Rheological and Microstructural Characterization of Some Norwegian Milk Products

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ABSTRACT

Milk is a natural oil-in-water emulsion. Several changes can occur due to physical, chemical, biochemical or microbial changes. At the dairy, milk is always processed. Of course, this processing creates changes that can be discreet or drastic. In this study rheological changes in milk were investigated due to processing caused by heat treatment, separation and homogenization. A rheometer was used to measure the viscosity of the milk products. In addition the droplet size and the droplet size distribution in the emulsions were characterized by use of a Mastersizer.

INTRODUCTION

Milk is defined as a secret of the mammary glands of mammals. A classification of the principal constituents of cow milk is given in Table 1.

Freshly drawn milk varies in composition, structure and properties. *Cooling* of the milk at the farm to about 2-4°C, directly after milking, inhibit especially growth of microorganisms and enzyme actions. The milk should be kept cold during storing and transport to the dairy. The most common processes applied at the dairy of interest for this study are briefly described in the following;

Heat treatment is always applied, primary to kill harmful microorganisms. It also causes numerous chemical and other changes depending on temperature and duration of heating. Low pasteurization (e.g. 72°C for 15 s) is a fairly mild treatment that kills most microorganisms and inactivates some enzymes. But it does not cause too many other changes. Ultrahigh temperature heating (UHT e.g., at 145°C for 2-4 seconds) is meant to sterilize milk while minimizing chemical and sensorial changes.

Table 1. Approximate composition of cow milk[1]

Constituent	Average (%ww)	Range (%ww)
Water	87.1	85.3-88.7
Solids not fat	8.9	7.9-10.0
Fat in dry mat	31	22-38
Lactose	4.8	3.8 -5.3
Fat	3.9	2.5-5.5
Protein	3.3	2.3-4.4
Minerals	0.7	0.6-0.8
Organic acids	0.17	0.12-0.21
Miscellaneous	0.15	-

The UHT process may be either based on direct systems or indirect systems. In the direct systems which are most common for milk processing, the product comes in direct contact with the heating medium. The direct systems are divided into 1) steam injection or 2) steam infusion. The systems differ from each other in the way of bringing the milk and steam together [2].

Separation, usually by means of a flow-through centrifuge called a cream separator, yields skimmed milk and cream. The skimmed milk has a very low fat content; usually below 0.1%. Unless stated otherwise, the term skimmed milk refers to centrifugally separated milk. By mixing skimmed milk and cream, milk may be standardized to desired fat content.

Homogenization of milk leads to a considerable reduction in the fat globule size which of course influence on the rheological properties of the milk. Such milk creams very slowly, but it is also altered in other aspects. The disruption of milk fat globules into smaller ones, leads to a considerably enlarging of the milk fat-plasma interface. The new interface is covered with milk protein, predominantly micellar casein.

Other effects of homogenization are;

1. The colour becomes whiter.
2. The tendency to foam increases.
3. Reduced fat autoxidation and formation of off-flavours.
4. Fat globules lose their ability to agglutinate upon cooling.

Regarding homogenization, different equipment exists depending on the pressure utilized. Pressure between 15-20 MPa is normally used in commercial milk treatment in combination with pasteurization at 72°C for 15 s. This treatment results in a dramatically reduction of the fat globule size mainly due to shear stress and cavitation[2].

Homogenization is applied to improve stability of the fat phase in milk during storage. The smaller milk fat globule formed during homogenization, dramatically decreases the cream separation rate caused by the density difference between milk fat and the aqueous phase (Stoke`s law). To some extent, it also prevents coalescence. Homogenization results in an emulsion more stable than milk directly from the udder. This phenomenon contributes also to increased shelf-life of the product, mainly caused by adsorbed milk proteins (basically casein micelles) at the interface of the smaller fat globules formed[3].

From the literature, the native milk fat globule size variation has been reported to span from < 1 to about 20µm. Average size is initially around 3-5 µm. Upon homogenization the average size is reduced to around 1 µm, resulting in a 4 to 10 fold increase of the interface between the fat droplets and the aqueous medium[4,5,6,].

The particle size of the fat droplets present in milk and other food emulsions is important in defining properties such as flavor release, mouth feel and the emulsion stability. Large emulsion droplets normally lead to poor flavor release, a greasy mouth feel and poor stability due to creaming. Emulsification to smaller droplet size tends to reduce creaming and improve the taste of a product.

The objectives with this study were as follows:

- Characterize different milk products regarding rheological behavior and droplet size measurements after traditionally processing in the dairy; heating, separation and homogenization.
- Investigate the feasibility of a rotational rheometer instrument equipped with a Bob Cup system to study texture characteristics in food emulsions with different fat content.
- Investigate the feasibility of using a laser diffraction particle size measurement instrument to characterize and distinguish between fine emulsion droplets and larger flocculated or coalesced droplets in different milk products.

