STUDY OF THE IMPACT OF THE PREPARATION OF CREAM FOR CHURNING USING VACUUM ATOMIZATION ON THE STRUCTURE OF BUTTER

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Received April 30, 2015; Accepted in revised form June 11, 2015; Published October 20, 2015

Abstract: In the process of the production of butter, glycerides of butterfat crystallize with the formation of different space lattices. Depending on the conditions of cooling, crystals of various sizes and configurations with different physical properties are formed, which determines the crystalline structure of solidified fat, its physical and chemical properties, and therefore, the consistency of the finished product. The paper explores the impact of the flow two-stage method for physical aging of cream on the pattern of the crystallization of glycerides of butterfat. Comparative X-ray crystallographic and differential-scanning studies of butter, produced using the method of churning, were carried out. The method of differential scanning calorimetry was used to study thermal effects of the test sample of butter (received by churning cream which was aged using the flow method) and the control sample (received by churning cream which was aged using the conventional method). When analyzing data, no exothermic peaks, corresponding to processes that release heat, were observed. The polymorphism and the type of crystalline lattice of glycerides in the butter samples were analyzed using the method of X-ray diffraction. The separate group character of solidification of butterfat – low-melting, medium-melting and high-melting glycerides – was determined. X-ray crystallography did not reveal fundamental differences in the pattern of the crystallization of glycerides and formation of polymorphic modifications with different types of crystalline structure. This indicates the uniformity of type of successive phase changes of butterfat in butter, both after fast cooling of cream by vacuum atomization, followed by aftercooling in a scraped heat exchanger, and in case of using the conventional method of physical aging of cream.

Keywords: Aging of cream, butter, differential scanning calorimetry, thermogram, X-ray diffraction, polymorphism, crystalline structure

DOI 10.12737/13124 *Foods and Raw Materials*, 2015, vol. 3, no. 2, pp. 23–28.

INTRODUCTION

The crystalline structure of solidified fat, its physical and chemical properties, and hence the consistency of butter depend on the presence of certain polymorphic forms and their relationship. Glycerides of butterfat possess the properties of monotropic polymorphism, i.e. the ability to crystallize with the formation of different space lattices. Depending on the conditions of cooling, crystals of various sizes and configurations with different physical properties are formed.

According to research, conducted by G.V. Tverdokhleb [1], in the solid phase of butterfat and its fractions there are four modifications: γ, α, β' and β. The transition of one modification to another is irreversible and occurs in one direction, from a metastable form to a stable form γ→ α→ β'→ β. The transition point is close to the melting temperature of a metastable modification.

In order to obtain objective data on the impact of the flow two-stage method of aging of cream [2] and its implementation on the pattern of the crystallization of glycerides of butterfat, differential-scanning and X-ray crystallographic studies of butter, produced using the method of churning, were carried out.

OBJECTS AND METHODS OF STUDY

Differential scanning calorimetry is a method based on the registration of energy necessary to establish zero temperature difference between the studied sample and the reference sample in time or depending on temperature, when heating or cooling them in identical temperature conditions with a certain speed.

The results are recorded in the form of a DSC curve. The difference of energies between the cells with the studied sample and the reference sample ($d\Delta Q/dt$) is plotted on the ordinate, time or temperature are plotted on the abscissa [3–5].

DSC curves were obtained using the differential scanning calorimeter "Shimadzu DSC-60" (Fig. 1), with the use of aluminium crucibles having a diameter of 6 mm and a height of 5 mm, weighing 49 mg. The device was calibrated with indium, stannum and lead.

This differential scanning calorimeter has the following technical characteristics:
– temperature range of measurement: from room temperature to 600°C (without liquid nitrogen cooling); from –140°C to 600°C (with liquid nitrogen cooling);
– limits of DSC signal measurement: ±40 MW;
– noise level of DSC signal: 1 MW;
– programmable heating/cooling rate: from ±0.1 to 99.9°C/min;
– cooling conditions: cooling agent – liquid nitrogen; drying gas – nitrogen with feed rate of 200–300 ml/min;
– atmosphere: air, inert gas (nitrogen);
– pressure: atmospheric;
– amount of sample: depends on the type of crucible;
– form of sample: solid or liquid.

