Rheological characterization of crystallized water-in-oil emulsions during storage and use.

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ABSTRACT

The scope of this study was to assess and compare two rheological measurement methods to characterize butter and margarine when repeating a number of time and temperature cycles during storage. A controlled stress oscillation rheometer and a penetrometer (texture analyser) were elected as measurement instruments.

INTRODUCTION

In a previous study 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].

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[2] caused for example by the crystallization temperature and in changes in the temperature of the product.

Consumer acceptance of these crystallized water-in-oil emulsions depends much on their textural characteristics such as spreadability – a measure of how easily and uniformly they can be deformed and spread at end-use temperature[3]. It is usually necessary for these table spreads to maintain their properties over a relatively wide range of temperatures; for instance between 4°C to 22°C. However regular butter requires approximately 15°C before it can be easily spread[4].

Spreadability as a rheological property, depends on the composition of the product and on the solid fat content of the product. The spreadability is also influenced by the morphology of the fat crystal network and the different forms this might adopt, as well as the type and strength of interactions that might occur between the phases of the emulsion at a given temperature[5].

Temperature has a considerable effect on firmness. For butter, large differences occur in firmness at the same temperature, even when the butters have the same chemical composition. After heating followed by subsequent cooling to initial temperature, crystallisation causes formation of solid networks, establishing an increase in firmness beyond the original level[6]. It is also known that milk fat has a long and variable melting range from -40°C to + 40°C because of the large differences in melting point of the many component triglycerides. However the pronounced melting occurs in the temperature regions between 0°C and 20°C[6]. Working of a fat product gives a sharp decrease in its firmness. This phenomenon is called work softening. The product obtains an increase in firmness again if kept undisturbed after the work softening. The new firmness is however less than before the work softening.[7].

Crystallization of water-in-oil emulsions is in general a complicated 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.

Rheological instruments are used to characterize these characteristics of butter and spreads, in order to measure and characterize their plastic behaviour. Thus they must have yield stresses below their elastic level, and above their plastic level. Commonly used measuring methods to characteristize the consistency of butter and similar products, either register the stress necessary to obtain a given deformation, or the time necessary to obtain a given deformation by a given stress[9].

The rheological properties of spreadable foods have been studied by a variety of methods[2]. In two previous studies[10,11] it was concluded that off-line oscillatory plate-plate rheometer measurement can be useful in grading the spreadability of fatty livers and similar products according to given quality parameters.

Another study pin points that crystal polymorphism has primordial 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[12].

Both margarine and butter are examples of food systems that are rather complex regarding measuring their 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[13]. This implies that it may be difficult to compare rheological results obtained by the use of different measuring methods.

The purpose of this study was as follows:

- To compare results from two rheological measurement instruments giving rheological information of fat spreads when repeating a number of time and temperature cycles during storage of the products.
- To investigate if storing of water-in-oil emulsions like butter (80 % milk fat), margarine (80 % vegetable fats and oils) and spreads (40 % fat) gets firmer by repeated "heating and cooling" in a temperature range between 4°C to 20°C.

MATERIALS AND METHODS

<u>Butter and margarine samples</u>

Butter and margarine were purchased from a local retailer in 400 grams plastic containers according to Table 1. The samples of each type of spread were from the same lot of production. Butter and spread with a mixture of milk fat and vegetable oil were 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 in the first run. Thereafter the samples were tempered once a week to 20 °C. After 4.5 hours at 20°C the samples were stored at 4°C for a week until the next rheological measurement run. This treatment was repeated several weeks and is named the "time temperature cycles", Fig. 1. Two storage series (I and II) were carried out during the period of 2010.10.18 – 2010.12.20.

Three replicate measurements were carried out for each product examined. All three replicates were taken from inside the same package.

Table 1. 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
Brelett	milk/rape/palm	40
Soft Flora	veg. fats & oils	80
Soft Light	veg. fats & oils	40

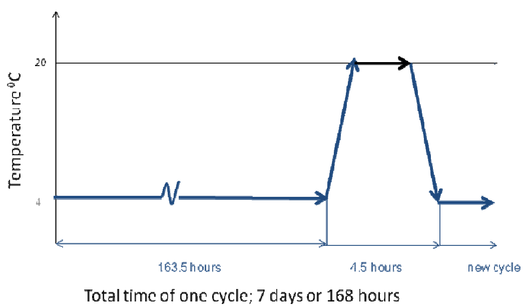

Figure 1. One of the repeated temperature/time cycles simulating the consumers handling of the products kept in the refrigerator and served at room temperature several times during some weeks (temperature range 4°C – 20°C).

