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NEW DEVELOPMENTS IN CRYSTALLIZATION PROCESSING

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Abstract

The intention of this work presented is to introduce new processing principles for the crystallization of watery or fatty phases in food systems, and in particular to quantify the process – microstructure – product quality relationships for such food systems. The crystallization processes demonstrated in detail are high shear crystallization (i), spray crystallization (ii) and spray powder based seed crystallization (iii). Crystalline, semi-crystalline and/or amorphous structures were analysed by calorimetric, mechanical/rheological and microscopical methods. Quality aspects of the final food products, which are related to the structure of the crystalline and/or amorphous components, were investigated additionally.

Keywords: glassy films, high shear crystallization, seed crystallization, spray crystallization, water movability

Shear crystallization

Shear induced pre-crystallization of polymorphous fat systems

Laboratory experiments showed that in shear fields which were generated in rheometric concentric cylindrical gaps, a significant influence on the crystallization kinetics and the resulting polymorphous crystal structure of polymorphic fat systems, like cocoabutter (Fig. 1), can be taken by varying the shear stresses acting in the flow field. Figure 2 demonstrates the viscosity – time functions for various constant shear stresses. With increasing shear stress, crystal nucleation is more rapid. If a certain mechanical power input is exceeded at shear stresses larger than approximately 0.9 Pa, in the experiment shown in Fig. 2, a viscosity plateau is found. As measured by differential scanning calorimetry (DSC), a cocoabutter melt which is cooled at 20°C (flow gap wall), crystallizes first in the so-called β_{IV}-type of the polymorphous crystalline cocoabutter structure.

In the viscosity plateau domain (Fig. 2) a transition from the β_{IV} to the β_V crystal modification is detected by direct DSC measurements [1]. In the laboratory device an increase of the acting shear stress from about 0.9 Pa to about 113 Pa decreased the transition time for the β_{IV} to β_V transition by a time factor of about 6. The physical explanation for this behaviour is the improved mass and heat transfer in the high shear field.

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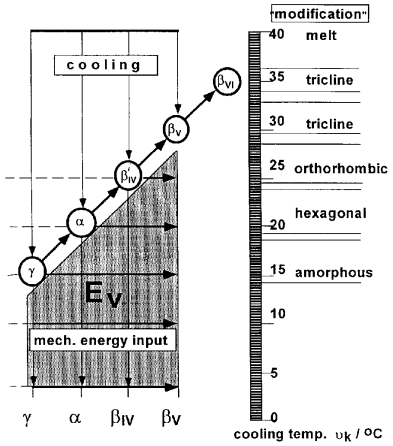

Fig. 1 Polymorphic fat crystal modifications of cocoabutter and influence of mechanical energy input (E_V)

Additionally, there is a mechanical 'activation mechanism' which allows for accelerating the modification transfer from the lower to higher stable crystalline state. This mechanism seems to be based on the high local energy dissipation between directly contacting but, relative to each other, moving crystals.

The principle of the rheometric laboratory crystallization device has been transferred to a continuous process device which is shown in Fig. 3. A 2 mm concentric cylinder gap was kept like in the experimental laboratory setup but additionally two wall scraping elements were installed to guarantee a long-time stability of the process without generation of crystal layers at the cooled wall. As demonstrated in the

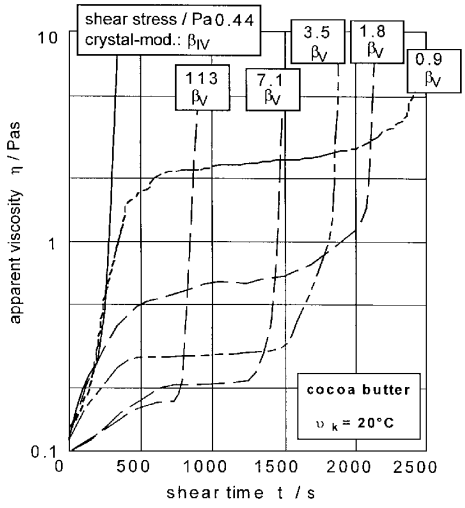

Fig. 2 Mechanical influence on the crystallization kinetics and resulting crystal modifications for a cocoabutter melt in a rheometric gap (stress-controlled)

