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Mini-Review

Crystallization technology for product design

S. Petersen[*,#], A. Abouzeid, P. T. N. Nguyen, K. Wendt and J. Ulrich[*,$]
Martin Luther University Halle-Wittenberg, Center of Engineering Science,
Thermal Process Technology, D-06099 Halle (Saale), Germany

ABSTRACT

The functionality of products in pharmaceutical, chemical and food industries is very broad and diverse. Besides modified release and drug targeting in the pharmaceutical industry, many food products with new and innovative functionality pertaining to looks, taste, particle/ crystal form, handling properties or shelf life such as in the field of sweets or nutritional supplement are created on a regular basis. Crystallization technology can be used in designing such new products for the food, pharmaceutical as well as chemical and fertilizer industries. Using the example of three different techniques namely melt crystallization (here *in-situ* coating), solution crystallization (liquid mediated phase transition) and freeze casting, it is shown that crystallization technology is suitable for the production of a wide range of new innovative products. It is, for instance, possible to design container systems either for pharmaceutical or food applications with various release characteristics or filling alternatives. Further, tablet bodies disintegrating very fast or controlled by pore volume design, coated tablets etc. can be successfully produced using crystallization technologies.

KEYWORDS: crystallization, product design, porous tablets, hollow needles, coating

1. INTRODUCTION

Crystallization is a thermal phase separation technology used for concentration and purification [1, 2]. There are various techniques, such as crystallization from solutions and melts, and furthermore different options to create super-saturation and induced nucleation. By controlling nucleation and crystal growth it is possible to achieve products of high purity as well as products with the desired design in terms of crystal shape, crystal size distribution or functionality. There is a high demand for new products or improved product formulations, especially in the food, pharmaceutical and fertilizer industries. This can be achieved by different methods or technologies, e.g. conventional coating [3, 4], melt extrusion [5-8] or polymer coating [9-11]. However, crystallization is a suitable tool for the design of new formulations and products with innovative functionalities. It enables the development of new technologies and products as well as product qualities. Here, three examples (case study 1 to 3) of new innovative products in combination with the newly used innovative technologies are presented. Melt or solution crystallization techniques are used to achieve the required supersaturation. Thermodynamics (solubility) as well as kinetics (nucleation and crystal growth) have to be controlled in order to realize the desired product form. Moreover, phase transition of different polymorphs or solvates can be the cause for defined shapes of crystals.

2. Case study no. 1: crystalline hollow needles as container systems

Solvent-mediated phase transformation can be used to produce crystalline hollow needles. Here, different transitions are possible: 1. solvate to another solvate [12], 2. solvate to unsolvate [13], unsolvate to solvate [14] and transition to the

*Corresponding authors
[#]sandra.petersen@iw.uni-halle.de
[$]joachim.ulrich@iw.uni-halle.de

vapor phase [15]. As developed by Dette *et al.* [13], the initial solvate in crystal form is immersed in an antisolvent. Subsequently, phase transition towards the needle shape occurs on the surface of the initial crystal. Besides the model system sodium-2-keto-L-gulonate [13, 16-18], there are various substances forming crystalline hollow needles and having importance in pharmaceutical and food industries, that have already been investigated successfully. Examples are glucose anhydrate [19] or theophylline monohydrate [14] as needle substance. It is possible to produce closed containers, which can be filled *inter alia* with an active pharmaceutical ingredient (API) or any other substance soluble in the crystallization medium [19]. Furthermore, the outer and inner diameters of these needle-like crystals [20, 21] as well as the stability [17] can be controlled.