Instrumental analysis

The Physica MCR 301 rheometer (Paar Physica, Anton Paar, Germany, 2010) fitted with a PP50 profiled top plate and a Peltier bottom plate was used as oscillation rheometer.

All the 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 in the in 400 grams plastic containers at +4°C, Fig. 3.

Rheometer experimental set-up

The sample at room temperature was gently placed on the Peltier plate of the Paar Physica MCR 301 instrument while the temperature of the Peltier was set to 20 °C. The top plate (PP50/P2-SN9573) was then gently lowered until the gap was approximately 1.0 mm. The excess spread was then gently removed from the rim of the MP31, Fig. 2.

The normal force on the sample was set to 0 N during the test which caused the gap to vary during the test as a result of thermal expansion effects. The sample was monitored at 10 radians/s at 0.01% strain during cooling and heating.

An amplitude sweep at 10 radians/s was first performed at 20 °C while the strain increased from 0.01-5%. The temperature was then reduced to 4 °C in 165.5 s and then left for 5 minutes to equilibrate. An amplitude sweep was then performed at 4 °C while the strain increased from 0.01-5%. The temperature was then increased to 20 °C in 165.5 s.

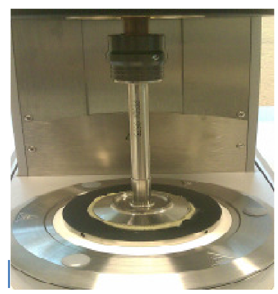

Figure 2. Spread sample in the Physica MCR 301 rheometer fitted with the PP50 top (PP50/P2-SN9573) plate and the Peltier bottom plate.

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, Fig. 3.

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.

Figure 3. The Texture Profile Analyser TA-HDi TPA showing the PO 5R ½" Delrin BS 757 probe.

RESULTS

Table 1 reports the average per capita consumption of margarine and butter within EU and Norway during the period from 1979 to 2007. 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 both in EU and in Norway, while the butter consumption seems quite stable over the last 4 decades.

Table 2. Average per capita consumption (kg) of butter (B) and margarine (M) in EU[14] and Norway[15] from 1979-2007.

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

*Estimates based on Statistics from IFMA and IMACE[16].

Fig. 4, 5 and 6 are presenting individual measurement results from the two instruments; TPA and Physica MCR respectively. The results show rheological characterics of the tested emulsions when simulating the consumers handling of these articles at home from buying them fresh until final use.

Fig. 4 show the TPA plot highlighting force (F) versus time at 4^oC for serie I and II of the crystallized water in oil emulsions. The results indicate more or less the same development between the two series and between the types of products tested. Butter is much firmer than all the other emulsions. It is about 7 times firmer than margarine with the same fat content, and about 23 times firmer than the low fat spread Soft Light.

Fig. 5 represents the storage modulus G´ (Pa) or the elastic properties of the sample, versus shear stress τ (Pa) for one of the measured emulsions at at 4^oC and 20 ^oC. Fig. 5 is important as an underlying explanation for all other MCR results presented, which are taken at 5% reduction in G´.

Fig. 6 show the MCR plot of shear stressvariation at 5% reduction in elastic properties G´ at 4^oC and 20^oC for the two series of tested emulsions. The results indicate more or less the same development between the two series and between the types of products tested. Regarding butter at 4^oC it was not possible to detect the upper limit of the linear viscoelastic range since this exceeded the maximum allowable working torque of the electronically commutated synchronous motor of the instrument.

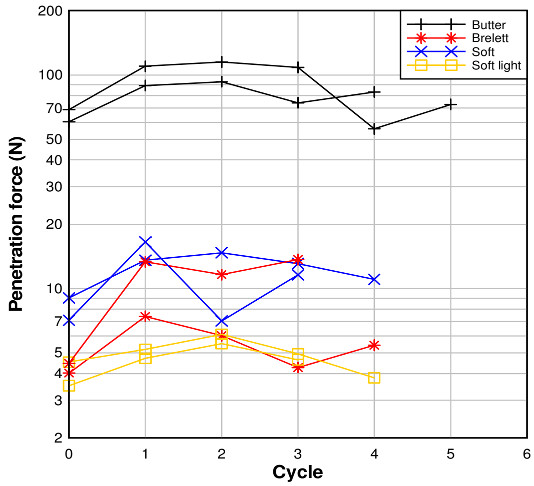

Figure 4. TPA plot highlighting force (F) versus time at 4°C for serie I and II. Crystallized water in oil emulsions after repeated temperature/time cycles simulating consumers handling of the products kept in the refrigerator at 4°C and served at 20°C (serie I; 4 repetitions, serie II; 3 repetitions, n=3).