The polymorphism and the type of crystalline lattice of glycerides in the butter samples were analyzed using the method of X-ray diffraction. The analysis was carried out using the X-ray diffractometer Shimadzu XRD7000 (Japan) with the X-ray tube having a cobalt anode (characteristic radiation wavelength 0.178897 nm, Fe-filter). The appearance of the device is presented in Fig. 2. Curve recording was implemented in the Bragg–Brentano geometry at the tube voltage of 40 kV and the current of 30 μA. The slit width during the recording of curves was 0.3 mm. The recording was implemented at the angular rate of 2 degrees per minute.

Fig. 1. The appearance of DSC-60.

Fig. 2. X-ray powder diffractometer Shimadzu XRD7000.

The condition for obtaining diffraction maximum on the x-ray spectrum is the fulfillment of the Wulff–Bragg's condition:

$$2d\sin\theta = n\lambda, \quad (1)$$

where d is the interplanar distance, nm; θ is the grazing angle; λ is the wavelength, and n (n=1, 2 ...) is an integer, called the diffraction order.

The identification of the modifications of butterfat is based on the system proposed by E. Latton [6]. X-ray structural characteristics of the modifications of triglycerides according to Latton are presented in Table 1.

RESULTS AND DISCUSSION

Study of thermal effects using the method of differential scanning calorimetry

The test sample of butter (received by churning cream which was aged using the flow method) was placed into the crucible, weighed and transferred into the measuring cell. The device was cooled to –70°C using liquid nitrogen. After exposure to this temperature, the program of heating with the rate of 2°C/min was launched, which ensures almost complete separation of melting peaks of various components of butter. Aluminium oxide was used as a reference sample. DSK-thermogram of the test sample is presented in Fig. 3.

When analyzing data, no exothermic peaks, corresponding to processes that release heat, were observed. In the thermogram there is a sharp endothermic peak with a maximum at a temperature of –1.5°C, corresponding to the melting of plasma. In terms of intensity this peak is comparable with the similar peak of the thermograms of the control sample (received by churning cream which was aged using the conventional method) (Fig. 4), but has a more pronounced, "narrow" character: in the control sample the beginning of this peak corresponds to the temperature of approximately –12.9°C, and the peak is more diffused, while for the test sample the beginning of the melting corresponds to the temperature of approximately –3.9°C.

Table 1. X-ray structural characteristics of the modifications of triglycerides according to Latton

Modification	Characteristics of small intervals
α	A single diffraction peak corresponding to the interval of 0.414 nm
β'	Usually two (sometimes more) diffraction peaks corresponding to the intervals of 0.42 nm (of high intensity) and 0.38 nm
β	Sharp (usually very sharp) diffraction maximum corresponding to the interval of 0.46 nm, along with peaks of lesser intensity

