ORIGINAL PAPER

The Effect of Capacity, Rotational Speed and Storage on Crystallization and Rheological Properties of Puff Pastry Butter

S. Rønholt · J. J. K. Kirkensgaard · K. F. Høyer · K. Mortensen · J. C. Knudsen

Received: 13 March 2013/Revised: 23 August 2013/Accepted: 14 September 2013 © AOCS 2013

Abstract In the margarine and butter industry, sustainable and more efficient refrigerants, such as CO₂, are introduced to industrial scraped surface heat exchangers, allowing an increased capacity compared to conventional use of NH₃. The effect of such changes in capacity and a varied rotational speed was studied in relation to the structural behavior of puff pastry butter during 4 weeks of isothermal storage at 20 °C. The physical properties of the fat crystal network were studied in detail at several length scales by combining X-ray diffraction with differential scanning calorimetry, confocal laser scanning microscopy, LR-NMR and rheology. Our data shows that a high capacity combined with high rotational speed decreases the brittleness of puff pastry butter after 7 days of storage. This effect is, however, diminished after 28 days of storage. Likewise, changes in capacity and rotational speed are shown to induce no microstructural and polymorphic differences after 28 days of storage. However, the degree of work softening is related to the manufacturing conditions: a

S. Rønholt (⊠) · J. C. Knudsen Department of Food Science, University of Copenhagen, Rolighedsvej 30, 5, Frederiksberg C 1958, Denmark e-mail: stine.roenholt@sund.ku.dk

Present Address:

S. Rønholt

Department of Pharmacy, Faculty of Health and Medical Sciences, University of Copenhagen, Universitetsparken 2, Copenhagen Ø 2100, Denmark

J. J. K. Kirkensgaard · K. Mortensen Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark

K. F. Høyer SPX Flow Technology, Soeborg, Denmark high capacity and a high rotational speed increase the ability of the puff pastry butter to resist structural breakdown during working. With this being the only observed difference; a wide operational window exists on an industrial level to produce puff pastry butter with similar structural behavior.

Keywords Food processing operation · Microstructure · Thermal analysis · Rheology · Fat · Crystallization

Introduction

Puff pastry butter is a commonly used as a bakery ingredient due to its functionality and unique taste. In dough, puff pastry butter separates the dough layers. Upon baking, water evaporates from the fat matrix and the dough layers separate, generating the typical flaky texture of baked products [1]. Puff pastry butter is, like regular butter, a water-in-oil emulsion where water droplets are dispersed within a partially crystallized fat phase, the fat crystal network. Two types of crystal-crystal interactions exist within a fat crystal network: the strong irreversible (primary) bonds formed upon crystal growth and the weaker reversible (secondary) bonds occurring due to van der Waals interactions [2]. The properties of the fat crystal network can be quantified using rheological measurements [3]. In milk fat, three main crystal polymorphs are identified: α , β ' and β in increasing order of stability [4]. The subcell structure is hexagonal for the α -polymorph, orthorhombic for the β ' and triclinic for β -crystals [5], and can be characterized using small and large angle X-ray scattering (SAXS and WAXS). The long spacings are related to the lamellar packing of the triglyceride chains in the longitudinal direction. Milk fat stacks most often as lamellae of 2 (2L) or 3 (3L) chain length periodicity [5]. The in-line packing within the lamellae is linked to the polymorphic structure [6].

As puff pastry butter is subjected to a high degree of shear when stretching and thinning the dough, certain product characteristics are essential [1]. The product needs to be plastic and not sticky. Moreover, β '-crystals are preferred over α and β , as they are associated with an increased firmness and a less grainy macroscopic structure [7]. From model systems produced on a laboratory scale, it has been shown that thermal treatment [3], mixing temperature [8] and shear during processing [9] affects the final structural properties of the products. Moreover, the effect of post crystallization during storage strongly influences the rheological behavior of milk fat-based products [10]. On an industrial scale, changing residence time in the manufacturing equipment or varying the rotational speed during mixing is shown to affect the applied shear on the products [11]. Depending on the shear applied to the fat crystal network upon an increased rotational speed, the reversible and irreversible crystal-crystal bonds will eventually break, hence decrease the hardness of the products [2, 11, 12].