The mechanism of the formation of hollow needles is almost fully investigated. The model substance for this study is sodium-2-keto-gulonate (skg). The anhydrate of skg forms the needles by an immersion of the monohydrate crystals in an antisolvent such as methanol (method 1). In Figure 1 such a process is displayed. Here, compact sodium-2-keto-gulonate monohydrate crystals are immersed in dry methanol (see Figure 1a). The skg monohydrate crystals partially dissolve and give grounds for the subsequent growth of the hollow skg anhydrate needles on the surface of the dissolving crystal (see Figure 1b) until skg monohydrate is completely dissolved (see Figure 1c). This mechanism is explained in detail by Dette [16] and Wachsmuth [17] from its start (the nucleation of each needle starts at one single defect), including optimization due to improved stability and the control of the inner diameter of the cavity from 500 nm-10 µm by variation of the water content in the methanol. Also, the growth rate is dependent on the solvent content in the antisolvent, here, water in methanol. It can vary in the case of skg anhydrate needles from 0.1-0.6 m/s until a complete inhibition at water contents higher than 8000 ppm [20, 21].

For a faster production with higher yields, an alternative method for the production of hollow needles, the so called antisolvent crystallization (method 2), was developed [22]. This method is carried out without the usage of initial crystals. Here, a saturated solution of the initial substance is dropped in an antisolvent and subsequently a phase transition occurs, for example, quinine sulfate needles in methanol (see Figure 2, right). Both technologies, method 1: conventional method and method 2: antisolvent crystallization, undergo different nucleation but the same growth mechanism. A local supersaturation created by dissolution of the initial crystal in the case of the method 1 or created by local mixing phenomenon in the case of method 2 leads to phase transition (see Figure 2, left). In the case of method 1, the nucleation starts at the surface of the initial crystal and the newly created crystal forms a hollow needle (hetereogeneous nucleation). In the case of method 2, there is no initial crystal present. Here, a homogenous nucleation takes place and the hollow needles are directly formed out of the supersaturated solution.

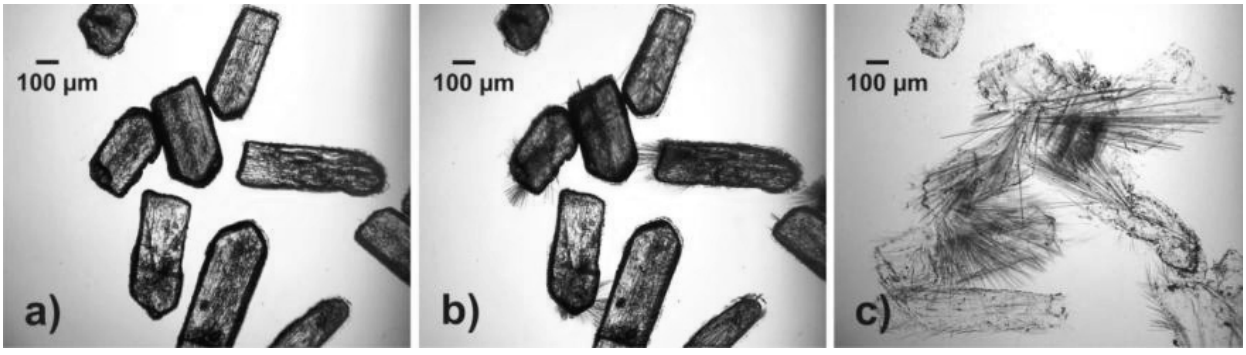

Figure 1. Mechanism of the formation of hollow needles of sodium-2-keto-gulonate anhydrate [18].

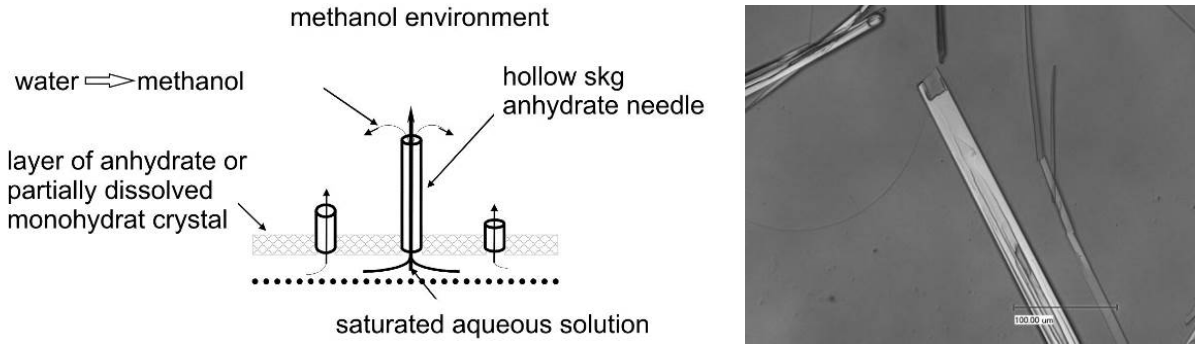

Figure 2. Left: mechanism of formation of hollow needles [16]; Right: microscopic image of quinine sulfate needles in a methanol solution.