MATERIALS AND METHODS

Milk and cream

Traditionally skimmed milk, low fat milk, H-milk, UHT milk, UHT Coffee Cream and Cream were purchased from a local retailer in carton containers produced by Tine BA Dairies, Norway according to Table 2. Freshly drawn milk (milk directly from the udder) – raw milk - was collected from the livestock at the University of Life Sciences, Aas, Norway. The milk was collected manually directly from farm tank at 4°C.

Table 2. Approximate composition (%ww) of the different milk products tested.

Product	Fat	Prot.	Lact.	Dry matter
Raw milk	4.9	3.5	4.7	14.1
Sk. Milk	0.1	3.4	4.7	8.9
Extra Light	0.5	3.4	4.8	9.4
Light	1.2	3.4	4.6	10.0
H-milk	3.9	3.3	4.3	12.6
Cream	38	2.1	2.9	43.1
UHT Light	1.2	3.3	4.7	10.0
UHT Coffee Cream	10	3.0	4.3	17.5

Figure 1. Milk sample measured by rotational viscometry using a Physica MCR 301 rheometer with a bob/cup measuring geometry.

<u>Instrumental analysis and experimental set-up</u>

The Physica MCR301 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany, 2010) fitted with a Titanium CC27 cup and a ST24-2D/2V/2V-30/129 stirrer was used for viscosity measurements. The stirrer was positioned with < 0.5 mm clearance from the bottom of the cup. The viscosity of the emulsions was measured by rotational viscometry.

Rotational shear rate sweeps from 0 1/s to 500 1/s were recorded at +4 °C. Temperature-sweeps from +4 °C to +20 °C were recorded at a shear rate of 100 1/s.

The Malvern Mastersizer 3000 (S.nr. MAL1083189, Malvern, UK, 2013) fitted with a Hydro LV dispersion unit, was used regarding measuring particle sizes in the different milk products investigated. The sample was dispersed in Millipore distilled water during measurement with the laser diffraction particle size measurement instrument.

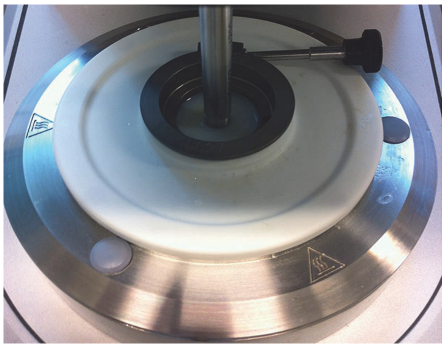

Figure 2. Milk sample in the Bob Cup System – A Titanium CC27 cup and a ST24-2D/2V/2V-30/129 stirrer.

<u>Statistical analysis</u>

All rheological measurements were carried out as a screening to investigate connections between viscosity levels and particle distributions in the samples tested.

Figure 3. Milk sample in the Malvern Mastersizer 3000 using the Hydro LV dispersion unit.

RESULTS

Typical results of the viscosity determination with the Paar Physica rheometer for the milk- and cream samples are shown in Fig. 4, 5 and 6. All figures are focusing on viscosity as a function of shear rate.

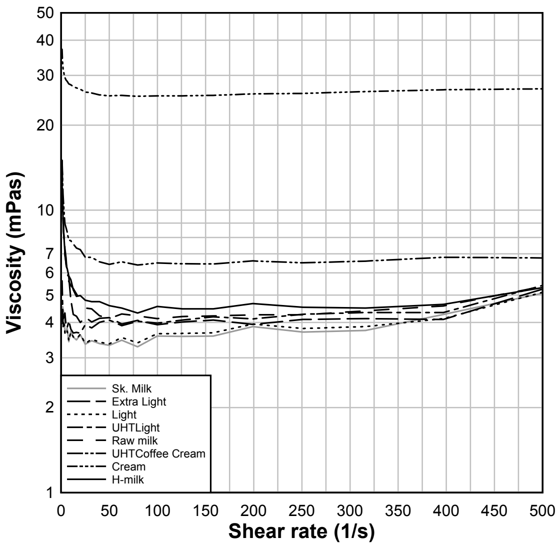

Figure 4. Flow curves at 4 °C - Rotational shear rate sweeps from 0 1/s to 500 1/s.