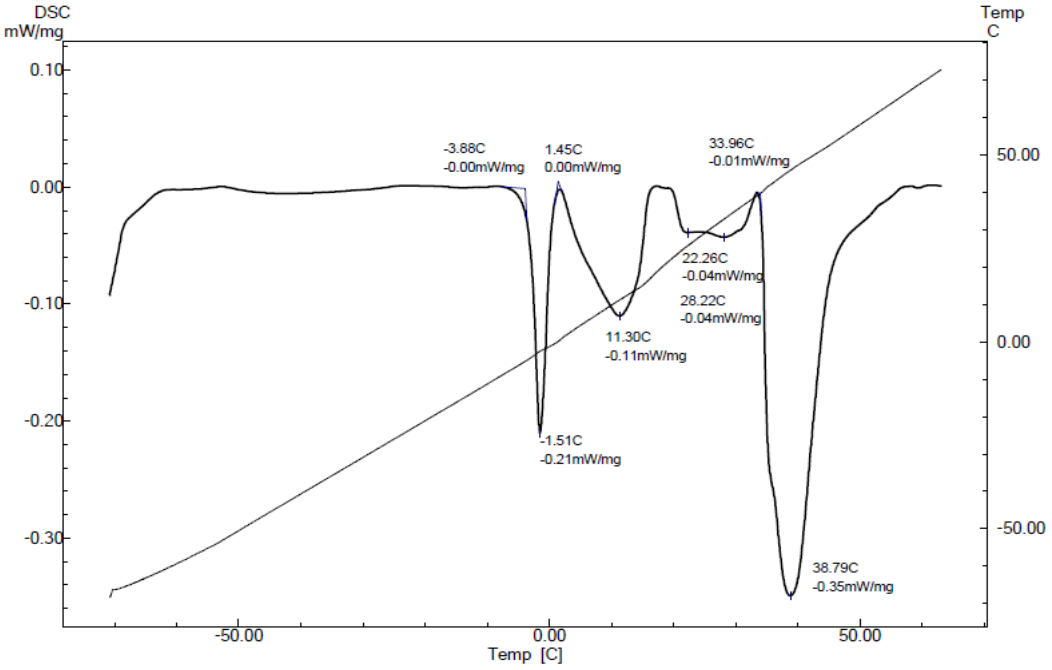

Fig. 3. DSC-thermogram of the test sample.

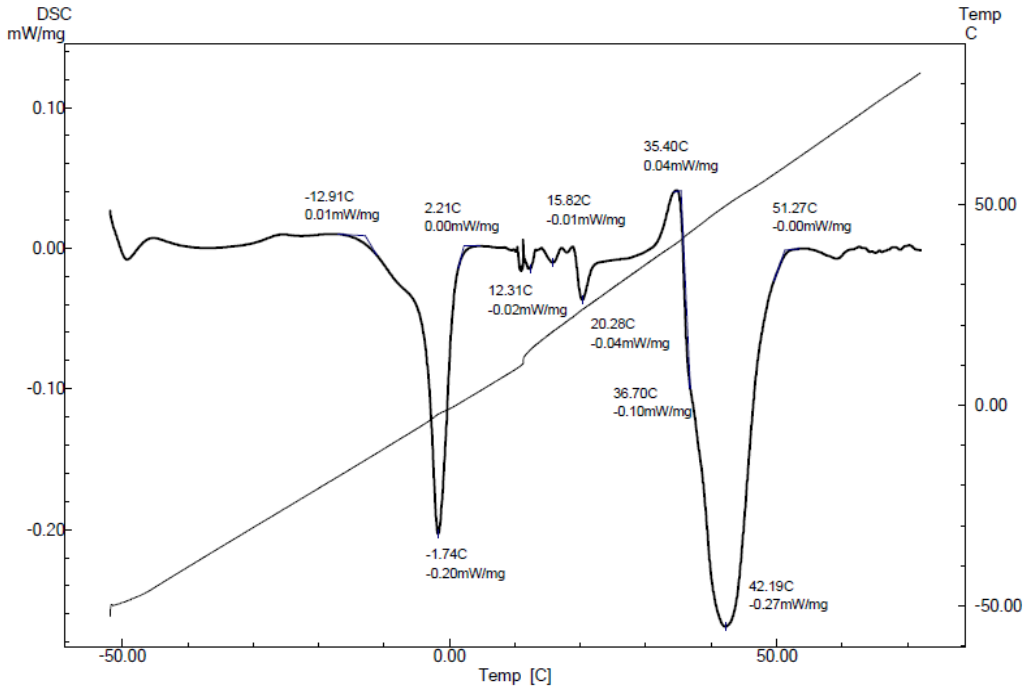

Fig. 4. DSC-thermogram of the control sample.

