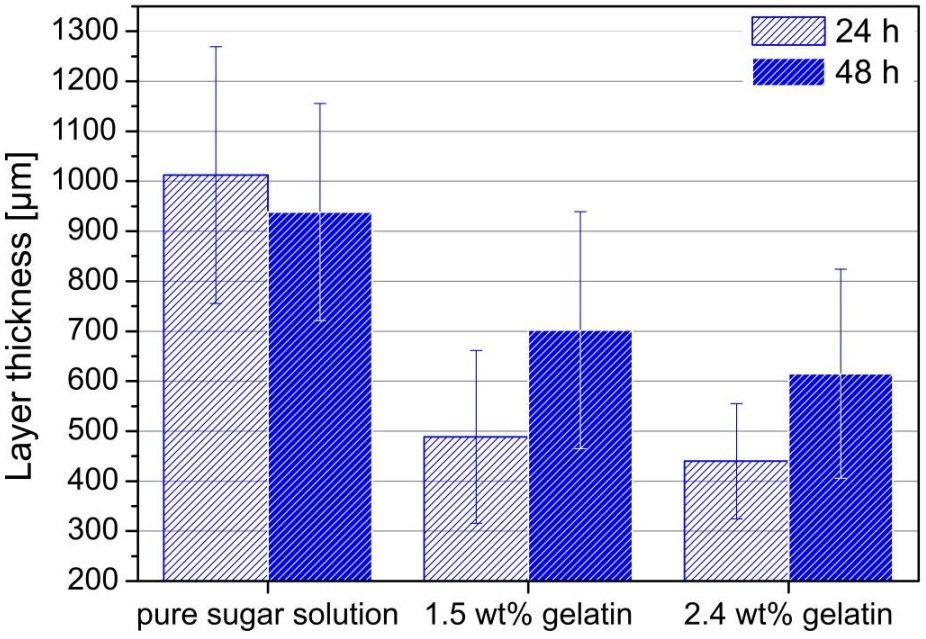

Figure 5.7-3: Layer thicknesses after 24 and 48 hours with different gelatin concentrations in a starch powder bed [Her16]

Different concentrations of carrageen lead to differences in the measured layer thicknesses after 24 and 48 hours (see Figure 5.7-4). Lower amounts (1 wt%) ι-carrageen show layer thicknesses of 1100 µm after 24 hours. Higher ι-carrageen amounts (1.7 wt%) decrease the layer thickness after 24 hours around 200 µm. After 48 hours of storage ι-carrageen products decrease in layer thickness for 1.0 wt% and increase for 1.7 wt% ι-carrageen. κ-carrageen products (0.2 wt% and 0.5 wt%) from Roth show comparable layer thicknesses of 900 µm. The values vary about 100 µm. κ-carrageen from Cargill shows more differences in dependency of the amount and time. The layers of products produced with 0.5 wt% κ-carrageen (C) show smaller values (625 µm) than higher κ-carrageen (C) (0.7 wt%) amounts with 800 µm after 24 hours. The layer thickness increases after 48 hours around 180 µm for both cases (0.5 and 0.7 wt% κ-carrageen (C)). 0.7 wt% κ-carrageen products (C) reach comparable values to pure sugar products (ca. 1000 µm) after 48 hours.

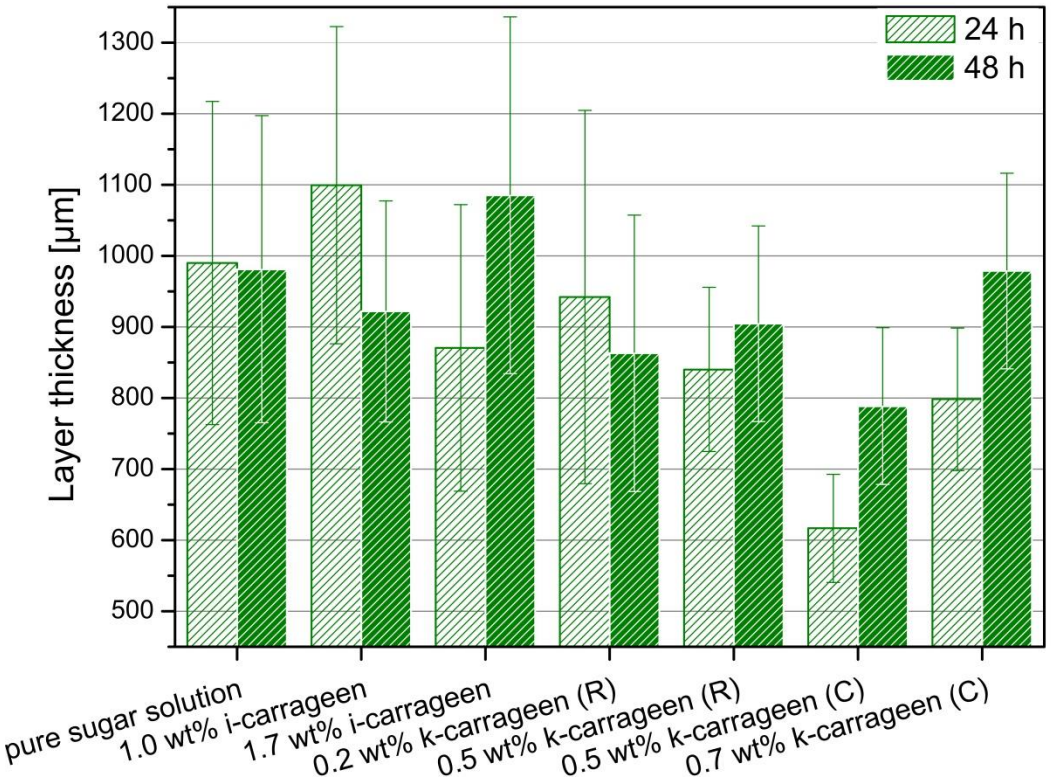

Figure 5.7-4: Layer thicknesses after 24 and 48 hours with different carrageen types and concentrations

Measurements of coated gels over a longer storage time (7 or 10 days) show the crystal layer growth and the changes in crystal layer thickness due to different processes.

For all products the highest amount of hydrocolloids (1.5 wt% agar, 2.4 wt% gelatin, 0.5 wt% κ-carrageen (R), 0.7 wt% κ-carrageen (C), 1.7 wt% ι-carrageen) were used to compare the layer thicknesses with the layer thickness of pure sugar products over a storage time of 240 hours at 22 °C (ambient conditions).

For agar products the layer thickness is similar to pure sugar products after 24 hours (see Figure 5.7-5). With longer storage times (> 7 days) the layer exceeds the layer thicknesses of pure sugar products. After 168 hours the layer thicknesses of 1.5 wt% agar products is about 400 µm higher compared to products produced without hydrocolloids. The standard deviation of products with agar is higher (350 µm) than for products produced with a pure sugar solution (220 µm).

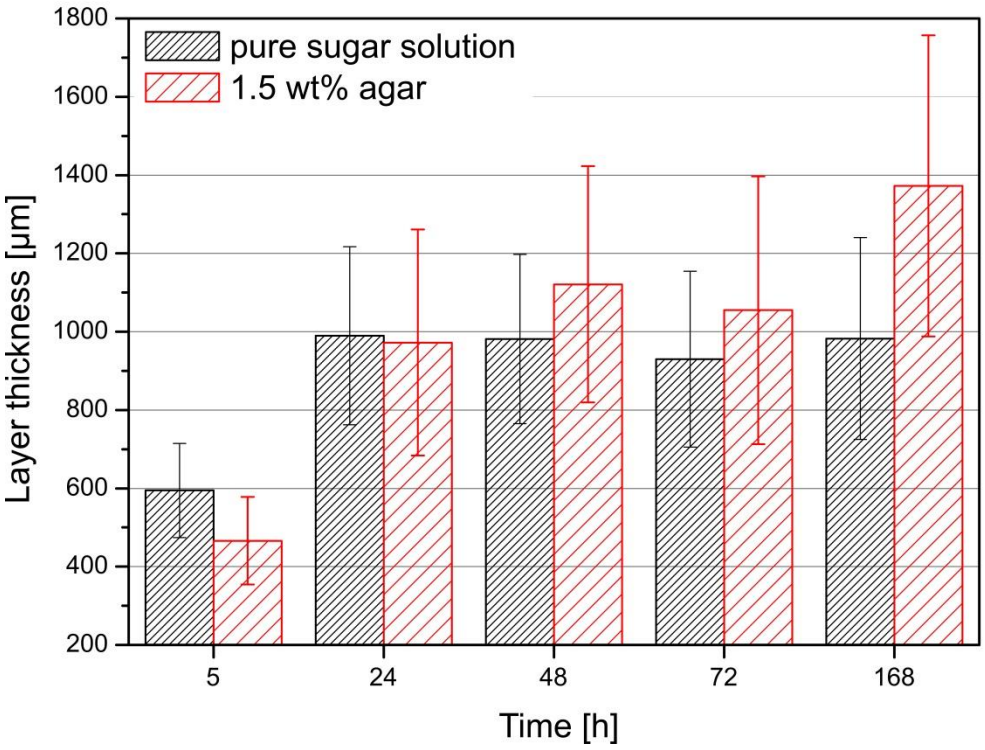

Figure 5.7-5: Sugar layers of agar products compared with pure sugar products over time

Products produced with gelatin show only after 168 hours comparable layer thicknesses to pure sugar products (see Figure 5.7-6). After 24 hours the crystallized layer of gelatin products is 400 µm thinner than products produced without a hydrocolloid.
After 168 hours the layer thicknesses of 2.4 wt% gelatin products and pure sugar products are comparable. Thereafter (storage time 240 hours), the layer thicknesses increase further (200 µm) for gelatin products and the layer thicknesses for pure sugar products stay constant at nearly 1000 µm (see Figure 5.7-3).

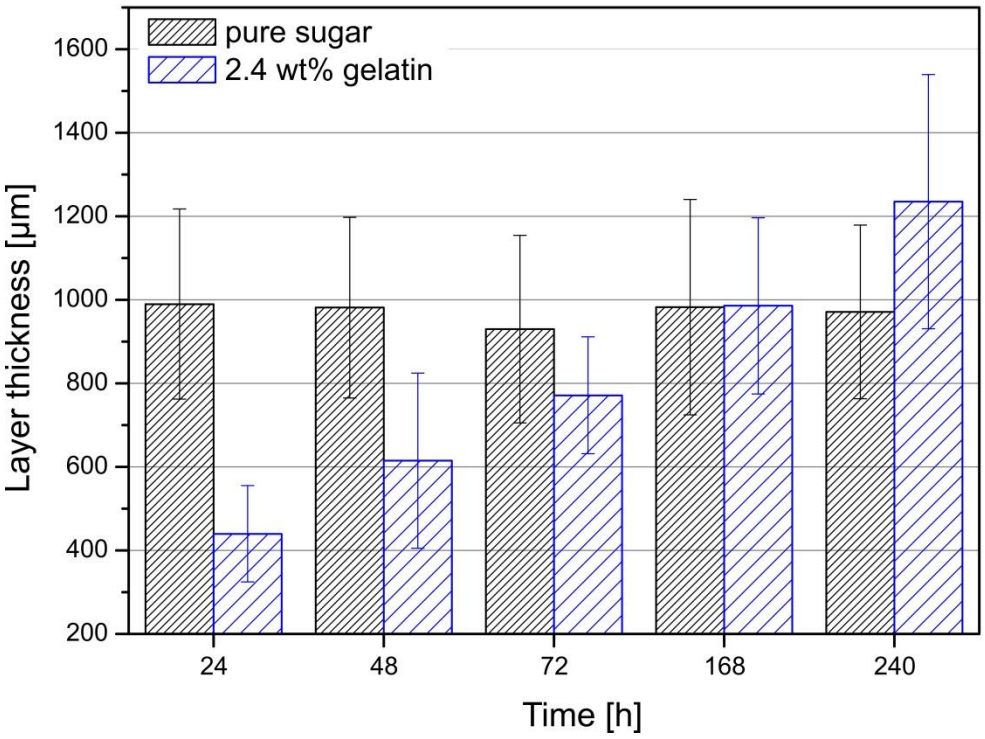

Figure 5.7-6: Sugar layers of gelatin products over time compared with pure sugar products

Products with carrageen show different layer thicknesses. The layers of ι-carrageen products (see Figure 5.7-7, orange bars) show after 48 hours the smallest layer thicknesses. The layer increases after 240 hours further and shows the thickest values compared to all other carrageen and pure sugar products.
κ-carrageen products (0.5 and 0.7 wt%) have after 24 hours similar layer thicknesses but thinner ones compared to products produced with pure sugar (see Figure 5.7-7). After 48 hours the layer of κ-carrageen products increases to comparable values of pure sugar products. Further storage lead to an increased sugar layer thickness. The average layer thicknesses of κ-carrageen products is 300 µm higher compared to products without hydrocolloids after 240 hours.

In general, the layer thickness of products produced with hydrocolloids excides the layer thickness of pure sugar products after 168 hours storage time, except for gelatin. Products with gelatin show only after more than 168 hours thicker layers (see Figure 5.7-6).

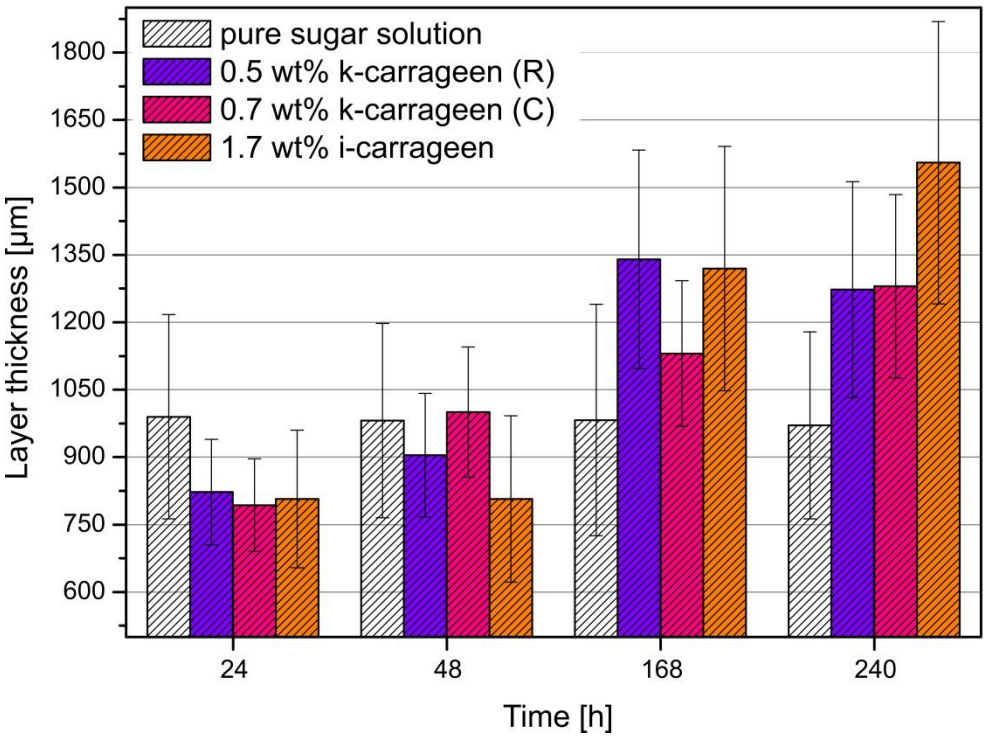

Figure 5.7-7: Layer thicknesses of products produced with carrageenan compared to pure sugar products over time

5.8 Temperature and time dependent storage stability of crystalline coated gels

Figure 5.8-1 shows exemplary the influence of 50 °C storage temperature on layer thicknesses of products produced with ι-carrageen. The storage at 50 °C leads to thinner layer thicknesses of ι-carrageen products compared to a storage temperature at ambient conditions (22 °C). The layer thicknesses of ι-carrageen products are comparable to layer thicknesses of pure sugar products stored at ambient conditions after 168 hours. Further storage time leads to increased layer thicknesses for ι-carrageen products. ι-carrageen products stored at 50 °C have with 1340 µm layer thicknesses in-between of 1.7 wt% ι-carrageen products stored at ambient conditions (1550 µm) and products without hydrocolloid 1000 µm stored for 240 hours (see Figure 5.8-1). The values for the standard deviation are similar for all cases.

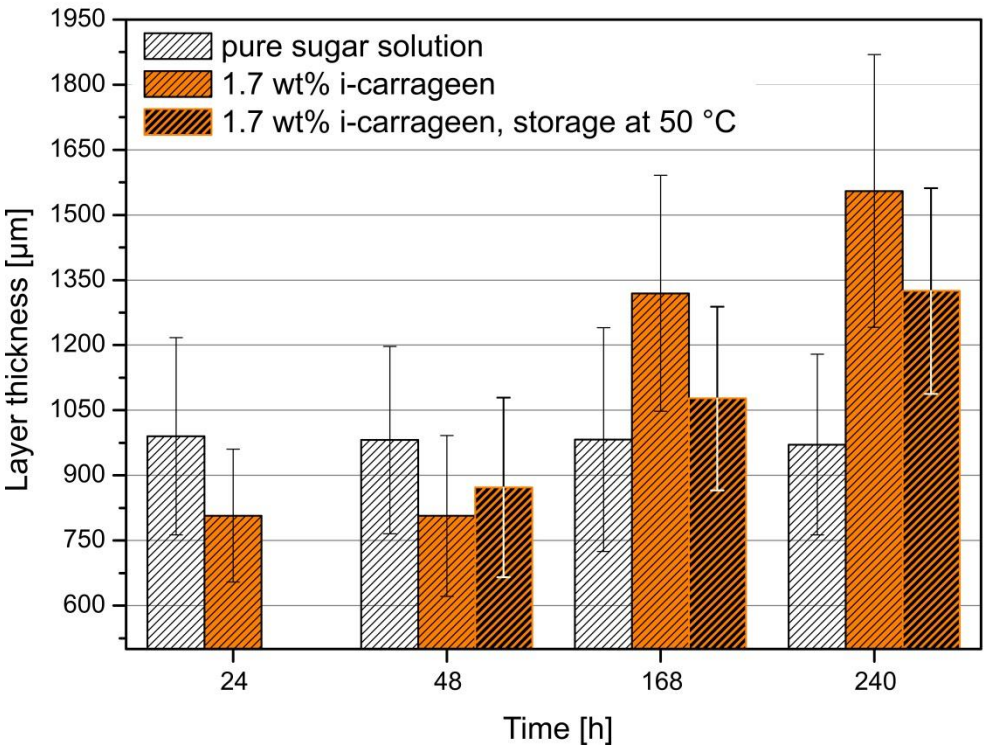

Figure 5.8-1: Storage of ι-carrageen products at different temperatures (22 °C and 50 °C) [Sin16]

Figure 5.8-2 shows the optical changes of ι-carrageen products after 28 days of storage at ambient conditions. After seven days at ambient conditions (22 °C) the layer starts to curve. The products loss water (syneresis happens) and some crystals appear within the gel core (see Figure 5.8-2, image a). Further storage time (10 days) at 22 °C increase the layer thicknesses and within the gel cores air holes appear (see Figure 5.8-2, image b). Storage at ambient conditions for 28 days results in a total drying of the gel core and a torn crystallized layer as well as a thick crystallized layer without a gel (see Figure 5.8-1, image c). Storage at 50 °C shows the clearest effects. The crystallized layer shows a strong curved appearance without a gel core. The color changes slightly to a light yellow (see Figure 5.8-1, image d).

Similar results show products produced with κ-carrageen (compared to ι-carrageen), also crystalline coated gels with gelatin lose their shape and syneresis happens during aging of the product (after 28 days at ambient temperature, different day and night temperature changes, several degrees) but without cracked edges. After 28 days holes and partially crystals within the gel (depending on supersaturation degree and crystallization process) can be found.

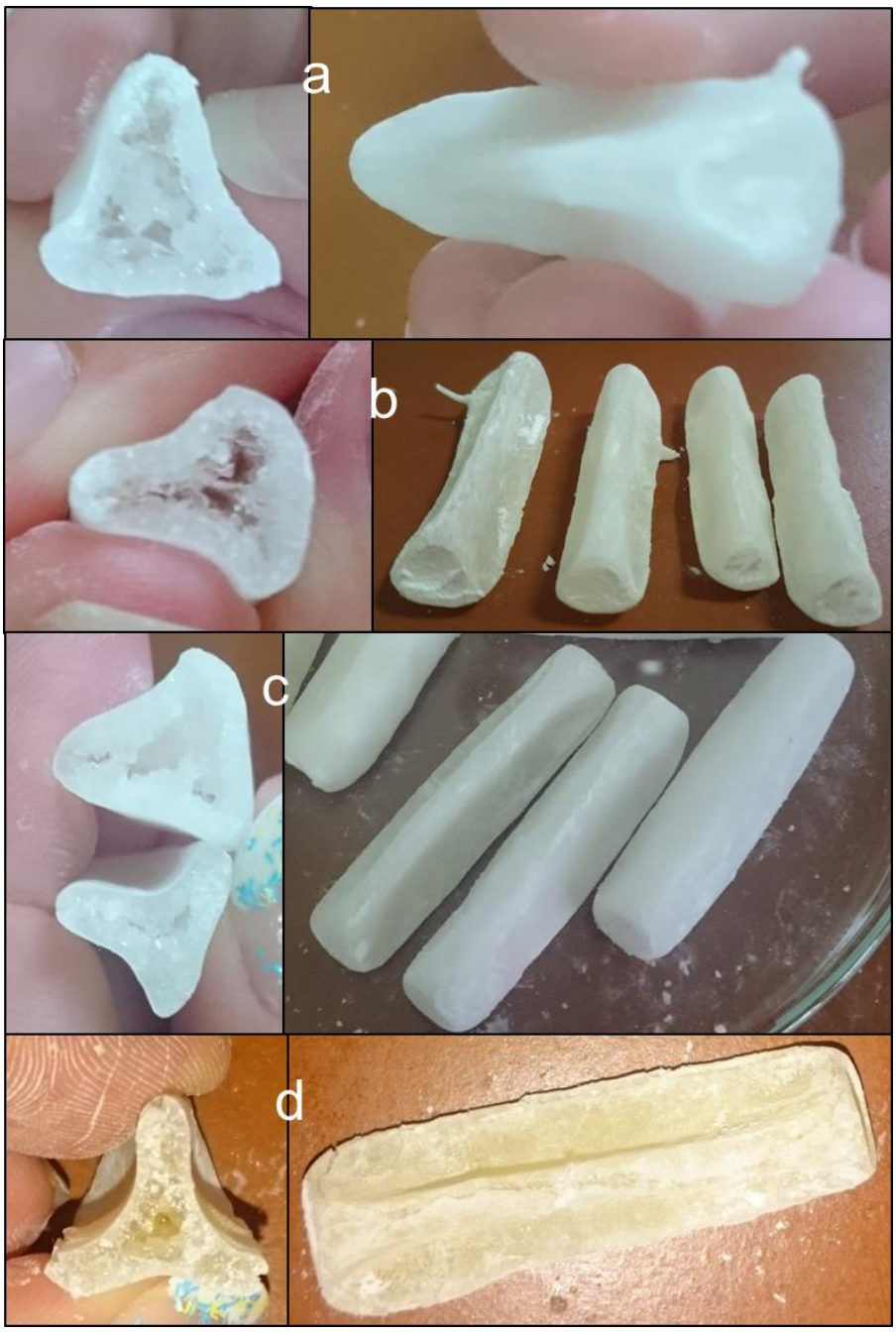

Figure 5.8-2: Aging phenomena of ι-carrageen bodies, a: After 7 days at 22 °C, b: After 10 days at 22 °C, c: After 28 days at 22 °C, d: After 28 days at 50 °C

Figure 5.8-3 shows the appearance of coated gels produced with 2.4 wt% gelatin. After 28 days storage at ambient conditions the gelatin products show similar aging phenomena to carrageenans. The shape changes and the crystallized layers becomes curved. The gel core is smaller due to syneresis over time.

