Rheological studies of butter and margarine exposed to repeated breaks in the cooling chain

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ABSTRACT
Rheological characteristics of food products, also regarding butter and margarine, may be utilized to optimize manufacturing processes, to achieve right quality of the products and to give information of fatty products during usage.

In this study a Physica UDS200 plate-plate rheometer was used to investigate rheological behavior of table spreads exposed to repeated breaks in the cooling chain. The instrument was utilized as a non-destructive measurement tool giving rheological information when repeating a number of time/temperature cycles.

INTRODUCTION
In fat or oil-continuous products, such as butter and margarine, the structure of the food is based on networks of crystalline particles. It is well known, both from research and from literature, that the nature of this crystal network can be dramatically altered by changes in crystallization conditions. In butter this crystallization is very complicated. Regarding its fatty acids and triglyceride composition, butterfat can be seen as one of the most complex fats in nature. The composition of butterfat is further complicated due to numerous isomers of monoenoic, dienoic and branched chain fatty acids. In addition there is seasonal variation and variations during the period of lactation.

Consumer acceptance of these products depends very 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. It is important that these table spreads retain their shape when they are removed from the refrigerator and for instance used at room temperature during serving. But they also have to spread easily at relatively low temperature when a knife is applied. It is usually necessary for these products to maintain their properties over a relatively wide range of temperatures.

Temperature has considerable effect on firmness. For butter, large differences occur in firmness at the same temperature, even when the butters have exactly the same chemical composition. After heating followed by subsequent cooling to initial temperature, crystallisation causes formation of solid networks, so that firmness will increase beyond the original level. From literature it is also well 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. But more pronounced melting is going on in the temperature regions between 0°C and 20°C.

From the literature it is also reported that as soon as one starts to work a fat its firmness decreases sharply. This is called...
work softening. On keeping, the fats set again, but not up to original firmness.

The crystallization of spreads is in general a complicated process which has to be explained with more than composition, temperature treatment and state of dispersion of the fat. The fact that lipids exhibit polymorphism is another phenomenon that contributes to the complexity of fat crystals and their rheological behaviour.

Rheological instruments are used to characterize these non-nutritional functions of butter and spreads, in order to measure and characterize their plastic behaviour. Thus they must have yield stresses below which they are elastic, and above which they are plastic.

The rheological properties of spreadable foods have been studied by a variety of methods. In two previous studies, 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.

The objectives of this work using a non-destructive measurement method were as follows:

To investigate if butter consisting of 80% milk fat gets firmer by repeated heating and cooling in a temperature range between 4°C to 20°C.

Compare the above with margarine consisting of 80% vegetable fats and oils.

Compare the mentioned objectives with spreads of the type of water in fat emulsions with 40% fat content.

Evaluate the robustness of rheological characteristics of butter and margarine when repeating a number of temperature/time cycles, thought to simulate the consumers handling of these products when bringing them in and out from the fridge a number of times for serving.

Investigate the feasibility of a rotational rheometer instrument equipped with a plate-plate system to study the texture characteristics mentioned above.

Using an objective non-destructive rheological measurement method to unveil texture differences between butter and margarine composed of a) fat from different sources (animal and vegetables) b) with different fat content (80% and 40%) c) influence of repeated heating and cooling in a temperature range between 4°C to 20°C.

MATERIALS AND METHODS

Butter and margarine samples

Butter and margarines were purchased from a local retailer according to table 1. Butter and spreads with a mixture of milk fat and vegetable oil were produced by TINE, an association of Norwegian dairies. Margarine based on vegetable fats and oils, mainly soy bean oil, were produced by Mills, Norway. The samples were stored at +4 °C until rheological measurements were carried out.

Three replicate measurements were carried out for each product examined. All three replicates were taken from inside the same package to avoid possible differences between productions.

Table 1. Name of spread, fat source and fat content in butter and margarine used in this study.