Reducing the residence time in the processing equipment increases the cooling rate. It has been shown that a reduced residence time is associated with formation of smaller emulsion droplets due to a stronger degree of super cooling. As smaller droplets are formed, the system is more likely to coalesce [2]. The effect of subsequent storage of milk fat-based products on their rheological behavior is not unambiguously determined. Both Haighton and Dolby have shown that the strength of the fat crystal network does not recover to the original level after strong mixing [2]. On the contrary. Sone has observed a more perfect recovery of butter after 10 days of storage at 16 °C [12]. Due to the wide range of triglycerides present in milk fat, the storage temperature has a high impact on the fat crystallization [13]. Butter stored for 28 days at 5 °C contains primarily β '-crystals with traces of β -crystals [10]. For margarine, having a higher melting point compared to butter, the temperature can be increased from 4 to 13 °C [14] and even 25 °C [13] without inducing any polymorphic transitions, as primarily β '-crystals are present.

In the present study, we produced puff pastry butter by using a scraped surface heat exchanger (SSHE). Sustainable and more efficient refrigerants, such as CO_2 , have now been introduced in industrial equipment, which allows an increase of 40 % in capacity compared to conventional use of NH₃. To exclude the effect on textural behavior caused by different physical conditions using two different manufacturing plants, the change in capacity caused by a change in the refrigerant was simulated using two different capacity settings (both using CO₂ as refrigerant): 60 l/h to simulate the use of regular NH₃ equipment and 90 l/h to demonstrate the increase in capacity obtained by using CO₂ as refrigerant. As the capacity was increased, the cooling rate increased correspondingly from 170 to 254 °C/min in the first cooling step, and from 29 to 44 °C/min in the second cooling step with the residence time decreasing correspondingly. When changing the cooling rate and residence time (i.e. capacity), the crystallization behavior was affected. In addition to capacity, the rotational speed during mixing was set to either 500 or 1,000 rpm at both capacity settings. As a majority of the present literature is based on model systems produced on a laboratory scale, the aim of the present work was to study the relations between capacity and rotational speed at industrial settings with crystal polymorphism, thermal behavior, microstructure and rheological behavior (hardness, brittleness and work softening) of puff pastry butter.

Materials and Methods

Materials

Puff pastry butter from Martens Backbedarf, Lübeck, Germany was used for sample manufacturing (82 % anhydrous milk fat, 16 % water, 2 % other components). Butter from Thise Dairy, Denmark was used as a commercial reference sample (80 % milk fat, max. 16 % water and 4 % other components). Fluorescein-5-isothiocyanate (FITC) (Merck, Darmstadt, Germany), Nile red and 1,1'dioctadecyl-3,3,3',3'-tetramethyl-indodicarbocyanine perchlorate (D307) (Molecular Probes, Paisley, UK) were used as fluorescent dyes for confocal laser scanning microscopy.

Puff Pastry Butter Manufacturing

The production of puff pastry butter was carried out using a Nexus pilot plant based on CO_2 as refrigerant (SPX Flow Technology, Soeborg, Denmark), with a total batch volume of 100 kg. The configuration during preparation of the samples was (1) high pressure pump (2) SSHE (3) pin rotor machine (4) SSHE and (5) resting tube. Two experimental parameters were varied: capacity (60 and 90 l/h) and speed of mixing in the SSHE (500 and 1,000 rpm). The combinations were as follows: 60 l/h and 500 rpm (S1), 60 l/h and 1,000 rpm (S2), 90 l/h and 500 rpm (S3), 90 l/h and 1000 rpm (S4). The emulsion inlet temperature to SSHE was 57 °C and a back pressure of 16 bar. The emulsion was cooled at 170 °C/min (60 l/h) or 254 °C/min (90 l/h) to 17 °C in the SSHE (500 or 1,000 rpm) to initiate the crystallization. Subsequently, the product was mixed in a

pin rotor machine set to a constant speed of 200 rpm (24 °C). To ensure similar residence time in the pin rotor machine, its volume was set to either 2 l for the 60 l/h production or 3 l or the 90 l/h production. Finally, the product was further cooled in the last SSHE (14 °C), before entering the resting tube. The cooling rates used were 29 °C/min for the 60 l/h capacity and 44 °C/min for the 90 l/h setting. Finally, the puff pastry butter was packed in plastic containers and stored at 20 °C for 28 days, and tested at day 7, 14 and 28 after production. The storage temperature was set to 20 °C, as the puff pastry butter produced is intended for use at 18–20 °C.