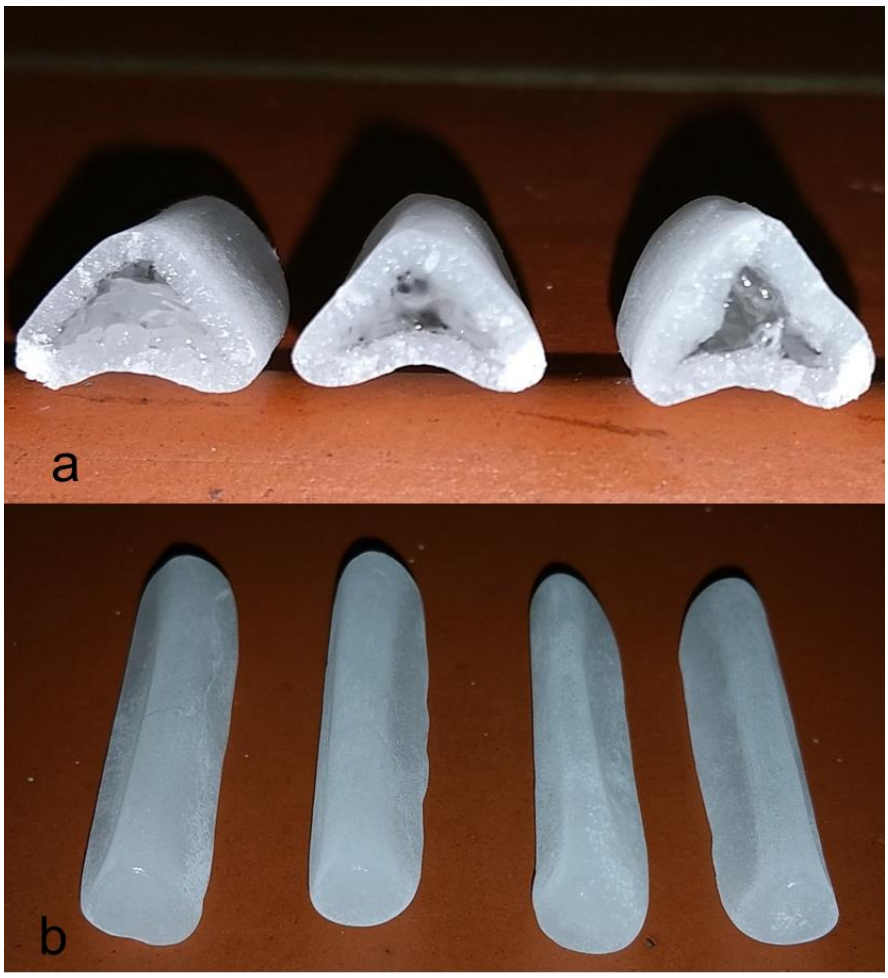

Figure 5.8-3: Aging phenomena of 2.4 wt% gelatin bodies after 28 days storage at 22 °C, a: Bisected with visible gel core and sugar layer; b: Curved appearance [Wel16]

Products produced with agar show different aging phenomena. The shape of the products does not change during aging of the product (see Figure 5.8-4, b). After 28 days at 22 °C the end products show water loses (little air holes) and crystals within the gel cores (see Figure 5.8-4, a1 and a2). But providing constant storage conditions leads to different results (here tested for gelatin and agar). Almost no shape changes (water loss) happens, a few or no crystals appear in the gel core after 28 days of storage at 21.5 °C ± 0.5 °C and relative humidity of 48 %H ± 2.5 %H. Depending on the production processes a complete crystallization of the gel core could occur (see Figure 5.8-4, a1). These effects can happen if the dissolution process is not completely finished before the solution is poured into the powder molds.

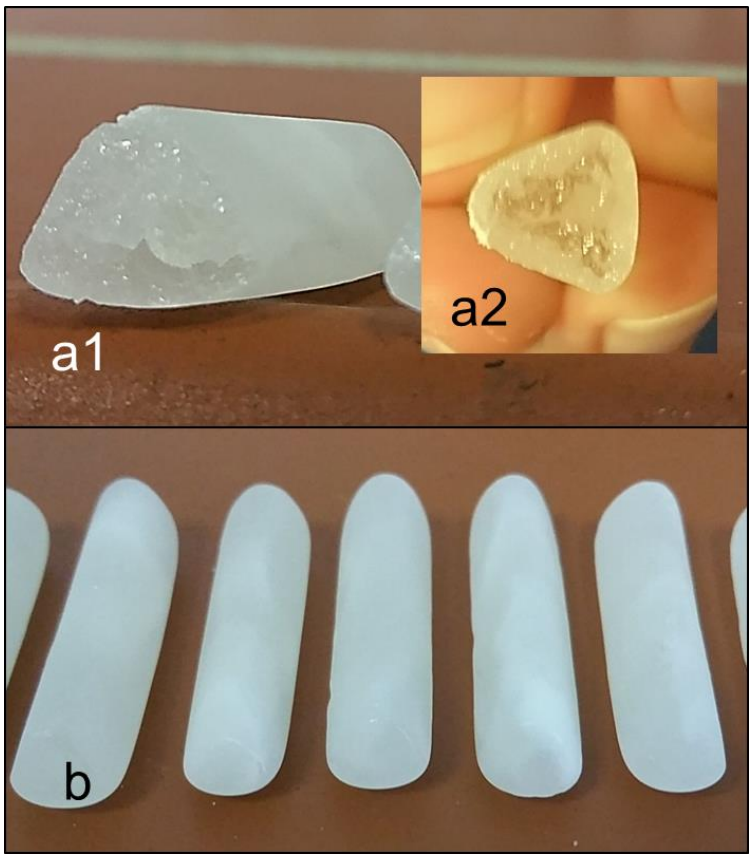

Figure 5.8-4: Aging phenomena of 1.5 wt% agar bodies after 28 days storage at 22 °C [Wel16]

Measurements of the layer thickness of products produced with 1.5 wt% agar at different storage temperatures were done (see Figure 5.8-5). Storage at 23 °C was carried out from beginning. The products were stored at ambient conditions (23 °C) for the complete time to compare the layer thicknesses with other temperature cases (50 and 70 °C). Higher temperatures (50 and 70 °C) were tested with the following conditions: For the first 3 hours the products were stored at 13 °C in the powder molds (speed up the gel formation). Thereafter, the products were removed from the powder molds and stored at 50 or 70 °C until two days after the production time. The layer thicknesses were determined after different times (see Figure 5.8-5). 48 hours after the production time all products (no matter which storage temperature was applied before) were stored at the same temperature conditions (23 °C). Beside the layer thicknesses at different storage conditions also the weight losses of 1.5 wt% agar products were determined (see Figure 5.8-6).

Smallest layer thicknesses were measured for the agar products stored partially at 70 °C. Even a removing after 48 hours does not lead to equal layer thicknesses compared to storage conditions at 23 or 50 °C (Figure 5.8-5, 168 hours). The layer thickness of products stored at 23 and 50 °C are 200 µm thicker compared to layers stored partially at 70 °C. The smallest standard deviations can be seen for the products stored partially at 70 °C.

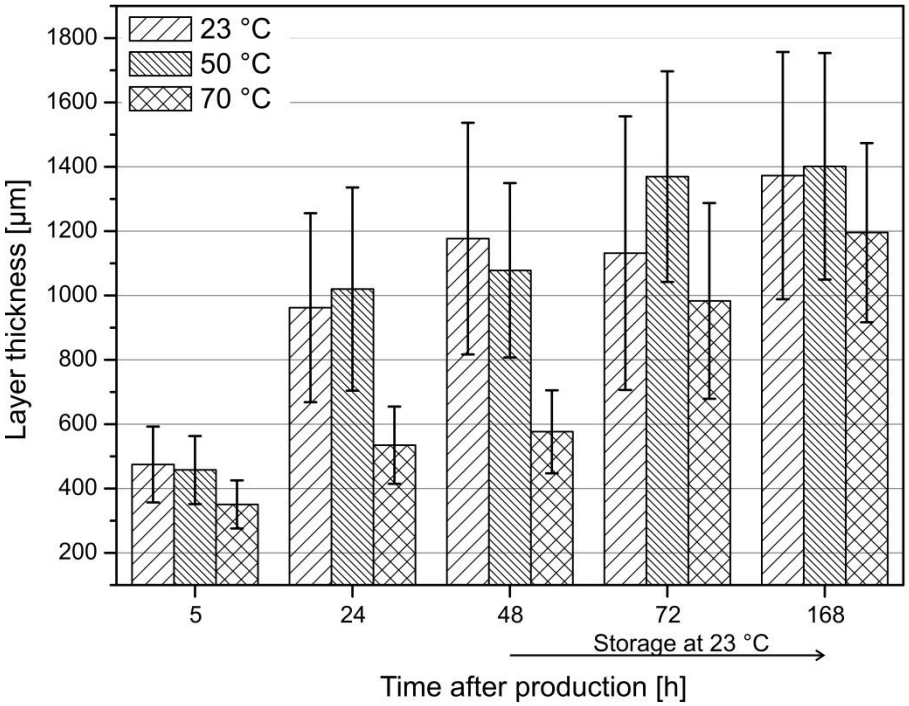

Figure 5.8-5: Layer thickness of 1.5 wt% agar products over time at different storage temperatures [Poe16]

Figure 5.8-6 shows the measured weight loss of 1.5 wt% agar products over time at different storage conditions (23, 50 and 70 °C). Partially storage at 50 or 70 °C leads to a lower weight loss after 28 days. The highest weight loss (> 4 %) occurred for 1.5 wt% agar products stored at ambient conditions (23 °C) for the complete examined time period.

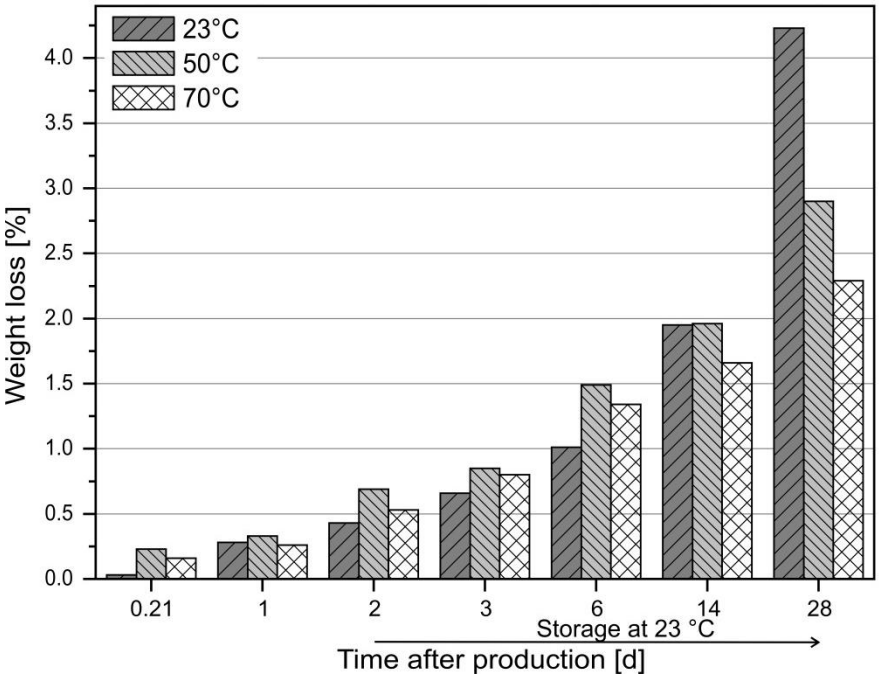

Figure 5.8-6: Weight loss of 1.5 wt% agar products at different storage temperatures over time [Poe16]

5.9 Purity of the crystalline material

Water loss (syneresis) during storage of coated gels happens after 28 days storage at 22 °C (see Figure 5.9-1). Gelatin and ι-carrageen containing products show the highest loss of water with 11.4 % and 16.9 % weight loss, respectively, during storage. κ-carrageen of different producers show similar weight loss (6.7 – 7.4 %) and agar the lowest weight loss (4.4 %) of all tested hydrocolloid containing products. Pure sugar shows nearly no weight loss (0.5 %) after a storage time of 28 days. All values for the weight loss can be found in the Appendix in Tables 11-16 and 11-17.

The effect of water loss leads to the idea to check the hydrocolloid content within the sugar layers of the coated gels.

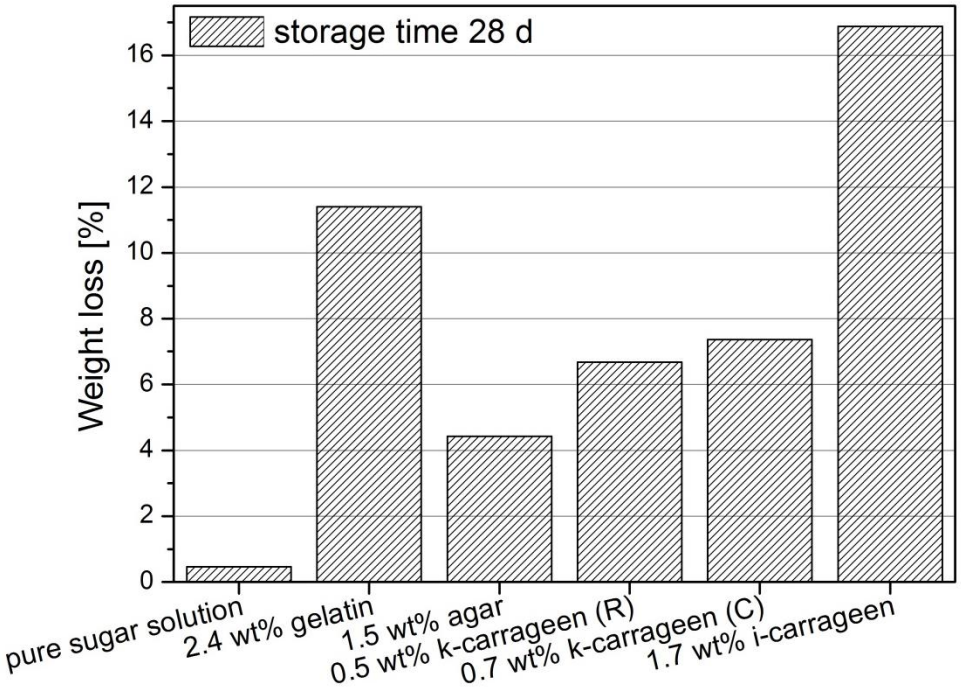

Figure 5.9-1: Weight loss of hydrocolloid bodies at ambient temperature (22 °C)

Crystallized layers (crystals), grown from sugar-hydrocolloid solutions show different looks in microscope images [Her17]. This is illustrated in Figure 5.9-2. Crystals grown in a hydrocolloid solution show irregular structures at the surface (see Figure 5.9-2, images b-f). Crystals in a pure sugar solution appear more clear (see Figure 5.9-2, image a).

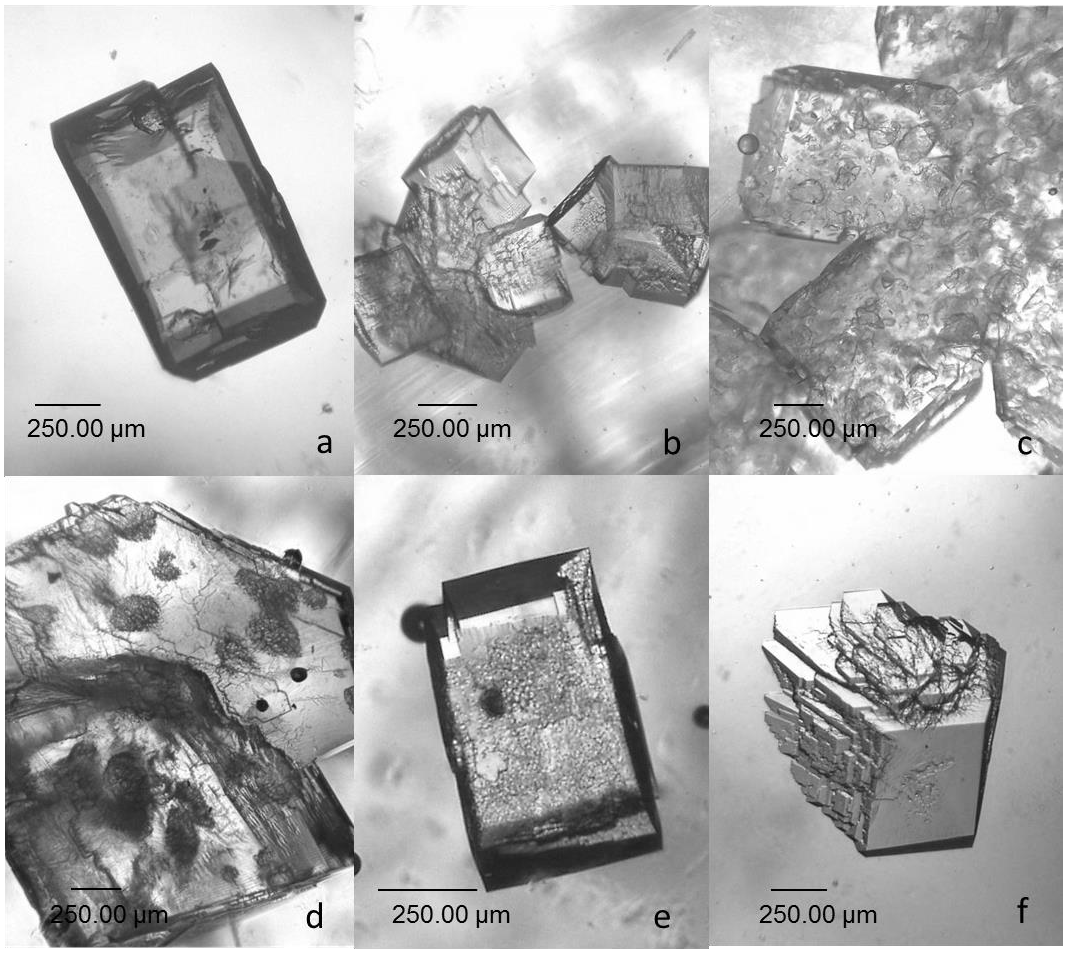

Figure 5.9-2: Sugar crystals grown in a hydrocolloid free solution (a: pure sugar solution) or hydrocolloid solution (b: 2.4 wt% gelatin, c: 1.5 wt% agar, d: 0.5 wt% κ-carrageen (R), e: 0.7 wt% κ-carrageen (C), f: 1.7 wt% ι-carrageen) [Her17]

The crystal grown in the presence of 1.5 wt% agar shows many irregularities and appears turbid [Her16] (see Figure 5.9-3).

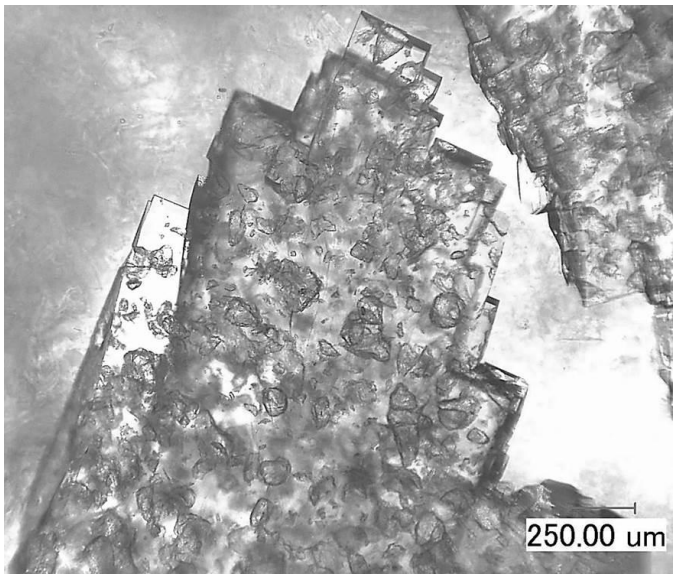

Figure 5.9-3: Sugar crystal grown in the presence of 1.5 wt% agar [Her16]

Based on these facts, experiments to analyze the crystalline material were developed.
All analyzed materials show a positive result that means the proof was successful.
The precipitation of agar with ammonium sulfate (AS) leads to a turbid solution as can be seen in Figure 5.9-4, left image. Coloring with methylene blue (see Figure 5.9-4, right image) shows blue colored agar clusters. This was illustrated by microscope images.

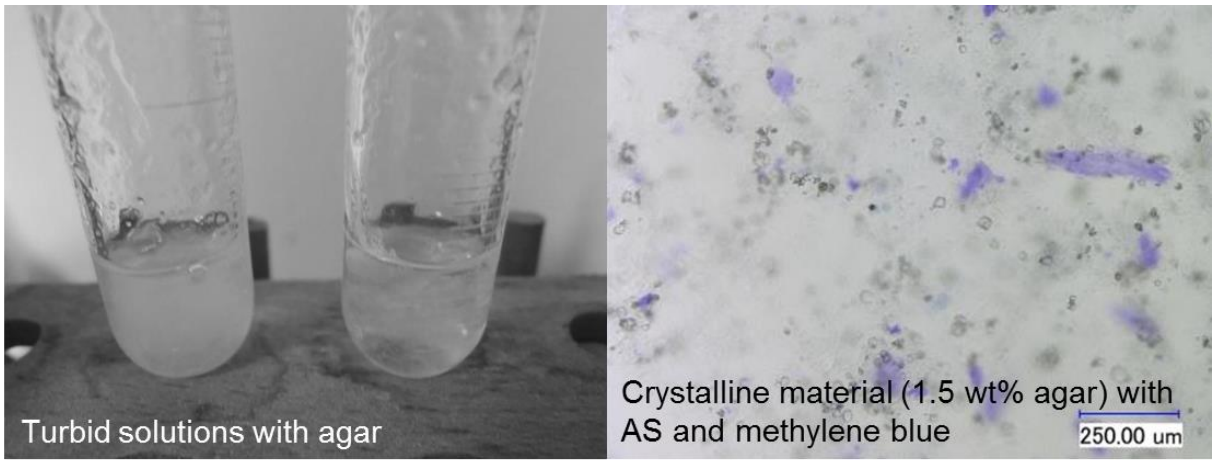

Figure 5.9-4: Precipitation of agar with AS (left image) and coloring with methylene blue (right image) [Her17]

The precipitation of gelatin with AS leads to turbid solutions as well as for agar (see Figure **5.9-5**). The left microscope image shows the precipitation result of the raw material gelatin with AS [Her17]. The right image illustrates the results for the crystallized material.