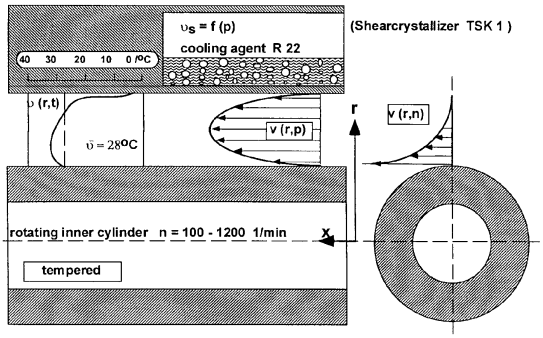

Fig. 3 Continuous shear crystallizer principle (biaxial shear in concentric cylinder gap; axial throughput)

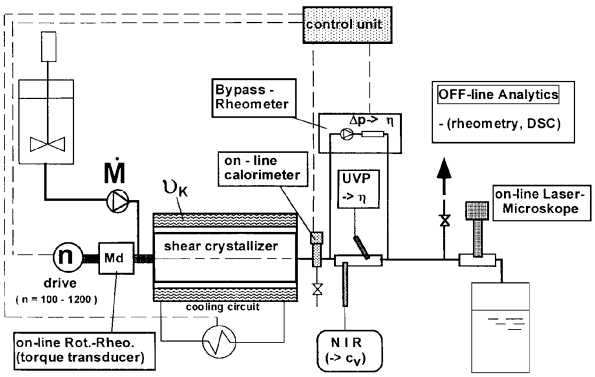

Fig. 4 Scheme of the shear crystallization process with adapted in-line measuring devices for rheology (direct) and calorimetry (indirect via DSC calibrated NIR)

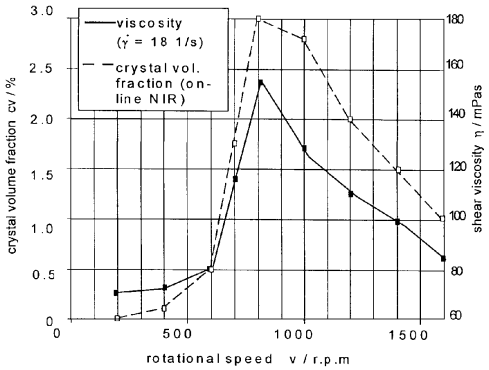

Fig. 5 On-line measured viscosity and fat crystal content in continuous shear crystallizer; wall cooling temperature constant (15°C); gap width 2 mm; mass flow rate 30 kg h^{-1}

process scheme (Fig. 4), process on-line measurements of viscosity (ultrasound velocity profile and pressure measurements (UVPP)) as well as on-line NIR-spectroscopy to determine the crystal content (calibration of the NIR device with a laboratory DSC) were installed. Figure 5 demonstrates how both viscosity and crystal content depend on the rotational speed of the high shear crystallizing unit. From Fig. 5 it is obvious that an increasing rotational speed and related shear stresses lead to an increased nucleation rate as already found in the laboratory experiments.

If the rotational speed exceeds a critical maximum, the mechanical energy dissipation leads to an increase of the local temperature within the shearing gap, thus remelting part of the crystals. As a consequence, viscosity and crystal content are then reduced. The optimum rotational speed depends on the wall cooling temperature and the gap size. For the chosen example shown in Fig. 5 the optimum rotational speed was 800 r.p.m.

Shear crystallization in frozen watery systems

Frozen watery systems such as frozen desserts (e.g. ice cream) are continuously frozen in so-called wall-scraping freezer devices. Primary heterogeneous nucleation takes place in such processes at the cooled wall of the wall-scraping units. In general, the watery phase contains solved components such as sugars or colloidally dispersed hydrocolloids (polysaccharides) and proteins.These ingredients lead to a freezing point depression. If water is crystallized, the remaining solution is concentrated, thus increasing the freezing point depression.

At the outlet of a continuous freezer system, temperatures of approx. –6 to –5°C are conventionally reached for ice-cream and, related to this temperature about 50% of water in a typical ice-cream recipe are frozen. If such a system is further frozen in the state of rest, e.g. in a cooling-/hardening tunnel, the liquid water crystallizes at the surface of the existing crystals and consequently increases them significantly in size.

This can lead to quality problems due to iciness and roughness of the related product.