Low Resolution-Nuclear Magnetic Resonance

A Bruker wide line LR-NMR system (Bruker Minispec mq 20) from Bruker Optik GmbH, Ettlingen, Germany was used to measure water droplet size distribution at day 7 and 28 after production. The LR-NMR was equipped with a pulsed gradient field unit and operated at 20 °C. The samples were prepared by punching a cylindrical glass (0.8 cm in diameter) into the sample at random locations, for the water droplet size distribution. Then, the samples were placed in the NMR tube and tempered at 20 °C prior to analysis. The size is reported as volume-weighted geometric mean diameter ($d_{3,3}$), according to Alderliesten [15].

Rheology

To characterize the textural behavior during storage, small deformation rheology was conducted at days 7, 14 and 28 after production, using an AR G2 Rheometer (TA Instrument, West Sussex, England). The rheometer was equipped with a temperature controlled serrated parallel plate geometry (25 mm in diameter). The choice of geometry was based on a methodical evaluation, where serrated parallel plates were considered as the most suitable for rheological characterization of fat-based systems [16]. The frequency sweeps were performed in an interval of 500–0.05 rad/s, with a constant oscillation stress of 500 Pa. The following stress sweeps were run at an oscillation stress of 1-800 Pa, and a constant angular frequency of 1.0 rad/s. Strain at fracture was determined from the stress sweep as the point where decrease of 50 % in the elastic modulus (G') was observed. All measurements were run at 20 °C, and within the linear viscoelastic region (tested, data not shown).

Large Deformation Rheology

A multiple extrusion cell (Stable Micro Systems Ltd., Surrey, UK based) was used to characterize plasticity, which was the work recorded upon multiple extrusions, of the sample. The plasticity was recorded during multiple extrusions in order to evaluate the effect of large deformations, thus intensive working, on breakdown and eventual re-bodying of the butter samples. The puff pastry butter was filled to 5–8 mm under the top edge of the vessel, and the piston was set to 25 cycles. The measurements were performed at room temperature (20 °C). The analysis was run in duplicate at day 7 and 28.

Confocal laser scanning microscopy

A confocal laser scanning microscope (SP5) from Leica Microsystems, Wetzlar GmbH, Wetzlar, Germany equipped with a $63 \times$ magnification water immersion objective was used to study the microstructure of the puff pastry butter. The dyes (FITC, Nile red and D307) were prepared in a (0.01 % (volume/volume) solution), and immersed on the object glass. After evaporation of the solvent, the puff pastry butter was placed on the slides and equilibrated at 20 °C for 30 min. Images were obtained on days 7, 14 and 28 after production.

X-Ray Diffraction

X-ray scattering was performed at the SAXSLAB instrument (JJ-Xray, Denmark), equipped with a 100XL + micro-focus sealed X-ray tube from Rigaku and a 2D 300 K Pilatus detector from Dectris. Measurements were performed with a pin-hole collimated beam with the detector positioned asymmetrically to obtain a single measurement q-range of 0.05–2.8 $Å^{-1}$ with the magnitude of the scattering vector defined by $q = 4\pi/\lambda \sin\theta$, where $\lambda = 1.54$ Å is the X-ray wavelength and θ is half of the scattering angle. In this way SAXS and WAXS were simultaneously measured, allowing all relevant peak information for both short and long spacings to be obtained during a single measurement. The d-spacings were calculated as $d = 2\pi/q^*$, where q* are the Bragg peak positions in the X-ray spectra. The puff pastry butter was mounted between two 5-7 µm thick mica windows, placed in sample holders at 20 °C. The sample spectra were corrected for the background scatter from the mica by subtraction. The sample holders were loaded onto a temperature controlled sample stage from Linkam, set to 20 °C. X-ray diffraction measurements were performed at days 2, 7, 14 and 28 after production.