The test sample is also characterized by a more pronounced peak corresponding to low-melting glycerides (the peak corresponds to the temperature of approximately 11.3°C). As is the case with the control sample, the thermogram shows rather diffused peaks of low intensity corresponding to the glycerides with a melting temperature of about 22.3°C and 28.2°C.

The test sample is also characterized by the dominance of high-melting glycerides, identified by the most intense peak with a maximum at a temperature of 38.8°C (the beginning of the peak is around 34.0°C). The content of this high-melting group of glycerides is higher than in the control sample, which as evidenced by the greater intensity of the peak (–0.35 MW/mg vs –0.27 MW/mg).

Study of the structure of butter using the method of x-ray crystallography

Samples for recording curves were prepared by pressuring butter into flat open aluminum ditches. Butter samples for the study were prepared in four ways:
I – spectra were recorded at a temperature of 4 ± 2°C without additional heat treatment;
II – samples were heated to a temperature of 15°C and conditioned for 10 h before recording spectra;
III – samples were conditioned for 24 h at a temperature of –18° before recording spectra;
IV – samples were heated to a temperature of 70°C, conditioned for 20 minutes and recorded spectra immediately, after which the repeated recording of spectra was carried out in 2 hours.

As a result of X-ray studies, the following data were obtained. Both samples in the area of small interplanar distances have two peaks corresponding to the interplanar distances of 0.38 and 0.42 (0.43) nm, wherein the second peak is more intense. This combination of peaks characterizes the β'- polymorphous modification, while the offset and asymmetrical extension in the area of 0.46 nm can indicate the presence of tiny centers of crystallization of β-modification or is a consequence of a large amount of liquid fat phase.

In the test sample (Fig. 5), as opposed to the control sample (Fig. 6), along with β'-modification, β-modification was also clearly seen, which is evidenced by the clear peak of 0.46 nm.

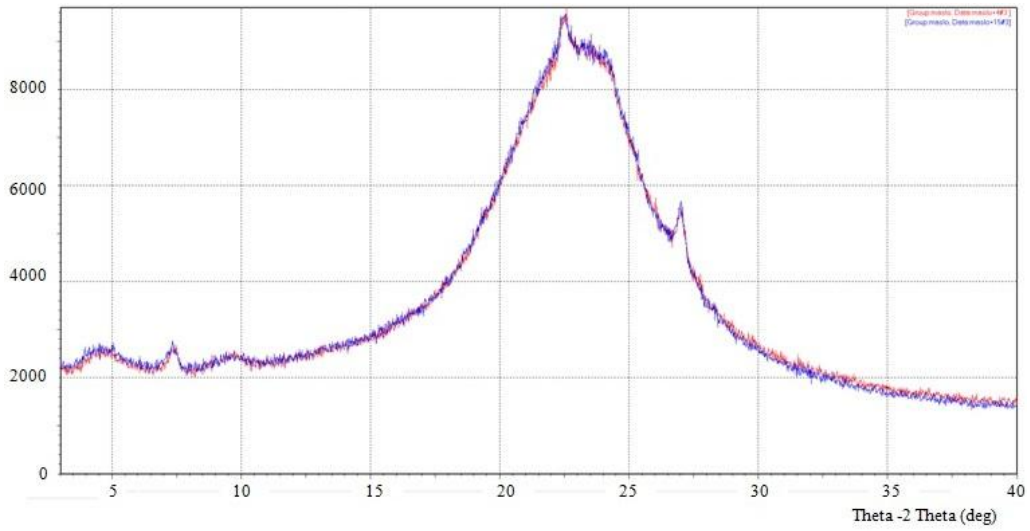

Fig. 5. The X-ray spectrum of the test sample at temperatures of 4 ± 2°C (red line) and 15°C (blue line).