High shear forces can be applied to such watery systems if there is some mechanical treatment at low temperatures (approx. –15°C). This can be reached in a newly developed low-temperature extrusion device which fulfills the condition of a homogeneous shear treatment due to locally narrowly distributed shear stresses and residence times. Under low temperature conditions additional crystal nuclei are formed at the extruder wall as well as by partly ‘milling’ larger crystal.

Furthermore small crystals which are close to each other are hindered from agglomeration due to their relative motion in the shear field. Figure 6 confirms this result in terms of measured ice crystal size distributions. Conventional freezing and additional hardening in the state of rest lead to a final ice crystal distribution which is shifted by a factor of more than 2.5 to coarser crystals, compared to the case of the low-temperature extrusion. This process leads to about the same mean ice crystal size at a frozen water fraction of 85–90% compared to a conventional freezer at a temperature of –5.5°C with a crystalline water fraction of 50%.

Extruded samples show significantly smaller crystals due to the described additional secondary nucleation. Industrial versions of the newly developed low-tem-

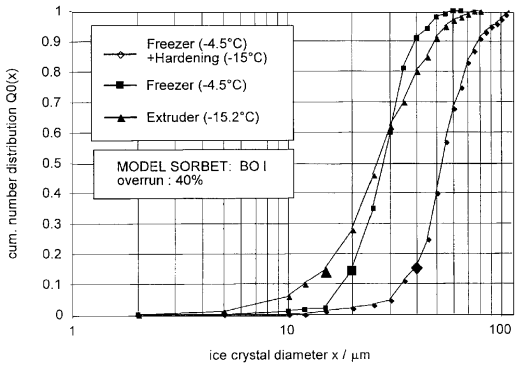

Fig. 6 Influence of high shear stresses acting in a low temperature extrusion process on the ice crystal size distribution compared to conventional freezing + hardening [14]

perature extrusion device have been successfully scaled-up to mass flow rates of 1000–1500 kg h^{-1}.

Cold spray crystallization

The basic idea of a newly developed cold spray-crystallization process is to spray a liquid into a cold atmosphere, thus solidifying the sprayed droplets. Figure 6 shows the principle of this cold spraying process. The solidified structure of the droplets strongly depends on the radial cooling gradient in the droplet and the droplet surface. This gradient is a function of the spraying temperature, the droplet size and the relative velocity of the droplet and the surrounding cooling gas flow. The droplet size depends on the spraying pressure, the spraying fluid temperature, fluid viscosity, fluid surface tension and density, as well as on the nozzle type used.

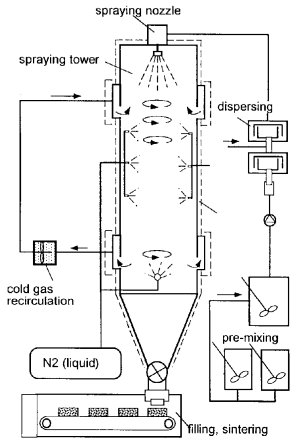

Fig. 7 Cold spraying tower including pretreatment of the fluid system (e.g. mixing, dispersing) and frozen powder treatment (e.g. partial sintering) [12]

In the case of very rapid cooling or under annealing conditions, besides crystals, amorphous solid structures (glassy state) result. For polymorphous systems the cooling gradient allows for 'adjusting' a certain variety of crystalline modifications.

Fat spray crystallization

As a polymorphous model fat system of specific interest for confectionary products, cocoabutter was spray-crystallized. The particle size of the sprayed and solidified droplets was varied in the range of 5 to 500 μ. Typical crystal modification distributions which were generated for cold-sprayed cocoabutter powders are shown in Fig. 8.

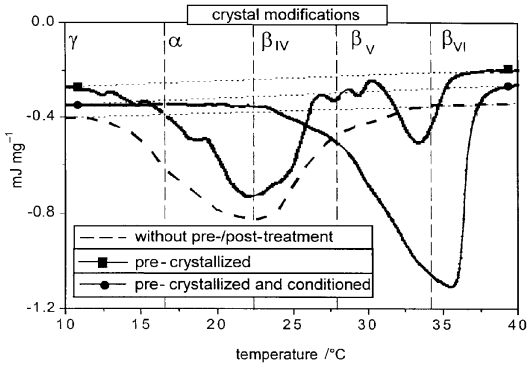

Fig. 8 Polymorphous crystal modification distribution of cold-sprayed cocoabutter powder with different pretreatment and conditioning

If fat powder samples with such crystal modification distributions are stored at temperatures of about 1–2°C below the melting temperature of the lowest melting fraction, there is no significant change of the modification distribution during long term storage.