An additional filling process can be applied for both techniques by dissolving the desired substance in the used antisolvent. By the dimensions of the cavity of the needles and the concentration of the dissolved substance, the amount of e.g. encapsulated API can be controlled. In order to verify the filling, investigations with a fluorescent dye was carried out [19].

Such hollow needles can easily be used as container system to enclose pharmaceutical compounds. As a result, bitter taste of the enclosed substance can be masked or the substance can be protected against external influences. Moreover, the drug release is controllable by the selection of the substance forming the hollow needles and its dissolution behavior. Besides in the pharmaceutical field, an encapsulation of oily liquids or flavors enables their application in food industry.

3. Case study no. 2: fast dissolving porous tablets

Fast dissolving products are of high interest in pharmaceutical industry due to drug delivery issues. In food industry such properties are of high interest for instant products. A high dissolution rate of tablets can be achieved by the addition of disintegrants or by controlling the porosity and thus the surface area of the tablet. The example of the in-practice already applied "Orally Disintegrating Tablets" with a desired dissolution time of 30 seconds [23] shows that a high porosity up to 80% [24] leads, however, to products with a low strength against breakage, which makes it very hard to handle. In order to increase the mechanical stability of such porous tablets, the freeze-casting process can be applied. Freeze-casting is a shape-forming technology, known in the field of ceramics, e.g. [25], which is suitable for the formulation of high porous dosage forms [26]. It is possible to control the porosity (30-50%) and thereby the breaking strength of the tablet (30-240 N) [27]. The procedure operates as follows: an aqueous suspension is frozen in molds, which represent the form-giving tool, and subsequently the ice is forced to sublimate. Due to a volume expansion caused by a change of the aggregate state of water, a cold compression of the system occurs. The pores are the negative images after the ice crystals are sublimated. This means that the initial ice crystals create the structure in terms of size, amount and distribution of the pores. The porosity and therefore the mechanical properties can be influenced by the control of the ice crystallization conditions, i.e. cooling rate and inclusion of additives which were dissolved in water, which stabilize the matrix when being crystallized inside the tablet after most of the water is transformed already to ice.

In previous works [26-30] different pharmaceutical systems have been investigated to show the potential of this technique. In the following, a new approach of this research topic is shown. Here, the food product cocoa was used for the tablet forming process of freeze casting. A product with enormous variety of properties and qualities in terms of tablet body properties or dissolution behavior could be achieved. Cocoa powder (Gepa The Fair Trade Co., Germany) was suspended in different densities in water and subsequently the

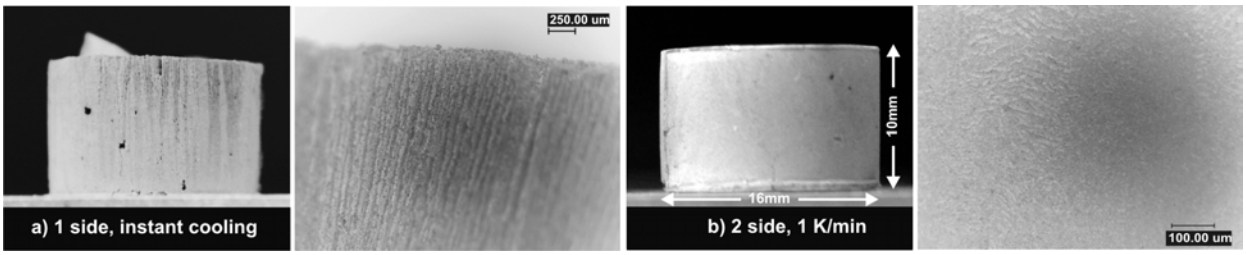

Figure 3. The effect of the freezing mode on the morphology of cocoa tablets produced by freeze casting; a) one side freezing mode with constant temperature, b) two side freezing mode with a cooling rate of 1 K/min; modified from [31].

