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Effect of cream cooling rate and water content on butter microstructure during four weeks of storage

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ABSTRACT

Crystallization, rheological properties and microstructure of butter with varying water content and subjected to different cooling rate were studied during four weeks of storage at 5 °C. Using small and large deformation rheology, the elastic modulus (G′) and Hencky strain at fracture was followed. When comparing samples with an equal water content, samples produced from fast cooled cream (7.5 °C/min) have a higher G′ compared to butter produced from slow cooled cream (0.4 °C/min), at day 1–7. However, no difference in G′ is observed as a function of time, even though the solid fat content increases. Increasing the water content from 20% to 32% decreases G′ at day 1–14, yet X-ray scattering and differential scanning calorimetry shows no difference in crystal polymorphism or crystallinity. After 21 days of storage, no difference in G′ is observed as a function of cream cooling rate or water content. For all samples, small angle X-ray scattering shows formation of 2L (41 Å) and 3L (57 Å) lamellar organization, while the wide angle spectra shows mainly β′-crystals (4.2 Å & 3.81 Å) together with traces of β (4.6 Å).

1. Introduction

In recent years one of the major challenges in food research has been to develop and create products covering the essential nutritional needs, being low fat based while maintaining an appealing texture and taste (Wassell, Bonwick, Smith, Almiron-Roig, & Young, 2010). In commercial butter-like products and spreads, vegetable oils, such as canola oil, have been added in order to obtain a soft and spreadable product (Kaufmann, Andersen, & Wiking, 2012). One way to lower the amount of fat per serving is to increase the water content in the products. The water percentage is closely related to the quality of the final product. Therefore, it has been discussed that presence of water might influence crystallization behavior, which in turn could influence the texture of the product (Vanhoutte, Dewettinck, Foubert, & Huyghebaert, 2002; Vereecken, Foubert, Meeussen, Lesaffer, & Dewettinck, 2009).

Butter, spreads and margarines are all multiphase water-in-oil emulsions, consisting of fat globules, crystalline fat and water droplets dispersed within a continuous oil phase (Juriaanse & Heertje, 1988). The fat crystal network strongly contributes to the product stability by physical stabilization of the water droplets dispersed within the fat phase, hence preventing microstructural changes (Rousseau, Zilnik, Khan, & Hodge, 2003). The organization of the fat crystals is in lamellar planes near the water and oil interfaces, almost parallel to the interface plane (Wassel et al., 2012). Both the properties of the fat crystals and the size of water droplets are crucial for the strength of the fat crystal network (Juriaanse & Heertje, 1988; Rousseau, Gosh, & Park, 2009). When the water content is increased, more interactions between the water droplets can occur and they might become deformed with a bimodal size distribution (van Dalen, 2002). Still, more knowledge is needed on how water impacts milk fat crystallization together with the colloidal stability of butter, butter-like products and spreads. Other factors, such as thermal history and storage conditions, also affect the properties of a fat crystal network (Kellens, Meeussen, & Reynaers, 1992; Rousseau, Marangoni, & Jeffreys, 1998) together with microstructure of the fat crystals (Litwinenko, Singh, & Marangoni, 2004; Narine & Humphrey, 2004).

In milk fat, the crystals primarily form three different polymorphs: α, β′ and β (Fig. 1) (Lopez, Bourgaux, Lesieur, & Ollivon, 2002). The triacylglycerol chains pack hexagonally in the α-crystals, orthorhombic in the β′-crystals and triclinic in the β-form (Chapman, 1962), in increasing order of stability. The crystalline structure formed in concentrated cream (40% fat) and anhydrous milk fat quenched from 60 °C to 4 °C has been studied during 6 days storage at 4 °C (Lopez et al., 2002). After 15 min of storage, α (4.14 Å & 4.17 Å) and β′-form (3.84, 4.26 & 4.28 Å) are formed in cream and anhydrous milk fat. In addition, traces of β-crystals (4.65 Å) were observed in the anhydrous milk fat. For long spacings, Lopez et al.

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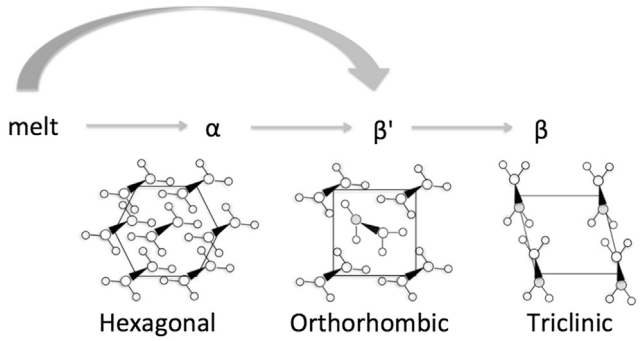

Fig. 1. Illustration of fat crystallization in milk fat. α-crystals (hexagonal subcell structure), forms directly from the melt, while β′-crystals (orthorhombic subcell) forms either via recrystallization of α to β′ or directly from the melt. β-crystals (triclinic subcell) are formed via recrystallization from β′.

(2002) observed peaks corresponding to 2L (39 Å) and 3L (70.5 Å) lamellar packing in cream. In the milk fat, a transition occurs from 3L (70.5 Å) → 2L (39 Å) and 3L (66 Å). After four days of storage, both α, β′ and β crystals are present in cream and anhydrous milk fat. In the long spacings, a coexistence of peaks corresponding to 2L (40.5 Å) and 3L (54.2 Å) is observed, demonstrating presence of a fast and slow transition in milk fat during storage at 4 °C, as more stable crystals are formed during storage.