Consequently the powder keeps free flowing without sintering. As a typical test for the powder flow characteristics, the so-called ffc value was determined. For this purpose a powder sample is pressed into a cubic form with a well-defined normal stress σ_1. Then the form is removed and the normal stress which is necessary for breaking the densified 'powder cake' σ_B is determined. The ratio σ_1/σ_B is defined as the so-called ffc-value. For ffc-values larger than 3–4, the powder system still behaves as a powder. ffc>5 means free flowing powder. Values lower than 2–2.5 represent partially sintered or strongly sintered powder structure.

The produced cocoabutter fat powders were either used as a powder ingredient in sintered multi-phase foods or as seed powder (for seed crystallization) in crystallization processing of chocolate masses. It was shown that due to the more clearly defined crystalline structure, better products with improved quality (e.g. storage stability, melting behaviour, consistency) can be developed.

Spray crystallization of watery systems

If watery systems are sprayed into a cold atmosphere, there is no polymorphous behaviour but depending on the cooling gradient and the droplet size, the solidification can lead to either amorphous (glassy) or crystalline structures. In general, the watery systems are solutions of sugars, polysaccharides and further soluble ingredients. As a consequence, there is a freezing point depression (FPD). If such a watery solution is cooled down, crystals start to form at about –2 to –1°C (at a dry matter concentration of about 35–40%). At the same time, the solution concentrates and consequently reduces the freezing point further. If a specific maximum freeze concentrated solution is reached, the system solidifies during further cooling in the glassy state.

Figure 9 shows SEM micrographs of cold sprayed watery droplet microstructures containing mainly sucrose as the soluble component.

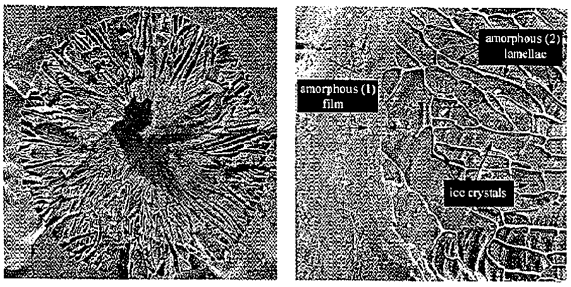

Fig. 9 SEM micrographs of inner particle structures from cold-sprayed watery sucrose solutions (spraying temperature 5°C, tower temperature (N2) –80°C). Magnifications (left: image side length=300 μm; right: image side length=50 μm) [11]

Some of the differently solidified components are visible after cryopreparation (partial sublimation/etching/sputtering). The outer shell of the droplet, where the largest cooling gradients are acting, is solidified in a glassy state (amorphous 1; Fig. 9), but not in the state of a maximum freeze concentrated solution.

This is confirmed by a few very small dentritic water ice crystals which are found in the outer particle shell zone. In the inner zone of the particle the cooling gradient is reduced. Consequently ice crystal nuclei are more efficiently generated. During crystal growth, the surrounding solution is increased in solute concentration. The maximum concentrated solution finally solidifies in a glassy state (amorphous 2, Fig. 9) as a lamella between the ice crystals. In these lamella there are no dentritic ice crystal nuclei found.

The glass transition can be detected for such cold-sprayed powders using Differential Scanning Calorimetry, which detects the changes in heat capacity c_P during the approximately second-order phase transition (glass transition), as demonstrated in Fig. 10. Another successfully tested method is based on the change in the mechanical behaviour during glass transition. This is the so-called Dynamic Mechanical Thermal Analysis (DMTA) which allows for measuring the significant reduction

in the elastic modulus E' (real part of E-modulus, measured in an oscillatory compression mode) when the glass transition temperature is exceeded [11].