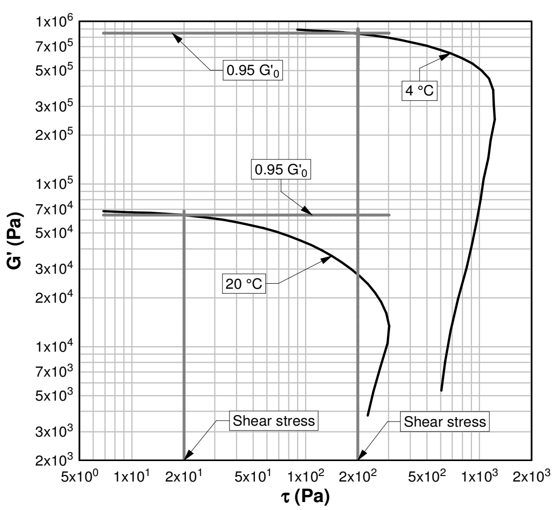

Figure 5. Example plot of G´versus shear stress for Soft Light at 4°C and 20 °C. All Physica MCR shear stress values presented in fig. 6 for all emulsions, are taken at 5% reduction in G´.

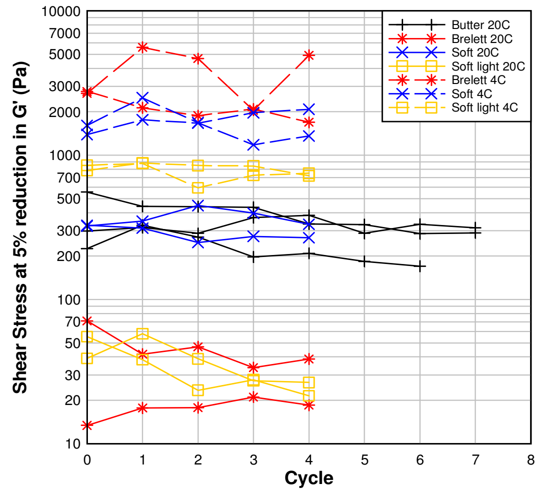

Figure 6. Physica MCR plot of shear stress variation at 5% reduction in elastic properties G´ at 4°C (- - -) and 20°C (––) for the tested emulsions, serie I and II. Number of repeated temperature cycles of 1 week along the x-axis, each (Fig. 1) monitored at constant 1% strain using the oscillatory plate-plate rheometer.

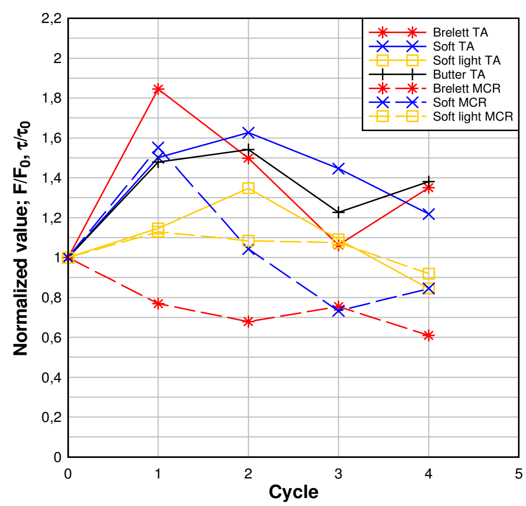

Figure 7. Time plot for TPA (––) and Physica MCR(----) from serie I of oil in water emulsions at 4 °C. Relative values from TPA (F/F_0) and Physica MCR 301 (τ/τ_0) instrument measurements.

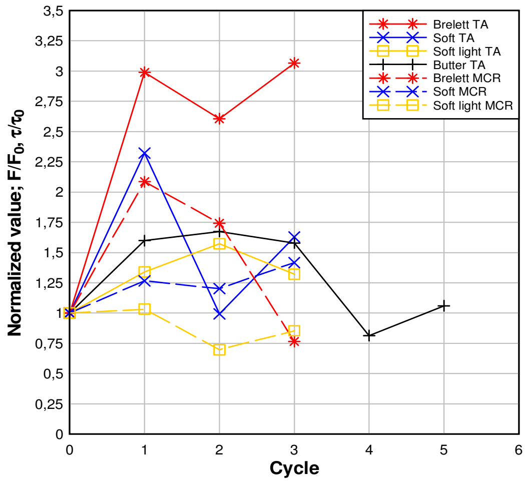

Figure 8. Time plot for TPA (——) and Physica MCR (----) from serie II of oil in water emulsions at 4 °C. Relative values from TPA (F/F_0) and Physica MCR 301 (τ/τ_0) instrument measurements.