In the present work, butter with different water content was prepared from fast and slow cooled cream. The objective of the study was to understand how water content and cream cooling rate affects the butter microstructure during storage. Therefore, butter was produced with a water content of 20%, 26% and 32% respectively. The butter was stored at 5 °C and characterized at day 1, 4, 7, 14, 21 and 28 after production. Low resolution nuclear magnetic resonance (LR-NMR) was used to study water droplet stability and solid fat content of the butter. Rheological characterization was used to quantify the effect of water content on the fat crystal network and confocal laser scanning microscopy to visualize the microstructure of the samples. Finally, the crystal polymorphism and stability was followed by small and wide angle X-ray scattering (SAXS and WAXS) and thermograms of the samples were obtained using differential scanning calorimetry.

By definition, butter contains maximum 16% of water (Codex Alimentarius, 2011). In the present study, the water content of the samples varies from 20 to 32%. However, to ease the reading all samples produced in this study will be referred to as butter.

2. Materials and methods

2.1. Materials

Pasteurized cream (38% fat) from ARLA Foods (Denmark) was used to butter manufacturing. To prevent microbial growth, 0.2 g/L sodium azide from Sigma Aldrich (St Louis, USA) was added. For the confocal laser scanning microscopy fluorescein-5-isothiocyanat (FITC) (Merck, Damstadt, Germany), Nile red and 1,1′-dioctadecyl-3,3,3′,3′-tetramethyl-indodicarbocyanine perchlorate (D307) (Molecular Probes, Paisley, UK) were used as fluorescent dyes.

2.2. Sample preparation

The butter samples were prepared in laboratory scale, all in triplicate. Two parameters were varied: the water content (20%, 26% and 32%) and the cream cooling rate (fast cooling at 7.5 °C/min and slow cooling at 0.4 °C/min) resulting in six different samples. A laboratory-scale butter making method developed in a previous study was systematically applied (Rønholt, Kirkensgaard, Pedersen, Mortensen, & Knudsen, 2012). First, the cream was kept at 65 °C for 10 min to erase all crystal memory. Afterward, the cream was cooled either slow or fast to a churning temperature of 10 °C. Finally, the cream was subjected to phase inversion at room temperature in a kitchen machine (CombiMax 600, Braun, Kronberg, Germany), equipped with a 2.0 L work bowl and a universal chopping blade. Churning time was defined as the time from the start of churning to phase inversion. The churning was considered complete, when butter grains appeared together with a liquid phase, the buttermilk. Water was then squeezed out of the butter to reach the desired water content. Finally, the butter was packed in plastic containers intended for butter, to avoid moisture loss during storage and placed at 5 °C in a refrigerator.

2.3. Water content

For each measurement, 5 g sample was spread on small pumice stones, placed in a porcelain crucible, in order to enhance water evaporation. The samples were placed in an oven at 100 °C for 2 h followed by 30 min in an exicator at room temperature. The procedure was continued until a stable weight was achieved e.g. all water was evaporated. Water content was obtained as the % difference in weight/weight before and after evaporation of the water. Water content (dry matter) was measured in duplicate on day 1, 4, 7, 14, 21 and 28 after production.

2.4. Low resolution nuclear magnetic resonance

Solid fat content and water droplet size distribution were determined during 28 days of storage at 5 °C. The measurements were conducted using a Bruker wide line low resolution nuclear magnetic resonance system (LR-NMR) (Bruker Minispec mq 20, Bruker Optik GmbH, Ettlingen, Germany) equipped with a pulsed gradient field unit, operated at 5 °C. The samples were prepared by punching a cylindrical glass (0.8 cm in diameter) into the sample at random locations, as described by Rousseau et al. (2009). Then, the samples were placed in an NMR tube. At least three replicates were prepared for each sample. The size is given by the volume-weighted geometric mean diameter ($d_{3,3}$), as defined by Alderliesten (1990). The determination of solid fat content by LR-NMR is possible since the transverse magnetization of solid fat decays faster than oil, resulting in faster spin–spin relaxation time for solid fat compared to oil (Balinov, Mariette, & Söderman, 2004). Even though the relaxation of water is faster than for oil, it is not possible to distinguish between their contributions to the signal (Balinov et al., 2004). Thus, the measured liquid content is the sum of water and oil. However, as the percentage water content is known for all samples in the present work, the reported solid fat content is corrected for the amount of water in each sample. In this way, the solid fat content represents the amount of solid fat relative to liquid fat.

2.5. Small deformation rheology

An AR G2 Rheometer (TA Instrument, West Sussex, England) equipped with a plate–plate geometry was used for all measurements, as described by Rønholt et al. (2012). Both upper and lower plate are temperature controlled and with serrated surfaces (25 mm in diameter). The frequency sweeps were performed in an interval of 500–0.05 rad/s divided into 21 steps. The oscillation stress was held constant at 500 Pa. The stress sweeps were performed in an interval of 1–800 Pa divided into 21 steps. Angular frequency was constant at 1.0 rad/s. All measurements were performed within the linear viscoelastic region (data not shown) at 10 °C. Cylindrical samples (25 mm in diameter) were punched out