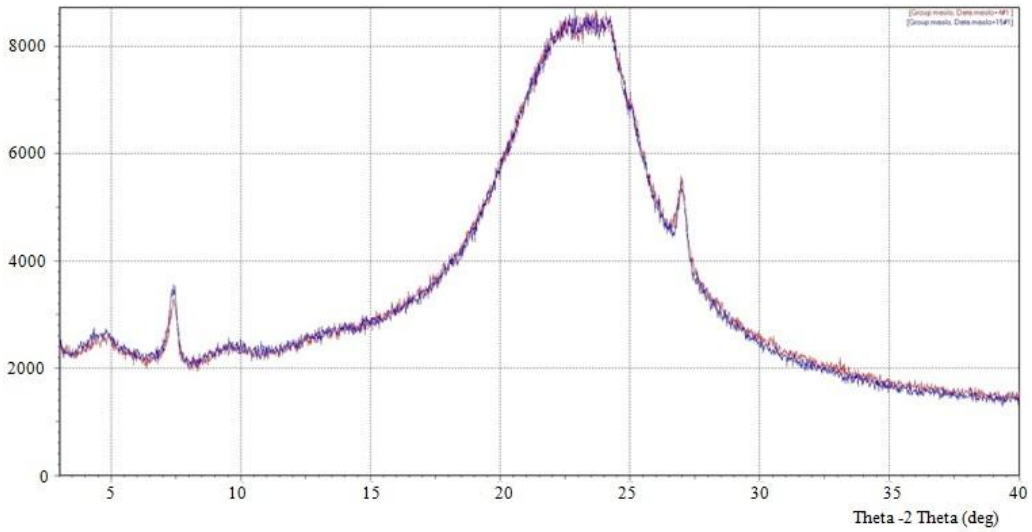

Fig. 6. The X-ray spectrum of the control sample at temperatures of 4 ± 2°C (red line) and 15°C (blue line).

In both samples, reflexes (of different order n) were identified in the area of large intervals, corresponding to the same interplanar distance of 4.1 (4.2) nm, which indicates the presence of the crystalline structure with double chain length (DCL).

When heating samples to a temperature of 15°C, no significant changes in the samples were identified.

When cooling samples to a temperature of –18°C there were also no significant differences in comparison with the samples, studied at 4 ± 2.1°C.

When heating samples to 70°C (Fig. 7 and Fig. 8) the following changes were identified: in the area of small angles the maximum of 0.43 nm transformed into the diffused halo within the boundaries of 0.40–0.47 nm, the maximum in the area of 0.38 nm also lost its sharpness, its intensity decreased.

In the area of large intervals, the intensity of reflexes, corresponding to the interplanar distance of 4.1 (4.2) nm, significantly decreased. These changes indicate partial melting and significant reduction of layered ordering of molecules in the structure with double chain length.

CONCLUSIONS

The studies determined the separate group character of solidification of butterfat – low-melting, medium-melting and high-melting glycerides. For mixed crystals of high-melting group of glycerides only structures with double chain lengths are typical. Low-melting glycerides are characterized by having structures with double and triple chain length, wherein the latter are rather stable.

The differentiation of mixed groups of solidified glycerides contributes to the formation of fat structure in individual fat balls and in butter, close to the structure of the control cream sample. X-ray crystallography did not reveal fundamental differences in the pattern of the crystallization of glycerides and formation of polymorphic modifications with different types of crystalline structure. This indicates the uniformity of type of successive phase changes of butterfat in butter, both after fast cooling of cream by vacuum atomization, followed by aftercooling in a scraped heat exchanger, and in case of using the conventional method of physical aging of cream.

