Thermal Influence on Rheological Characteristics of Butter and Margarine during Distribution, Storage and Use

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ABSTRACT

Investigation of thermal behavior of emulsion systems are essential in order to understand changes when the systems are exposed to different temperature cycles during storage and use. In fat emulsions, like butter and margarine, the amount of crystallized fat is greatly dependent on temperature, and so is the firmness. Even at constant temperature, a slow recrystalization may occur since the fat crystals in such products seldom are in thermodynamic equilibrium. A slight temperature increase often causes some melting of the fat crystals. Upon subsequent slight cooling, newly formed crystals will deposit on existing crystals, often referred to as "sintering". Consequently, the fat product may markedly increase in firmness due to small temperature fluctuations during storage.

A Texture Profile Analyzer (Stable Micro Systems, UK, 1998) was used to measure rheological changes in firmness of the tested spreads caused by changes of the storage temperatures. The measurement equipment was feasible for the purpose.

INTRODUCTION

In two previous studies, it was investigated if butter (80 % milk fat), margarine (80% vegetable fats and oils) and spreads (40% fat) became firmer by repeated "heating and cooling" in a temperature range between 4°C and 20°C [1,2].

From a theoretical point of view it was expected that the firmness of butter, would increase considerably beyond the original level, due to temperature increase followed by subsequent cooling to original temperature[3]. This was not confirmed in the previous studies, partly related to the holding time at 20 °C. Milk fat is partially solid at temperatures between approximately 5 and 25°C, and its consistency is caused by the presence of a network of fat crystals in liquid fat[4]. In another study[5], the solid fat contents of butter at different temperatures between 0 to 35°C were determined by pulsed nuclear magnetic resonance. Table 1 summarize these findings for salted types of butter[5,6] and for a typical soft table margarine.

Table 1. Solid fat content (%) of butter*[5] and soft table margarine**[6] at different temperatures.

5°C	10°C	15°C	20°C	25°C	30°C
63*	56*	40*	22*	12*	5*
	28**		14**		3**

In general the structure of products with a continuous face of fat or oil, such as butter and margarine, is based on a network of crystalline particles. The nature of this crystal network can be dramatically altered by changes in crystallization conditions[7] ; for example by changes in the temperature of the product. Accurate data for thermal properties of butter is a prerequisite for the prediction of thermal behavior of food under industrial conditions.

Crystallization of water-in-oil emulsions is a complex process which is influenced for instance by composition of the emulsion, temperature treatment and state of dispersion of the fat. The fact that lipids exhibit polymorphism[8] is another incident that contributes to the complexity of fat crystals and their rheological behaviour.

Crystal polymorphism is of fundamental importance for final product consistency and acceptability. By cooling anhydrous milk fat at different cooling rates from 60 °C to -10 °C, it was found that the triglycerides crystallized in 4 different polymorphic subcell types; sub-α, α, β´, and β with some reversible and some irreversible transitions[9].

Regarding butter, both polymorphism and rheology are largely determined by the treatment of the cream prior to the butter manufacturing. Slow and fast cooling of the cream may result in similar rheological properties and polymorphic forms, α,- and β´-crystals , but different microstructure[10]. In addition this is further complicated by formation of mixed crystals. Mixed crystals form when different kind of molecules are incorporated into the lattice of one crystal [11].

After production, different crystallization processes proceed in semi-solid fat products that consist of solid crystals dispersed in a liquid oil. These post-crystallization processes include nucleation of new crystals and crystal growth; so-called Ostwald ripening which mean dissolution of small crystals and growth of big ones. In addition polymorphic transformation (a property that gives rise to various aggregation of lipids), migration of oil, and migration of small crystals are ongoing. Crystal growth during post-crystallization may sometimes lead to formation of solid bridges (sintering) in narrow gaps of fat crystal networks. Such fat crystal bonds are divided into primary bonds (solid bridges), which are very strong and dissociate up on mechanical work. Secondary bonds are much weaker[12]. Such sintering has been mentioned in the literature, but less studied extensively.