<table>
<thead>
<tr>
<th>Spread Type</th>
<th>Fat source</th>
<th>Fat content (%)</th>
</tr>
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<tbody>
<tr>
<td>Butter</td>
<td>milkfat</td>
<td>81</td>
</tr>
<tr>
<td>Brelett</td>
<td>milk/rape/palm</td>
<td>40</td>
</tr>
<tr>
<td>Soft Flora</td>
<td>veg. fats &amp; oils</td>
<td>80</td>
</tr>
<tr>
<td>Soft Light</td>
<td>veg. fats &amp; oils</td>
<td>40</td>
</tr>
</tbody>
</table>

Instrumental analysis

The Physica UDS200 rheometer (Paar Physica, Anton Paar, Germany, 2003) fitted with a MP31 top plate and a Peltier bottom plate was used. The Peltier temperature was set to +4 °C. The butter and margarine samples were placed on the Peltier plate and gently formed to cover the plate. The MP31 was then lowered very slowly squeezing the
samples gently to obtain the desired plate – plate clearance of 1 mm. The excess spread was then gently removed from the rim of the MP31.

Experimental set-up
The instrument was programmed to perform 19 repeated temperature scans at constant 1 % strain (γ) with frequency (ω)=10 s⁻¹ in the temperature range from 4 °C to 20 °C and back again.

Every scan or cycle took place in 210 minutes (3.5 hours). During this period of 210 minutes each sample was kept 120 minutes at 4°C. Then the temperature increased to 20°C within 15 minutes. After 30 minutes at 20°C the temperature decreased back to 4°C within 15 minutes. Then the temperature was kept 30 minutes at 4°C in front of next cycle. This cycle which was repeated 19 times, simulates the situation which spreads undergo during everyday use by the consumer keeping the butter or spreads in a refrigerator between servings.

Figure 1. Graphic illustration of one of 19 repeated programmed temperature/time cycles simulating the consumers handling of the products kept in the refrigerator and served at room temperature several times (temperature range 4°C – 20°C).

Figure 2. Spread sample in the Physica UDS200 rheometer fitted with a MP31 top plate and a Peltier bottom plate.

Statistical treatment
One-way ANOVA (Minitab 15 and Fisher 95% individual confidence intervals, pair-wise comparisons) was used to determine if statistically significant differences were observed.

RESULTS
Results of the elastic properties of the butter and of the spread products containing fat of different origin and at different levels, are shown in Fig. 3, 4, 5 and 6. Fig. 3 and 4 are plots of average storage modulus G’ (elastic properties) variation at respectively 4°C and 20°C (n=3) for the tested spreads. The results represent average measurements of each of the 19 repeated temperature/time cycles of 210 minutes each at constant 1 % strain. Differences in storage modulus G’ between the 4 spreads, are clearly illustrated using this non-destructive measurement method both in Fig. 3 and 4.

No significant differences between the values from the first and from the 19th temperature/time cycle were observed for any of the products using the non-destructive plate-plate Physica UDS200 rheometer.
Figure 3. Average storage modulus $G'$ (elastic properties) variation at 4 °C (n=3) for the tested spreads. 19 repeated temperature cycles of 210 minutes each at constant 1 % strain using a non-destructive oscillatory plate-plate rheometer.

Figure 4. Average storage modulus $G'$ (elastic properties) variation at 20 °C (n=3) for the tested spreads. 19 repeated temperature cycles of 210 minutes each at constant 1 % strain using a non-destructive oscillatory plate-plate rheometer.

Figure 5. Average initial and final (n=3) storage modulus for each spread at 4 °C and 20 °C; 19 repeated temperature cycles of 210 minutes each at constant 1 % strain.

Fig. 5 is a plot of average initial and average final (n=3) storage modulus in each of the tested spreads at 4 °C and 20 °C. The results represent measurement of 19 repeated temperature cycles of 180 minutes each at constant 1 % strain.

Figure 6. Variation of storage modulus $G'$ in 4 spreads within one part (180 minutes) of one temperature/time cycle of 210 minutes at constant 1 % strain using a non-destructive oscillatory plate-plate rheometer (number 1 of 19 repeated cycles).
Fig. 6 shows clear changes in the values of the storage modulus $G'$ when the temperature increase and decrease between 4°C and 20°C, during the first 180 minutes of one temperature/time cycle of 210 minutes. But as in Fig. 3 and 4, figure 6 also indicates no change in $G'$ between start- and end values for any of the tested table spreads.