In Fig. 7 and 8 the results from the two instruments are compared regarding rheological information when measuring the same product at the same time during a number of repeated time and temperature cycles. The relative values given by the oscillation rheometer are lower than the values from the penetrometer for all samples tested. However, the trends are the same regarding the two instruments used.

DISCUSSION

The TPA plot in Fig. 4 highlighting force (F) versus time at 4 °C for serie I and II, give more or less the same trends for the two series of spreads tested. Both margarine and butter seemed to be a bit firmer after repeated temperature/time cycles when simulating consumers handling of the products kept in the refrigerator at 4°C and served at 20°C. The full fat emulsions containing 80% fat were firmer than the low fat variants at all measurement points. Butter was much firmer than the corresponding margarine with exactly the same fat content. The results are consistent with other mechanical chracterisations of food materiels which have been based on texture analysis[17]

Fig. 6 also indicates more or less the same results as mentioned above between the two series tested, regarding elastic properties or shear stress variation at 5% reduction in G´. The Physica MCR shear stress measurements, both at 4°C and 20°C, showed distinct differences between the tested emulsions. In general the low fat spreads seemed to maintain the biggest differences in shear stress when measurements performed at 4°C and 20°C are compared.

Compared to margarine, butter has a limited plastic range at low temperature. At refrigerator temperature, butter essentially behaves brittle and it has poor palatability. At room temperature (18-22°C) it oils off and exhibits moisture exudation[4]. Shear stress measurements can therefore be useful for the industry as a process parameter for instance whether such emulsions will be difficult to pump or stir or in any way handle in the packaging line. This result is also in agreement with some of the restrictions mentioned regarding direct strain oscillation measurements at very small deflection angles and torques. The method is especially valuable for measurements on samples with low viscosity and a weak structure such as gels, emulsions, suspensions, colloids, surfactant solutions and foams[18]. Butter at 4 °C, seems to be too firm for this oscillation method.

In Fig. 7 and 8 the results of the two rheological measurement instruments are compared according to the main objective of this study. The comparisons are given as relative values measured at 4°C for serie I in Fig. 7 and for serie II in Fig. 8. The measurements with the two instruments show the same development for the emulsions studied, when repeating a number of time and temperature cycles.

Increased firmness between start- and end values for all of the products investigated was observed. From a theoretical point of view it was expected that the firmness, especially of butter, would increase considerably beyond the original level, due to temperature increase followed by subsequent cooling to original temperature[6]. One reason that this did not happen as anticipated, is probably related to the temperature increase to 20 °C used in this study. 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[19]. It means that it could be interesting to repeat the study with temperatures > 25°C, for instance at 28 °C.

CONCLUSION

This investigation compared the measurement results from two different rheological instruments characterizing butter and margarine when repeating a number of time and temperature cycles. Texture analysis and dynamic oscillatory rheology were used to measure the mechanical properties of the crystallized water-in-oil emulsions. The conclusions can be summarized as follows:

1. Both the TPA- and the Physica MCR rheological measurement instruments are feasible giving objective rheological information of fat spreads when repeating a number of time and temperature cycles. But regarding butter at 4°C it was not possible to detect the upper limit of the linear viscoelastic range since this exceeded the maximum allowable working torque of the electronically commutated synchronous motor of the instrument.
2. It was possible to compare the results from the two instruments using relative values and getting the same trends regarding description of the samples.
3. The measurements may be used by the industry for instance to:
   - 3.1 Contribute to aid more optimal formulation of spreadable water-in-oil emulsions. Spreadability of butter and margarine can be easily assessed by measurement of its complex viscosity at different temperatures.
   - 3.2 Shear stress measurements can be useful as a process parameter; for instance whether such emulsions will be difficult to pump, stir etc.
4. The firmness of both butter and margarine seemed to increase after repeated temperature/time cycles when simulating consumers handling of the products kept in the refrigerator at 4°C and served at 20°C.
5. The full fat emulsions containing 80% fat were firmer than the low fat variants at all measurement points. Butter seemed much firmer than the corresponding margarine with the same fat content.
6. Low fat spreads (40% fat) seemed to maintain the biggest differences in shear-stress values comparing measurements performed at 4°C and 20°C.

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