A model that can be used to describe the formation and interaction among structural elements that affect the macroscopic properties of fat crystal network, is shown in Fig. 1.

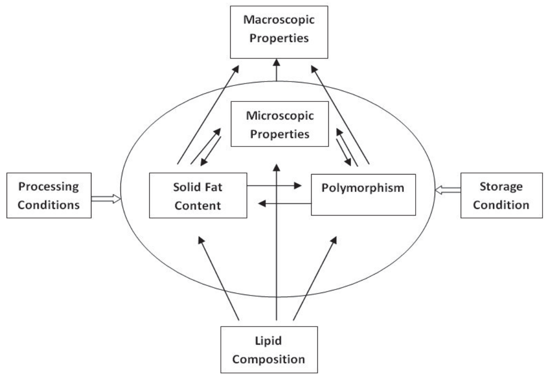

Figure 1. Model describing factors with strong- ⇨ and potential ➔ influence, affecting macroscopic properties of fat crystal network[13].

This model suggests that lipid composition, directly under influence of storage conditions, will affect the solid fat content, polymorphism and microstructure of a fat crystal network[13]. The model also suggest that interactions among these factors play an important role, since they affect the structure of the fat crystal network, and in turn influence physical properties and sensory perception of the fat product.

Triglyceride composition of fats and their solubility has also been studied. Solubility of fats in soybean oil has for instance been calculated as a function of temperature[12]:

$$X_M = e^{-\frac{\Delta HM}{R}(\frac{1}{T}-\frac{1}{Tm})} \quad (1)$$

where X_M is the dissolved mole fraction, ΔH_M the enthalpy, R the gas constant, Tm the melting point of the pure fat, and T the temperature. The equation is valid for ideal solutions.

Both margarine and butter are examples of food systems that are rather complex regarding measuring rheological properties. During processing they are made from liquids with different viscosity, which may or may not exhibit elasticity. In addition these products are quite heterogeneous, consisting of two or more phases as emulsions[14].

The objectives of this work are divided in three main parts;

1. Theoretical approaches and understanding of mechanisms appearing during temperature fluctuations in fat emulsions caused by storage of fat emulsions.
2. Simulation of the effect of variation in storage temperature on the firmness of butter and margarines using a transient temperature calculation program based on a finite element modeling system.
3. Experimental documentation to validate both the simulation, and the theoretical understanding of the phenomenon of firmness development in fat emulsions during storage at fluctuating temperature and use.

MATERIALS AND METHODS

Butter and margarine samples

Butter and margarine were purchased from a local retailer in 500 grams wrapped packages according to Table 1. The samples of each type of spread were from the same lot of production. Butter was produced by TINE, Norwegian Dairies Association, Norway. Margarine based on vegetable fats and oils, mainly soy bean oil, were produced by Mills, Norway. The samples were stored at +4 ºC until rheological measurements were carried out as measurements of "fresh products". Thereafter the samples were tempered 5 hours to 20, 25 and 30°C respectively; three packages at each temperature. After 5 hours extension at the mentioned temperatures the samples were stored at 4°C for 48 hours until the next rheological measurement.

Four replicate measurements in each package were carried out for each product examined. All three replicates were taken from inside the same package. These measurements were compared with measurements on butter and margarine samples from the same lots kept continuously at 4°C.

Table 2. Name of spread, fat source and fat content in butter and margarine investigated in this study.

Spread	Fat source	Fat content(w%)
Butter	milkfat	81
Soft Flora	veg. fats & oils	80

Instrumental analysis

Penetration tests of the fat samples were performed with the Texture Profile Analyser TA-HDi TPA (Stable Micro Systems, United Kingdom, 1998). The measurements were carried out on one surface of the 500 grams rectangular butter and margarine packages at +4°C.

