Influence of freeze storage on rheological properties in Quark

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ABSTRACT

Quark is a traditional fresh acid coagulated cheese produced from milk and/or cream by biological acidification to around pH 4.6. This pH causes the casein proteins to coagulate at their isoelectric point pH 4.6. The coagulum may or may not be cooked during manufacturing. The curd is not pressed. Acid coagulated cheeses are characterized by a high moisture content. They are usually consumed soon after manufacture as Quark belong to the so-called fresh dairy products.

In this introductory study, several rheological methods were used to investigate and characterize the texture of fresh and freeze stored Quark samples. A Physica MCR301 rheometer was used both in rotation and oscillation mode with a PP50 measuring cell, to characterize fresh- and freeze stored Quark. Conventional amplitude sweeps were used to determine stiffness, strength and strain limit. Viscosity was measured in rotation at different shear rates, hence also determining the linear viscoelastic range.

The results show how freezing may influence the rheological behavior of Quark. Both the strength, the strain limit and the stiffness (G’) of the Quark samples seem to increase a bit after freezing. From a commercial point of view these findings are positive, since they indicate that sensory properties did not deteriorates during freezing.

INTRODUCTION

Fermented milk products are popular in many parts of the world. They are produced by fermentation of milk by adding starter cultures of Lactic acid bacteria. The fermentation of lactose to lactic acid results in a pH drop, which causes coagulation of milk proteins to a gel[1]. Acid-curd cheeses were probably the first cheeses produced. Such products may result from natural souring of milk. This is caused by the natural lactic acid bacterial flora from the udder and the environment. Acidification is usually achieved by the action of an added mesophilic starter culture. But direct acidification is also practiced. A small amount of rennet may be used in certain varieties, but this additive is not essential. Rennet serves to increase the firmness of the coagulum and to minimize casein losses in the whey fraction[2].

Quark may be manufactured in many ways; by batch methods, separator processes, thermo processes, filtration, recombination technology etc. The majority are produced by acid (and/or rennet) coagulation, separation of the curd from the skim milk or whey, various heating and homogenising steps. Fresh cheese preparations are often added with different ingredients[3].

Various cuisines feature quark as an ingredient for appetizers, salads, main dishes, side dishes and desserts. In Germany, quark is sold in cubic plastic tubs. Usually it comes in three different varieties, *Magerquark* (skimmed quark, <10% fat by dry mass.), "regular" quark (20% fat in dry mass) and *Sahnequark* (40% fat in dry mass) with added cream. Similar gradations in fat content are also common in Eastern Europe[4].

While *Magerquark* often is used for baking (Fig. 1) or is eaten for breakfast with a side of fruit muesli, *Sahnequark* also forms the basis of many quark desserts. Much like yoghurt in some parts of the world, these foods mostly come with fruit flavoring (fruit quark), sometimes with vanilla and are often also simply referred to as quark.

Figure 1. Käsekuchen - a famous German cheesecake based on quark as an essential ingredient (*Photo Wordpress.com)*

As quark is an essential ingredient in many dishes, it is of great interest to maintain a steady supply of this product throughout the seasons. Quark as a fresh cheese, should be stored at 0-4 °C. Initially, this product has a longer shelf life than the expiry date on the packaging. But the manufacturers do not guarantee the shelf life beyond this. Regarding composition, see Table 1.

Table 1. Approximate composition pr. 100 g of fresh natural Quark produced in Norway. Values declared by the manufacturer.

Content	Amount	Unit
Energy	325	kJ
Protein	11	g
Sugar	4	g
Fat total	1.9	g
Saturated fat	1.3	g

Sensory quality (odour, taste, appearance) deteriorates after expiry. The changes may be related to more sour taste, whey syneresis and changes in texture. Freezing of quark is therefore interesting to extend the shelf life of this product. The dairy industry has made a tremendous success of the frozen dessert category. But freezing has been used to much smaller extent for other dairy products. From the literature it is reported that Quark can be frozen for up to 6 months. To optimize texture, it should be thawed slowly in the refrigerator. After thawing it can be used in e.g. pastries or waffle batter.

The main objective with this introductory study was to:

- investigate eventually structural effects of long time freezing on Quark, both as a product by itself and/or as an ingredient in other dishes.
- observe if some acidic additives during the diafiltration process applied in the production, would affect the rheological measurements of Quark samples before- and after freezing.

MATERIALS AND METHODS

Quark manufacture

Skimmed milk was pasteurized (A3-HRB, Alfa Laval, Lund, Sweden) at 73 °C/15s, microfiltered (MF) and diafiltered with different water media (UF/MF pilot MCC RV 01118340, APV, Silkeborg, Denmark) using a 0.14 µm ceramic membrane (INSIDE CéRAM™, TAMI Industries, GEA, Nyons, France) at 50 °C ± 0.1 and uniform trans-membrane pressure (UTMP) to produce 8% ±0.1 casein concentrates (CC), following the process described by Gaber et al. [5].