Differential Scanning Calorimetry

The thermal behavior of the puff pastry butter was studied using a differential scanning calorimeter from Mettler Toledo, Greifensee, Switzerland. Fifteen to twenty-five mg of the puff pastry butter was placed in an aluminum pan that was hermetically sealed. The procedure was as Fig. 1 Representative thermogram obtained using differential scanning calorimetry after 7, 14 and 28 days of storage at 20 °C for the puff pastry butter. Moreover, a commercial butter was tested as reference. The samples were heated from 20 to 65 °C at 2 °C/min (only the segment from 20 to 40 °C shown). S1 = 60 l/h and 500 rpm, S2 = 60 l/h and 1,000 rpm, S3 = 90 l/h and500 rpm, S4 = 90 l/h and 1,000 rpm



follows: 10 min at 20 °C followed by heating to 65 °C with a scan rate of 2 °C/min. An empty sealed pan was used as a reference.

Statistical Analysis

The statistical analysis of the data was conducted using a one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison tests using GraphPad Prism (Version 5.02, GraphPad Software, Inc., La Jolla, CA, USA). For the rheological analysis, the elastic modulus (G') (n = 5) and strain at 50 % decrease in G' (n = 5) was used as variables, while for differential scanning calorimetry the melting point of the high and low melting fraction, respectively (n = 2) was used as variable and water droplet size from the LR-NMR analysis (n = 2). In addition, time was used as a variable within the same batch.

Results and Discussion

Capacity

In the present study, the capacity was set to 60 and 90 l/h in order to simulate the effect of using CO_2 and NH_3 as refrigerants. Such increase in capacity resulted in an increased cooling rate and decreased residence time. It is known, that the crystallization behavior of milk fat-based products is affected by both cooling rate [3, 17] and shear [9, 17, 18] (the latter will be further discussed in Sect. 3.2).

Therefore, crystallization behavior was monitored using differential scanning calorimetry (Fig. 1).

In the thermograms (Fig. 1), two distinct melting points can be observed, the high and low melting fraction of the triacylglycerols, independent of processing conditions. Additionally, a middle melting fraction is observed. The melting points of the high and low melting fractions are not altered by changes in capacity (Fig. 1). Applying a fast cooling rate during processing by increasing the capacity however, induces formation of a narrower melting point in the thermogram, also when compared to commercial butter (Fig. 1). The same tendency has previously been observed by Kaufmann et al. [17]. This can be a consequence of the different crystal sizes obtained when changing the residence time in the SSHE [19].

In the meantime, the crystal polymorphism was monitored during storage using SAXS and WAXS (Fig. 2).

For S3 and S4, both produced at 90 l/h, a peak corresponding to an α -related 3L stacking (55.5 Å) is identified only at day 2. At all days of measurement, two separate 2L stackings related to β ' (41.1 Å) and α (45.7 Å), respectively are observed. These long spacing distances are in good agreement with those usually found in cream, butter and other milk fat-based samples [3, 10, 20, 21].

For the short spacings observed within the WAXS spectra, primarily β '-crystals are observed with a population of α -crystals and minor traces of β in all samples independently of capacity (Fig. 2).

The mechanical properties of the fat crystal network were quantified using both small and large deformation rheology. Using small deformation rheology, a frequency **Fig. 2** SAXS and WAXS spectra from all samples from days 2, 7, 14 and 28. See text for details



sweep was run to characterize hardness (G') (Fig. 3 top), followed by a stress sweep. The stress sweep was used to evaluate the brittleness of the puff pastry butter. In this case brittleness was recorded as the strain at 50 % decrease in

elastic modulus (G') relative to the (G') in the linear viscoelastic region [3] (Fig. 3 bottom). In addition to small deformation rheology, a multiple extrusion cell was used to study the work softening of the puff pastry butter (Fig. 4).