Rheometer experimental set-up

The Texture Profile Analyser (TPA) TA-HDi equipped with Texture Expert Exceed data computing programme was programmed to measure compression and penetration force. The probe PO 5R ½” Delrin BS 757 was used in all the experiments. The TPA - test settings were;

Pre-test speed: 2.0 mm/s, test speed:1.0 mm/s, post-test speed: 2.0 mm/s, distance: 5.0 mm, time: 5.0 s, force: 0.98 N, Load Cell: 25.0 kg, trigger type: Auto, data acquisition rate: 200 pps.

Temperature calculations

Temperature calculations is based on Comsol Multiphysics* version 4.3a.
Comsol Multiphysics is an engineering, design, and finite element analysis software for modeling and simulation of any physicbased system. This study used transient temperature calculations made on a 3D model of butter in the tray as shown in Fig. 2. Account was made for the nonlinear temperature dependent thermal properties of butter in the calculations.

The thermal properties, in SI units, of butter were taken[5] as:

$$t = T - 273.15 \quad [°C] \tag{2}$$

$$k = 0.183 + 0.0025 \cdot t \tag{3}$$

$$\rho = 949.8 - 0.7 \cdot t \tag{4}$$

$$c_p = 1000 \cdot (1.6 + 0.0611 \cdot \mathrm{t} + \frac{6.75}{1 + 0.1 \cdot (\mathrm{t} + 6.32)^2} + \frac{3.42}{1 + 0.0269 \cdot (\mathrm{t} - 17)^2}) \tag{5}$$

where T is temperature [K], k is the thermal conductivity of the material [$Wm^{-1}K^{-1}$], ρ is the relative density [kgm^{-3}] and c_p is specific heat capacity at temperature T [$Jkg^{-1}K^{-1}$].

* www.comsol.no

Statistical treatment

One-way ANOVA (Minitab 16) and 95% Tuckey simultaneous confidence intervals, pair-wise comparisons, was used to determine if statistically significant differences were observed after measurements.

RESULTS

Table 3 reports the average per capita consumption of margarine and butter within EU and Norway during the period from 1979 to 2010. The table gives at least three important informations;

- Butter and margarine are essential food products in the diet both in EU and in Norway.
- The European pr. capita consumption of these crystallized emulsions is less than the consumption in Norway.
- The consumption of margarine seems to decrease in Norway, while the butter consumption seems to increase in EU.

Table 3. Average per capita consumption (kg) of butter (B) and margarine (M) in EU[15] and Norway[16] from 1979-2010.

Year	EU		Norway	
	B	M	B	M
1979-80	2.0	5.0	5.0	15.0
1989-90	2.0	4.9	3.0	13.0
1999	2.2	3.6	3.0	12.0
2007	2.4*	3.3*	3.0	9.0
2010	3.6*	5.0*	3.0	9.0

*Estimates based on Statistics from IFMA and IMACE[14].

Fig. 2 show the calculated meshed 3D model of butter in container with lid removed. The grid is relatively tight. The calculated heat transfer follows the connecting lines between the many nodes.

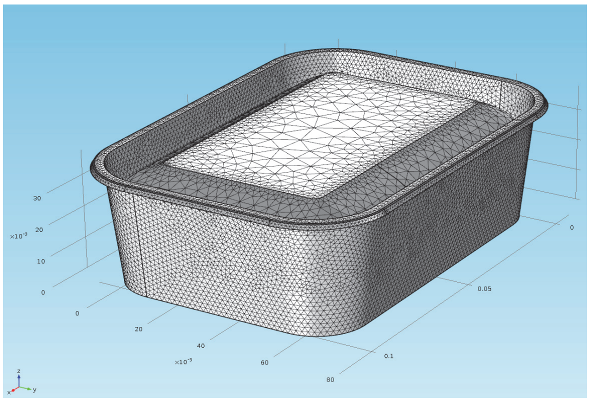

Figure 2. Comsol Multiphysics meshed 3D model of butter in container with lid removed.