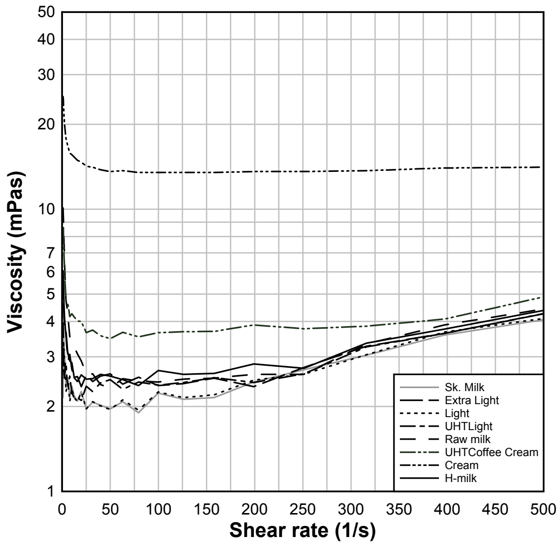

Figure 5. Flow curves at 20 °C - Rotational shear rate sweeps from 0 1/s to 500 1/s.

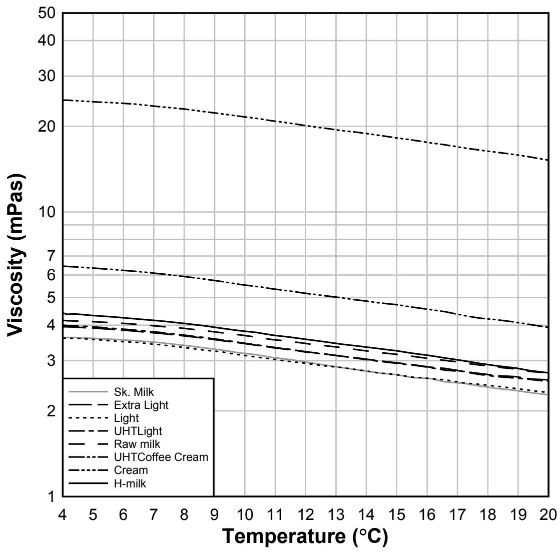

Figure 6. Temperature plots - Temperature-sweeps from +4 °C to +20 °C at a shear rate of 100 1/s. A relatively small decrease in viscosity is observed for all the samples when increasing temperature from +4 °C to +20 °C.

Fig. 7 and 8 and table 3 characterize the droplet size distribution in the different milk and cream samples. The results are all obtained from the Malvern Mastersizer 3000 measurements by adding some droplets of the tested sample into a known volume of distilled air free water.

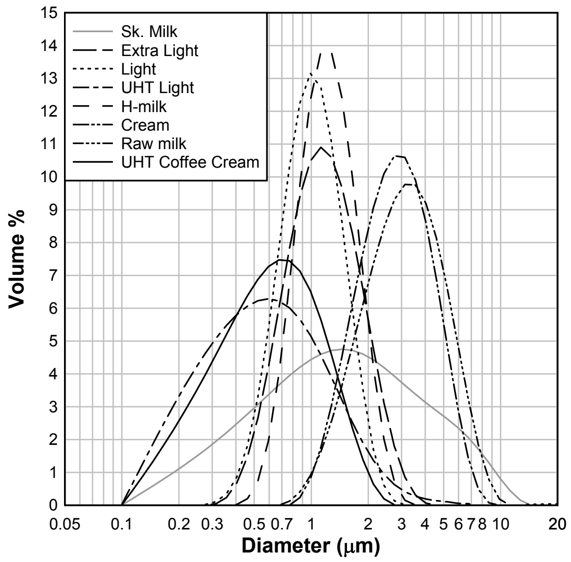

Figure 7. Size distribution of particles in the different milk samples measured by the Malvern Mastersizer 3000.

Regarding the Dx values expressed in Fig. 8; Dv 10 – the size of particle below which 10% of the sample lies. Dv 50 – the size in microns at which 50% of the sample is smaller and 50% is larger. This value is also known as the Mass Median Diameter (MMD), or the median of the volume distribution. Dv 90 – the size of particle below which 90% of the sample lies.

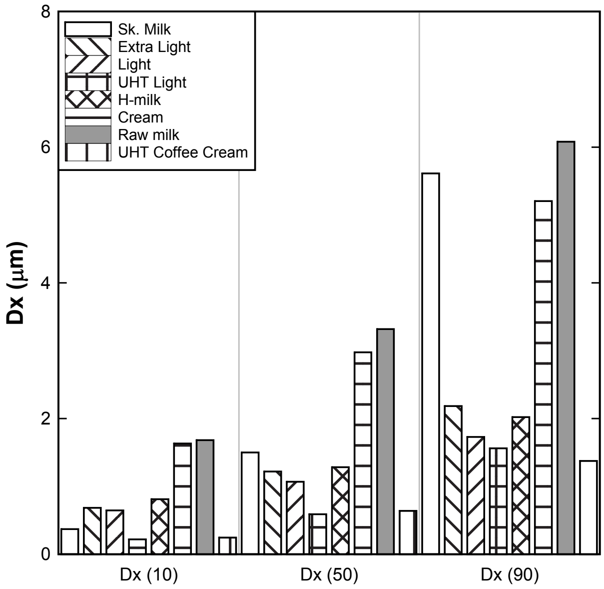

Figure 8. Groups of particle sizes expressed in the different milk samples measured, expressed as Dx values (μm).