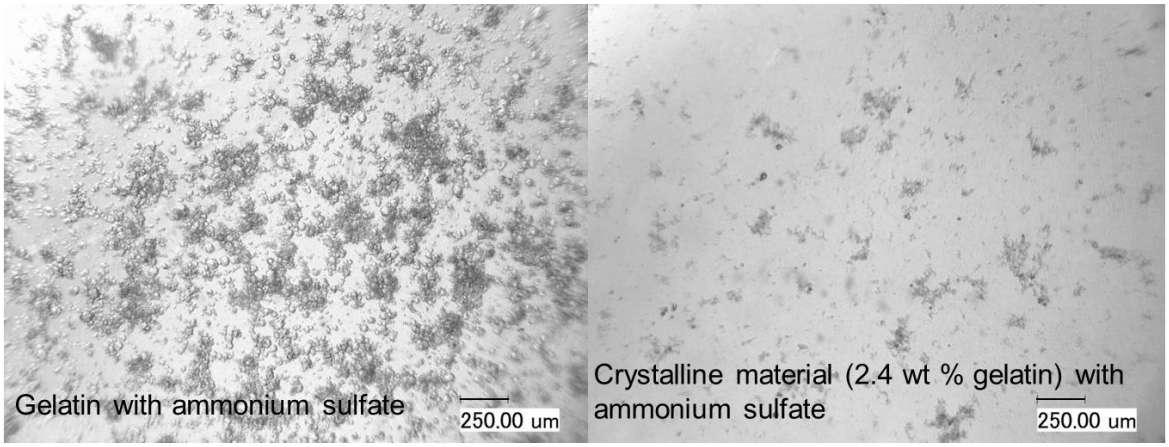

Figure 5.9-5: Precipitation of gelatin with AS (left image) and precipitate of crystalline material obtained with AS (right image) [Her17]

The proof of polysaccharides (agar and carrageen) show different colors with methylene blue coloring. The diluted solution of methylene blue is light blue. Carrageenans show a purple color and agar a light blue color with the addition of methylene blue [Her17].

Figure 5.9-6 shows the absorption of different tested samples with polysaccharides (carrageenans). The black line shows the values without hydrocolloids. Sugar absorbs at 660 nm. The black lines with an arrow illustrated the shift of the absorption with hydrocolloids (κ- and ι-carrageen).

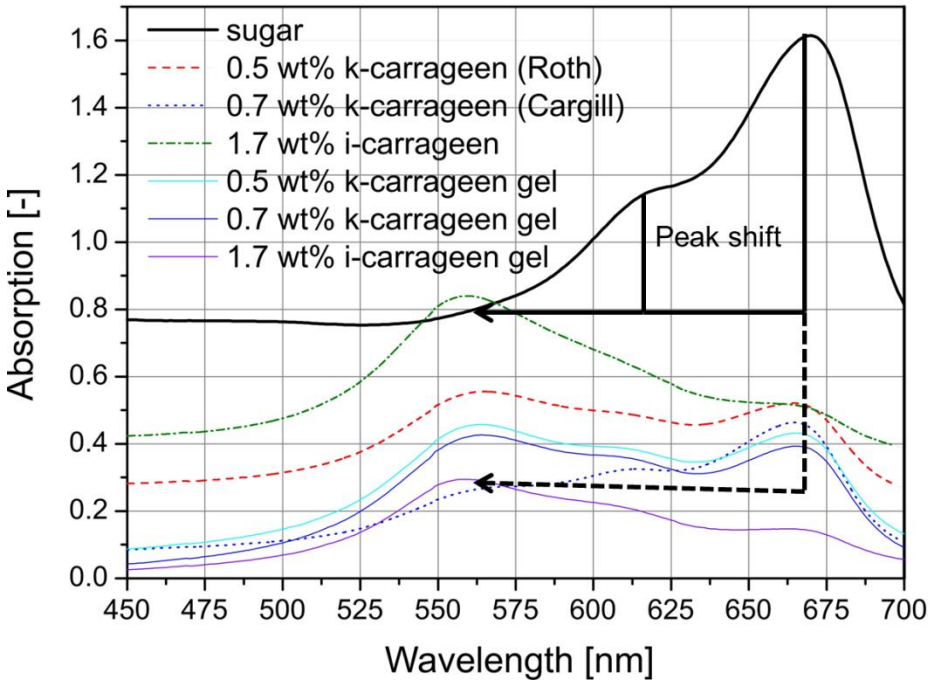

Figure 5.9-6: Absorption of different carrageenans and sugar [Her17]

The smaller lines give the positive control that means the measured gel cores of the crystallized products. ι-carrageen samples show the clearest shift due to a high amount of sulfate groups. The absorption changes from 664 nm and 610 nm to 559 nm. Since agar shows no shift in absorption during measurement with a photometer, agar was precipitated with AS as shown before (see Figure 5.9-4, left side). Afterwards, it was colored with methylene blue (see Figure 5.9-4, right image).

Figure 5.9-7 (image a and b) shows the precipitation for the two κ-carrageenans from Cargill and Roth and ι-carrageen. The κ-carrageenans show the clearest result concerning the precipitation. ι-carrageen solutions change the color from blue to purple without a high amount of precipitation (see Figure 5.9-7, image c).

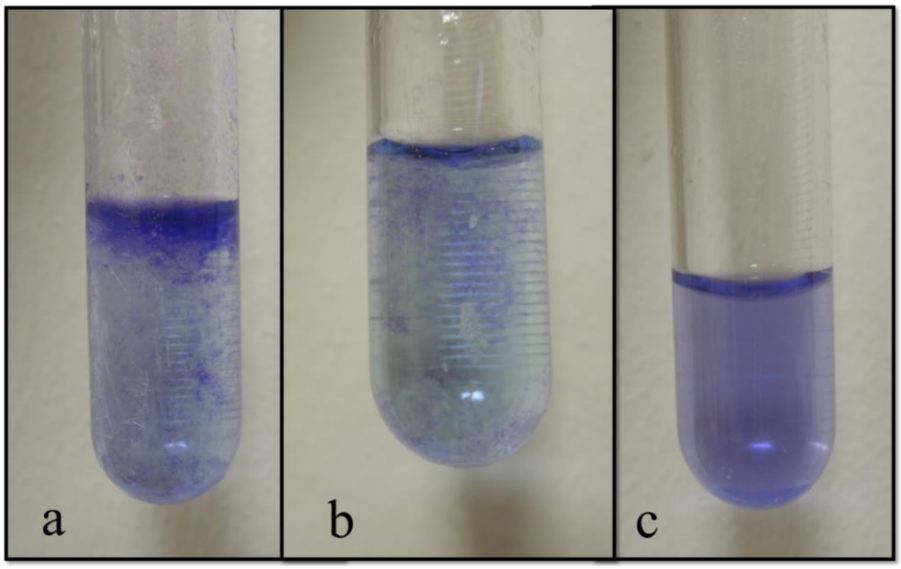

Figure 5.9-7: Precipitation of crystalline material with AS proof of a: 0.5 wt% κ-carrageen (Roth); b: 0.7 wt% κ-carrageen (Cargill) and c: 1.7 wt% ι-carrageen [Her17; Kat16]

5.10 Stability of sugar layers

The sensitivity to pressure is important after the production of coated gels. To facilitate a save transportation without loss of quality a stability as high as possible must be reached.
The following four Figures (5.10-1, 5.10-2, 5.10-3 and 5.10-4) show the stability of the end products over time.
Depending on the type of hydrocolloid and hydrocolloid concentration the measurements of 30 products per time show different results. Beside the average values the minimal stability and the maximal stability is shown with blank symbols. The dotted lines should help to distinguish between the different average values and are supportive for the clarity.

At the beginning of the measurement (5 hours) the values are very close to each other. With increasing amount of agar the stability of the coated gels increases during the first 72 hours after the production (Figure 5.10-1). Noticeable are striking high values for 1.5 wt% agar-sugar products after 24 hours (red triangles). After 48 and 72 hours the stability decreases. Compared with the products produced with pure sugar the products with 1.0 and 1.5 wt% agar show a higher stability. Adding 0.5 wt% agar to the sugar solution (purple circles), result in lower stability values than for pure sugar products (black squares). The minimal and maximal values show very big differences.

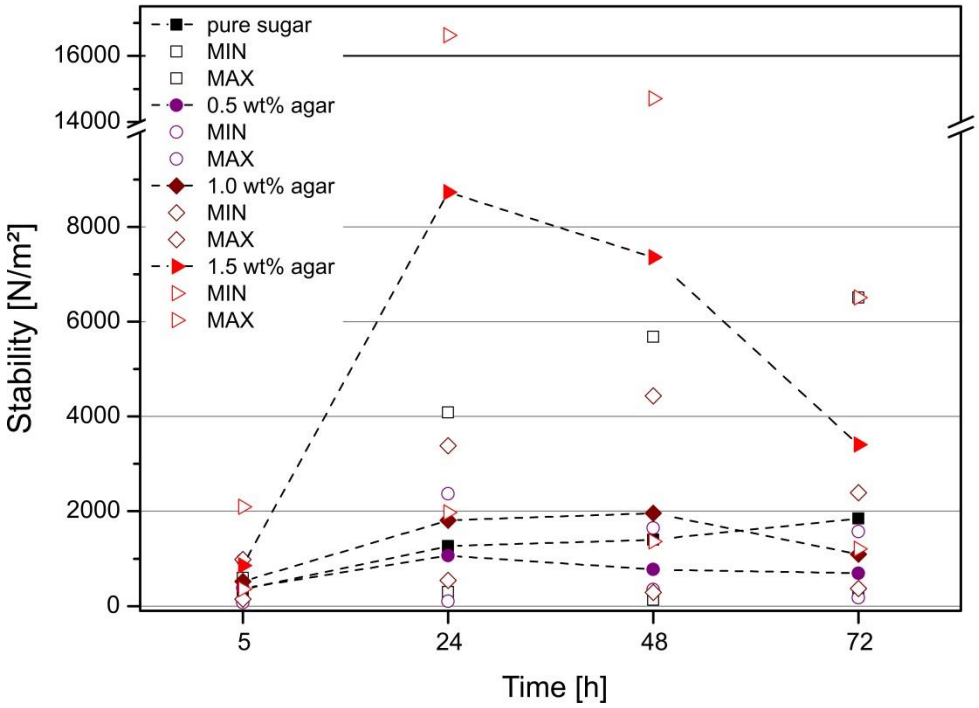

Figure 5.10-1: Average stability and minimal and maximal values of sugar bodies and agar products [Wel16]

A clearly different trend in stability of products with gelatin can be seen in Figure 5.10-2 compared to products with agar. After 5 hours the stability is for all products (pure sugar and gelatin) similar. With increasing time and gelatin amount the stability increases. Initially, the stability of pure sugar products after 24 hours is higher but after 48 hours the stability of the products produced with gelatin exceeds the stability of products produced without the hydrocolloid. The highest gelatin amount (2.4 wt%) shows the highest values in stability. The minimal and maximal values differ significantly from each other. The longer the storage time (72 hours) of products with gelatin the higher becomes the maximal values in stability (> 9000 N/m²) as can be seen in Figure 5.10-2.

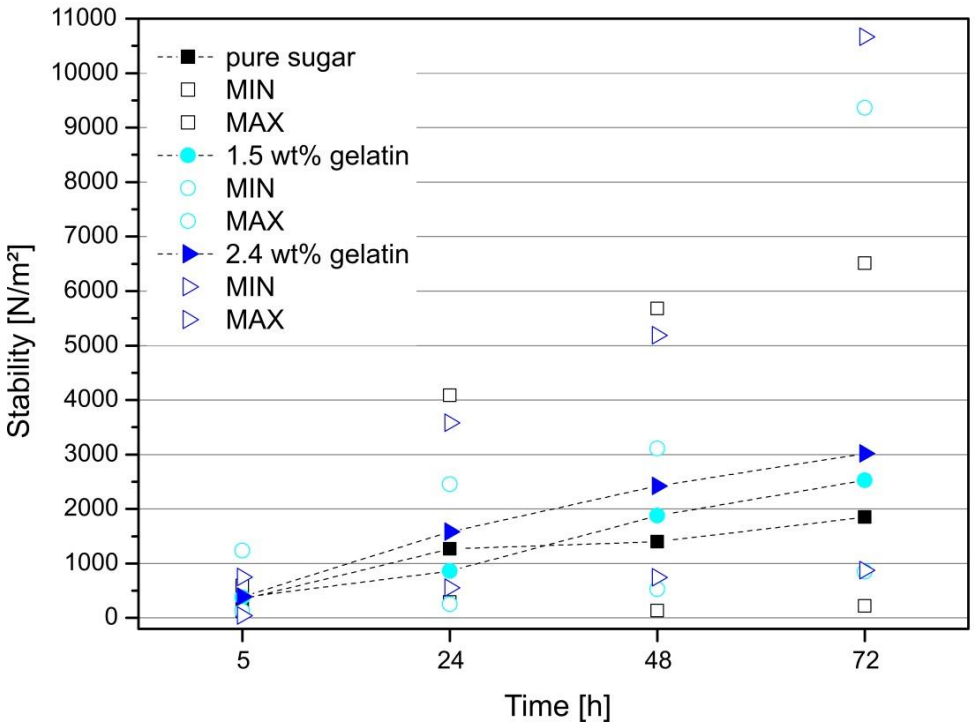

Figure 5.10-2: Average stability and minimal and maximal values of sugar bodies and gelatin products [Wel16]

The average stability with minimal and maximal values of products containing ι-carrageen is shown in Figure 5.10-3.

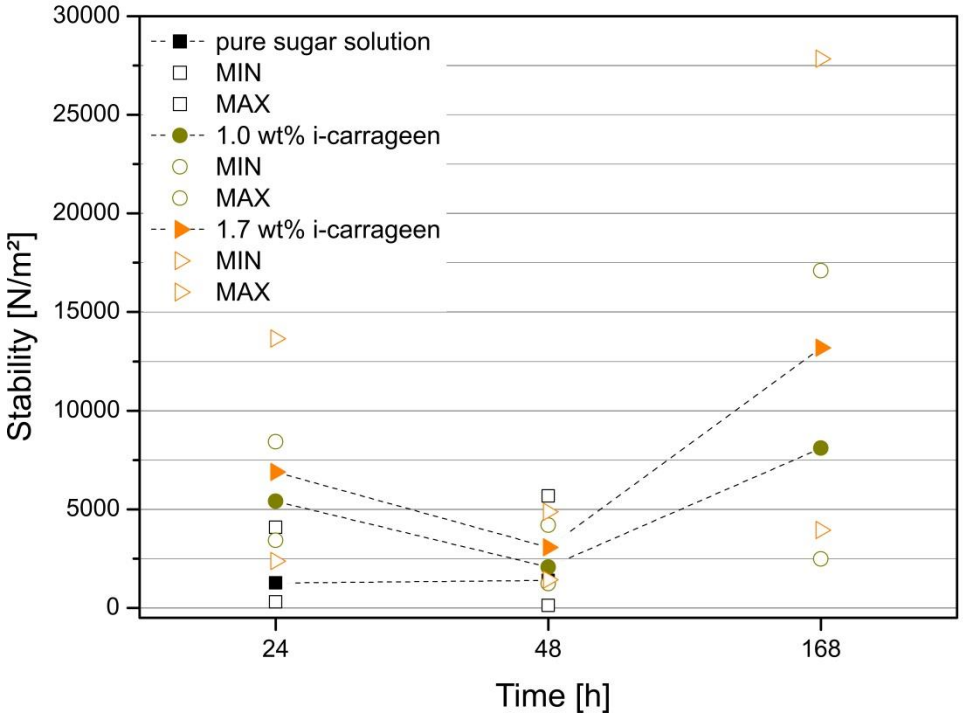

Figure 5.10-3: Average stability and minimal and maximal values of sugar bodies and ι-carrageen products [Sin16]

After 48 hours the stability of ι-carrageen products decreases slightly and subsequently (after 168 hours) increases again (see Figure 5.10-3). The difference between 1.0 wt% and 1.7 wt% ι-carrageen increases noticeable after 168 hours. The minimal and maximal values differ depending on the storage time. After 24 hours the difference is much higher than after 48 hours. After 168 hours the minimal and maximal values change and show a wider distribution compared to the stability after 48 hours (see Figure 5.10-3).

The products produced with κ-carrageen show different results in stability (see Figure 5.10-4). Depending on the producer the stability varies. κ-carrageen from Cargill (C) shows a constant increase in stability over time. κ-carrageen from Roth (R) shows after 48 hours a decrease in stability and increases subsequently (168 hours). κ-carrageen (C) shows higher stability values than κ-carrageen (R). The more carrageen was used the more the stability increases. Products without hydrocolloids have similar stabilities to 0.2 wt% κ-carrageen (R) after 24 hours. All other tested concentrations and carrageen types show higher stability values after 24 hours than products without hydrocolloid (pure sugar) (see Figure 5.10-4). The minimum and maximum values are very different from each other during the storage time. All mean values for the stability are summarized in the Appendix in Tables 11-18 and 11-19.

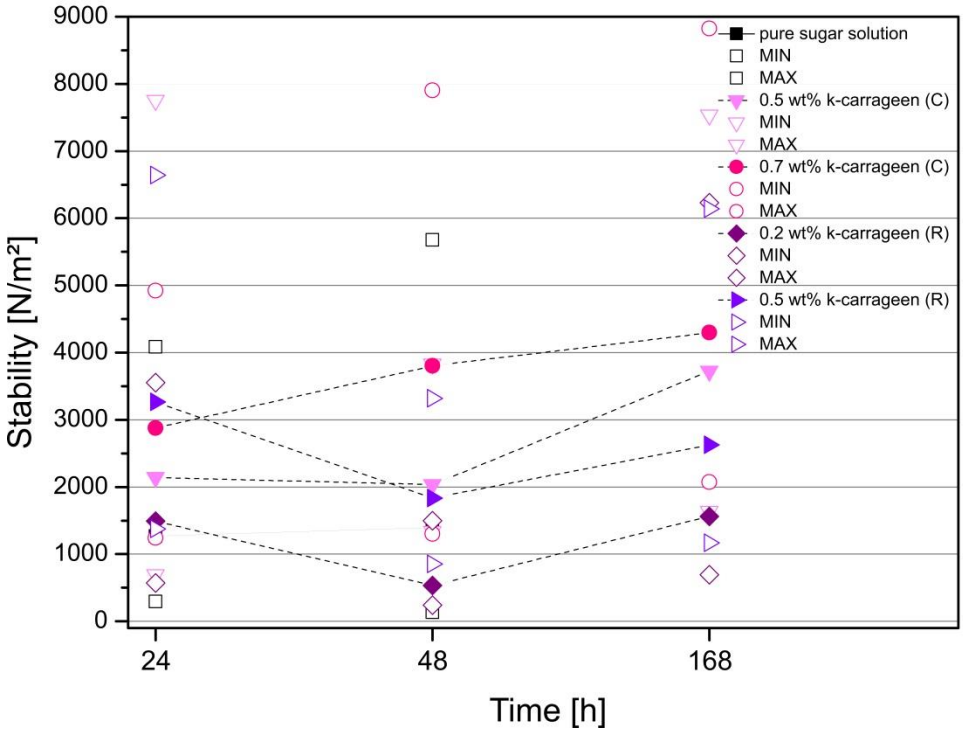

Figure 5.10-4: Average stability and minimal and maximal values of sugar bodies and κ-carrageen bodies [Sin16]

6. Discussion

In principle, a combination of crystallization and gelation is possible. Both processes can be realized to produce coated gels. Different parameters (hydrocolloid type, hydrocolloid amount, temperature, etc.) show different effects on the inner gel core and the outer crystallized coat. Especially, temperature conditions and the type of hydrocolloid as well as its amount influence the crystallization process.

The use of different seed materials (other powders than the commercially used corn starch) was applicable. A different initiation of the crystallization of a supersaturated sugar solution shows different results depending on e.g. the material properties of the external seed materials (starches, flours and icing sugar).

6.1 Material properties of hydrocolloid-sugar solutions

Experiments show that the process of crystallization in combination with gelation is more controllable with the use of thermo-reversible hydrocolloids. These hydrocolloids are able to form gels when cooled and can be transformed into sol when heated. By temperature control the crystallized material can be crystallized more pure. High temperature conditions (> 50 °C) lead to lower viscosities in the system and less supersaturation followed by a fewer driving force so the material crystallizes slower and more pure than with other not thermo-reversible hydrocolloids. Mobilization of sugar molecules within the three-dimensional network of a gel is possible provided the supersaturation (driving force) is high enough. Without a sol formation due to heating, the gel would be build irreversible and the crystallization process is negatively influenced and not as pure as with thermo-reversible hydrocolloids. Mobilization of sugar molecules to create a crystallized layer would not be possible or the formation of the crystallized layer would include much incorporated hydrocolloids (gels) due to insufficient separation of gel and sugar molecules in the system.

The dissolution process during the preparation of the supersaturated hydrocolloid-sugar solutions is very important. If the sugar amount is not completely dissolved, small not visible nuclei occur, which grow during storage of the end product. The end product would contain big crystals within the gel core (undesired crystals) and a thinner layer thickness without undesired crystals of sugar would be formed. The supersaturation will be consumed not only from the outer crystallized core but also from the undesired crystals within the gel core. However, unstable and not reproducible end products have to be avoided (see Table 6.1-1).