The temperature versus time development in a butter container is shown in Fig. 3. As illustrated in the figure, measured data are compared with calculated data. The two set of calculated data are based on heat transfer from the surroundings at 20 ^{o}C into the butter center according to two different external heat transfer coefficients (5 W/m^{2}K through all surfaces, and 10 W/m^{2}K through the bottom with 7 W/m^{2}K through other surfaces – numbers selected to match real heat transfer).

To obtain the rate of heating of butter when left in room temperature, a container of butter from TINE was taken out from a refrigerator at 1 °C and left on a wooden table located in closed room at 21.5 °C. Temperature was measured by a thermocouple type K inserted at the center of the container. The same pot was drawn at scale for the FEM analysis and it is shown on Fig. 2 Temperature was measured in fuction of time and it was used to estimate the heat transfer coefficients shown on Fig. 3.

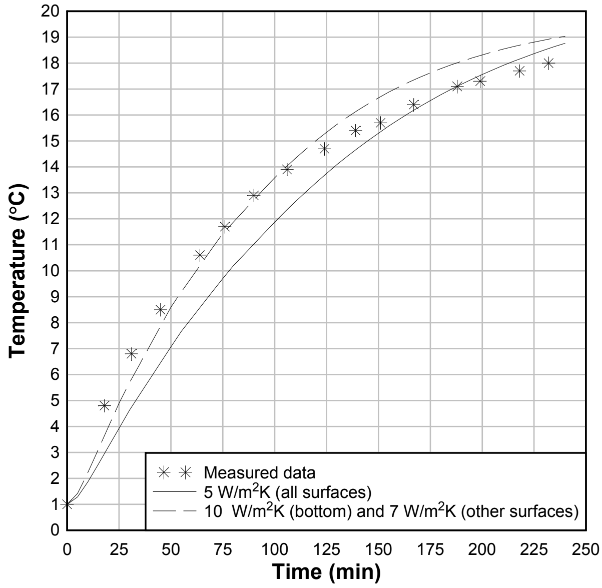

Figure 3. Butter center temperature versus time for different external heat transfer coefficients. Surrounding temperature was 20 °C.

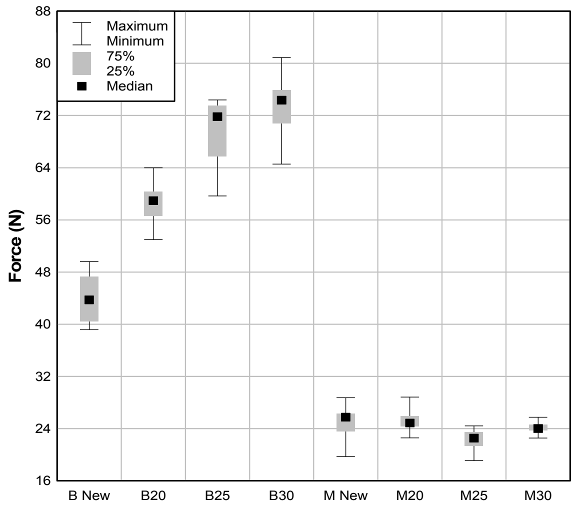

Figure 4. TPA boxplot highlighting firmness (N) in butter (B) and margarine (M). The samples were measured at 4^{o}C as fresh (new), and after 5 hours extension of the samples at 20, 25 and 30^{o}C stored at 4^{o}C for 48 hours.

Fig. 4 shows a TPA plot highlighting firmness (N) at 4^{o}C for butter (B) and margarine (M). The samples were stored at +4 ºC until rheological measurements were carried out as reference measurements of "fresh products"; B New and M New. Then the samples were tempered 5 hours at 20, 25 and 30°C respectively; three packages at each temperature. After 5 hours extension at the mentioned temperatures the samples were stored at 4°C for 48 hours until next TPA measurement.

Four replicate measurements in each package were carried out for each product examined.Butter increased the firmness extremely after 5 hours at 20, 25 and 30 °C followed by 48 hours storage at 4 °C. This is in intense contrast to the rheological characteristics of margarine which seems more or less unaffected of the thermal influence.