Fig. 3 The elastic modulus (G') at 5 rad/s (*top*) and strain at 50 % decrease in G' (*bottom*) as function of time. The analysis was run at 20 °C using serrated parallel plate. The samples were produced at two different capacities (60 and 90 l/h) using two different speeds at the pin rotor machines (500 and 1,000 rpm). The *letters* indicate differences (P < 0.05) as between samples within 1 day of measurements while the *numbers* indicate difference within one sample as a function of time. The *error bars* indicate standard deviation. Moreover, a commercial butter was tested as reference



Fig. 4 The work per extrusion as a function of number of extrusions for the different products after 7 and 28 days of isothermal storage at 20 °C. The analysis was done at 20 °C

The main application of puff pastry butter is, as previously mentioned, for baking purposes. The application involves continuous bending and kneading of the puff pastry butter and therefore requires plastic behavior from the product. Therefore, in order to evaluate the plasticity of the puff pastry butter in relation to baking purposes, it is important to understand the effect of intensive working on the fat crystal network and to which extent the product can keep its body intact [1]. Combining the data obtained using small deformation rheology with those obtained from cell extrusion provides a detailed understanding of the relations between rheological terms plasticity, hardness and brittleness.

When changing the capacity from 60 to 90 l/h, no systematic effect is observed on any of the rheological parameters studied (Fig. 3, 4). Comparing the rheological properties of puff pastry butter with those of commercial butter, the puff pastry butter has a significantly higher G' and strain at 50 % decrease in G' when measured at 20 °C.

Additionally, the macroscopic behavior of the fat crystal network formed in the puff pastry butter was studied using confocal laser scanning microscopy (Fig. 5). The images reveal a microstructure consisting of a fat crystal network, seen as dark black/gray shadows, distributed throughout the continuous fat phase. A high cooling rate (7.5 °C/min) versus slow cooling rate (0.4 °C/min) has been shown to induce a different microstructure as well as rheological properties of butter within 24 h after production. Fast cooling rates may result in the formation of many small crystals and a high G' value, whereas slow cooling rates may result in formation of fewer, but larger crystals and a low G' value [3]. In Fig. 5, no major differences in crystal size or water droplet size could be identified as a function of capacity. The microstructure of the commercial butter, however, shows presence of less solid fat present (Fig. 5), corresponding to a low G' when compared to the puff pastry butter (Fig. 3).

Figure 6, depicting the average water droplet size as quantified using LR-NMR, confirms the findings from confocal laser scanning microscopy, since no difference is observed in water droplet size as a function of capacity changes. Summing up, the capacity during puff pastry butter production can be increased from 60 to 90 l/h without affecting product hardness, microstructure and average water droplet size.

Rotational Speed

As mentioned in Sect. 3.1, the crystallization behavior and formation of fat crystal network is affected by shear and rotational speed [9, 17, 18]. In the present work, however, no difference is observed in thermal behavior when changing the rotational speed from 500 to 1,000 rpm



Fig. 5 Representative images of the microstructure of the samples at day 28 and commercial butter captured using confocal laser scanning microscopy, showing the fat crystal network (*arrow* 1), milk fat

globules (*arrow* 2) and water droplets (*arrow* 3). No microstructural differences is observed in the puff pastry butter between day 7, 14 and 28. The *scale bar* is the same for all puff pastry butter images



Fig. 6 Average water droplet size (μ m) as a function of time, measured using LR-NMR. The samples were produced at two different capacities (60 and 90 l/h) using two different speeds at the pin rotor machines (500 and 1,000 rpm). The *letters* indicates differences (P < 0.05) between samples within 1 day of measurements. Moreover, a commercial sample was tested as reference

(Fig. 1). Previously, the application of shear rates between 0 and 2,880 s⁻¹ for 30 min at 50 °C to milk fat and milk fat triglycerides, has been shown to accelerate the transition from α to β '-crystals, when measured after cooling at 3 °C/min to a crystallization temperature of 17-17.5 °C. Shear was maintained during both cooling and crystallizing, in total 60 min [6]. When shear is applied, the initially formed crystallites are segregated and changes in the already formed α -crystals are induced. Consequently, nucleation sites for β '-crystals are formed [6]. In the present study, *a*-crystals are still present after applying a rotational speed of 500 or 1000 rpm. The observed acceleration of polymorphic transitions due to shear is likely not occurring in the present work, as both the degree of shear and also time under shear was far from what was used in the present setup. The only difference observed in the WAXS spectra is for S2 at day 2. Here, the peak at 3.83 Å is slightly shifted towards a higher q-value (lower Å), and is likely an artifact due to drift in temperature during measurement.