The casein concentrates were pasteurized at 73 °C for 15 s, cooled down to 30°C and transferred into cheese vats. Starter culture Probat 505 (Probat 505 FRO 500 DCU, CHOOZIT™ Cheese Cultures, Danisco) at 2% was inoculated to single cheese vat. Incubation conditions: 18hr at 25-30 °C.

After reaching a pH of 4.7, the curd was cut and separated using hanging cloth. It was left for draining at 4-5 °C for 4 hrs. The drained curd was further mixed using a colloid mill and packaged into several small containers about 250 g. Some samples were stored as fresh at 4-5 °C. Other were stored at -20 °C until analysis after six months. The frozen samples were thawed slowly in a refrigerator at +4 ºC before analysis.

The Quark samples are denoted following the used media for diafiltration: citric acid (CDR), lactic acid (LDR), carbonation (ODR) and just water as the reference (RDR)

Different types of milk, denoted A or B, were used in this study. Milk type A is from the normal lactation period, while type B is very early lactation milk. The RDR variant is only made from milk type A.

Instrumental analysis and experimental set-up

The Physica MCR301 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany, 2010) was used in oscillation to characterize fresh quark and quark after 6 months of freezing.

A PP50 plate/plate system was used with a Peltier for temperature control. Amplitude sweep tests were performed at an increasing strain from 0.001 to 0.1 at a constant frequency of 1 Hz and temperature of 5 °C to determine the stiffness of the gel and the linear viscoelastic range.

Samples were stirred prior of placing them on the plate using a plastic spoon. Fresh samples stored at 4-5 °C were measured within 7 days after manufacturing. Frozen samples were thawed at +4ºC during 40 hours prior to measurement. For each experimental quark batch duplicates were tested, and an average value was calculated[6].

Data analysis

The data were analysed in RheoPlus and exported to Excel for plotting. The analysis determined the limit of the linear viscoelastic range by running a macro that determined the point where the value of the stiffness, G', was reduced by 3%. The value of the strain and the stress at this point were denoted the strain limit and the strength. The reported value of stiffness, is the value of G' at the start of the amplitude sweep[7].

RESULTS

As mentioned in the introduction Quark is a typical acid-curd cheese. In this case acidification was achieved by the action of an added mesophilic starter culture. In addition, the different agents CDR, LDR, ODR and RDR were used during diafiltation. Table 2 summarizes the start- and end pH after fermentation of the curd.

Table 2. Start- and end pH after fermentation of the microfiltrated casein concentrates diafiltrated with different additives (CDR, LDR, ODR and RDR).

pH	Start	End
Citric acid, CDR	6.58	4.6
Lactic acid, LDR	6.55	4.6
CO2, ODR	6.61	4.6
Ref. water, RDR	6.66	4.8

The results from the rheological analysis are shown in Figure Figure , Figure and 4. The samples are named according to the treatment during processing and according to type of milk (A and B).

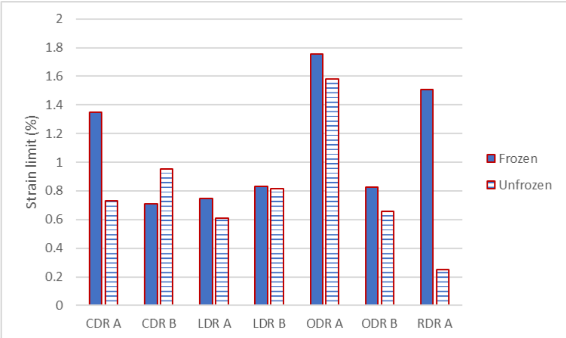

Figure 2. Strain limit results of unfrozen and frozen Quark made from casein concentrates produced by diafiltration. Media used for

diafiltrating; RDR - water as the reference; (CDR) citric acid; (ODR) CO_2; (LDR) lactic acid. Samples made from normal milk are denoted A including the RDR sample. Milk from very early lactation is denoted B. The six months frozen Quark samples at -20 °C were thawed slowly at +4 °C before measurement.

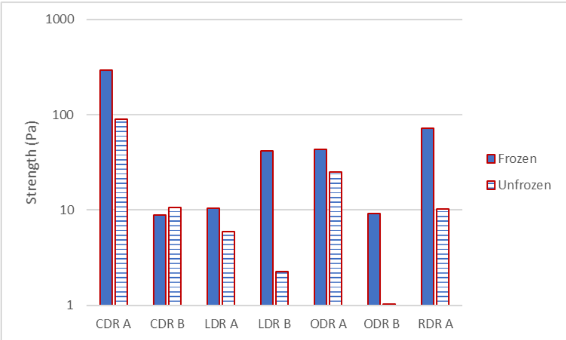

Figure 3. Strength results of unfrozen and frozen Quark made from casein concentrates produced by diafiltration. Media used for diafiltrating; RDR - water as the reference; (CDR) citric acid; (ODR) CO_2; (LDR) lactic acid. Samples made from normal milk are denoted A including the RDR sample. Milk from very early lactation is denoted B. The six months frozen Quark samples at -20 °C were thawed slowly at +4 °C before measurement.