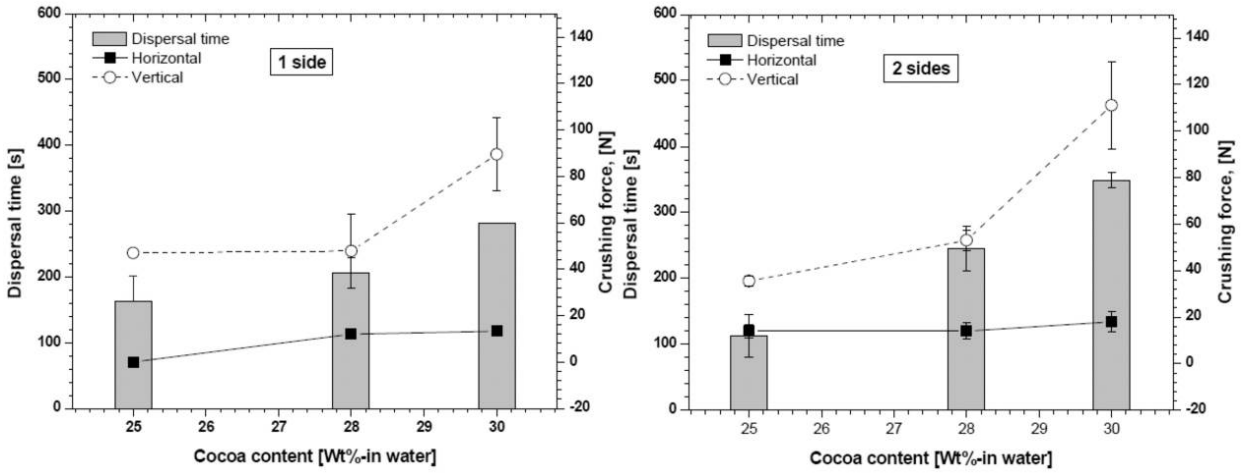

Figure 4. Dissolution behavior and mechanical stability of cocoa tablets produced by freeze casting, Left: One size freezing mode, Right: Two side freezing mode [31].

suspension undergoes the above-described freeze-casting procedure. By a variation of the mode of freezing, the appearance of the tablet body and the pore structure can be modified (see Figure 3).

The freezing took place on a temperature-controlled surface. Such a temperature-controlled surface can also be positioned on top of the mold in order to achieve a freeze mode from two sides (namely top and bottom). Freezing from two sides leads to a more lamellar pore structure (see Figure 3b) in comparison with a needle columnar structure, which can be obtained by using the one side freezing mode (see Figure 3a). A freezing just from one side will lead to a more homogenous appearance of the tablet surface and a modified dissolution behavior (see Figure 4). The dissolution time was determined by the immersion of one tablet in a vessel with boiled water under slow stirring (100 rpm). Both, the freezing mode and the solid content of the dispersion play an important role either for the dissolution behavior or for the hardness of the tablet. These two factors interact in a complex way. At a lower content of cocoa in the dispersion (25 wt-%), tablets produced with the two side freezing mode show lower mechanical stability in comparison with tablets produced with the one side freezing mode. However, the dissolution of these tablets is faster. By increasing the cocoa content up to 30 wt-% in the initial dispersion, the two side freezing mode leads to tablets with high mechanical stability or vertical crushing force of approximately 120 N. At the same time, the dissolution time is considerably increased. Nevertheless, through both freezing modes, tablets of 16 mm length and 10 mm height with a

dissolution time less than 2 minutes can be produced.

This dissolution time is still higher than for conventional lyophilizates in pharmaceutical industry (about 30 s [32]), but the tablets meet the requirements for food products, such that a hot chocolate can be easily prepared without the agglutination problem of normal cocoa powders. Big rather stable agglomerates floating on the surface of a drink which are disliked by the consumer can easily be avoided by the use of tablets made by freeze casting instead of using conventional powder in the case of e.g. instant drinks. Moreover, these tablets are adequately stable for food use and are thus easy to handle and to store.