In terms of rheological behavior, the hardness and brittleness of the fat crystal network formed is not affected by changes in rotational speed (Fig. 3). However, the plasticity of the puff pastry butter is increased when increasing the rotational speed from 500 to 1,000 rpm (Fig. 4), meaning that the fat crystal network is kept more intact during working. Changing the rotational speed during mixing is likely to alter the primary and secondary crystal–crystal bonds [2, 11, 12] and therefore, the rheological properties. The plasticity as measured using large deformation rheology is related to the primary crystal–crystal bonds [22], where a rotational speed of 1,000 rpm seems to induce formation of stronger primary crystal–

crystal interactions compared to a rotational speed of 500 rpm upon recovery (Fig. 4).

Moreover, the average water droplet size is affected by the rotational speed during manufacturing (Fig. 6), as applying 1,000 rpm induces formation of smaller water droplet compared to 500 rpm and commercial butter. Besides the change in average water droplet size, the microstructure of the puff pastry butter is identical (Fig. 5). Comparing the observed changes in plasticity and average water droplet size as a function of rotational speed, a correlation exists between strong primary crystal–crystal interactions related to mechanical interlinking between crystals and presence of small water droplets. It could be speculated, that large water droplets partly hinder mechanical interlining between the fat crystals hence formation of fewer and/or less stable primary bonds.

Summing up, changing the rotational speed from 500 to 1,000 rpm does not affect the polymorphic behavior in the produced puff pastry butter. However, such increase results in a reduced average water droplet size and a more elastic product.

Effect of Storage

As mentioned earlier, the puff pastry butter was followed at days 7, 15 and 28. In addition to days 7, 14 and 28, SAXS and WAXS were also monitored at day 2, as the crystal polymorphism in butter is likely to change within the first few days of storage [3, 10]. While no evolution is observed in the thermograms as a function of time, Fig. 2 illustrates, that polymorphic changes occurs in puff pastry butter from days 2 to 7.

For S2, S3 and S4, the intensity of the α -peak decreases from day 2 to 14 which corresponds to the observed disappearance of the 3L peak. From day 14 to 28, however, no changes are identified in either short or long spacings. For S1, the WAXS spectra remain the same during 28 days of storage. Both a high cooling rate and/or a high rotational speed during manufacturing induces a higher population of α -crystals. After 28 days of storage, no polymorphic differences are observed between samples.

In cream, both α - and β '-crystals have been found with minor traces of β -crystals immediately after cooling from 65 to 10 °C at either 0.4 °C/min or 7.5 °C/min [3]. However, after 48 h further storage at 5 °C, a transition to primarily β '-crystals with minor traces of β has occurred. In butter produced initially after cream cooling and tested after 24 h storage at 5 °C, primarily β '- crystals with traces of β are identified [3]. In the present work, a fraction of α crystals remains during the 28 days of storage (20 °C), independently of capacity and rotational speed. Previously we have shown, that a polymorphic transition from α - to β '-crystals occurs upon storage at 5 °C [3]. It can be concluded, that storage temperature can be used as a tool to control the polymorphic transitions in milk fat-based products.

Even though a high rotational speed during mixing affects the plasticity of the puff pastry butter, a strong degree of mixing is previously reported to reduce the fat crystal networks ability to recover [2, 6]. In the present work, a full recovery of the secondary bonds is observed after 7 days of isothermal storage (Fig. 3 top), as no difference is observed in G' when comparing 500 with 1,000 rpm. The recovery of the primary bonds is, however, delayed compared to the secondary ones. As the primary bonds are related to mechanical interlinking of the fat crystals, the delayed recovery could likely be ascribed to post crystallization, strengthening the crystal network. The observed difference in brittleness observed at day 7 may be related to differing number of nuclei formed due to changed rotational speed and capacity. Both rotational speed and increased capacity increases the shear applied on the product. According to the finding by Mazzanti et al. [6], the numbers of nuclei are increased which facilitate formation of crystallization and mechanical interlinking between the fat crystals and strain at 50 % decrease in G' is increased accordingly.

Second, storage of the puff pastry butter increases the ability of the fat crystal network to maintain its body during continuous working, independently of processing conditions.