The technical production of hydrocolloid-sugar solutions as a basic step to achieve the coated gels is possible without a loss of water. Even with the occurrence of water evaporation due to high temperatures (> 100 °C) to dissolve the sugar and the hydrocolloids

the production is possible. Despite covered beakers evaporation occurs during addition of ingredients and the cooling process. This water evaporation is partially balanced by cleaning the walls of the beakers with water and a brush. The high temperatures support a great evaporation of water, which is not negligible and should be considered. The measured sugar contents are therefore higher, than the expected sugar concentrations (see Chapter 5.2, Table 5.2-1).That loss of water leads to a lower content of solvent and a more concentrated solution (higher supersaturation), which tends to crystallize more easily. The higher driving force in a very concentrated (high supersaturated) sugar solution is on the one hand desired because the highly viscous solutions are hard to crystallize with very slow mass transportation of sugar molecules. On the other hand, the very high supersaturation can lead to incomplete dissolution of sugar molecules and hydrocolloids. That can result in an undesired nucleation before pouring the solution into a starch mold. Both components (sugar and hydrocolloid) within the system compete for the water molecules to dissolve. An incomplete dissolution of the sugar molecules initiates the crystallization in undesired ways and crystals appear in the gel cores, which have a grainy mouthfeel. Sugar contents (Brix%) change noticeable. The measured values differ from the “calculated” values. Generally, the standard deviation is high, with values between 0.4 and 1.1 Brix%. Water evaporation changes the sugar-water relation and therefore the Brix%. The sugar content is measured only locally and can have different values at different places. A total homogeneous sugar molecule distribution is not achievable and therefore the values fluctuate depending on the place where the sample was taken and also differs depending on the end product sample, which was used. Therefore, it is important to choose different end products of the same hydrocolloid randomly for the measurements and calculate a mean value.
A determination of the sugar content during the production of crystalline coated gels should be carried out in order to control the process conditions. Ensuring the same condition is a requirement to produce desired, reproducible end products.

Problems during the production of crystallized coated gels can occur due to undesired tailing of the prepared solutions (see Table 6.1-1). The fast cooling process (under ambient conditions) after the heating step leads to the formation of gel strings, which can change the shape of the products and contaminate the powder molds. This must be avoided by a fast molding process.

Changing the pH with adding some acid flavors can affect the supersaturation and the gel process. Sugar inversion takes place and the macromolecules of the hydrocolloids can be destroyed (degradation) due to reactions with acids. The addition of flavors for a good taste of the end product is necessary but if the conditions are too acidic, the end product

properties can be changed, that means a degradation of the gel texture and thinner crystallized coat (see Table 6.1-1, unstable end product) will be the result.

Table 6.1-1: Influencing factors that have to be considered enabling the maximal possible storage stability of the desired coated gel bodies

Process Step	Conditions	Effects/ Recommendations	Final State
Composition	Optimal sugar amount	High supersaturation for layer formation (78 wt% sugar)	Stable and desired end product
	Optimal hydrocolloid amount	Full dissolution and desired texture	
	Acidic conditions (flavors)	Buffer and addition of acid at the last moment or neutral pH conditions	
Preparation of the solution and pouring into molds	Wrong dissolution of components	Sugar: Inversion, Coloring (maillard reaction) and Nuclei (grindy mouthfeeling in gel core) Hydrocolloid: Degradation and lumps formation	Unstable and not desired end product
	Wrong stirring conditions	Air bubbles in solution and on top of the end product (permeability of the layer increases)	
	Wrong temperature during pouring	Tailing (formation of jelly strings) and undesired nucleation in gel core	
Storage conditions after production	Fluctuating temperatures and humidity	Syneresis (water loss)	
		Fast coating with chocolate or wax	Stable and desired end product

Differences of the crust appearance of the hydrocolloid-sugar end products can be described. Beside different gel textures due to different hydrocolloid types also different crust appearances are shown. Agar and κ-carrageen products show brittle gel textures due to a high hydrogen bond formation and a strong interaction between the macromolecules. Whereas gelatin and ι-carrageen build a soft and sticky gel core. The crust of a gelatin product is after 24 hours very thin compared to the other hydrocolloid products. The three-

dimensional network within the gelatin gel inhibits the mass transport of sugar molecules in a stronger way than for the other hydrocolloid products. The hard and crunchy coats of products produced with κ-carrageen and agar can be explained by a fewer strong bounding of sugar molecules and a better mobilization of the sugar molecules to the outer crust due to hydrogen bonds. Taking the macromolecules of hydrocolloids together with the sugar molecules by hydrogen bond formation leads to incorporations and bigger and hard crusts. The crunchy properties of end products are strongly influenced by the incorporation of hydrocolloid within the crystallized sugar coat. The more macromolecules are incorporated (unpure coat) into the crystallized material, the harder the crust will be over the storage time. The incorporated hydrocolloid areas on the outer shell can dry at ambient conditions and increase the crunchy properties of the end product (syneresis occurs). To avoid this kind of product changes Figure 6.1-1 gives an overview on tools that can be used to control the processing conditions and the product properties.

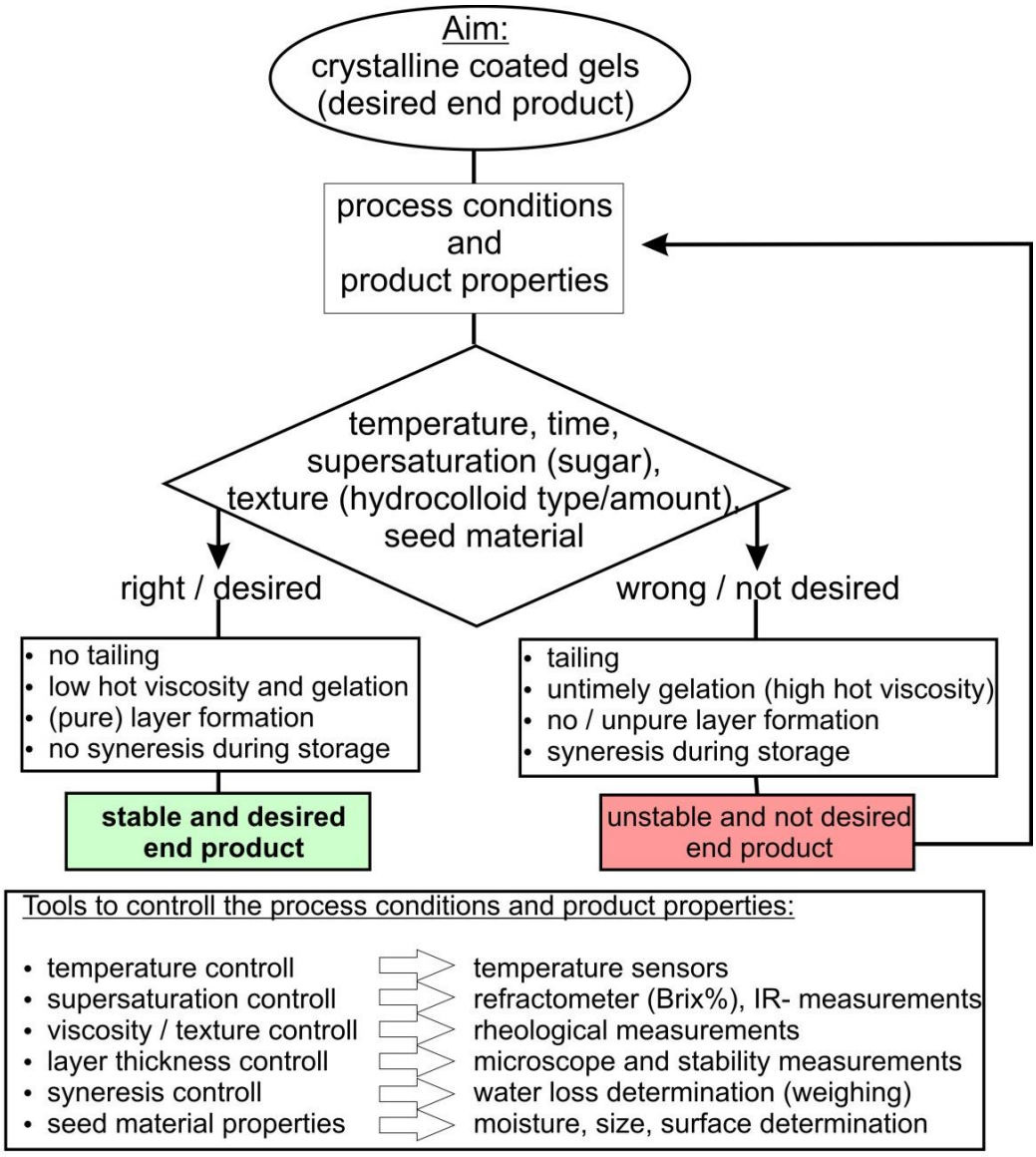

Figure 6.1-1: Tools to control the production process and product properties

During the production a recycling of broken and undesired products is beneficial for cost and economic values (material and money saving). Therefore, rework treatment is necessary, that means the addition of e.g. undesired gelled products into the heating step. To control the rework treatment, the determination of the melting point of gels and end products is necessary. The determination of the melting point of the produced coated gels was not successful. Measurements with DSC (Differential Scanning Calorimetry) were not reproducible because very low amounts of samples including local changes in composition of the samples had to be used and a fast water evaporation which changes the composition during the DSC measurement is happening.
Measurements with a “Kofler bench” to determine the melting temperature of a sample were also not successful. This heat plate has a scale with a range from 50 to 260 °C. Depending on the place where the sample is located different temperature ranges can be scanned. Water evaporation during the measurement changes the values significantly and the results were therefore not reproducible. Above a temperature of 100 °C the gel samples (agar and carrageenans) start to form strong bubbles and probably the sugar and gel components are negatively influenced. For the gelatin gel the melting point was also not measurable because the scale starts at 50 °C and a gelatin gel melts under this temperature. But in general, it should be possible to melt the products again because the gels are thermo-reversible. Attention must be paid to the hysteresis and the evaporation of the water in the sugar-hydrocolloid system at very hot temperatures if the products should be reused after undesired plant stops during production. To reuse the gelled products getting desired end products, a closed vessel with pressure regulation is necessary. Furthermore, higher temperatures are necessary to transform the gel into sol again (hysteresis) than for the formation of the gel directly after the preparation of the solution. The controlling of the sugar content (Brix% values) is necessary to get the desired supersaturation in the system. Attention must be payed to the pH values within the system during heating. The more acid is used, the higher the inversion rate of the sugar will be and the degradation of the macromolecules will happen. Therefore, the neutral conditions in the system are beneficial for rework treatment.

Viscosity measurements were taken before the gelation process of the hydrocolloid-sugar solution occurred. Solutions with a low molecular weight (non-polymeric materials) and low concentrated high molecular weight polymers show Newtonian behavior [Pan10]. That means the viscosity is independent of the rate of shear [Pan10]. Viscosities less than 100 mPas have Newtonian flow properties but at higher viscosities the solution shows shear thinning behavior (shear rate specification necessary) [Sta87]. Rheological experiments done by Schwarzlos et al. [Sch97] describe Newtonian behavior of agar solutions (0.2 - 1.5 wt%).

During cooling from 80 °C to temperatures close to the gel temperature the viscosity is shear independent [Sch97].

Panda [Pan10] summarized ten viscosity changing factors in hydrophilic systems. Important factors are concentration, temperature, degree of dispersion, solvation, electrical charge, previous thermal or mechanical treatment, presence of other lyophilic colloids, age of lyophilic sol or presents of electrolytes or non-electrolytes [Pan10].

The determination of the viscosity is important for the production process. The casting pressure must be adjusted depending on the viscosity. The viscosity depends not only on the temperature but changes also with hydrocolloid type, hydrocolloid amount and sugar content. Stanley [Sta87] describes that the viscosity depends on concentration of hydrocolloids and sugar, temperature, presence of cation, type of carrageenan and its molecular weight. The correlation between the viscosity and the molecular weight can be described by the Mark-Houwink equation (see Equation 6.1-1).

$$[\eta] = K\, M^{a} \qquad \text{(Eq. 6.1-1)}$$

η is the intrinsic viscosity, M is the average molecular weight and K and a are constants.

Stanley [Sta87] summarize that salts lower the viscosity of carrageenan solutions due to a reduction of electrostatic repulsion among the sulfate groups. Calcium lowers the viscosity stronger at higher temperatures [Sta87]. The solutions contain different amounts of ions since tap water (pH 7.37) was used (no distilled water!). Table 6.1-2 gives an overview on viscosity values from hydrocolloid solutions with and without sugar. Gelatin shows generally the lowest measured viscosity compared to the other solutions. Schrieber et al. [Sch07] describe gelatin solutions as shear stable and easily pumpable without quality loss. High viscosities lead to the conclusion that more molecule interactions occur. Application of shear stress leads to different reactions of hydrocolloid solutions. κ- and ι-carrageen gels show a pseudoplastic (shear thinning) shear effect. κ-carrageen gels break irreversible by shear stress and ι-carrageen gels break and recover after shear stress [Wue15].

Table 6.1-2: Classification of the viscosity of different hydrocolloid-sugar solutions

Viscosity values	Hydrocolloids without sugar	Hydrocolloids with sugar (78.5 g)
Low (50 - 250 mPas)	gelatin	gelatin
Middle (< 1500 mPas)	κ-carrageen (R, C)	agar, κ-carrageen (R, C)
High (> 1500 mPas)	agar, ι-carrageen	ι-carrageen

Maurer et al. [Mau12] describes the elastic modulus (G´) of 1 % agarose gels. The first changes in G´ (increase from 2 to 38 Pa) occur at 76 - 60 °C. Therefore, the gelation temperature can be changed by the use of sugar. Sugar interacts with its hydroxyl groups linking to the macromolecules of agaropectin and agarose [Mau12].
Due to the addition of sugar, more molecule interactions can be described and result in higher values of viscosity. Tables 6.1-3 and 6.1-4 show the measured effects of sugar on different hydrocolloid solutions.

Table 6.1-3: Overview of effects on the viscosity of hydrocolloid containing sugar solutions

Influencing factors on the viscosity	agar	gelatin	κ-carrageen (R, C)	ι-carrageen
Influence of sugar	high* (decreasing)	low*	high*	high*
Influence of hydrocolloid amount	high*	low*	middle*	high*
Influence of temperature	high*	low*	middle*	high*

*high effect: increasing viscosity of > 500 mPas, middle effect: increasing viscosity of 250 mPas, low effect: increasing viscosity of < 100 mPas

Measurements of the metastable zone show different effects of hydrocolloids during the crystallization of sucrose. The sugar solutions containing different amounts of agar show a slight decrease in the metastable zone the more agar was used. Due to high standard deviations this effect is not significant. Beside the negligible effect of agar on the metastable zone, the other hydrocolloids (carrageenans and gelatin) show different effects. On the one hand, a shift of the metastable zone to lower temperatures or on the other hand a shift to higher temperatures occurs depending on the used cooling and heating rate as well as on the used hydrocolloid amounts. Gelatin leads to a shift to lower temperatures as well as ι-carrageen compared to pure sugar solutions. Both hydrocolloids built soft and elastic gels. These three-dimensional network increases the solubility of sugar in the system. More sugar can be dissolved because interactions of hydroxyl-groups from the sucrose with the water occur (hydration shell can be built). Nucleation and solubility of e.g. a gelatin sugar solution changes because the gelatin binds water to dissolve the sugar (solubility changes from 86 (1.5 wt% gelatin) to 76 °C (2.4 wt% gelatin)). Both components (hydrocolloids: gelatin and ι-carrageen and sugar) compete for the water in the system to be dissolved (sugar) or to form a gel structure (hydrocolloids). The shift of the metastable zones to lower temperatures occurs also for 0.5 wt% κ-carrageen (C) cooled and heated with 6 K/h. The high amount of κ-carrageen and the cooling and heating rate support these results. The system becomes viscous and the interactions with sugar and water lead to a shift to lower temperatures. Important factors to interpret the results in the right way are the cooling and heating rates.

Different temperature rates can affect the metastable zone, especially, the nucleation temperatures (kinetic influence) but less the thermodynamic characteristic of the measured solutions (that means solubility temperature).

Different results can be shown for lower κ-carrageen (R and C) amounts and cooling and heating rates of 9 K/h. The metastable zone is shifted to higher temperatures compared to a pure sugar solution measured with the same heating and cooling rate. This effect can be explained by the competition of sugar and hydrocolloid for water. The hydrocolloid amount is high enough to take up enough water. This water is missing for the dissolution of sugar. The hydrocolloid is “stronger” in taking up water than the sugar. That results in a shift of the metastable zone to higher temperatures. Less sugar can be dissolved.

The metastable zone width (MZW) changes noticeable depending on the used hydrocolloid type, hydrocolloid amount, cooling and heating rate as well as measuring technique. The MZW increases due to high hydrocolloid amounts. The heat distribution is a key fact to determine the nucleation and solubility temperature. Cooling leads to gel formation and at some point the stirrer stops to work. This is disadvantageous for the heat distribution in the vessel and leads to differences in results (standard deviation > 2 °C). But ultrasound measurements show a little bit lower standard deviation values with approx. 1 °C. With an infrared device the little gap where the sample reflects light or not is small and that can change the values more noticeable between the measurements compared to a larger ultrasound gap (the place where nucleation starts is unpredictable but crucial for the obtained measured values). The amount of the sample, which is measured, is therefore different for the different methods.

It is crucial, which molecular interactions happen between the macromolecules of the hydrocolloids and sugar together with the water as third component. Binding of the sugar from macromolecules together with the dissolution due to water, leads to an effect on the nucleation. If the cluster formation of sugar molecules is possible the nucleation appears at higher temperatures (more sugar is dissolved). If the cluster formation of sugar molecules is inhibited due to a strong bounding of water by macromolecules with the effect of dissolution of sugar, the nucleation appears at lower temperatures (higher supersaturation is necessary).

Measurements of pure sugar solutions with the infrared method show very big differences compared to the measurements of the ultrasound technique. To compare both methods the same cooling and heating rate was used. The infrared method shows higher nucleation and solubility temperatures than the ultrasound technique. If the cooling and heating rate is decreased (from 9 K/h to 6 K/h) using the ultrasound technique the measured values increase a little bit (4 - 6 K). That leads to the conclusion that differences can be explained by the specific devices.

6.2 Nucleation enforced by external seed materials

An example from the food industry shows the importance of the issue that nucleation of a high viscous supersaturated solution has to be enforced. In the production of candies from e.g. gels the starch mogul technique is commonly used [Hof04a]. Different starch types as powder beds are used in this technique to generate desired shapes of the sweets. Beside the ability to shape the products, these powders can be used to enforce the nucleation of supersaturated liquids. Depending on the moisture content, particle size and surface structure of the seed materials different results can be shown. Basic requirements to enforce the nucleation and to estimate the nucleation behavior of sugar solutions are the dimension of energy input into a supersaturated solution to build nuclei. This energy input can be by mechanical irritation of molecules in a supersaturated sugar solution with sharp and edged surfaces (provided by different external starch materials). The removal of water in the supersaturated sugar solution can enhance the nucleation process. Properties like e.g. moisture of the seed materials are important influencing factors, too.

It is important to choose beside the right hydrocolloid also the right external seed material to achieve the desired products. Every hydrocolloid and external seed materials have advantages and disadvantages during the formation of crystalline sugar layer products. It is important to choose inexpensive and good applicable seed materials to optimize the production process. That means external seed materials must initiate the nucleation uniformly and simultaneously at all locations at the surface of the solution. The commonly used corn starch as external seed material to induce the nucleation of supersaturated ($\beta \approx 1.16$ at 20 °C) sugar solutions shows the best results (production of a crystallized layer in short times and uniformly). This corn starch provides a surface, which leads to a uniformly distributed initiation of nucleation over the surface of a supersaturated sugar solution. The edged surfaces of the seed material particles are energetically favorable for the nucleation process (formation of volume without increasing the surface) so that the sugar starts crystallizing when it contacts the surface of the particles. The angle of edges on the particle surface is therefore an important property. The particle size of corn starch is small enough to create an even surface were crystal clusters grow uniformly together. Smaller particles (10 µm) are able to float on the surface of the sugar solution without sinking into the solution or interact with the solution. If the surface of the seed materials is too smooth, e.g. with potato starch, the angle of slope will be different. Therefore, different molds to shape the product are not applicable, e.g. with the use of potato starch.

Too small particle sizes (< 10 µm) tend to form agglomerates (e.g. rice starch), so that a too small size has got no additional beneficial effect concerning the nucleation step. During the measurement of the particle size distribution in dry state with the Mastersizer the air flow is

not able to separate the single particles from each other so the agglomerates were measured as bigger particles (20 - 100 µm) in the case of rice starch.

The moisture content plays an important role during the induction of the nucleation. If the moisture content of the seed material is too high the seed material sticks on the crystallized layer (especially, for corn starch). If the seed materials is dissolvable in the solution molded in it, the materials (icing sugar) dissolves on the outer sugar layer and increases the layer thickness. Different external seed materials can influence therefore the thickness of sugar layers. Icing sugar is connected with the solution and increases layer thicknesses, whereas starch is almost totally inert and acts only as nucleation seed material. Overall, both seed materials (icing sugar and corn starch) induce the nucleation of hydrocolloid-sugar solutions to build up a sugar layer. These results for icing sugar were not expected because icing sugar shows more sharp edges and corners with an irregular surface compared to corn starch with rounder particles. Due to the external appearance it was expected that the icing sugar disturbs the supersaturated solution better than the corn starch. Results show that this material is not more effective than corn starch. That could be explained by a partial dissolution of the particles during pouring the hot solution (evaporation takes place at 80 °C) into the prepared icing sugar mold. The materials lose their strong nucleation properties. This additionally layers stick on the crystallized coat of the gels. Such an effect could be desired or not wanted. If no interaction from seed material with the solution is desired the starch particles are the better external seed material. They could be removed completely under these conditions and do not increase the layer thickness. Generally, the moisture content does not influence the sugar contents (Brix% values) within the produced products provided that the nucleation was enforced and the coated layer (shell) starts to grow.

Seed powders need a few drying cycles to loss all mobilizable water (especially, for tapioca and potato starches) and are affected by ambient conditions (humidity and room temperature). At “hot” conditions (50 °C), crystallization on the surface of a sugar solution with e.g. rice, tapioca wheat, potato starch as well as for the flours (wheat type 405 and instant) and icing sugar as alternatives to corn starch is possible and results in two different effects for the crystallization of a sugar solution. These higher temperatures (50 °C) lead to water evaporation at the surface between sugar solution and seed material. Therefore, the local supersaturation becomes higher. Additionally, the higher temperatures lead to lower moisture contents at the materials, so the seed materials are able to absorb water from the sugar solution, when the solution is poured into the mold. This water uptake leads to a higher local supersaturation at the interface between solution and seed material. A higher supersaturation supports the process of nucleation and the crystallization can be enforced more easily. High moistures (> 6 %) within the seed materials influence the nucleation

process negatively because the diffusion of sugar into a wet area of the mold is promoted and as shown in the Chapter 5.5 of the Results, empty shells of the products without a crystallized sugar layer occur at higher moisture (15 %). It can be concluded that a limit in moisture content exists. However, the crust thickness and stability seems to be higher at moistures of 10 %. Therefore, the moisture of corn starch should be less than 10 %, because of holes and starch incorporations within the end products. It is important that all seed materials are heat resistant to dry them and reuse them after the production process. Hoffman et al. [Hof04a] describe that seed materials have to withstand high mechanical and thermic stress during the drying step for reuse. This step can lead to changes in material structure and, especially, high molecular starch degradation products can be built up [Hof04a, p.127].