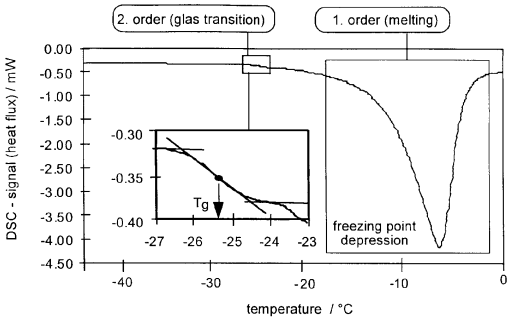

Fig. 10 DSC curve showing the glass transition and melting behaviour of a typical ice cream ('sorbet') mix (watery solution of sucrose + stabilizing polysaccharides) [13]

An improved modified DMTA method allows for sharply detecting the glass transition if the breakdown of the so-called pre-load force is detected [11].

As described for fat-based cold-sprayed powders in 'Fat spray crystallization' paragraph, the sintering behaviour of water-based powders was tested with the same 'ffc-value method'. Systematic experiments showed that the storage of water-based frozen powders at about –2°C below the glass transition temperature keeps those powders in a free-flowing state without sintering effects on a time scale of several months. Closer to the glass transition temperature T_g, or at temperatures above T_g, there is sintering observed (Fig. 11).

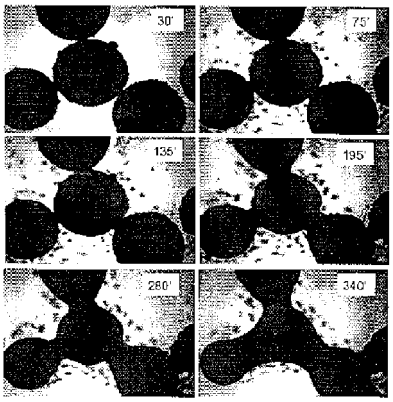

Fig. 11 Sintering of cold-sprayed sucrose/polysaccharide solution (T_g=–19°C) particles at –15°C (cold stage light microscopy, initial particle diameter 730 μm) [13]

In the case of frozen food products (such as frozen desserts) there is interest in 'ice powders', but glass transition temperatures which are relevant for such frozen foods are approximately in the range of –18 to –15°C. It could be shown that specific macromolecular ingredients, such as polysaccharides, proteins etc., allow for adjust-

ing a glass transition temperature in the temperature range of –15 to –5°C [11, 12]. Consequently such 'High T_g Cold Spray Powders' (HTCSP) is a new component in multiphase frozen food systems [12].

Seed crystallization

The seed crystallization is, in principle, a traditional method in many fields of crystallized food products (e.g. saccharose crystallization). The specific focus of recent research work at ETH Zurich was to use cold sprayed powders as seed particles for polymorphous fat crystallization. The specific aspect was to modify crystallization behaviour and related product properties of fat systems depending on the polymorphous state of the seed powder particles.

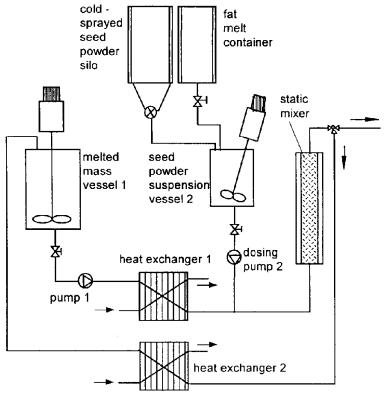

Fig. 12 Basic principle of a cold-spray powder based seed crystallization process (here pilot plant circuit)

Figure 12 shows a pilot-plant process scheme for seed crystallization of confectionary masses. From the seed powder, a concentrated suspension is produced, which is then dosed into the main stream of the non-crystallized mass. Depending on the seed crystal modification, the temperature of the seed crystal suspension, as well as of the mass which is crystallized, have to be adapted. From a processing point of view e.g. in cocoabutter based systems like chocolates, it is of interest to use highly stable β_{VI} crystals or eventually β_V crystals (which are as well stable but have a lower melting temperature range) and feed them into the chocolate mass at the highest possible temperature to enable the further processing (e.g. coating, moulding, filling) at lowest possible viscosity. It was shown that satisfying seed crystallization with β_{VI} seed crystals can be carried out for chocolates at temperatures of up to 34°C. Conventional pre-crystallization of chocolate masses in so-called tempering devices (pre-crystallizer) reaches a maximum of about 30–31°C. Consequently, with seed crystallization, lower viscosities at higher temperatures or even comparable viscosities at lower fat-content as well as a strongly reduced temperature sensitivity of the pre-crystallized state can be reached.

* * *

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