During storage, the fat crystal network is strengthened, and the work per extrusion is increased for all processing combinations. The relation between them does, however, remain unchanged. Contrary for small deformation rheology, no systematic differences between the tested samples are observed after 28 days of storage. This deviation at day 28 between the rheological methods used highlights the complexity of the fat crystal network and the methods available to characterize it. Moreover, the different experimental setup during rheological analysis implies varied handling of the samples, which is likely to induce a certain degree of variation to the methods used.

Moreover, G' is stable during storage. A previous study has followed the rheological behavior of puff pastry margarine during 4 weeks of storage at 10, 18 and 25 °C [14]. At 10 °C, the puff pastry margarine was subjected to super cooling, and an increase in hardness was observed during the 4 weeks of storage. Contrary for 18 and 25 °C, only a limited or no increase in G' was observed. Upon storage within this temperature range, no further nucleation occurs.

In the present study, no difference is observed in polymorphism after 7 to 28 days of storage, similarly no microstructural differences are observed between those days or as a function of capacity and rotational speed (Fig. 5). Previous studies have been reported on relationship between polymorphic compositions and microstructure of milk fat-based systems [6, 23]. β '-Crystals tend to form large, platelet-like crystals which is associated with a grainy, unwanted macroscopic structure. In the present work, however, this microstructural difference has effectively vanished due to post crystallization occurring during storage. This explains why no microstructural differences are observed between days 7, 14 and 28 in the present study.

General Discussion

For the strain at 50 % decrease in G', a correlation between rotational speed and capacity exists. Figure 3 (bottom) shows, that an increased degree of working and a higher capacity results in less brittle puff pastry butter at days 7 and 14 (Fig. 2 bottom), as the fat crystal network breaks at a higher strain for S2-4. A similar tendency was observed by Madsen [14], when studying the rheological behavior of puff pastry margarine produced at different capacities (50 and 100 %) in a laboratory scale SSHE. The puff pastry margarine produced at half capacity was shown to be softer compared to puff pastry margarine produced at full capacity, as the cone penetration value increases up to 90 % (i.e., a softer product) during 4 weeks of storage at 18 °C. This behavior is explained by insufficient cooling and mixing at highest capacity, hence more pronounced post crystallization and consequently hardening of the fat produced at high capacities [14]. In newer equipment, such as the SSHE used, high rotational speed and high flow rates are shown to increase the homogenization of temperature gradient during processing [24]. Consequently, the explanation by Madsen [14] does not seem valid for the present work. Additionally, applying low rotational speed to the 60 l/h samples, results in a more brittle puff pastry butter compared to the other settings tested. This increased brittleness is reflected in the work softening, as the fat crystal network is more prone to fracture when applying a workload.

Conclusions

The present study implies that the capacity of an industrial scale SSHE can be increased without compromising crystal polymorphism, microstructure and rheological behavior. At day 2 only, a peak corresponding to 3L stacking is observed for samples produced at 90 l/h. For all samples during the 28 days of storage at 20 °C, primarily β '-crystals are formed with a population of α -crystals and minor traces of β -crystals. Increasing the capacity from 60 to 90 l/h does, in turn, increase puff pastry butters capability to maintain its body during work softening tests. The

brittleness of the puff pastry butter is, however, affected by rotational speed during manufacturing. Combining a low rotational speed with a low capacity increases the brittleness. These findings show, that while the secondary bonds within the fat crystal network recovers during the first 7 days of storage, the primary bonds develop more slowly upon storage at 20 °C. However, post crystallization during storage eliminates the initially observed rheological differences after 28 days of isothermal storage. Consequently, a wide operational window exists to produce puff pastry butter with a similar structural behavior.

Acknowledgments Thanks to the Danish Dairy Research Foundation and The Danish Food Industry Agency for financial support. Thanks to the Danish Agency for Science, Technology and Innovation, Carlsberg and Lundbeck for the funding of our SAXSLABinstrument. Ann Sofie Madsen and Naja Søndergaard (University of Copenhagen) are acknowledged for their help with small deformation rheology and differential scanning calorimetry, and Mai Sørensen (SPX) for running the LR-NMR analysis and large deformation rheology.