DISCUSSION
Referring to Fig. 3 and 5 this measurement study prove that butter (80% fat from cows milk) at 4°C had the highest level of average storage modulus of the 4 tested products. This result was expected.

Fig. 5 also indicates that margarine consisting of 80% vegetable oils and fats was softer than butter at 4°C. This is also in accordance with the fact that milk fat is composed by an average amount of 69% saturated-, 27% mono unsaturated- and 2.5% polyunsaturated fatty acids. This is in contrast to the fatty acid composition in soybean oil which is reported to be composed of an average of 14% saturated-, 50% monounsaturated- and 35% polyunsaturated fatty acids.

Fig. 5 also shows that both the 40% fat spreads had the lowest average storage modulus at 4°C. This phenomenon is due to the fact that the amount of fat is decreased from 80% to 40%, while the amount of dispersed phase (water) is increased. But since these products also contain emulsifying agents like mono-, diglycerids and phospholipids there may be difficult to do a direct comparison of their rheological behaviour concerning original composition.

Regarding Fig. 4 and 5 and average storage modulus at 20°C, the results seem a bit surprising since both the milk fat based spreads with 80% and 40% fat content have lower level of storage modulus compared to respective margarines. But according to the melting behaviour of milk fat which takes place at lower temperature than the vegetable fat in the margarines, the results in Fig. 5 may be reasonable.

Fig. 3 and 4 show the average storage modulus variation through 19 repeated temperature cycles (n=3) at 4°C and 20°C respectively. As already mentioned there were no significant differences between start and end values for any of the products investigated. From a theoretical point of view it was expected that firmness of butter would increase beyond original level, due to temperature increase followed by subsequent cooling to original temperature.

Reasons why this phenomenon did not appear in this study may be:

1. Increasing the temperature of butter to 20°C and a holding time of 30 minutes, may be insufficient to affect fat crystallization which is crucial for structure and texture of butters. Mulder and Walstra pinpointed that if fat crystals melt, many of the globules disappear and aqueous droplets coalesce because they are no longer held apart. Then after cooling to initial temperature, the structure of the products are different from the original. In this study the fat phase was not melted.

2. The non destructive instrumentation set up was not optimal for measuring and describing foods that exhibit plastic behaviour.

We assume that point 1 above is the most reliable explanation for the results presented in this paper. Looking at Fig. 6 it clearly demonstrates how the measurement equipment registers changes in $G'$ during one cycle, caused by raising, holding and lowering the temperature according to Fig. 1. Fig. 6 even indicates that the storage modulus $G'$ increased during the holding phase at 20°C for 30 minutes. This
phenomenon demonstrates effects of so-called setting. Temperature is an important factor in setting. It is also known that higher temperatures in the range from 0°C–16°C favour setting in butter. The results also indicate the feasibility using a non-destructive rheological measurement method, to unveil texture differences between different table spreads investigated in this study.

CONCLUSIONS

Investigation on thermal behaviour of emulsions like that in table spreads is essential to understand changes occurred when the system is subjected to a temperature cycle during handling, storage as well as utilization. The conclusions from this non-destructive measurement study can be summarized as follows:

- Butter at 4°C had the highest level of average storage modulus of the 4 tested table spreads.
- Margarine consisting of 80% vegetable oils and fats was softer than butter at 4°C. But at 20°C the same margarine achieves the highest levels of storage modulus of the tested table spreads.
- 40% fat spreads had the lowest average storage modulus at 4°C.
- There were no significant differences at a level of 5% significance, between start and end values for the first and the 19th cycle of repeated heating and cooling for any of the examined products in the temperature range 4°C to 20°C.
- This study indicates that the non-destructive off-line Oscillatory Plate-Plate Rheometer may be feasible as an objective rheological measurement method to unveil texture differences between butter and margarine composed of a) fat from different sources (animal and vegetable) and b) with different fat content (80% and 40%) c) influence of repeated heating and cooling in a temperature range between 4°C to 20°C.

REFERENCES