4. Case study no. 3: *in-situ* coated pastilles

Coatings are very important in many chemical industries (pharmacy, fertilizers, etc.) as well as in food industries in order to protect the product against external influences (e.g. humidity or UV radiation), mask bitter taste and to impart elegant appearance, or for a controlled drug release for pharmaceutical purposes [33-36]. Conventionally, a tablet is coated by spraying or by immersing the tablet in a solution of the coating material and subsequent drying [33]. This means additional process steps with many different technologies, e.g. granulation, tablet compression, spraying and drying, for the production of one coated product. Moreover, thermal sensitive ingredients cannot be compressed. For all these reasons, an alternative method using melt crystallization to form coated tablet bodies is being developed. By using this so-called "*in-situ* coating" process it is possible to form and coat the tablet body simultaneously. Thereby, the required process steps can be reduced [37, 38]. The *in-situ* coating process uses melt crystallization combined with a pastillation process in order to form tablets or pastilles by dropping a molten mixture of the desired core and coating materials. A pastillation device is shown in Figure 5. Subsequently, the molten drop will be cooled down to create a supersaturation and to initiate nucleation. The crystallization process enables a phase separation, which leads to a crystallization of the pure coating material on the surface of the drop and the resulting mixture remains in the core either as a solid or liquid, depending on the physical properties of the mixture. The coating material has to fulfill certain requirements for this process. The most important requirement is the existence of a eutectic phase diagram for the desired mixture. According to the phase diagram, the composition has to be carefully selected to achieve a crystallization of the coating material on the surface. Furthermore, the coating material has to have the right functionality in terms of sealing and appearance and an approval to comply with regulations for the desired application, i.e. health and environment. The key points that have to be optimized are the initiation of the nucleation and the associated degree of phase separation. Two different techniques,

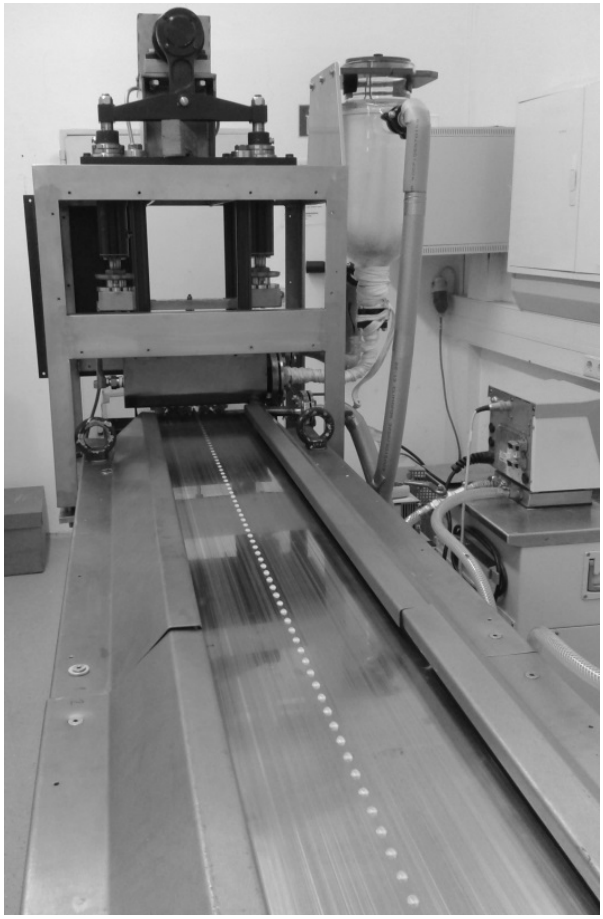

Figure 5. Photograph of an industrial pastillation device used in the lab of Thermal Process Technology of Martin Luther University Halle-Wittenberg, Germany for *in-situ* coating; one line of freshly produced pastilles.

seeding and ultrasound treatment combined with cooling can be used in order to reproducibly initiate nucleation in the metastable zone. By controlling the point of nucleation, the phase separation can also be reproducibly enforced and controlled.