Table 3. Dx (μm) variation in the different tested milk and cream samples

	Sk. Milk	Extra Light	Light	UHT Light	H-milk	Cream	Raw milk	UHT Coffee Cream
Dx (10) (micrometer)	0.37	0.69	0.65	0.22	0.81	1.63	1.68	0.25
Dx (50) (micrometer)	1.50	1.22	1.07	0.59	1.28	2.98	3.32	0.64
Dx (90) (micrometer)	5.61	2.18	1.73	1.56	2.02	5.21	6.08	1.38

DISCUSSION

In emulsions like milk and cream, several types of instability can occur; like creaming, flocculation, coalescence, aggregation and disruption. These processes often take place simultaneously. To prevent the phases from separating, milk is usually homogenized[6].

As mentioned, homogenization of milk causes disruption of milk fat globules into smaller ones. The milk fat-plasma interface is thereby considerably enlarged, usually by a factor of 4 to 10. The new interface is then covered with milk protein, predominantly micellar casein[1]. This treatment creates stable milk during storage whether homogenization is performed for milk treated with low pasteurization (72°C in 15 seconds) or Ultra High Temperature Treatment (UHT - 145°C for 2-4 seconds). Traditional dairy homogenization normally takes place at a pressure of about 18 MPa.

Looking at the flow curves given in fig. 4 and 5, the results indicate that the viscosity for all samples are a bit lower at 20°C compared to the measurements at different shear rates at 4°C. This is also expected because;

1. Increasing temperature will normally contribute to solve the different components better in a solution[5]. This normally indicates reduced viscosity provided that none of the components undergo chemical and/or physical changes during "heating"; like for instance coagulation of proteins etc.
2. Increasing temperature from 4 to 20°C, will melt some of the triglycerides in the milk fat. This will reduce the viscosity of the samples; especially for the samples with highest fat content like the UHT Coffee Cream (10% Fat) and Cream (38% Fat).

Regarding processing like heating and homogenization, fig. 4, 5 and 7 give no clear indications that these treatments influence on the viscosities of the different samples. The main factor influencing the viscosity seems to be the content of dry matter in the different samples.

Fig. 7 and 8 including table 3 give information about the size and the size distribution of the different particles in the measured milk samples. As shown in fig. 7 the samples seem to be divided into 4 groups;

1. Raw milk and Cream have the same distribution of particles (0.7- 10 µm). This is also as expected since these samples are not homogenized.
2. Extra light-, Light- and H-milk have also more or less the same distribution of the particles (0.3-4 µm). These samples are also treated the same way regarding pasteurization (72°C in 15 seconds) and homogenisation
3. UHT Light milk and UHT Coffee Cream form another group – having particles in the range 0.1-6 µm. These products have also undergone the same treatment regarding homogenization and heating (145 °C for 2-4 seconds)
4. Skimmed milk pasteurized at 72 °C for 15 seconds without homogenization, seems to be different from the other samples since the particles cover the whole range of particle diameters from about 0.1 - 15 µm. There is almost no fat in the sample which indicates that the present milk proteins may have aggregated. The small particles in the area around 0.1-0.7 µm, may be the smallest fat globules in milk beyond the critical diameter of globules that are recovered by separation or centrifugation. In addition, some non-globular fat is also present in milk; about 0.025% according to Walstra et al.[1].

CONCLUSIONS

Using a rheometer to characterize different "sweet" milk products, the conclusions from this study can be summarized as follows:

- The results indicate that the main factor influencing the viscosity of the characterized milk products seems to be the content of dry matter in the different samples which are in the range from 9-43%.
- Increasing temperature from 4 to 20°C, reduced the viscosity of the samples; especially for the samples with highest fat content like the UHT Coffee Cream (10% Fat) and Cream (38% Fat).

- A dramatic influence of the droplet size on viscosity was not observed in these non-acidified milk drinks.
  This finding was a bit unexpected. However, this phenomenon may be an important factor regarding the taste of the different milk products.

Based on the laser diffraction particle size measurements, the conclusions can be summarized like:

- Mastersizer measurements are feasible to characterize and distinguish between fine emulsion droplets and larger aggregated or coalesced droplets in different milk products.
- The Mastersizer managed to group the different milk samples according to droplet size and droplet size distribution.
- The Mastersizer also calculated the amount of particles according to the diameter (µm) of the particles. This knowledge may be of great importance regarding production of different food emulsions; either during product development or as a regular product control.
- The results also confirm the theory regarding homogenization of H-milk, which pin-point that the fat particles average size is reduced to around 1 µm, resulting in a 4 to 10 fold increase of the interface between the fat droplets and the aqueous medium.

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