References

- Cavillot V, Pierart C, De Meerendré MK, Vincent M, Paquot M, Wouters J, Deroanne C, Danthine S (2009) Physicochemical properties of European bakery margarines with and without trans fatty acids. J Food Lipids 16:273–286
- Haighton AJ (1965) Worksoftening of margarine and shortening. J Am Oil Chem Soc 42:27–30
- Rønholt S, Kirkensgaard JJK, Pedersen TB, Mortensen K, Knudsen JC (2012) Polymorphism, microstructure and rheology of butter. Effects of cream heat treatment. Food Chem 135: 1730–1739
- Larsson K (1966) Classification of glyceride crystal forms. Acta Chem Scand 20:2255–2260
- Lopez C, Bourgaux C, Lesieur P, Ollivon M (2002) Crystalline structures formed in cream and anhydrous milk fat at 4°C. Lait 82:317–335
- Mazzanti G, Marangoni AG, Idziak SHJ (2009) Synchrotron study on milkfat crystallization kinetics under shear flow. Food Res Int 42:682–694
- Bell A, Gordon MH, Jirasubkunakorn W, Smith KW (2007) Effects of composition on fat rheology and crystallization. Food Chem 101:799–805
- Buldo P, Wiking L (2012) The role of mixing temperature on microstructure and rheological properties of butter blends. J Am Oil Chem Soc 89:787–795

- Kaufmann N, De Graef V, Dewettinck K, Wiking L (2012) Shear-induced crystal structure formation in milk fat and blends with rapeseed oil. Food Biophys 7:308–316
- Rønholt S, Kirkensgaard JJK, Mortensen K, Knudsen JC (2014) Effect of cream cooling rate and water content on butter microstructure during four weeks of storage. Food Hydrocol 34:169–176
- Heertje I, van Bendenburg J, Cornelissen JM, Juriaanse AC (1988) The effect of processing on some microstructural characteristics of fat spreads. Food Microstruct 7:189–193
- Sone T (1961) The rheological behavior and thixotropy of a fatty plastic body. J Phys Soc Jpn 16:961–971
- Segura JA, Herrera ML, Añón MC (1990) Storage of commercial margarine at different temperatures. J Am Oil Chem Soc 67:989–992
- Madsen J (1971) Proceedings: Changes in margarine and bakery compound caused by physical transformation in the fat phase during storage. In International symposium on deterioration of lipids 147
- Alderliesten M (1990) Mean particle diameters. Part II: standardization of nomenclature. Part Part Syst Char 7:233–241
- Rønholt S, Mortensen K, Knudsen JC (2013) Small deformation rheology for characterization of anhydrous milk fat/rapeseed oil samples. J Texture Stud. doi:10.1111/jtxs.12048
- Kaufmann N, Andersen U, Wiking L (2012) The effect of cooling rate and rapeseed oil addition on the melting behavior, texture and microstructure of anhydrous milk fat. Int Dairy J 25:73–79
- Mazzanti G, Guthrie SE, Sirota EB, Marangoni AG, Idziak SHJ (2003) Orientation and phase transitions of fat crystals under shear. Cryst Growth Des 3:721–725
- Russel AB, Chenney PE, Wantling SD (1999) Influence of freezing conditions on ice crystallisation in ice cream. J Food Eng 39:179–191
- Lopez C, Lesieur P, Bourgaux C, Ollivon M (2005) Thermal and structural behavior of anhydrous milk fat. 3. Influence of cooling rate. J Dairy Sci 88:511–526
- Lopez C, Bourgaux C, Lesieur P, Bernadou S, Keller G, Ollivon M (2002) Thermal and structural behavior of milk fat 3. Influence of cooling rate and droplet size on cream crystallization. J Colloid Interf Sci 254:64–78
- Rønholt S, Mortensen K, Knudsen JC (2013) The effective factors on the structure of butter and other milk fat-based products. Compr Rev Food Sci Food Saf 12:468–482
- Saadi S, Ariffin AA, Ghazali HM, Abdulkarim MS, Boo HC, Miskander MS (2012) Crystallisation regime of w/o emulsion [e.g. multipurpose margarine] models during storage. Food Chem 4:1485–1493
- Dumont E, Valle DD, Fayolle F, Legrand J (2000) Influence of flow regimes on temperature heterogeneities within a scraped surface heat exchanger. J Food Process Eng 23(207):220