A suitable system with food market relevant application is a mixture with eutectic behavior (see Figure 6, left) of the two sugar alcohols, xylitol and isomalt. Coating these sugar substitutes with each other creates an extraordinary and unexpected feeling in mouth. Due to the negative value of the heat of solution of xylitol [39], there will be a cooling effect. In contrast, isomalt has a slight positive value of dissolution enthalpy [39] and thus the consumer will experience a warm effect in the mouth. First investigations were carried out by choosing xylitol as a coating material due to its crystallization behavior, which makes it easier to handle, since isomalt tends to remain amorphous.

The pastillation process was simulated in lab scale. Therefore, a mixture of 80 wt-% xylitol (Xylisorb 90^{TM}, Roquette Pharma, Lestrem, France) and 20 wt-% isomalt (IsoMaltidex^{TM}, Cargill Cerestar BVBA, Mechelen, Belgium) was molten at a temperature of 103 °C. Subsequently, single drops were generated and placed on a temperature controlled steel surface with a constant temperature of 25 °C. Besides this procedure, nucleation initiation tests were carried out by seeding and power ultrasound treatment on the surface of the drops. For seeding xylitol powder particles were distributed on the cooling surface or on the surface of the drops. The used ultrasound homogenizer, Bandelin Sonoplus HD 3100, was working at a frequency of 20 kHz and a sonotrode tip with a diameter of 3 mm was used.

Without an external initiation of nucleation, a fast, reproducible and uniform nucleation process will not be possible for the xylitol-isomalt system. The nucleation kinetics of this mixture in a pastillation process would require process periods longer than 7 days. For an industrial use the shell of the pastille has to crystallize within 6-8 minutes. The usage of seeding or ultrasound to initiate nucleation at desired conditions and points of time enables such process times. The crystallization time of the outer shell is enormously decreased and a visible phase separation can be achieved. It is possible to get pastilles with good quality in shape and phase separation by the sole use of ultrasound. Tests with an ultrasound treatment between 1 and 10 seconds were carried out. In every case a phase separation can be visually

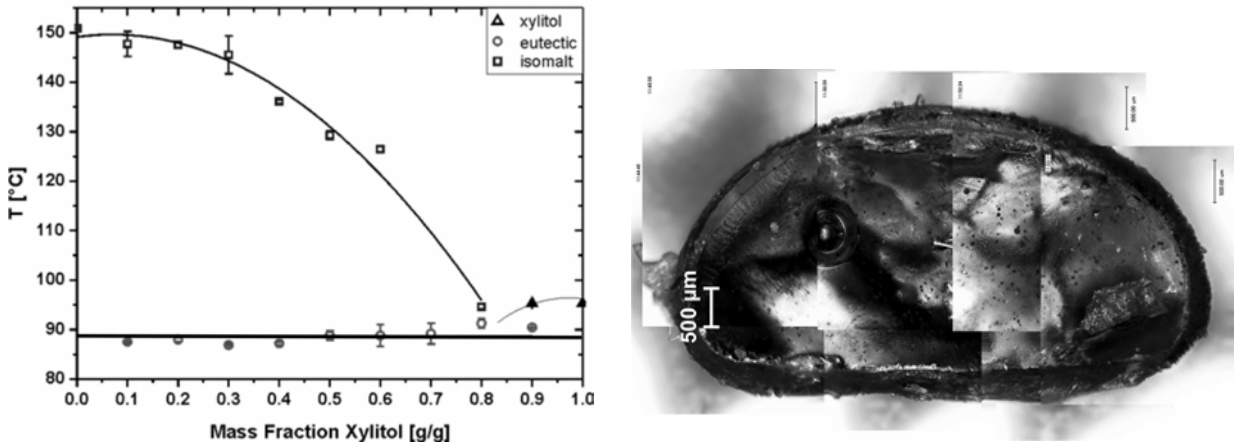

Figure 6. Left: Phase diagram of the xylitol-isomalt mixture [40]; Right: Cross-section image of a pastille initially consisting of homogeneous mixture of 30 wt-% xylitol and 70 wt-% isomalt; the picture is made by combining a number of single microscopic images and thus some optical defects are visible; initiation of nucleation by placing the molten drop on a seeded cooled surface and performing an ultrasound treatment on the top of the drop. A dark shell can clearly be seen [40].