The particle size and surface of the tested materials have different effects during the initiation of the nucleation of a sugar solution. The surface quality given by the seed materials, however, is affected by the particle size distribution. It is important to control the nuclei sizes during the layer formation. Larger particles create rougher and less smooth surfaces of the crystalline material, but this property is negligible when the moisture content of the seed material is too high to generate a supersaturation at the surface. The water content of the sugar solution and the moisture of the seed materials tend to change due to diffusion of water molecules between these interphases and into the ambient air and therefore, the nucleation process is affected by lower local supersaturations at the interface.

Larger particles and a rounder appearance (e.g. potato and tapioca starch) are not effective concerning the crystallization of sugar because enforcing and indentation of the surface tension of the sugar solution are only with restrictions possible (higher energy input necessary). Very large and round particles lead to more rough crystallized surfaces compared to smaller and more edged particle properties. The crystallization of a sugar solution can be easier triggered by small and edged particles. Therefore, different results concerning the crystallization of sugar can be ascribed to the surface appearance of the starch particles. Round and even surfaces of tapioca starch particles are not effective in enforcing the nucleation of a supersaturated sugar solution. More edged surfaces (as e.g. for corn starch particles) are necessary to initiate the nucleation process, independent of the particle size of the starch materials (similar sizes of corn and tapioca starches). Larger particles interact with the sugar solution when sprinkled thereon. The particles tend to settle and connect somehow with the solution which leads to a situation where there is no possibility to remove the seed materials from the end product.

It is important to achieve the desired shapes of the end products. Especially, bigger particles (> 10 µm) with a smooth surface show limitations in shaping the end products. Side walls

slide down during the formation of negative imprints. The interaction of moisture, particle size and particle surface play an important role in forming negative imprints.

In order to achieve a perfect crystalline end product many physical properties of the seed materials have to be considered. In this case, nucleation is the key parameter to be controlled to reach a desired process and end product. The conclusion is therefore, that the moisture content of seed materials, which covers the sugar solution, plays next to particle size and surface quality of the particles a key role during the nucleation process of a sugar solution.

To estimate the effect of the storage of end products in a powder mold the layer thickness of products were determined after 168 and 240 hours. The depowderation of end products after different times shows no clear differences. That leads to the conclusion that a later depowderation (after one week or later) is not negative for the end products. Normally, end products were depowdered after 24 hours. The powder mold shows no isolating effect for the end products and their layer thickness. Generally, it is not necessary to store the end product longer than 24 hours in a starch powder mold. However, it is important to depower the end products only after a specific time while paying attention to the stability of the end product. The stability of the end product must be high enough to avoid some damages (cracks in the crystallized layers) of the end product.

6.3 Influence of hydrocolloids on sugar layer growth

Sugar contents within the gel core (Brix% values) decrease slower with the application of hydrocolloids. Depending on the type of hydrocolloid, little differences in sugar content decrease over time are noticeable. After 24 hours the sugar content shows the slowest decrease with gelatin and ι-carrageen. Gelatin products show higher Brix% values after 72 hours than all the other tested products. The equilibrium for gelatin products is reached more slowly and needs more time to be achieved. The solubility of sugar changes due to the use of gelatin. More sugar can be dissolved within the gel core. Even the metastable zone confirms this fact. Generally, the standard deviations of products with hydrocolloids are higher. The distribution of sugar within the gel core is more heterogeneous and the place where the sample is taken plays an important role. It is important to measure many samples to create a reproducible mean value. Additionally to the shown sugar contents in the Chapter Results, the Appendix shows sugar contents of κ-carrageen products stored at 50 °C, over one week or ten days. The values are higher compared to storage at ambient conditions due to equilibrium at hot conditions (50 °C). These values confirm that a different equilibrium is reached at 50 °C. More sugar can be dissolved at 50 °C compared to ambient temperature

(22 °C). The measurements of the sugar content decrease in Brix% enables conclusions on the crystal layer growth. The sugar content in the gel core correlates with the grown crystallized sugar shell. The higher the decrease in sugar content in the gel core, the thicker will be the crystallized layer. A slower decrease in sugar content over time leads to the conclusion that the crystallized layer as an outer shell needs more time to be built up. The slower mass transport due to high viscosities consumes more time for the crystallization process and the mobilization of sugar molecules from the gel core to the outer crystallized layer.

Experiments with crystallized end products produced without hydrocolloids (pure sugar solution) show that the measured layer thickness varies depending on the time and the used method (evaluation of the images). After 24 hours it can be expected that the equilibrium in the system (water and sugar) is reached. All sugar molecules were mobilized to the crystallized layer and the remaining sugar amount in the core at ambient conditions (22 °C) stays constant. The measured layer thicknesses after more than 24 hours are almost the same (± 20 µm) and the standard deviation, which shows the roughness of the crystallized layer is similar, too. The method in general, is a good tool to measure the layer thickness and generates reproducible values provided that the quality of the images is good and the same evaluating person uses the method.

There are many factors, which have an effect on the shown layer thicknesses. These facts are summarized in Figure 6.3-1. Besides the changing layer thickness values due to the used methods also the crystallization process itself or the general process conditions can change the shown layer thicknesses of the measured hydrocolloid-sugar end products.

The standard deviation of all thicknesses is for all measurements with around 100 - 200 µm comparable, no matter which storage time or which kind of hydrocolloid was used. The standard deviation shows the roughness of a layer because the layer growth is not smooth and some crystals are more prominent than others. A higher standard deviation allows conclusions on bigger protruding crystals with hydrocolloid inclusions.

The quality of the taken images to evaluate the layer thickness is very important. Dark pictures with low contrast are difficult to analyze. The sample preparation is therefore a key factor for a reproducible examination of the crystallized layer thicknesses. If the same images of the layers are evaluated two times deviations of 50 µm are possible. Because different lines at different places within the image can be drawn leading to slightly different average layer thickness values. The time can change the layer thickness because at the beginning the building of the layer consumes time till equilibrium is reached. This equilibrium can be changed by different storage temperatures. The higher the temperatures the more sugar can

be dissolved within the gel core and a thinner layer thickness results. If the products differ much in their size (are larger and heavier) thicker layer thicknesses are measurable because the scale changes. However, the initial sugar content (Brix%) plays an important role for the formation of the crystallized sugar layer. If the measured sugar content is much higher (water evaporation occurs) the resulting layer thickness will be thicker compared to products produced with lower sugar contents.

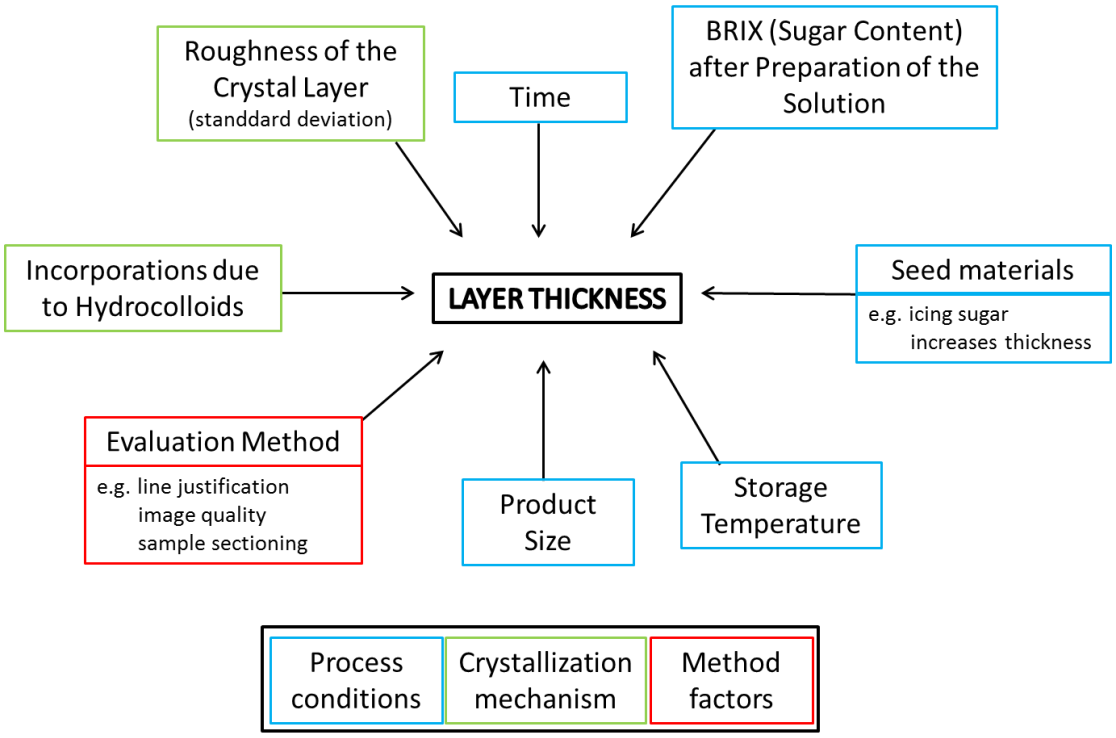

Figure 6.3-1: Influencing factors on layer thicknesses of crystallized coated gels

Even the used seed material can have an influence on the layer thickness. Icing sugar e.g. leads to thicker average layer thicknesses because the seed material dissolves partially in the sugar solution and sticks additionally to the layer. This additional icing sugar coat is not removable. Measurements of end products produced with a pure sugar solution show the same values after 24 hours (equilibrium is reached) but fluctuations due to the previous explained facts occur and are shown in Figure 6.3-1.

It can be said that the purity of the crystalline layer is changed by the use of hydrocolloids. The crystallized layer consists not only of sugar which should be crystallized but also of hydrocolloid material. Therefore, the crystallization mechanism is influenced by the used hydrocolloids (different types and amounts). A successful evaluation of a proofing method of hydrocolloids within the crystallized sugar was possible. Incorporations in the crystallized layer were detected by salting out with ammonium sulfate (AS) and coloring with methylene

blue (photometer evaluation). The three-dimensional network of the hydrocolloids acts like a system which interacts with the sugar molecules. It is shown in literature [Ala05; Gek92; Nis90; Nis92; Nor03; Oak86; Sch07; Wat90] that sugar interacts with the macromolecules of hydrocolloids. The hydroxyl-groups of sugar can modify the junction zones of the hydrocolloids directly. Or the compounds can affect each other indirectly by the competition of water molecules. It is necessary that these molecules can move (mobilizable) while crystallization of sugar happens. During the production of crystalline coated gels the crystallization of sugar for coating purposes and gelation (gel core) occurs simultaneously and therefore the hydrocolloids can be incorporated in the crystallized layer during these processes. The hot solutions (100 °C) are poured into the starch molds and cooled down to ambient temperatures (22 °C). The mobilization of the sugar molecules is limited due to high viscosities and the crystallization occurs around the hydrocolloid clusters. The sugar molecules are not able to move without taking some hydrocolloid clusters into the crystalline material. But not all hydrocolloids lead to an increase in layer thickness after 24 or 48 hours. Gelatin and carrageenans lead to a decrease in layer thickness after 24 hours except for the highest amount of agar (1.5 wt%) compared to layers produced with pure sugar. These results can be explained by the different gel structure and the intensity of incorporations within the crystallized layer. Agar incorporations (for 1.0 and 1.5 wt% agar-sugar solutions) are very numerous and extent the layer thickness noticeable. Bigger clusters are incorporated and increase the measured layer thickness. Therefore, the measured sugar layer appears thicker but it is a mixture of agar and sugar material. A slight effect of the different sugar concentrations (see Chapter 5.2) must be considered, but could not be the only reason for a 200 µm thicker layer thickness of 1.5 wt% agar products compared to products produced without hydrocolloids (pure sugar solution) measured after 48 hours. Such layer increasing effect happens not for the cases of the other tested hydrocolloids. Gelatin and ι-carrageen built a soft and sticky gel and the mobilization of sugar molecules is inhibited. Also the sugar molecules in a κ-carrageen network are not easy to mobilize and interactions with the hydroxyl-groups of sugar and macromolecules of the hydrocolloids inhibit the formation of a thicker layer compared to products without hydrocolloids.

The thermodynamically data (solubility temperature) could confirm the measured layer thicknesses of different gelatin-sugar solutions after 48 hours. With an increasing amount of gelatin the layer thickness decreases. The layer, however, did not reach the thickness of a pure sugar layer after 48 hours. This shows that beside the kinetic effect a thermodynamic change has a great importance for the growth of layers from highly viscous liquids. After 48 hours the equilibrium is probably not yet reached and a further growth of the layers is to be expected. But the overall layer of a 2.4 wt% gelatin-sugar solution will stay thinner than the other tested solutions at equilibrium because more sugar will be solvated within the gel and

remains in a saturated gelatin-sugar core. The gelatin will bind the water so that this water is available to dissolve the sugar molecules in the gel. Fewer molecules can be mobilized for layer growth. This assumes that the amount of solvent stays constant and does not decrease during storage and equilibrium.

Explanations of the different layer thickness (especially, for gelatin and agar) cannot be found by looking at the viscosity values of gelatin and agar solutions. The viscosity of an agar solution is higher than the viscosity of a gelatin solution. The sugar molecule transportation must be better for gelatin products at the beginning (directly after pouring the solution into the molds) under worm conditions (before the gelation process starts). But the overall layer thickness of the gelatin containing solution is thinner than the layers from the agar containing solution although an agar-sugar solution shows a higher viscosity (750 mPas at 80 °C) than the gelatin-sugar solution (150 mPas at 80 °C). Agar products show thicker layers due to faster molecule transportation (higher supersaturation) compared to thinner layers (gelatin). The more agar is used the higher the layers become after 24 and 48 hours. An explanation is that agar molecules are incorporated so the measured layer is thicker (200 µm for 1.5 wt% agar compared to pure sugar products). This model of incorporations is shown in Figure 6.3-2. The unpure crystallized layers (with incorporations) can explain the effect of syneresis. Loss of water during storage takes place for all produced hydrocolloid-sugar products. The crystallized layer of hydrocolloid-sugar solutions is more permeable for water and not as pure as in the cases for layers grown without a hydrocolloid. Therefore, the products containing hydrocolloids are more permeable to release some water out of the gel core (see Figure 6.3-2).

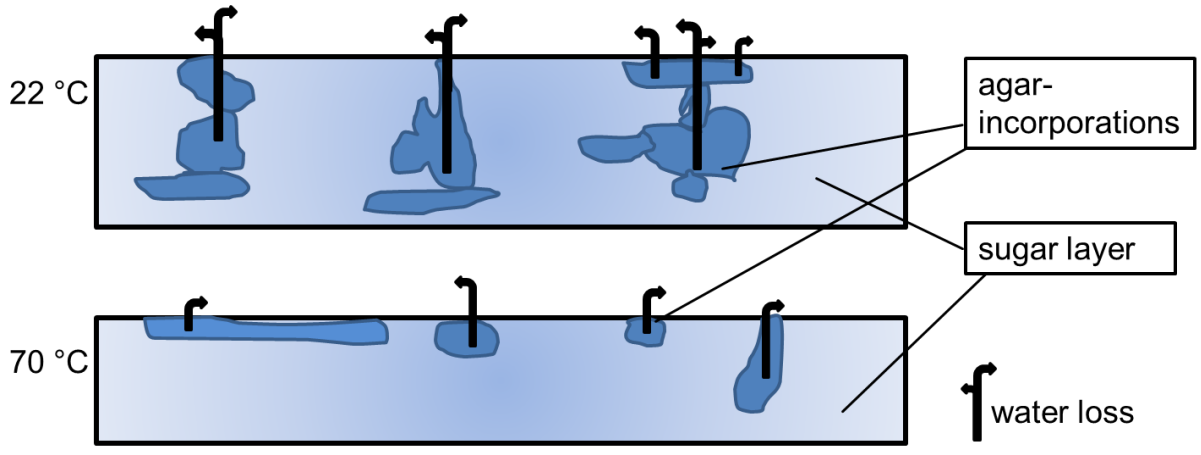

Figure 6.3-2: Model of water loss in a crystallized sugar- hydrocolloid layer

Further growth (> 168 hours) of the layers of end products with hydrocolloids shows that all thicknesses exceed the thickness of end products produced with pure sugar. The increase (250 µm – 600 µm higher values) after > 168 hours (one week) compared to pure sugar layers can be explained by the occurrence of syneresis. The produced end products

containing hydrocolloids lose water over time. The loss of water is possible due to an unpure crystallized layer as shown in the model of water loss (Figure 6.3-2). Evaporation of the solvent (water) leads to a further increase of the crystallized layer. More and more sugar crystallizes due to a lack of solvent. Maurer et al. [Mau12] examined that the addition of sugar (60 %) can increase the water holding capacity of agarose gels. But the experiments showed that even higher sugar amounts (75 %) lead to a loss of water within the gel-sugar system.

Experiments with different storage temperatures (50 °C and ambient temperature) show different results concerning the layer thicknesses. Exemplary, the layer thickness of end products produced with 1.7 wt% ι-carrageen are shown in the Chapter 5.7 of the Results. Higher storage temperatures lead to slightly higher layer thicknesses after 48 hours and thinner layer thicknesses after 168 and 240 hours compared to layers grown at ambient temperature (22 °C). The slightly higher values in layer thicknesses of end products stored at 50 °C can be explained by a better mass transportation at hot conditions (50 °C) due to lower viscosities and higher water evaporation and therefore, a higher supersaturation with more driving force for the crystallization of the layer. The equilibrium between sugar amount in the gel core and at the sugar layer is different at higher temperatures. Storage at higher temperatures leads to a higher dissolution of sugar in the gel core. Therefore, the sugar layer should be thinner at hot conditions (50 °C). But the effect of a different equilibrium at higher temperatures (50 °C) is overlapped by the evaporation process, which increases the supersaturation within the end product and leads to a slightly thicker (75 µm) layer than for end products with ι-carrageen stored at 22 °C for 48 hours. The layer thicknesses of products stored at 22 °C increase more extensively (> 150 µm) after 168 and 240 hours than for end products stored at 50 °C due to a different purity. An explanation is that the hot conditions (50 °C) enable a formation of a more pure crystallized layer and the evaporation is not as high as for end products stored at ambient temperatures (22 °C). At 22 °C more incorporation within the crystallized layers can occur and evaporation of water is higher and more solvent get lost. This lack of solvent supports the crystallization process. The layer thickness is higher due to a high supersaturation. These effects of layer thickness in combination with water loss were also confirmed by experiments with agar containing end products. After 168 hours (storage for 48 hours at 70 °C and afterward at 22 °C) the crystallized layer thickness is thinner (175 µm) compared to end products stored at 22 °C. It was expected that the storage at 22 °C for all end products no matter if they were stored at 70 °C or not reach the same values in layer thicknesses. The layer thickness (about 175 µm) of products stored at 70 °C at the beginning show after 168 hours thinner thicknesses. That can be explained by a more pure crystallized layer with less incorporations and a lower evaporation of water during the storage time.

A certain amount of water loss has no negative effects on the formation of crystallized layers. The loss of water has a stabilizing effect on the end product (thicker layer). But if the loss of water is too high, beside the changes of layer thicknesses over time during storage of the end products other phenomena were seen. The crystallized layers and therefore the appearance of the end product are changed during the storage and water loss process. The crystallized layer is curved after 28 days and the gel core is smaller. The degree of shape loss due to syneresis depends on the temperature fluctuations. The more fluctuations the more syneresis happens. The incorporations of hydrocolloids make the crystallized layer more flexible and less fragile/brittle. The crystallized layer is not as pure as for products produced without hydrocolloids and the volume of the end product can change. Images of the crystals confirmed that the surfaces of crystals grown in hydrocolloid solutions are affected. The unpure layer is less dimensionally stable than a pure sugar layer.

Important requirements for good storage stabilities of the crystallized end products are a complete dissolution of sugar during the preparation of the solution. Invisible little nuclei lead to crystallization within the gel core, which can grow undisturbed during the storage of the final product. Constant storage conditions (humidity and temperature) are beneficial to avoid syneresis within the gel core. It is also important to avoid air bubbles on the top of the poured sugar bodies because these air bubbles lead to an increased permeability for water of the layers. Therefore, the possibility of water loss increases because the formed sugar layer is not uniform and not completely crystallized. A fast further processing of the end products by coating with chocolate or other coating agents like e.g. wax can prevent product changes (water loss). While producing the solution the used sugar amount should not be too high to enable the dissolution of sugar (avoid undesired crystallization in gel core, which leads to a granular mouthfeel). The sugar amount, however, must be high enough to enable the process of layer formation as coating of the gel core. Beside the factors of the neutral system additionally requirements within an acid consisting product have to be considered. Acid leads to a damage of the three-dimensional network of gels (degradation) so the acid has to be added at the last possible moment within the production process and the use of buffers (e.g. Trinatriumcitrate (TNC)) is helpful to avoid inversion and gel degradation. All these influencing factors are summarized in Table 6.1-1.

Stability measurements of the end product´s layers and standard deviations show different effects. The highest stability was measured for 1.5 wt% agar and for ι-carrageen products (after 24 hours, stability > 5000 N/m²). The smallest stability values were shown for gelatin end products. The stability depends on the used hydrocolloid type, hydrocolloid amount and storage time. A decrease in stability from 1.5 wt% agar, κ- and ι-carrageen products from 24 to 48 hours and further for agar till 72 hours can be shown. Different products

(κ-carrageenans) from different producers (Roth or Cargill) can lead to different values in stability. Products with κ-carrageen from Cargill show higher stability values than from Roth. The crystallized layer shows another composition of sugar and hydrocolloid and the gel structure can be different, what results in different stability values for the carrageens. Generally, these changes in stability of hydrocolloid containing products were explained by two different facts. On the one hand, these products are not as crunchy as pure sugar products. That leads to a not hearable breaking of the crust during the stability measurement. The examination of a damaged crust is somehow subjective by notice a visible crack within the crystallized layer. On the other hand, the voluminous hydrocolloid clumps, which are incorporated in the crystallized layer, can dry after 48 hours after production. This drying process of the hydrocolloid incorporations lead to a decrease in volume (water loss and shrinking) and some “microcracks” appear. These “microcracks” lead to an unstable product which tends to break easier with less pressure application. Therefore, these stability values decrease after 48 hours depending on the combination of hydrocolloid incorporations and purity of the crystallized sugar layer. Gelatin products show a linear increase in stability over time (from 5 to 72 hours). That behavior can be explained by the slow mass transport and a slow increase in layer thickness. Gelatin products need more time to reach a constant stability. Further storage of κ- and ι-carrageen products for 168 hours shows an increased stability. This increasing stability is due to water loss over time. The water evaporates slowly through the unpure crystallized layer and solvent gets lost. More and more sugar crystallizes due to a lack of solvent. This increased crystallization leads to higher stability values after storage of 168 hours.
It is necessary to measure as much as possible end products because there are differences between different batches and between different products of the same hydrocolloid. Not all end products have a totally equal shape. Little differences in shape, size or supersaturation of the end products can change the measured stability values. This was shown by the high differences in maximum and minimum values of the stability values.

