Food Chemistry 135 (2012) 1730–1739

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Polymorphism, microstructure and rheology of butter. Effects of cream heat treatment

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ARTICLE INFO

Article history:
Received 5 March 2012
Received in revised form 25 April 2012
Accepted 23 May 2012
Available online 30 May 2012

Keywords:
Butter
Milk fat
X-ray diffraction
Fat crystallization
Rheology

ABSTRACT

The effect of cream heat treatment prior to butter manufacturing, fluctuating temperatures during storage and presence of fat globules vs. no fat globules was examined in laboratory scale produced butter. X-ray diffraction and differential scanning calorimetry was used to study crystallization behaviour and nuclear magnetic resonance to measure solid fat content and water droplet size distribution. Furthermore, the crystal structure was linked to the rheological properties and microstructure of the butter using confocal laser scanning microscopy. Butter produced from non-matured cream mainly formed α- and β′-crystals with minor traces of β-crystals. Maturing of the cream caused a transition from α- to β′- and β-form. The rheological behaviour of slow cooled butter deviated from the matured ones by having a lower elastic modulus, caused by a weaker crystal network. Presence of fat globules did not affect the rheological properties significantly.

1. Introduction

Butter is produced by a mechanical phase inversion of cream, an oil-in-water emulsion, to reach a water-in-oil emulsion. More precisely, butter consists of a continuous fat phase in which water droplets; fat globules and a network of fat crystals are dispersed. The fat crystal network is essential, since it determines the spreadability, appearance and mouthfeel of the butter and is strongly related to the butter composition and overall structure. The ratio between the solid and liquid fat is of outmost importance for the rheological properties of butter and spreads: without solid fat, butter is fully liquid. Without liquid fat, the butter would appear hard and brittle (Narine & Marangoni, 1999). Even though the solid fat content is the same, fat can have very different physical characteristics (Haighton, 1965; Shama & Sherman, 1970). Since a greater part of the solid fat is inside the fat globules, not all fat crystals are able to form a network outside the globule. Due to the large volume fraction of fat globules in butter, their presence is thus believed to influence the firmness of the product although results are not conclusive as to what extent (Fedotova & Lencki, 2010; Mulder & Walstra, 1974).

Recently, there has been an increasing awareness on the nutritional aspects of milk fat. However, before changing fat content (and potentially the microstructure) of the butter, it is essential to gain more information on how the individual parameters, such as presence of milk fat globules, cream heat treatment and fluctuating temperature during storage, all contribute to the textural properties of butter. Therefore, we aim to simulate the industrially applied continuous butter making process (Fritz-method) to gain knowledge of the structural and rheological properties arising from such conditions. In the Fritz-method the cream is separated into buttergrains and buttermilk in a churning cylinder, followed by processing of the buttergrains and finally evacuation (Frede & Buchheim, 1994). Our aim was to investigate the effect of cream heat treatment on the final butter texture. Hence, we study how the thermal history of the cream affects rheological properties, solid fat content, microstructure and the crystallization characteristics of the butter, i.e. the structural organization of the solid fat. Further, we compare samples with and without fat globules.

The exact crystallization characteristics of the fat is influenced by many factors such as the way in which the sample is cooled from the bulk fat (Herrera & Hartel, 2000a, 2000b, 2000c; ten Grotenhuis, van Aken, van Malassen, & Schenk, 1999) and the mechanical treatment (Heertje, 1993). Also, the broad range of triacylglycerols found in milk fat results in different polymorphic forms as a result of varying chain length and degree of saturation of fatty acids. The polymorphism of the various constituents can be identified by X-ray diffraction and has been the topic of numerous studies (Fredrick et al., 2011; Lopez, Lavigne, Lesieur, Keller, & Ollivon, 2001; Lopez, Lesieur, Bourgaux, & Ollivon, 2005; Lopez et al., 2002; ten Grotenhuis et al., 1999; Wiking, De Graef,

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http://dx.doi.org/10.1016/j.foodchem.2012.05.087

Rasmussen, & Dewettnick, 2009). The main structural characteristic of the molecular arrangements of triacylglycerols is that they pack into lamellar structures in the longitudinal direction; most often in stacks either two or three fatty acids long (termed 2L or 3L respectively). The chains lie perpendicular to the lamellae planes (possibly tilted) and the in-plane packing of the chains gives rise to various polymorphic forms. The three most important of these found in fats are denoted α, β′ and β in order of increasing stability (Mazzanti, Marangoni, & Idziak, 2009). The different polymorphic forms are characterized by the short and long *d*-spacings of their crystal lattice which constitutes an identifying structural fingerprint (Larsson, 1966; ten Grotenhuis et al., 1999; Vaeck, 1960). To determine this fingerprint and describe the crystal structure one needs knowledge of both the lateral packing and the longitudinal stacking.