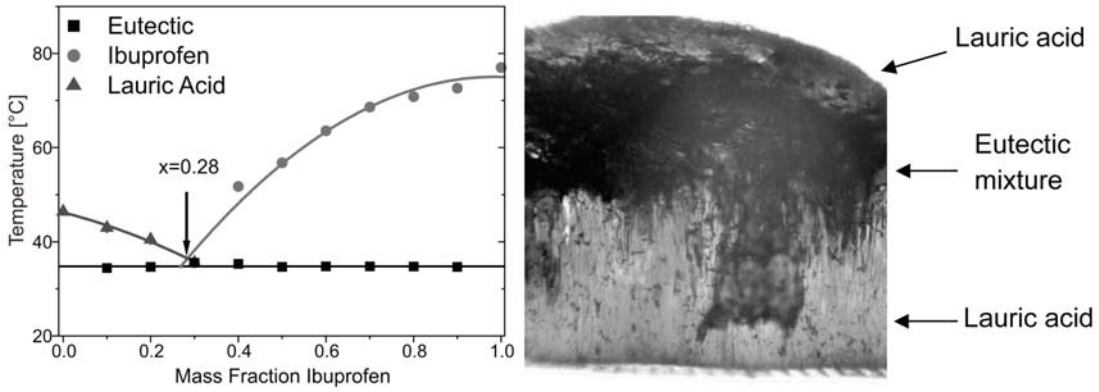

Figure 7. Left: Phase diagram of the ibuprofen-lauric acid system [42]; Right: Cross-section image of a pastille initially consisting of a homogenous mixture of 10 wt-% ibuprofen and 90 wt-% lauric acid, application of an air flow from with a temperature of 16 °C [41].

verified. By using ultrasound and seeding simultaneously, it is possible to use a high content of isomalt (see Figure 6, right; here 70 wt-% of isomalt and seeding with isomalt powder). The shape of the pastille is well defined and a sharp phase border can be achieved. Optimization regarding quantification of phase separation or scale up to industrial scale has to be done, but this technology and especially this product shows high potential for a future market launch.

Apart from food application, coated drugs can also be developed with the *in-situ* coating technology. First investigations with a model system of lauric acid and ibuprofen have already been carried out [41]. These two substances form a eutectic mixture. In order to see the phase separation more clearly, the lauric acid was colored by chemical complex reaction with cobalt-(II) ions. According to the phase diagram (see Figure 7, left), the pastillation of a melt with a composition of 10 wt-% ibuprofen and 90 wt-% lauric acid leads to coated pastilles as shown in Figure 7, right. Such a result can be achieved by an application of an additional cooling from the top. An air flow with a temperature of 16 °C is applied on the top of the drops that are placed on a temperature controlled surface with a temperature of 25 °C. Crystallization takes place in a time of one minute. The black part inside the pastilles (see Figure 7, right) represents the eutectic mixture of ibuprofen and lauric acid and the light part is pure lauric acid. An optimization in terms of phase separation has to be done. The proof of the concept was herewith successfully done with this system and as the next step a product with market relevance can be tested.

CONCLUSION

Crystallization is a well-known and common phase separation technology. Besides this, crystallization enables the design of new innovative products and the development of new technologies for the production of new as well as conventional products. Based on examples of three different technologies, it is shown that its range of application in various fields is very wide and has by no means been fully exploited. It is easily conceivable to design products in pharmaceutical industry for formulation with modified drug release as well as food products in the field of sweets or instant products. However, these are just examples. Crystallization and especially the technologies presented here are not limited to the production of only one type of product. Depending on the system of substances, it is possible to design products with different functionalities for every industry with a need for new innovative products or with a need for a new technology.

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