It can be summarized that hydrocolloids affect the crystallization process and at the same time the crystallizing material (sugar) has also an effect on the gelation of hydrocolloids. Figure 6.3-3 gives an overview of all already explained parameters (influencing factors) concerning the combination of crystallization and gelation. Ulrich [Ulr93] gives influencing factors like supersaturation, temperature, flow rate, additives, surface quality, time of growth and the history of the crystals on crystal growth. Some factors could be explained by experiments of this work (see Figure 6.3-3).
Besides influencing factors, Ulrich [Ulr93] describes also the properties of the crystal growth being influenced by different factors. It could be summarized that purity, firmness, shape,

size distribution, flowability, storage properties and the appearance of crystals are affected during the crystal growth [Ulr93]. These effects occur of course by the use of hydrocolloids during the crystallization of sugar. Here, these effects were confirmed.

Experiments showed that the purity of the crystalline material was influenced by hydrocolloids and therefore, the firmness of the layer was changed. The shape of the sugar crystals was not influenced by hydrocolloids but the appearance of sugar crystals changes due to a changed surface structure. These cracked appearances on the surface are caused by the polymeric structures of hydrocolloids. As well as storage properties are influenced by the use of hydrocolloids.

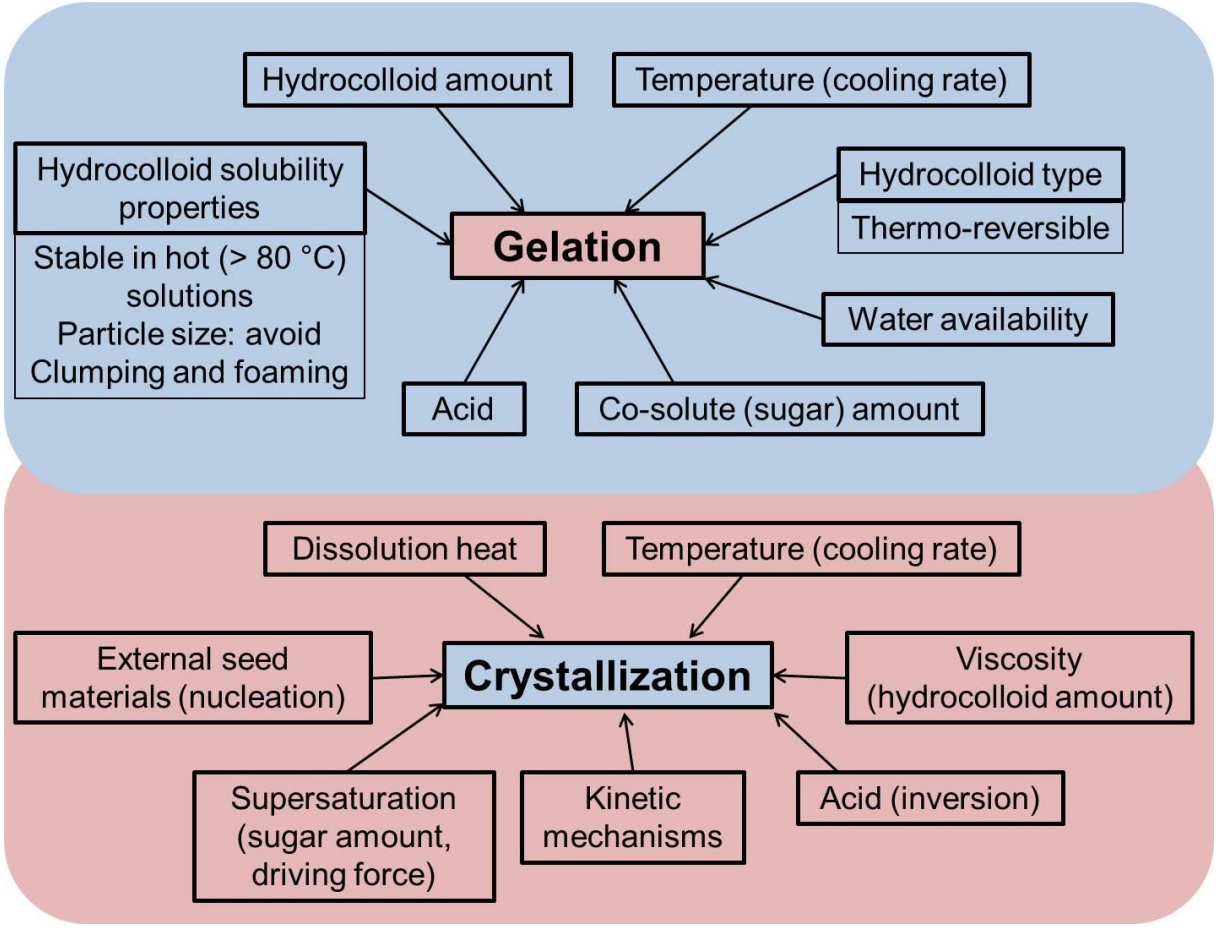

Figure 6.3-3: Influencing factors on gelation and crystallization processes

6.4 Summary of the results

Crystallization of sugar is possible while gelation occurs. The application of different hydrocolloids during the process of product modification and development, especially, in confectionary industry, to achieve a crystalline coated gel is possible. Especially, the application of thermo-reversible hydrocolloids shows desired results. These crystalline coatings can be realized in **one production step**. It was shown that, generally, the addition of texturizing material (hydrocolloids) affects the crystallization of sugar. If a few parameters are fulfilled the **first aim** (named in Chapter 3) that means the **combination of the crystallization process and the process of gelation** is possible.

The **second aim** of this work that means to describe and summarize the changes during the **crystallization process of sugar** (especially, for a coating purpose) in the **presents of hydrocolloids** (agar, gelatin and carrageenans) was successful. Hydrocolloids can **affect** the **liquid phase** by changes in the **diffusion process** (slower molecule transportation) and the **solid phase** that means the **formation of crystals** (installation kinetics with effects on the purity of the layer). These effects result in different product properties (see Table 6.4-1). The Table can be seen as a guideline to choose the most suitable hydrocolloid according to the desired end product properties. The addition of e.g. gelatin leads to changes in solubility and results in a thinner crystallized sugar layer compared to products produced with agar (see Table 6.4-1). Depending on the desired properties (texture, viscosity, layer thickness, storage stability) different hydrocolloids can be selected.
The existence of hydrocolloid structures within the crystalline sugar coat was detected. The storage conditions (temperature and humidity) have to be kept constant and due to a temperature controlled production (high temperatures, > 50 °C) the purity of the crystalline material is increasable. A pure crystalline material (without hydrocolloids) should be achieved due to the undesired process of syneresis and the phenomena of aging of the end products. The aging and syneresis are processes, which should be avoided because the layer thicknesses of the crystalline materials change and the gel core shrinks due to a lack of water. Possible operations against the aging are additional coatings with materials such as chocolate. Changes in layer thicknesses can occur due to the loss of water and due to a change in the metastable zone. Gelatin e.g. leads to an increase in solubility for sugar and the equilibrium changes. More sugar can be dissolved within the gel network and less sugar is transported to the crystalline layer. The layer becomes thinner.

Neutral (with respect to pH) conditions during the production process are beneficial because acid can damage the sugar molecules (called inversion) and degrade the macromolecules of the hydrocolloids. Therefore, the supersaturation is reduced and the crystallization of the desired layer is affected. Degradation of the macromolecules of hydrocolloids leads to

undesired changes in textures (e.g. liquefaction) of the gel core. The addition of flavors and other ingredients which might have an influence on the pH value of the end product have to be well-considered.

Table 6.4-1: Summarized properties of end products by using different hydrocolloids

Desired characteristics:		Agar	Gelatin	κ-carrageen	ι-carrageen
Gel properties	Firm and brittle gel texture	×	-	×	-
	Soft and flexible gel texture	-	×	-	×
Coating properties	Crunchy/hard (high stability > 2000 N/m²)	×	-	×	×
	Soft (low stability < 2000 N/m²)	-	×	-	-
	Causes changes in layer thicknesses	× (+)	× (-)	-	-
Handling during production	High hot viscosity (> 300 mPas)	×	-	×	×
	Low hot viscosity (< 250 mPas)	-	×	-	-
	Dissolving process slow	-	-	×	×
Storage stability (syneresis)	High water loss (>10 %)	-	×	-	×
	Lower water loss (< 8 %)	×	-	×	-

The **third aim** was to screen on new materials for the production process of coated gels. The knowledge on the **suitability of seed materials** (other starches, flours or icing sugar) for the **initiation of the crystallization of sugar** are essential for the potential to lower costs and to optimize the production process of e.g. sugar confectionary. Generally, the use of other seed materials than the commonly used corn starch is possible. Seed materials (starches, flours or icing sugar), lead to changes in the end product qualities. The moisture content is an important property of the seed materials because low moisture contents (< 6 %) support the supersaturation which is necessary at the phase boundary between sugar solution and seed material. This supersaturation is necessary to initiate the nucleation of the sugar molecules. Furthermore, the surface structure of the materials should be edged to form imprints into the seed molds and to initiate the nucleation. Small particles (10 µm) of the seed material are beneficial for the crystallization process due to a uniform nucleation mechanism and a smooth crystallized surface.

7. Summary

The crystallization of sugar seems to be a widely investigated topic but nevertheless in practice there are still some difficulties (unresolved issues). The application of sugar in the food industry is often as one component in a complex mixture. New ingredients are often used during the development of new products. This replacement or addition of new ingredients can change the product properties and the manufacturing process in a desired or undesired way. These can lead to problems during the production of e.g. confectionaries. The influence of hydrocolloids on the crystallization of sugar has been investigated because they are potential additives which certainly change the rheological properties of products.

The coating of food is often realized by the use of an additional production step. The aim of the work was to reduce this additional production step and to realize the coating and shaping of e.g. gel materials at the same time. The combination of the processes of crystallization and the formation of gels was successfully implemented on the basis of commercially available products with an outer crystallized sugar layer and a liquid core inside. Changes in the process and also in the product, which occur through the use of different hydrocolloids, have been identified. The used hydrocolloids are thermo-reversible like e.g. gelatin, agar or carrageenan. The use of different types of hydrocolloids and different amounts shows significant influences on the crystallization of sugar.

The results of this work show different aspects, which help to avoid difficulties while crystallizing sugar in the presence of hydrocolloids. The properties of the initial hydrocolloid-sugar solutions containing different types and amounts of hydrocolloids were investigated. Beside the pH-value, the knowledge on the supersaturation (sugar concentration in Brix%), nucleation, solubility as well as on the viscosities (at temperatures > 70 °C) play an important role while crystallizing highly viscous supersaturated solutions. Effects of hydrocolloids on crystalline sweets (end products) were evaluated by determining the sugar decrease within the gel core over time, layer thickness measurements, stability measurements of the end products, storage stability evaluation as well as the proof of the purity of the crystallized layers. Beside the composition of the end product also the use of different seed materials has got an influence on the shaped and crystallized end products. The properties of the used seed materials (size, surface and moisture content) are important to enforce the crystallization of sugar.

Neutral conditions (with respect to pH) are beneficial because inversion of sugar and degradation of macromolecules of hydrocolloids is prevented. The viscosity is increased by the use of hydrocolloids. A strong increase in the viscosity (at 70 - 110 °C) of a sugar solution was shown by the application of ι-carrageen. Gelatin shows the smallest viscosity increase

(70 - 100 °C) compared to the other tested hydrocolloids. These texture changes due to the application of hydrocolloids can lead to problems (tailing) during the filling of the solutions into the powder molds. It is therefore important, to avoid these problems by a suitable controlling of the temperature.

The measured sugar concentration of the initial sugar solutions with hydrocolloids is slightly increased due to water evaporations during the production process. But generally, this water evaporation can be avoided by a closed system. Furthermore, the decrease of the sugar concentration within the gel core is slower than without the application of hydrocolloids. The mass transport within a three-dimensional network of a gel is hindered and therefore slowed down. The solubility (metastable zone) of a sugar solution with gelatin and ι-carrageen is shifted to lower temperatures whereas the use of agar and κ-carrageen shows only little effects on the metastable zone. The changed solubility of sugar in a gelatin containing solution affects the formation of crystallized layers. A shift to lower temperatures means a higher solubility of sugar in the three-dimensional network of gelatin and therefore a lower amount of sugar can crystallize. The resulting layer thickness is thinner than for products without gelatin. A contrary effect was shown for the layer thicknesses of agar. The layer thicknesses are thicker due to detectable incorporations of agar cluster within the crystallized layer. The proof of gelatin and carrageenan was successful. Mostly, the addition of all hydrocolloids leads to unpure crystallized sugar layers. The detectable occurrence of hydrocolloids in the crystalline sugar layer can explain the reduced storage stability. End products produced with hydrocolloids show an increased loss of water during storage time. Therefore, the products lose their initial nature and properties. The layer crystallizes further during the storage time due to a loss of solvent and the gel core decreases in volume till no loss of water is possible anymore. Therefore, it is essential to protect the end product against the loss of water by e.g. additional coating with chocolate or wax as well as the enabling of constant storage conditions (temperatures and humidity).

The conventional used corn starch as a powder for shaping of gel articles as well as for the production of crystallized sweets (crust pralines) can be altered by other materials. Therefore, different starches, powdered sugar and flours were tested as seed materials to enforce the crystallization. Beside the used materials (hydrocolloid types and sugar) the used external seed material has got an effect on the end products. Particle size (< 10 µm), moisture content (< 6 %) and surface appearance of the seed particles have to be controlled to achieve an enforced, desired crystallization of the supersaturated sugar solution as well as good shaped end products. The crystallization can thus be triggered in a uniformly, controlled and reproducible way. Round and big particles lead to worse crystallizing and shaping results than small and edged seed material particles. Too high moistures within the seed materials (> 10 – 15 %), however, are not beneficial.

The knowledge on the influence of additives (hydrocolloids) on the crystallization of sugar, especially, in confectionary industries is demonstrably essential.
In summary can be said, that the scientific problems:

1. The **combination of crystallization** of sugar **and** the **gelation** of hydrocolloids in **one production step**,
2. Description of changes during the **crystallization process of highly viscous supersaturated sugar solutions** (especially, for a coating purpose) in the **presents of hydrocolloids** (agar, gelatin and carrageenans), with the clarification of the effects of hydrocolloids on:
   2.a: The **liquid phase** by changes in the **diffusion process** (slower molecule transportation) and
   2.b: The **solid phase** that means the **formation of crystals** (installation kinetics with effects on the purity of the layers),
3. **The enforcement of the nucleation process in the crystallization of high viscous supersaturated sugar solutions** by **external seed materials**,

could be described and solved successfully, based on crystalline coated gels (end products). The results lead to a summary of important product properties, which are achievable and desired as well as process parameters, which can be adapted. These important parameters, which should be controlled during the production of crystalline coated gels, are e.g. temperature, time, supersaturation, viscosity and texture properties, layer thicknesses of the crystallized material, as well as storage stability after the production of the end products by e.g. detecting the weight losses (syneresis quantification). Only a testing of different process parameters and adjusting them according to the used materials leads to a consistent product quality.

8. Zusammenfassung

Die Kristallisation von Zucker scheint ein weitgehend untersuchtes Thema zu sein, aber in der Praxis stößt man noch auf einige Schwierigkeiten (ungelöste Probleme). In der Lebensmittelindustrie wird Zucker oft als eine Komponente in einer komplexen Mischung eingesetzt. Während einer Produktneu- oder -weiterentwicklung werden häufig neue Inhaltsstoffe eingesetzt. Dieser Austausch oder die Zugabe neuer Inhaltsstoffe kann die Produkteigenschaften und den Herstellungsprozess auf eine gewünschte oder unerwünschte Weise verändern. Es kann somit zu Problemen bei der Produktion kommen. Es wurde der Einfluss von Hydrokolloiden auf die Zuckerkristallisation untersucht, weil sie potentielle Zusatzstoffe sind, die rheologische Eigenschaften mit Sicherheit verändern.

Werden Lebensmittel beschichtet, dann meist in einem zusätzlichen Arbeitsschritt. Ziel der Arbeit war es, einen Arbeitsschritt zu reduzieren und das Ummanteln und Ausformen von z. B. Gelartikeln gleichzeitig zu realisieren. Die Kombination des Kristallisationsprozesses und der Gelbildung wurde erfolgreich, in Anlehnung an handelsübliche Produkte mit einer äußeren kristallisierten Zuckerschicht und einem flüssigen Kern im Inneren, realisiert. Es konnten Veränderungen im Prozess und auch am Produkt festgestellt werden, die durch den Einsatz von Hydrokolloiden auftreten. Die verwendeten Hydrokolloide sind thermoreversibel wie z. B. Gelatine, Agar oder Karrageen. Die Verwendung verschiedener Hydrokolloidarten und auch unterschiedlicher Mengen zeigt deutliche Einflüsse auf die Kristallisation von Zucker.

Die Ergebnisse dieser Arbeit zeigen die unterschiedlichen Aspekte, die bei der Zugabe von Texturierungsmaterialien (Hydrokolloiden) zu berücksichtigen sind. Die Eigenschaften der Ausgangs-Hydrokolloid-Zucker-Lösungen mit verschiedenen Hydrokolloidtypen und Mengen, wurden untersucht. Neben dem pH-Wert, spielen auch die Kenntnisse über die Übersättigung (Zuckerkonzentration in Brix%), die Keimbildung, die Löslichkeit sowie die Viskosität (bei Temperaturen > 70 °C) eine wichtige Rolle bei der Kristallisation hochviskoser übersättigter Lösungen. Der Einfluss von Hydrokolloiden auf die kristallin beschichteten Gele (Endprodukte) konnten durch die Bestimmung der zeitabhängigen Zuckerabnahme innerhalb des Gelkerns, die Schichtdickenermittlung, Stabilitätsmessungen der Endprodukte, die Lagerstabilitätsbewertung sowie die Beurteilung der Reinheit kristallisierter Schichten gezeigt werden. Neben der Zusammensetzung des Endprodukts wirkt sich auch die Verwendung verschiedener Pudermaterialien auf das geformte und kristallisierte Endprodukt aus. Die Eigenschaften der Pudermaterialien (Größe, Oberfläche und Feuchtegehalt) beeinflussen das Auslösen der Keimbildung für die Kristallisation von Zucker.

Neutrale Bedingungen sollten angestrebt werden, weil die Invertierung von Zucker und der Abbau von Hydrokolloid-Makromolekülen dadurch verhindert werden. Die Viskosität wird durch Hydrokolloidverwendung erhöht. Ein sehr starker Viskositätsanstieg (70 - 110 °C) wurde durch den Einsatz von ι-Karrageen festgestellt. Gelatine hingegen zeigt die kleinste Viskositätszunahme (70 - 100 °C) verglichen mit den anderen getesteten Hydro-kolloiden. Die gelbildenden Eigenschaften der Hydrokolloide führen zu Texturänderungen, die beim Füllen der Lösungen in Puderformen zu Problemen wie „Tailing“ führen, was jedoch durch eine geeignete Temperaturführung vermeidbar ist.
Die gemessene Zuckerkonzentration der Ausgangszuckerlösungen mit Hydrokolloiden ist aufgrund von Wasserverdunstungen während des Herstellungsprozesses leicht erhöht. Ein Wasserverlust in der industriellen Praxis kann jedoch durch geschlossene Behälter vermieden werden. Weiterhin ist die Abnahme der Zuckerkonzentration innerhalb des Gelkerns verlangsamt. Der Massetransport innerhalb eines drei-dimensionalen Netzwerkes eines Gels wird behindert. Die Löslichkeit (metastabile Zone) einer Zuckerlösung mit Gelatine und ι-Karrageen wird zu niedrigeren Temperaturen verschoben, während Agar und κ-Karrageen nur geringe Auswirk-ungen auf die metastabile Zone zeigen. Die veränderte Löslichkeit von Zucker in einer Lösung, die Gelatine enthält, führt zu einer veränderten kristallisierten Schichtdicke des Endprodukts. Eine Verschiebung der metastabilen Zone zu niedrigeren Temperaturen bedeutet, dass eine höhere Löslichkeit von Zucker im drei-dimensionalen Netz von Gelatine möglich ist und deshalb weniger Zucker auskristallisiert. Die resultierende Schichtdicke der Endprodukte ist dünner, als die der Produkte ohne Gelatine. Eine entgegengesetzte Wirkung auf die Schichtdicke kann für Agar gezeigt werden. Die Schichtdicken der Endprodukte mit Agar sind aufgrund der nachweisbaren Einlagerungen von Agar-Cluster innerhalb der kristallisierten Schicht dicker. Der Nachweis von Gelatine und Karrageen war ebenso erfolgreich. Die Zugabe aller Hydrokolloide führt zumeist zu unrein kristallisierten Zuckerschichten. Das nachweisbare Auftreten von Hydrokolloiden in der kristallinen Zuckerschicht bewirkt auch eine verminderte Lagerstabilität. Die Endprodukte zeigen einen erhöhten Wasserverlust während der Lagerung. Die Produkte verlieren ihre ursprüngliche Beschaffenheit und Eigenschaften. Die Schicht des Endproduktes kristallisiert während der Lagerung weiter, aufgrund des Wasserverlustes wodurch der Gelkern schrumpft, bis kein Wasserverlust mehr möglich ist. Deshalb ist es wichtig, das Endprodukt gegen Wasserverlust zu schützen z. B. durch zusätzliche Beschichtung mit Schokolade oder Wachs sowie die Einhaltung konstanter Lagerungsbedingungen (Temperaturen und Luftfeuchtigkeit).

Der herkömmliche Einsatz von Maisstärke als Puder zur Formgebung von Gelartikeln sowie zur Herstellung von Krustenpralinen kann durch den Einsatz anderer Materialien (Formpuder) verändert werden. Deshalb wurden unterschiedliche Stärken, Puderzucker und

auch Mehle für den Einsatz als Materialien zur Auslösung der Kristallisation getestet. Die Partikelgröße (< 10 µm), der Feuchtegehalt (< 6 %) und die Oberflächenstruktur der Partikel des Saatmaterials müssen gesteuert werden, um eine erzwungene, gewünschte Kristallisation der übersättigten Zuckerlösung zu erzielen sowie gut geformte Endprodukte zu erreichen. Die Kristallisation kann dadurch gleichmäßig, kontrolliert und reproduzierbar ausgelöst werden. Runde und große Partikel führen zu schlechteren Kristallisations- und Formgebungsergebnissen als kleine und scharfkantige Partikel. Zu hohe Feuchtigkeiten (> 10 – 15 %) im Saatmaterial sind dagegen unvorteilhaft.