In previous studies, the polymorphic characteristics of milk fat are typically studied in model systems with focus on the effect of temperature treatment and processing conditions on the crystallization kinetics. In the present study, we study polymorphism, microstructure and rheology of butter. Moreover, we study the crystal polymorphism in cream, subjected to different temperature treatments prior to butter making. We quantify the properties of the butter using a variety of characterization tools. Small and Wide Angle X-ray Scattering (SAXS and WAXS) is to describe the crystallization state before (i.e. of the cream) and after butter manufacturing. Further, we combine the SAXS and WAXS with Differential Scanning Calorimetry (DSC) to follow the thermal evolution of the crystallinity on subsequent heating. Light scattering is used to study milk fat globule size and zeta potential. Rheological measurements are used to quantify the mechanical properties of the fat crystal network and confocal laser scanning microscopy to visualize the microstructure of the butter. Finally, using Low Resolution Nuclear Magnetic Resonance (LR-NMR) we measure the water droplet size distribution and solid fat content of the butter.

2. Materials and methods

2.1. Materials

Cream (38% fat) and skimmed milk (0.1% fat) were collected from the local supermarket. They were all from ARLA Foods Dairy in Slagelse, Denmark. Sodium azide from Sigma Aldrich, St. Louis, USA was added to avoid microbial growth (0.2 g/L cream). Anhydrous milk fat from ARLA Foods, Götene, Sweden was used for the reference samples. Fluorescein-5-isothiocyanat (FITC) (Merck, Damstadt, Germany), Nile red and 1,1′-dioctadecyl-3,3,3′,3′-tetramethyl-indodicarbocyanine perchlorate (D307) (Molecular Probes, Taastrup, Denmark) was used as fluorescent dyes for the confocal laser scanning microscopy images.

2.2. Sample preparation

Five butter samples with differing cream heat treatment were prepared in laboratory scale in triplicate. Furthermore, three reference samples of anhydrous milk fat and skimmed milk were prepared, also in triplicate, and subjected to different heat treatments according to the butter samples. The various treatments were: slow cooling (butter and reference), fast cooling (butter and reference), slow cooling and maturing (butter only), fast cooling and maturing (butter only) and finally fast cooling and storage at fluctuating temperatures (butter and reference). In order to control the heat treatment of the cream, a laboratory-scale butter making method was developed and systematically applied. To erase all crystal memory the cream was heated to 65 °C for 10 min followed by either fast (7.5 °C/min) or slow cooling (0.4 °C/min) to churning temperature (10 °C). For the matured samples, the cream was stored at 5 °C for 48 h. Non-matured samples were prepared from the cream immediately after reaching 10 °C. The samples stored at fluctuating were produced from fast cooled cream, and after manufacturing stored at 5 °C for 3 h, 20 °C for 3 h, followed by nine cycles of 1 h at 5 °C and 1 h at 20 °C. The cream was subjected to phase inversion in a kitchen machine and worked in a food grinder (Beem, Gigant ES-10/12) followed by vacuum treatment to remove air. The reference samples were prepared from anhydrous milk fat melted at 65 °C for 15 min and skimmed milk according to the water content in the butter samples. It should be noted, that butter by definition contains maximum 16% of water. In this work the water content varies from 24.6% to 27.3% (w/w). Even though our samples do not meet the formal requirements we will still refer to the samples as butter.

2.3. Light scattering

Initially, the milk fat globule size and zeta potential of the cream was measured using light scattering (Malvern Mastersizer connected to a 50 ml stirring unit and Malvern Zetasizer, Malvern Instruments Ltd., Malvern, UK). For determination of zeta potential the refractive index (RI) of the cream must be known. For all samples it was assumed that the RI was 1.39 (Calhoun, Maeta, Roy, Bali, & Bali, 2010). The zeta potential generated from the samples is a combination of the signal from the fat globules as serum phase in which they are dispersed. Consequently, the signal obtained from the serum phase must be subtracted to get the zeta potential of the fat globules. A serum phase was therefore prepared by centrifugation at 16,100 rpm for 1 h at 4 °C (SL16R centrifuge from Holm&Halby, Brøndby, Denmark). The serum phase was removed with a syringe. Any proteins remaining in the bottom of the centrifuge tube were removed and redispersed in the plasma phase during ultrasonication for 30 min followed by centrifugation at 3400 rpm for 0.5 h, as described by Wade and Beattie (1997). All measurements were done in triplicate on samples diluted 1:10 with water. The distributions of fat globule sizes were derived from measurements on cream diluted in deionised water. The volume-surface mean diameter ($d_{3,2}$) was calculated using the Malvern Mastersizer software. The measurements of zeta potential and globule sizes were conducted the day the samples were prepared.

2.4. Dry matter

Water content (dry matter) was measured in duplicate on all samples. The samples were placed in an oven at 100 °C for 2 h followed by 30 min in an exicator at room temperature. The water content was calculated as the % w/w difference before and after heating.

2.5. Conductivity

Conductivity was measured with a hand-held conduct meter in the final butter sample (Cond.330i/SET, WTW Wissenschaftlich-Technische Werstätten GmbH, Weilheim, Germany). The results are the average of three measurements.

2.6. Low resolution nuclear magnetic resonance

The solid fat content and water droplet size distribution were determined in all butter and reference samples using a Bruker wide line LR-NMR system (Bruker Minispec mq 20, Bruker Optik GmbH, Ettlingen, Germany) equipped with a pulsed gradient field unit, operated at 5 °C. The samples were obtained by pressing the NMR tubes (0.8 cm in diameter for water droplet size distribution