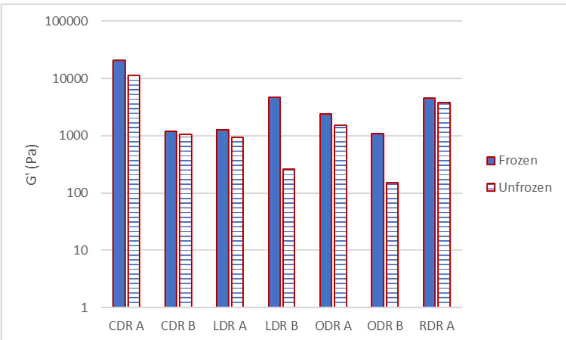

Figure 4. Stiffness results of unfrozen and frozen Quark made from casein concentrates produced by diafiltration. Media used for diafiltrating; RDR - water as the reference; (CDR) citric acid; (ODR) CO_2; (LDR) lactic acid. Samples made from normal milk are denoted A including the RDR sample. Milk from very early lactation is denoted B. The six months frozen Quark samples at -20 °C were thawed slowly at +4 °C before measurement.

DISCUSSION

A previous study investigated the effect of freezing temperatures (-20, -40, -80 °C) on micro filtrated milk casein concentrates (CC) during 15 days of storage. The study focused on different changes in this concentrate focusing later use as raw material for various productions[6]. The study demonstrated that CC with 8% protein were destabilized during the period of frozen storage, especially in the initial phase of freezing.

Regarding rheological behaviour the storage modulus G' of acid gels made from freeze-thawed CC-samples, had higher values compared with unfrozen CC-samples. Another factor connected to rheological behaviour, was the observed formation of larger aggregates in the freeze-thawed CC-samples.

In this study the fresh casein concentrate was used as raw material for Quark production. The motive for this investigation was to look at eventually rheological effects after freezing Quark for 6 months, both as a product by itself and/or as an ingredient in other dishes.

Looking at Fig. 4 it seems that these G' results (stiffness) confirm the previous study mentioned above, although the differences before- and after freezing are very small in this case for some of the samples (CDR *B*, LDR *A* and RDR). From a commercial point of view these findings are positive. It means that frozen Quark is OK both for the consumer market, and for further processing in the industry.

Fig. 3 summarizes the strength of the Quark products before- and after freezing. A general trend seems to be that the strength of the products has increased after freezing. One exception is Quark produced from milk very early in the lactation period (CDR *B*). The measurement for this variant shows about the same strength value before- and after freezing.

When it comes to the strain limit in Fig. 2, most of the samples observed had an increase after freezing. Also, here the Quark sample produced from milk very early in the lactation period added citric acid (CDR *B*) was an exception. The strain limit was higher before-, than after freezing.

At the other end of the measurement results, the strain limit of the reference (RDR) became much higher after freezing compared to fresh Quark. From a commercial point of view these results are positive. Freeze storage seems to maintain or increase the strain limit for Quark. An opposite behaviour during freeze storage will in many cases be negative in terms of commercial use of those frozen products.

It is known from the literature that freezing of cheese usually remains the flavour unless lipid oxidation occurs. Freezing of Mozzarella was suggested to damage the micro- and protein structure of the product, especially during slow freezing. This phenomenon seemed to cause an alteration in the stretch- and melting properties of the Mozzarella after thawing[8].

In this study it was also of interest to observe if some acidic additives during the diafiltration process would affect the structure of Quark before- and after freezing. The rheological measurements did not provide clear answers to this, although both the values for strength and strain limit appeared to increase after freezing. Detection of correlations between texture properties and the microstructure of the acid gel produced with various additives, seems to be a complicated issue. From the literature it is also known that such investigations are challenging and requires further research[9].

According to Table 2, the pH after fermentation of the microfiltrated casein concentrates diafiltrated with different additives (CDR, LDR, ODR and RDR), are almost the same in all samples. They are at the isoelectric point for casein which is pH 4.6. It is just water as an additive during diafiltrating that contribute slightly higher pH; pH 4.8. Possibly the 0.2 pH unit difference after fermentation of the casein concentrate, may explain some of the differences in the rheological measurements results for the RDR-sample before and after freezing.

Some acidic additive may contribute to stability of product characteristics during long frozen storage, as compared to the reference which was prepared without any acidic modification to the starting material. But in order to determine this, further repetitions/research are needed.

CONCLUSIONS

This screening study of six months frozen Quark samples at -20 °C thawed slowly at +4 °C indicates the following:

- Both the strength, the strain limit and the stiffness (G') of the Quark samples seemed to have increased a bit after freezing.
- From a commercial point of view these findings are positive regarding sensory properties which did not deteriorates, but rather achieved some improvements.
- The above-mentioned trends seemed to be the same for Quark made from both milk from normal lactation period and for milk from very early lactation. The reference sample showed more or less the same development before- and after freezing

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