The results in Fig. 4 also show that butter is much firmer than margarine as fresh products. It is about two times firmer than margarine measured as fresh at 4 °C. This ratio increase dramatically during for instance consumers treatment of butter at home when leaving butter on the table or outside the fridge for some hours.

DISCUSSION

Fig. 4 presents individual average TPA measurements. The results show rheological characterics and differenent behaviour between butter and margarine when simulating the consumers handling of these articles at extreme time and temperature combinations. But such temperature/time cycles happens from time to time at home during activities of daily living

The TPA plot in Fig. 4 highlight firmness or force (N) at 4 °C for margarine and butter. The measurements reported give a clear trend for the two types of full fat spreads. Butter was much firmer than margarine both as fresh, and after thermal treatment at 20, 25 and 30 °C followed by 48 hours storage at 4 °C .

From a theoretical point of view, it was expected that the firmness of butter should increase beyond the original level, due to temperature increase followed by subsequent cooling to original temperature[2,3]. As pin pointed in Table 1, milk fat is partially solid at temperatures between approximately 5 and 30°C, and its consistency is caused by the presence of a network of fat crystals in liquid fat[17].

Information about temperature versus time development in the spread container, was calculated on a 3D model as shown in Fig. 2. Both measured- and calculated temperatures versus time in butter center for different external heat transfer coefficients are illustrated. Surrounding temperature was 20 °C. Based on this documentation, 5 hours was used as extension of the samples at temperatures tested (20, 25 and 30°C).

The rheological characteristics of margarine seemed to be more or less unaffected of the thermal treatment in this study. This is also as expected. Modern margarines are tailor-made products, which differ significantly from classical margarine and butter regarding properties and fat composition. These new properties are in line with present-day market requirements, like spreadability from the refrigerator and high content of polyunsaturated fatty acids . In the past, margarine was purely regarded as a substitute for butter. Its physical properties were much like those of butter, which is plastic and spreadable at ambiente temperatures, but very hard under cooler conditions.

Rheological characteristics of margarine and butter are expressed in terms such as consistency, texture, plasticity, hardness, structure and spreadability[18]. These characteristics are related to a number of variable factors; temperature, solid fat content, crystal size, crystal size distribution, crystal shape, interparticle forces and mechanical treatment of the emulsion. The two dominating factors are the amount of solid triglycerides and the processing conditions during production. But in this study, we just investigated the storage conditions; Fig. 1.

The results prove the declared phenomenon related to setting of butter. An increased temperature of butter and a following cooling will re-crystallize the melted fat which make the crystal network stiffer, resulting in firmer consistency[19]. In contrast to butter, margarine is formulated of oil blends which allow control of the solid fat content. This control is directly related to the consistency and type of crystalline structure formed during processing, storage and use.

In this study only deformation rheology was used as method for characterization of changes in the microstructure of butter and margarine caused by thermal influence. In further studies of this phenomenom, polarized light microscopy will be utilized to analysis changes in fat crystal network as a supplement to this rheological investigation.

CONCLUSIONS

This study investigated thermal influence in rheological characteristics of butter and margarine during simulated distribution, storage and use. The conclusions can be summarized as follows:

- The firmness of butter at 4 °C increased dramatically beyond the original level, due to temperature increase between 20 and 30 °C followed by subsequent cooling to original storage temperature at 4°C.
- Margarine remained unaffected of this treatment.
- Theoretical temperature calculations based on Comsol Multiphysics Simulation of the effect of storage temperature of butter corresponded well with real temperature measurements. These findings were used to prove both the simulation, and the theoretical understanding of the phenomenon of firmness development in fat emulsions during storage and use.
- The TPA-measurement instrument was feasible giving objective rheological information about changes in firmness of fat spreads when repeating a number of time and temperature cycles.
- The measurements may be used by the industry for instance to contribute to aid more optimal formulation of spreadable water-in-oil emulsions. Spreadability of butter and margarine can easily be assessed by measurement of its complex viscosity at different temperatures.

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