Das Wissen über den Einfluss von Additiven (Hydrokolloiden) auf die Kristallisation von Zucker, insbesondere in der Süßwarenindustrie, ist nachweislich von Bedeutung.
Zusammenfassend kann gesagt werden, dass die bereits erwähnten wissenschaftlichen Fragestellungen:

1. **Kombination** der **Zuckerkristallisation** mit der **Gelierung** von Hydrokolloiden in **einem Prozessschritt**,
2. Beschreibung der **Veränderungen** während der **Kristallisation** hochviskoser, übersättigter Zuckerlösungen (zur Ummantelung) in Anwesenheit von verschiedenen **Hydrokolloiden** (Agar, Gelatine und Karrageen) mit der Fokussierung von Hydrokolloideffekten auf:
   2.a: Die **flüssige Phase**, durch Veränderungen im Diffusionsprozess (langsamerer Molekültransport) und
   2.b: Die **feste Phase**, das heißt auf die Einbaukinetik beim Kristallwachstum (Reinheitsveränderungen der ausgebildeten Schichten),
3. **Erzwingen der Keimbildung bei der Kristallisation von hochviskosen, übersättigten Zuckerlösungen** durch **Saatmaterialien (Formpuder)**,

erfolgreich beschrieben und gelöst werden konnten. Die Ergebnisse zeigen die resultierenden Produkteigenschaften, sowie auch unterschiedliche, kontrollierbare Prozessparameter, die während der Produktion von kristallin ummantelten Gelprodukten angepasst werden müssen. Diese zu kontrollierenden Parameter sind beispielsweise Temperatur, Zeit, Übersättigung, Viskosität, Schichtdicken des kristallisierten Materials sowie die Lagerungsstabilität nach der Produktion durch Erfassung des Gewichtsverlustes (Quantifizierung der Synärese). Denn nur, wenn unterschiedliche Prozessparameter getestet und angepasst werden, kann bei jeder Veränderung der Produktzusammensetzung eine gleichbleibende Produktqualität erreicht werden.

9. Symbols and abbreviations

Latin symbols

g	[m/s²]	acceleration of gravity
l	[cm]	length of solution the light passes through
t	[s]	time
T	[°C]	temperature

Greek symbols

ε	[m² mol $^{-1}$]	molar absorption coefficient
ŋ	[Pa s]	dynamic viscosity or intrinsic viscosity
κ	[-]	kappa
ι	[-]	iota

Other symbols

A	[L mol^{-1} cm $^{-1}$]	extinction
A	[-]	constant
c	[mol/L]	concentration of the solution
kD	[-]	Kilodalton
K	[-]	constant
I_0	[Wm^{-2}]	intensity of incoming light
I	[Wm^{-2}]	intensity of transmitted light
M	[g/mol]	molecular weight
q_3	[%]	Particle size distribution density
Q_3	[%]	Cumulative size distribution
x	[µm]	Particle diameter

Abbreviations

AS	ammonium sulfate
DSC	differential scanning calorimetry
MZW	metastable zone width
MFG	manufacturing date
R	producer Roth
C	producer Cargill
SEM	scanning electronic microscope (under atmospheric conditions)
wt%	weight percent
G´	elastic modulus (storage)

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11. Appendix

Table 11-1: Viscosity of initial solutions in dependency of different temperatures with standard deviation

Additive	Temperature [°C]					
	70	80	85	90	100	110
	Viscosity [mPas]					
pure sugar solution	187.70 ± 10.31	107.55 ± 4.18	-	66.14 ± 3.05	44.63 ± 2.11	-
0.5 wt% agar	302.06 ± 10.45	176.69 ± 5.43	-	110.95 ± 3.37	75.23 ± 2.41	-
1.0 wt% agar	632.23 ± 50.72	372.52 ± 27.39	-	234.49 ± 16.88	158.16 ± 13.54	-
1.5 wt% agar	1306.22 ± 233.90	730.71 ± 152.11	-	464.19 ± 92.35	320.75 ± 66.97	-
3.5 wt% agar (20 g sugar)	1320.20 ± 204.13	917.84 ± 103.27	-	669.59 ± 57.66	483.65 ± 22.47	-
6.5 wt% agar (no sugar)	1941.65 ± 115.07	1540.04 ± 100.88	-	1136.52 ± 105.00	472.33 ± 134.50	-
1.5 wt% gelatine	239.06 ± 17.70	141.84 ± 6.95	-	87.90 ± 5.97	57.80 ± 3.85	-
2.4 wt% gelatine	232.69 ± 41.67	140.88 ± 23.29	-	91.18 ± 13.36	62.04 ± 8.83	-
5.2 wt% gelatin (20 g sugar)	18.11 ± 1.70	13.89 ± 0.56	-	10.87 ± 0.50	10.03 ± 1.71	-
8.9 wt% gelatin (no sugar)	7.52 ± 0.78	6.14 ± 0.64	±	5.28 ± 0.41	4.11 ± 0.34	-
0.2 wt% κ-carrageen (R)	706.03 ± 11.88	541.41 ± 8.23	-	384.13 ± 9.42	271.77 ± 7.49	-
0.5 wt% κ-carrageen (R)	-	-	1120.12 ± 39.71	877.34 ± 39.17	592.51 ± 34.48	-
1.2 wt% κ-carrageen (R) (20 g sugar)	232.40 ± 23.76	172.38 ± 12.36	-	132.98 ± 9.20	106.13 ± 6.37	-

Additive	Temperature [°C]					
	70	80	85	90	100	110
	Viscosity [mPas]					
2.3 wt% carrageen (R) (no sugar)	155.89 ± 5.26	123.51 ± 5.00	-	95.55 ± 3.80	73.36 ± 1.76	-
0.5 wt% κ-carrageen (C)	792.13 ± 98.59	532.77 ± 66.61	-	353.53 ± 39.92	253.57 ± 26.19	-
0.7 wt% κ-carrageen (C)	1117.00 ± 45.90	766.44 ± 24.52	-	505.31 ± 17.37	358.96 ± 11.63	-
1.7 wt% κ-carrageen (C) (20 g sugar)	239.91 ± 16.05	182.75 ± 13.34	-	144.98 ± 8.17	117.17 ± 6.61	-
3.2 wt% κ-carrageen (C) (no sugar)	160.98 ± 4.39	126.10 ± 3.28	-	99.57 ± 2.28	78.24 ± 1.61	-
1.0 wt% ι-carrageen	-	1689.14 ± 70.76	-	964.64 ± 98.14	615.25 ± 24.89	-
1.7 wt% ι-carrageen	-	-	-	2296.56 ± 144.91	1283.60 ± 59.91	363.42 ± 37.84
3.9 wt% ι-carrageen (20 g sugar)	1717.42 ± 147.25	1042.90 ± 165.53	-	900.94 ± 48.38	674.30 ± 15.02	-
7.3 wt% ι-carrageen (no sugar)	2018.47 ± 146.36	1334.44 ± 43.13	-	1212.91 ± 29.24	808.66 ± 93.37	-

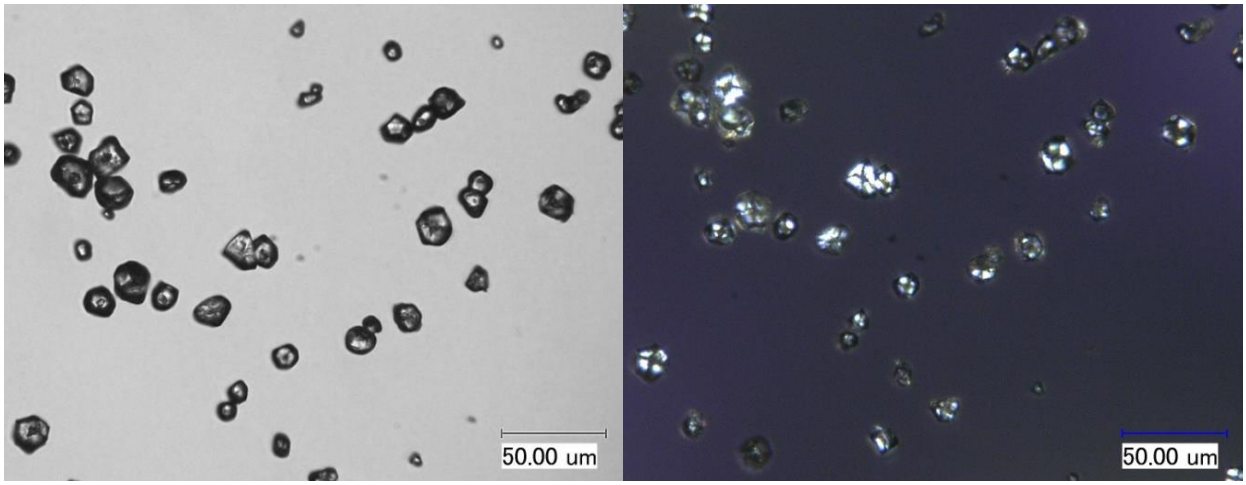

Figure 11-1: Corn starch (left: Without polarization, right: Polarization) [Kat16]

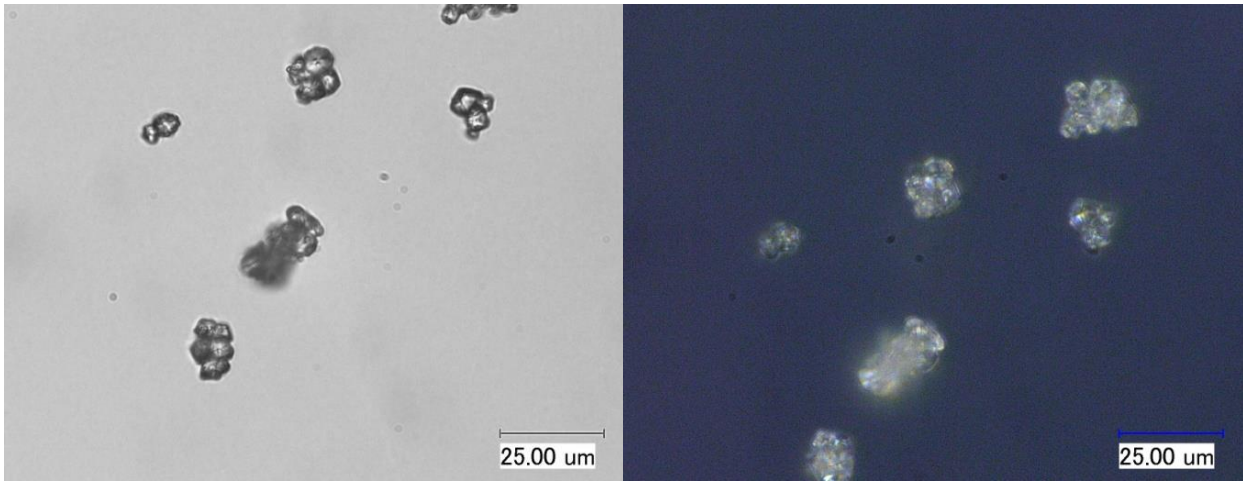

Figure 11-2: Rice starch (left: Without polarization, right: Polarization) [Kat16]

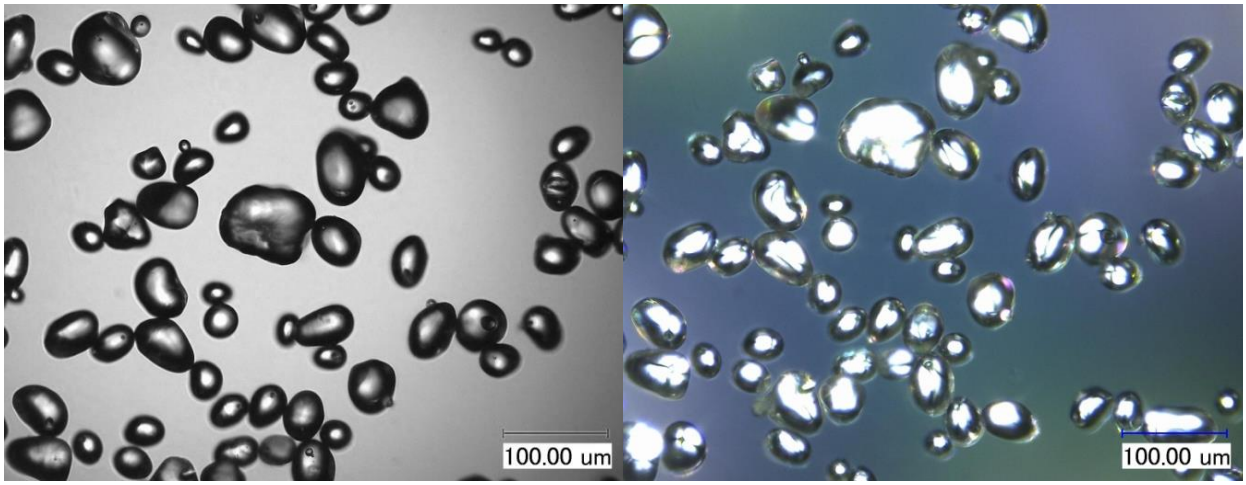

Figure 11-3: Potato starch (left: Without polarization, right: Polarization) [Kat16]

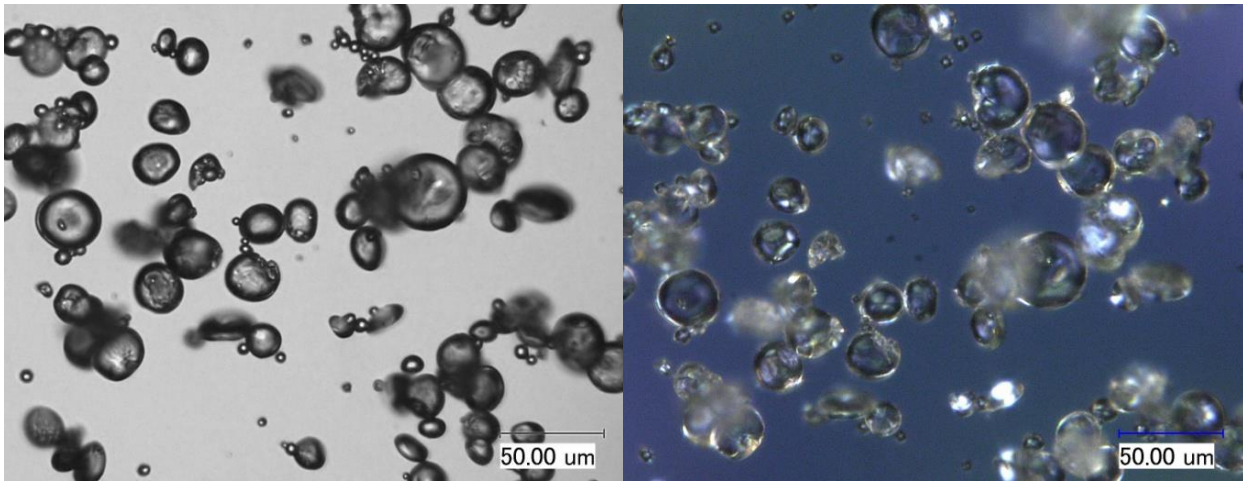

Figure 11-4: Wheat starch (left: Without polarization, right: Polarization) [Kat16]

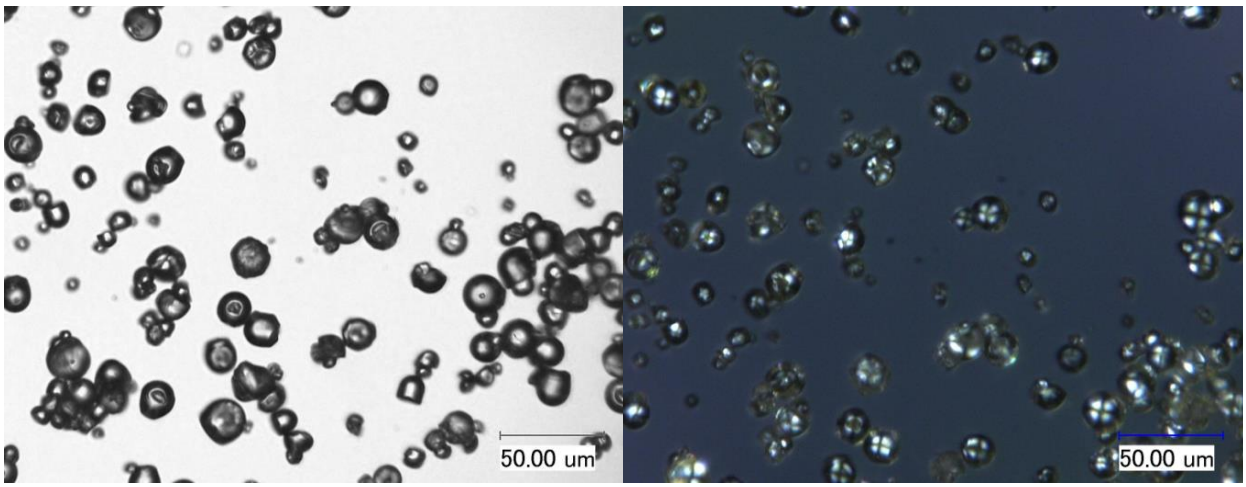

Figure 11-5: Tapioca starch (left: Without polarization, right: Polarization) [Kat16]

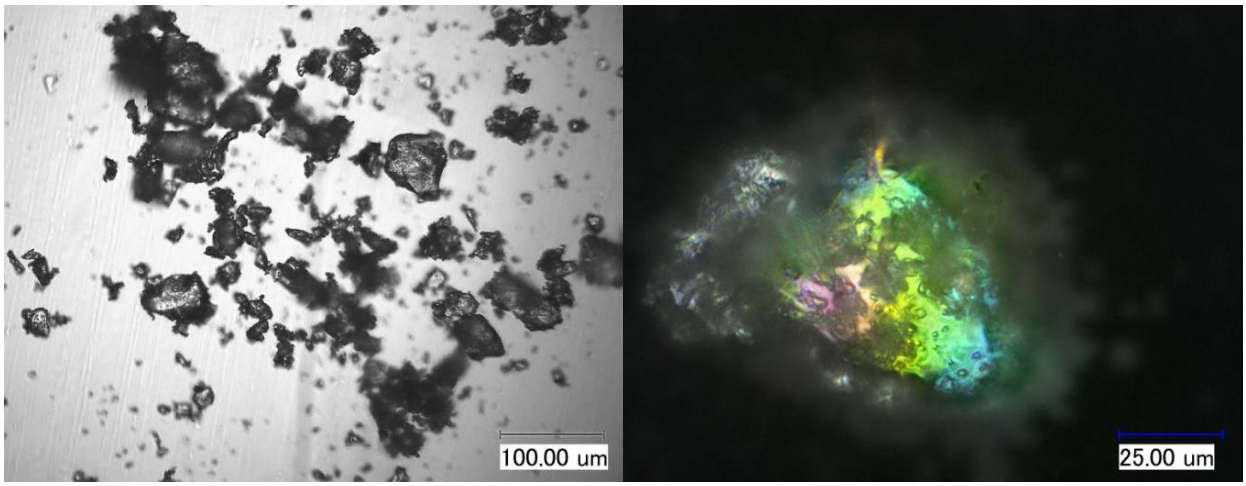

Figure 11-6: Icing sugar (left: Without polarization, right: Polarization) [Kat16]

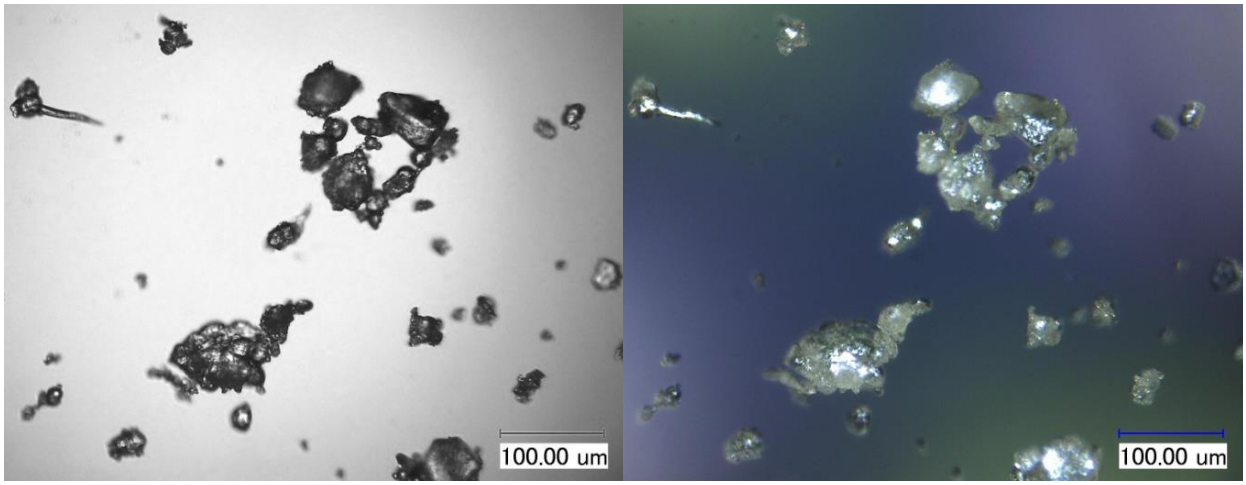

Figure 11-7: Wheat flour type 405 (left: Without polarization, right: Polarization) [Kat16]

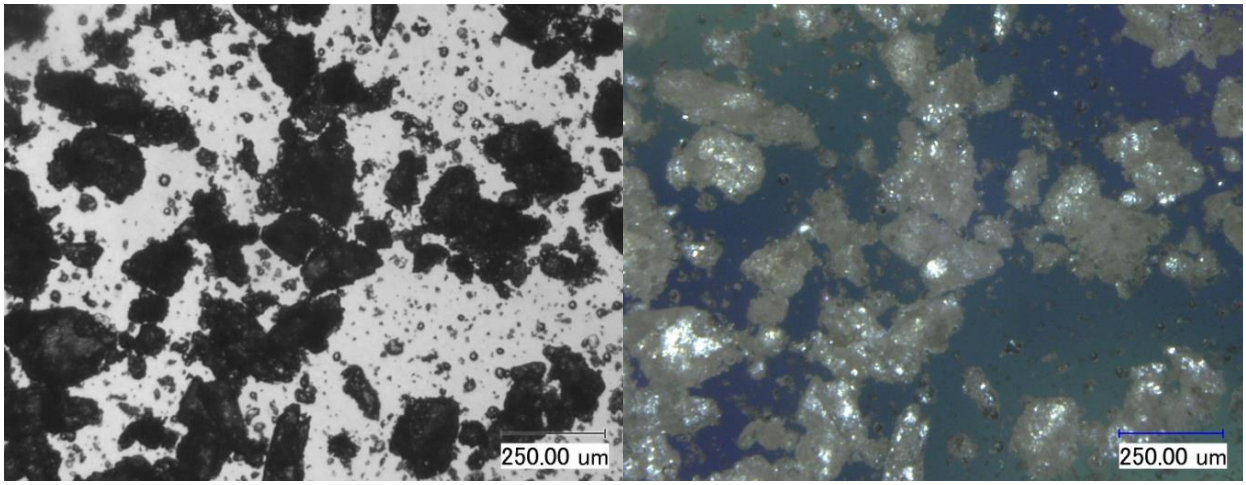

Figure 11-8: Wheat flour instant (left: Without polarization, right: Polarization) [Kat16]