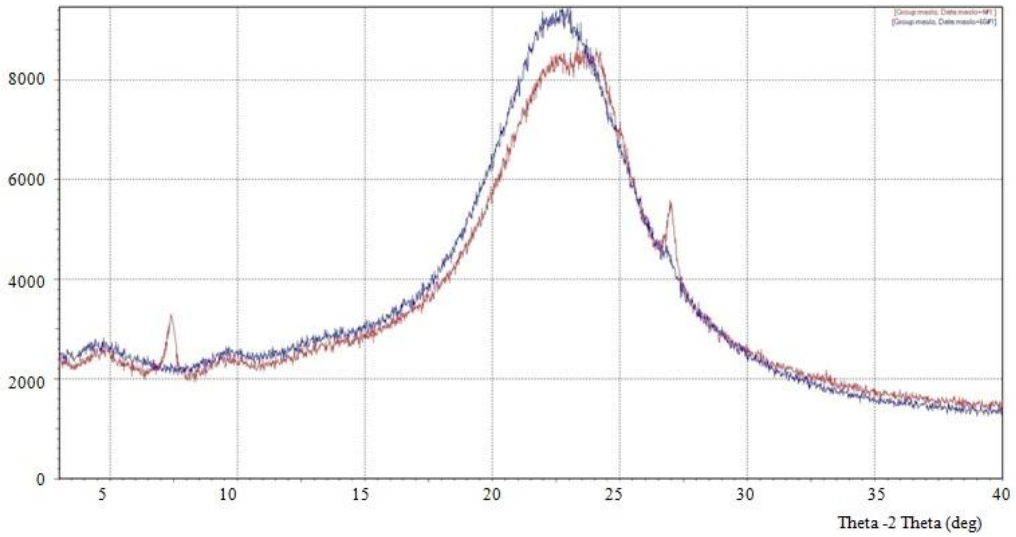

Fig. 7. The X-ray spectrum of the control sample at temperatures of 4 ± 2°C (red line) and 70°C (blue line).

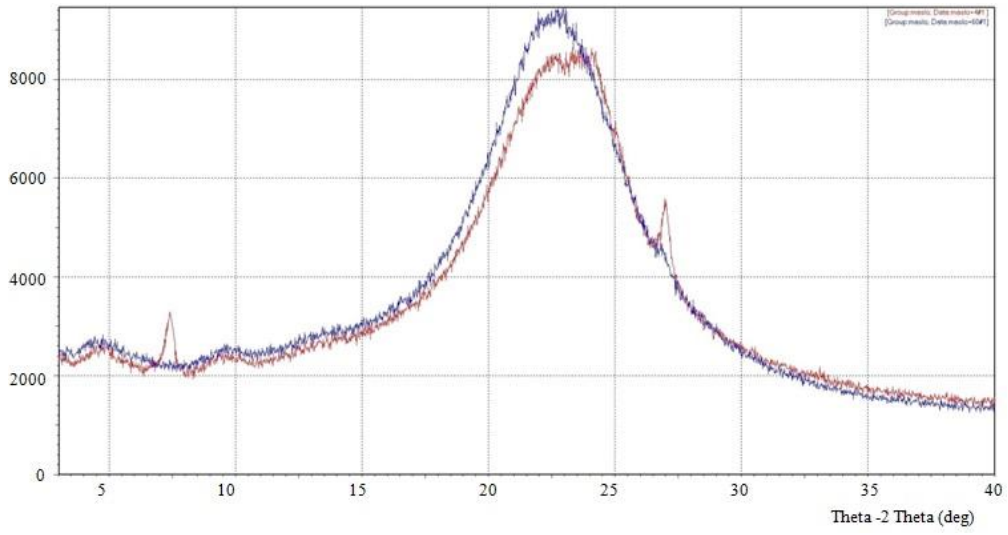

Fig. 8. The X-ray spectrum of the test sample at the temperatures of 4 ± 2°C (red line) and 70°C (blue line).

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Please cite this article in press as: Chervetsov V.V., Kulenko V.G. and Rattur E.V. Study of the impact of the preparation of cream for churning using vacuum atomization on the structure of butter. *Foods and Raw Materials*, 2015, vol. 3, no. 2, pp. 23–28. doi: 10.12737/13124.