Table 11-2: Sugar concentration of κ-carrageen at 50 °C [Sin16]

Sugar content [Brix%] at 25 °C			
Storage time [h] at 50 °C	**0.5 wt% κ-carrageen (R)**	**0.7 wt% κ-carrageen (C)**	**1.7 wt% ι-carrageen**
168	71.8 ± 1.1	71.4 ± 0.7	71.8 ± 0.8
240	72.2 ± 0.5	71.3 ± 0.8	71.1 ± 0.7

Table 11-3: Sugar concentration of κ-carrageen with depowdering or not

Sugar content [Brix%] at 25 °C		
Storage time [h]	**0.5 wt% κ-carrageen (R) depowdered after 24 h**	**0.5 wt% κ-carrageen (R) not depowdered after 24 h**
168	68.4 ± 0.4	68.4 ± 0.3
240	68.1 ± 0.2	67.9 ± 0.2
672	67.8 ± 0.2	67.9 ± 0.5

Table 11-4: Influence of seed materials on Brix%

	Sugar content [Brix%] at 25 °C and standard deviation of pure sugar products		
Time	**10 % corn starch moisture**	**6 % corn starch moisture**	**Icing sugar as powder mold**
0	77.3 ± 0.2	78.3 ± 0.7	80.6 ± 0.8
1	76.0 ± 0.5	76.9 ± 1.7	-
2	75.2 ± 1.4	74.3 ± 1.0	-
3	74.8 ± 0.6	74.0 ± 0.5	-
4	74.5 ± 1.0	74.2 ± 0.5	-
5	72.4 ± 0.7	73.7 ± 0.8	-
6	72.3 ± 1.2	71.9 ± 1.8	-
7	71.9 ± 0.6	71.6 ± 1.3	-
23	68.0 ± 0.2	67.9 ± 0.1	-
24	67.9 ± 0.1	68.1 ± 0.4	68.0 ± 0.2
28	67.7 ± 0.5	67.8 ± 0.1	-
30	67.7 ± 0.3	67.7 ± 0.1	-
47	-	67.4 ± 0.2	-
48	67.2 ± 0.4	-	67.6 ± 0.1

Table 11-5: Influence of seed materials and their properties on layer thickness

Layer thickness at different conditions and after different times	Mean [µm] ± Standard deviation	Min [µm]	Max [µm]
6 % corn starch moisture (24 h)	863.3 ± 151.9	470.2	1515.4
10 % corn starch moisture (24 h)	1169.6 ± 181.0	673.3	2077.1
pure sugar solution in corn starch (24 h)	1012.2 ± 256.9	529.6	1655.8
pure sugar solution in corn starch (48 h)	938.4 ± 217.4	554.7	1746.6
pure sugar solution in icing sugar mold (24 h)	1484.7 ± 73.1	545.0	2621.8
pure sugar solution in icing sugar mold (48 h)	1596.5 ± 194.7	570.6	2759.9
2.4 wt% gelatin in corn starch (24 h)	439.8 ± 115.2	231.5	819.4
2.4 wt% gelatin in corn starch (48 h)	615.0 ± 209.3	126.0	529.6
2.4 wt% gelatin in icing sugar (24 h)	528.6 ± 110.9	250.9	1101.3
2.4 wt% gelatin in icing sugar (48 h)	759.74214 ± 141.9	277.4	1373.8
1.5 wt% agar in corn starch (24 h)	962.1 ± 293.5	283.0	1923.4
1.5 wt% agar in corn starch (48 h)	1176.6 ± 359.9	467.3	2812.1
1.5 wt% agar in icing sugar (24 h)	990.0 ± 239.8	480.8	1966.6
1.5 wt% agar in icing sugar (48 h)	1256.5 ± 344.1	393.8	2326.6
1.5 wt% gelatin depowdered after 24 h (168 h)	1002.5 ± 236.0	377.9	1759.1
1.5 wt% gelatin not depowdered (168 h)	1040.3 ± 224.5	424.5	1828.7
2.4 wt% gelatin depowdered after 24 h (168 h)	985.9 ± 211.0	409.0	1617.9
2.4 wt% gelatin not depowdered (168 h)	997.0 ± 203.0	509.7	1691.8
1.5 wt% gelatin depowdered after 24 h (240 h)	1163.3 ± 299.4	556.9	2087.0
1.5 wt% gelatin not depowdered (240 h)	1157.0 ± 277.7	447.1	2005.8
2.4 wt% gelatin depowdered after 24 h (240 h)	1235.0 ± 304.4	325.0	2388.9
2.4 wt% gelatin not depowdered (240 h)	1215.5 ± 247.4	732.8	2065.8

Table 11-6: Influence of seed materials on sugar contents of 1.5 wt% agar products at different storage temperatures [Poe16]

Time after production [h]	**Seed material**					
	Corn starch			**Icing sugar**		
	Temperature [°C]					
	23	50	70	23	50	70
	Sugar content [Brix%] of 1.5 wt% agar products					
0	80.8 ± 0.4	81.6 ± 0.3	80.8 ± 0.4	80.4 ± 1.4	80.1 ± 0.6	80.6 ± 1.4
24	72.3 ± 1.0	73.8 ± 0.4	77.8 ± 0.6	73.7 ± 0.8	73.3 ± 0.5	77.3 ± 0.3
48	68.9 ± 0.5	73.4 ± 0.1	77.6 ± 0.7	68.3 ± 1.3	73.1 ± 0.5	77.4 ± 0.2
72	68.0 ± 0.2	73.4 ± 0.2	77.8 ± 0.7	68.0 ± 0.3	73.1 ± 0.2	77.1 ± 0.4
after 72 h: storage of the agar products at 23 °C						
168	67.6 ± 0.2	67.8 ± 0.5	68.1 ± 0.3	67.7 ± 0.6	68.6 ± 1.4	69.7 ± 1.2

Table 11-7: Influence of different sugar amounts on sugar content of 1.5 wt% agar products [Poe16]

Time after production [h]	**Sugar amount [g] in 1.5 wt% agar products**		
	78.50	74.58	82.43
	Sugar content [Brix%] at 25 °C		
0	81.6 ± 0.3	77.4 ± 0.7	84.6 ± 0.4
24	73.8 ± 0.4	73.9 ± 0.3	73.6 ± 0.7
48	73.4 ± 0.1	73.2 ± 0.5	72.2 ± 0.2

Table 11-8: Sugar content of hydrocolloid-sugar solutions at different times

Sugar content [Brix%] at 25 °C												
time [h]	pure sugar solution	0.5 wt% agar	1.0 wt% agar	1.5 wt% agar	1.5 wt% gelatin	2.4 wt% gelatin	1.0 wt% ι-carrageen	1.7 wt% ι-carrageen	0.2 wt% κ-carrageen (R)	0.5 wt% κ-carrageen (R)	0.5 wt% κ-carrageen (C)	0.7 wt% κ-carrageen (C)
0	79.4 ± 0.6	80.0 ± 0.6	80.3 ± 0.7	80.2 ± 0.6	78.6 ± 0.6	78.0 ± 0.8	81.5 ± 1.1	81.8 ± 0.7	81.8 ± 0.7	81.4 ± 0.8	80.8 ± 0.6	80.8 ± 06
3	-	-	-	-	-	-	78.0 ± 0.6	77.5 ± 0.7	77.4 ± 0.4	77.9 ± 1.2	77.4 ± 0.6	77.9 ± 0.6
4	72.8 ± 0.7	77.1 ± 1.1	78.2 ± 0.8	79.1 ± 0.4	77.3 ± 0.6	76.3 ± 0.6	-	-	-	-	-	-
24	68.2 ± 0.7	70.8 ± 0.8	71.0 ± 1.1	71.8 ± 1.2	73.2 ± 0.5	74.1 ± 1.0	72.6 ± 0.8	74.0 ± 0.8	71.9 ± 0.3	73.1 ± 0.4	72.3 ± 1.0	71.8 ± 1.0
48	67.8 ± 0.1	68.1 ± 0.5	68.4 ± 0.5	69.1 ± 0.6	70.1 ± 1.3	71.7 ± 0.8	68.7 ± 0.4	69.8 ± 0.3	70.3 ± 0.3	70.5 ± 0.4	69.3 ± 0.5	69.8 ± 0.3
72	67.8 ± 0.2	68.0 ± 0.4	68.3 ± 0.4	68.7 ± 0.3	69.4 ± 0.5	70.8 ± 0.5	68.5 ± 0.4	68.3 ± 0.3	69.1 ± 0.2	68.9 ± 0.7	68.5 ± 0.6	68.7 ± 0.2
168	67.2 ± 0.1 -	-	-	69.7 ± 1.2	-	-	68.3 ± 0.3	68.3 ± 0.3	67.8 ± 0.1	68.4 ± 0.2	67.7 ± 0.3	68.0 ± 0.2
240	67.3 ± 0.1	-	-	-	-	-	-	68.8 ± 0.9	-	67.9 ± 0.2	-	67.5 ± 0.3
672	67.1 ± 0.1	-	-	-	-	-	-	-	-	67.6 ± 0.2	-	67.7 ± 0.1

Table 11-9: Layer thicknesses of hydrocolloid-sugar products after different times

Layer thickness [µm] after different times								
Time [h]	pure sugar solution	1.5 wt% agar	2.4 wt% gelatin	0.7 wt% κ-carrageen (C)	0.7 wt% κ-carrageen (C) at 50 °C	0.5 wt% κ-carrageen (R)	1.7 wt% ι-carrageen	1.7 wt% ι-carrageen at 50 °C
5	594.6 ± 120.4	466.1 ± 111.8	-	-	-	-	-	-
24	989.9 ± 227.4	972.3 ± 288.5	439.8 ± 115.2	793.4 ± 102.9	-	822.5 ± 117.6	807.1 ± 153.0	-
48	981.3 ± 216.1	1120.9 ± 301.8	615.0 ± 209.3	1000.1 ± 144.8	890.3 ± 134.6	904.5 ± 137.5	806.9 ± 185.3	872.4 ± 206.9
72	929.9 ± 224.7	1054.7 ± 341.6	771.2 ± 139.8	-	-	-	-	-
168	982.6 ± 257.6	1372.7 ± 384.5	985.9 ± 211.0	1130.3 ± 162.3	976.2 ± 128.3	1339.7 ± 243.3	1319.6 ± 271.4	1077.1 ± 211.4
240	971.0 ± 208.1	-	1235.0 ± 304.4	1280.3 ± 204.2	971.0 ± 119.4	1272.8 ± 240.1	1555.2 ± 314.1	1324.7 ± 237.2
672	977.6 ± 208.6	-	-	1274.8 ± 165.3	1108.7 ± 130.1	1466.5 ± 261.5	-	-

Table 11-10: Layer thicknesses of hydrocolloid-sugar products with different hydrocolloid amounts

Additives	**Layer thickness [µm] in dependence of hydrocolloid amounts after 24 (left) and 48 h (right)**	
pure sugar solution	989.9 ± 227.4	981.3 ± 216.1
0.5 wt% agar	835.2 ± 274.8	914.4 ± 313.3
1.0 wt% agar	865.3 ± 227.7	1036.0 ± 344.5
1.5 wt% agar	972.3 ± 288.5	1120.9 ± 301.8
1.5 wt% gelatin	488.8 ± 172.8	702.1 ± 237.3
2.4 wt% gelatin	439.8 ± 115.2	615.0 ± 209.3
1.0 wt% ι-carrageen	1099.5 ± 223.1	922.0 ± 155.6
1.7 wt% ι-carrageen	807.1 ± 153.0	806.9 ± 185.3
0.2 wt% κ-carrageen (R)	941.9 ± 262.6	863.1 ± 194.4
0.5 wt% κ-carrageen (R)	822.5 ± 117.6	904.5 ± 137.5
0.5 wt% κ-carrageen (C)	616.6 ± 76.2	788.6 ± 110.4
0.7 wt% κ-carrageen (C)	793.4 ± 102.9	1000.1 ± 144.8

Table 11-11: Differences between multiple measurements of layer thicknesses of the same hydrocolloid

Layer thickness [µm] of different charges after 24 h		
Additives	**First measurement**	**Second measurement**
pure sugar solution	1012.2 ± 256.9	967.6 ± 198.0
1.0 wt% ι-carrageen	1095.2 ± 221.3	1086.8 ± 174.2
1.7 wt% ι-carrageen	856.5 ± 141.3	786.2 ± 144.1
0.2 wt% κ-carrageen (R)	998.4 ± 288.8	871.0 ± 232.4
0.5 wt% κ-carrageen (R)	861.7 ± 116.8	841.0 ± 109.0
0.5 wt% κ-carrageen (C)	659.9 ± 77.5	563.9 ± 73.7
0.7 wt% κ-carrageen (C)	785.1 ± 95.8	808.5 ± 97.6

Table 11-12: Layer thicknesses of 1.5 wt% agar products at different storage temperatures produced in corn starch molds [Poe16]

Time after production [h]	**Temperature [°C]**		
	23	50	70
	Layer thickness [µm] of 1.5 wt% agar products produced in corn starch molds		
5	474.7 ± 118.2	457.6 ± 105.5	350.5 ± 75.2
24	962.1 ± 293.5	1019.8 ± 315.9	535.0 ± 120.0
48	1176.6 ± 359.9	1078.1 ± 271.3	576.3 ± 129.2
After 48 h: storage at 23 °C			
72	1131.5 ± 425.2	1369.7 ± 327.4	983.3 ± 304.2
168	1372.7 ± 384.5	1401.4 ± 352.3	1195.5 ± 278.6

Table 11-13: Layer thicknesses of 1.5 wt% agar products at different storage temperatures produced in icing sugar molds [Poe16]

Time after production [h]	**Temperature [°C]**		
	23	50	70
	Layer thickness [µm] of 1.5 wt% agar products produced in icing sugar molds		
5	448.7 ± 116.8	381.5 ± 91.8	346.3 ± 81.9
24	990.0 ± 239.8	932.1 ± 291.2	504.2 ± 99.3
48	1256.5 ± 344.1	921.7 ± 312.3	524.4 ± 105.0
After 48 h: storage at 23 °C			
72	1390.0 ± 384.4	1401.9 ± 355.7	1043.9 ± 267.1
168	1350.8 ± 375.6	1388.5 ± 385.2	1072.2 ± 387.5

Table 11-14: Layer thickness of 1.5 wt% agar products with different sugar amounts [Poe16]

Time after production [h]	**Sugar amount [g]**		
	78.50	74.58	82.43
	Layer thickness [µm] of 1.5 wt% agar products		
5	457.6 ± 105.5	266.9 ± 67.2	680.5 ± 180.9
24	1019.8 ± 315.9	490.5 ± 141.0	1030.0 ± 350.8
48	1078.1 ± 271.3	695.5 ± 186.8	1060.2 ± 374.9

Table 11-15: Weight loss of 1.5 wt% agar products over time at different storage temperatures [Poe16]

Time after production [d]	**Temperature [°C]**		
	23	50	70
	Weight loss [%] of 1.5 wt% agar products		
0.21	0.03	0.23	0.18
1	0.28	0.33	0.26
2	0.43	0.68	0.53
3	0.66	0.85	0.79
6	1.01	1.47	1.32
After 6 days storage at 23 °C			
14	1.95	1.96	1.66
28	4.23	2.90	2.29

Table 11-16: Weight loss of different hydrocolloid-sugar products over time

Storage time [d]	**Weight loss [%]**								
	pure sugar solution	1.5 wt% gelatin	2.4 wt% gelatin	0.5 wt% agar	1.5 wt% agar	1.0 wt% ι-carrageen	1.0 wt% ι-carrageen; (50 °C storage)	1.7 wt% ι-carrageen	1.7 wt% ι-carrageen; (50 °C storage)
2	0.14	0.30	0.39	0.11	0.18	1.19	2.41	0.99	2.21
3	0.17	-	-	0.11	0.21	2.50	3.89	2.29	3.70
4	0.17	-	-	0.17	0.44	-	-	-	-
5	-	1.35	1.84	-	-	-	-	-	-
7	0.20	2.15	2.63	0.31	1.09	7.24	8.07	6.67	9.99
9	0.25	2.90	3.36	0.42	1.42	-	-	-	-
11	0.25	-	-	0.42	1.76	-	-	-	-
12	-	3.91	4.92	-	-	-	-	-	-
13	-	4.43	-	-	-	-	-	-	-
14	0.28	4.56	5.63	0.42	2.21	12.67	13.08	12.44	17.52
15	0.28	-	-	-	-	-	-	-	-
16	0.33	-	-	0.64	2.70	-	-	-	-
19	-	6.44	8.10	-	-	-	-	-	-
21	0.46	-	-	0.70	3.62	-	-	-	-
26	-	8.56	10.47	-	-	-	-	-	-
28	0.47	9.37	11.41	1.20	4.43	18.69	18.39	16.88	19.47

Table 11-17: Weight loss of different hydrocolloid-sugar products over time

Storage time [d]	**Weight loss [%]**							
	0.2 wt% κ-carrageen (R)	0.2 wt% κ-carrageen (R); (50 °C storage)	0.5 wt% κ- carrageen (R)	0.5 wt% κ-carrageen (R); (50 °C storage)	0.5 wt% κ-carrageen (C)	0.5 wt% κ-carrageen (C); (50 °C storage)	0.7 wt% κ-carrageen (C)	0.7 wt% κ-carrageen (C); (50 °C storage)
2	0.38	0.61	0.17	0.92	0.60	0.50	0.51	0.84
3	0.59	1.19	0.51	1.86	1.63	0.97	0.88	1.64
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
7	1.55	3.11	1.66	4.86	3.14	1.69	2.25	3.74
9	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-
14	2.89	9.05	3.45	10.52	7.02	3.25	4.20	7.45
15	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-
26	-	-	-	-	-	-	-	-
28	6.25	20.86	6.68	20.58	16.64	5.81	7.36	18.80

Table 11-18: Stability of hydrocolloid-sugar products over time with standard deviation [Wel16]

	Stability [N/m²] and Standard deviation					
Time after production [h]	pure sugar solution	1.5 wt% gelatin	2.4 wt% gelatin	0.5 wt% agar	1.0 wt% agar	1.5 wt% agar
4	345.82 ± 142.81	374.50 ± 215.97	390.58 ± 181.23	377.45 ± 211.24	520.84 ± 227.99	857.80 ± 414.41
24	1268.05 ± 934.50	861.41 ± 387.62	1585.52 ± 669.74	1064.97 ± 503.30	1813.32 ± 723.81	8734.25 ± 3099.49
48	1398.22 ± 1349.41	1877.18 ± 674.51	2418.65 ± 1003.43	771.43 ± 310.47	1955.14 ± 1054.11	7355.94 ± 3144.56
72	1850.15 ± 1700.37	2526.09 ± 1702.86	3015.23 ± 2086.57	690.75 ± 336.68	1093.00 ± 473.36	3408.81 ± 1289.38

Table 11-19: Stability of different hydrocolloid-sugar products over time [Sin16]

	Stability			
Hydrocolloids	**Time [h]**	**Mean [N/m²]**	**Maximum [N/m²]**	**Minimum [N/m²]**
1.0 wt% ι-carrageen	24	5411.15 ± 1101.60	8430.09	3428.70
	48	2074.23 ± 691.91	4191.43	1229.46
	168	8102.06 ± 3694.94	17097.17	2478.90
1.7 wt% ι-carrageen	24	6881.21 ± 2810.40	13648.50	2366.31
	48	3064.35 ± 839.87	4869.73	1420.15
	168	13184.58 ± 5434.51	27831.82	3942.64
0.2 wt% κ-carrageen (R)	24	1492.34 ± 757.79	3554.00	572.96
	48	531.71 ± 238.16	1495.51	243.35
	168	1559.10 ± 1107.25	6229.04	691.01
0.5 wt% κ-carrageen (R)	24	3263.16 ± 1254.50	6638.56	1374.75
	48	1831.88 ± 642.95	3317.01	852.63
	168	2624.07 ± 1111.98	6141.87	1169.53
0.5 wt% κ-carrageen (C)	24	2143.66 ± 1571.52	7753.61	695.55
	48	2034.94 ± 651.29	3830.95	1340.24
	168	3725.10 ± 1612.28	7534.78	1635.35
0.7 wt% κ-carrageen (C)	24	2874.47 ± 911.11	4918.76	1239.45
	48	3803.56 ± 1666.64	7901.62	1300.29
	168	4299.13 ± 1745.13	8825.99	2072.11

Statement of authorship

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Halle (Saale), 20/03/2017

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Paper

J. Herfurth, J. Ulrich: Analysis of Hydrocolloids in Crystalline Material, Chemical Engineering and Technology, (DOI: 10.1002/ceat.201600546), in press.

J. Herfurth, J. Ulrich: Surface Nucleation in Complex Rheological Systems, Journal of Crystal Growth, 469 (2017), 13-17.

J. Herfurth, K. Mahnken, J. Fabian, J. Ulrich: Crystalline Layer Formation of Highly Viscous Supersaturated Liquids, Chemical Engineering and Technology, 39 (2016) 7, 1219 - 1223.

S. Selbmann, J. Herfurth, S. Petersen,J. Ulrich: Saccharose inversion and metastable Zone, Chemical Engineering and Technology, 38 (2015) 6, 1088 - 1091.

Conference contribution

Poster:

J. Herfurth, J. Ulrich: Analysis of Hydrocolloids in Crystalline Material presented at BIWIC 2016 (23rd International Workshop for Industrial Crystallization) 06 – 08/09/2016, Magdeburg (Germany), Max-Planck-Institute.

J. Herfurth, J. Ulrich: Surface Nucleation in Complex Rheological Systems presented at ACTS 2016 (Asian Crystallization Technology Symposium) 25 – 27/05/2016, Tianjin (PR China), Tianjin University.

J. Herfurth, K. Mahnken, J. Fabian, J. Ulrich: Crystalline Layer Formation of Highly Viscous Supersaturated Liquids presented at BIWIC 2015 (22nd International Workshop for Industrial Crystallization) 09 - 11/09/2015, Dajeon (South Korea), Hanbat National University.

S. Selbmann, J. Herfurth, J. Ulrich: Saccharose inversion and metastable zone presented at ISIC 2014 (International Symposium on Industrial Crystallization) 16 – 19/09/2014, Toulouse (France), University of Toulouse.

Presentation:

J. Herfurth, J. Ulrich: Surface Nucleation in Complex Rheological Systems presented at ACTS (Asian Crystallization Technology Symposium) 25 - 27/05/2016 in Tianjin (PR China).

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