DSC analysis of tvarogs depending on the fat content

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ABSTRACT:

Differential Scanning Calorimetry (DSC) allows qualitative and quantitative determination of changes heats flow in a sample by physicochemical changes such as melting or oxidation as a function of time and temperature, during heating or cooling of the sample. The aim of the study was to determine the use of DSC in the evaluation of tvarogs. To the analysis were used 9 tvarogs with differed fat content (skimmed, half-fat and full-fat). The basic chemical composition of tvarogs was determined (FoodScan™Lab), and tvarogs were freeze-dried (Alpha LD plus), then their chemical composition was calculated on the grounds of dry matter concentration. A Differential Scanning Calorimeter (TA Instruments DSC Q10) with the closed cooling system (RCS) was used to determine the heat transfer rate. Two tests were conducted. The first one in ranges of temperature from -30 to 60°C and the second in ranges from -40 to 80°C. The graphical representations to illustrate the dependence of heat transfer in function of temperature of the analyzed tvarogs were obtained. The full-fat tvarogs were characterized by significant differences, as opposed to the skim and half-fat tvarogs. In the half--fat and full-fat tvarogs were occurred the peaks of phase change in the temperature range of 3.68 to 18.33°C. The most peaks was observed in full-fat tvarogs, where exothermic reactions were observed more often than in the other tvarogs. The protein content in the tvarogs was not influenced to the results of DSC analysis in the range of used temperature. Differential Scanning Calorimetry can be used to determine and compare the thermal properties of tvarogs with different fat content.

Analiza DSC twarogów w zależności od zawartości tłuszczu

słowa kluczowe: skaningowa kalorymetria różnicowa, twaróg, analiza termiczna, przemiany fazowe

STRESZCZENIE:

Skaningowa kalorymetria różnicowa (DSC) pozwala na jakościowe oraz ilościowe określenie zmian przepływu ciepła w badanej próbce, które zachodzą w wyniku przemian fizykochemicznych np. topnienia czy utleniania, w funkcji czasu i temperatury, podczas ogrzewania lub chłodzenia tej próbki. Badania miały na celu określenie możliwości wykorzystania DSC w ocenie twarogu. Do analiz wybrano 9 twarogów, które różniły się między sobą zawartością tłuszczu (chude, półtłuste i tłuste). Dokonano oznaczenia podstawowego składu chemicznego (FoodScan™Lab), twarogi zliofilizowano (Alpha LD plus), a następnie na podstawie koncentracji suchej masy wyliczono ich skład chemiczny. Do określenia zależności przepływu ciepła od zmieniającej się temperatury próbki użyto skaningowego kalorymetru różnicowego (TA Instruments DSC Q10) z zamkniętym układem chłodzącym (RCS). Przeprowadzono dwie próby. Pierwszą w zakresie stosowanych temperatur od -30 do 60°C, a drugą od -40 do 80°C. Otrzymano wykresy zależności przepływu ciepła od temperatury analizowanych twarogów. Twarogi tłuste charakteryzowały się znacznymi różnicami uzyskanych wyników, w przeciwieństwie do twarogów chudych i półtłustych. W twarogach półtłustych i tłustych odnotowano piki przemian fazowych, które występowały w zakresie temperatur od 3,68 do 18,33°C. Najwięcej pików zaobserwowano w twarogach tłustych, gdzie wystąpiło także więcej reakcji egzotermicznych niż w pozostałych twarogach. Zawartość białka w badanych twarogach nie wpłynęła na wyniki analizy DSC w badanym zakresie temperatur. Metodę skaningowej kalorymetrii różnicowej można wykorzystać do porównania twarogów, ze względu na różną zawartość tłuszczu.

1. INTRODUCTION

The physicochemical properties of food to changes under the influence of temperature, during the production, transport, storage and prepare for consumption. The examples of technological processes related with change of temperature are pasteurization, freezing, drying, baking etc. The changes of temperature of raw materials and intermediate products cause to modify the physical and chemical properties of their structure, which affects to properties of the final product, including properties such as appearance, taste, smell and consistency. The action of temperature causes the occurrence of such chemical processes as hydrolysis and oxidation and physical such as evaporation, crystallization, melting. The thermal behavior of foods strongly depends on their composition, in particular the major food constituents: carbohydrates, lipids, proteins, water, the degree of advancement of food processing [1]. Understanding of the effect of temperature changes for food properties will allow manufacturers to optimize the processing conditions and improve the quality of products. The techniques, which include differential scanning calorimetry, are grouped together and called the Thermal Analysis. The methods of thermal analysis allow to determine the changes in the condition of the tested sample in different measurement with the change of temperature [2]. These methods in food technology is relatively new. In the past they have been used mainly as a standard method for testing polymers. During various technological processes in food production is a lot of phase transitions in raw food and products. In food testing, where using differential scanning calorimetry, many physicochemical effects can be observed in the temperature range between -50°C and 300°C [1]. The reactions in the processed material can be exothermic or endothermic, often with very little energy change, which makes them very difficult to detect [2]. The example of endothermic reactions is: melting, denaturation, evaporation, and exothermic: crystallization, oxidation, fermentation [1]. The better understanding of the physicochemical changes, which occur in food products will allow to production more secure, customer friendly, and also having improved organoleptic properties of products. The physicochemical changes of foods strongly depend on their composition including the major food constituents: proteins,

lipids, carbohydrates, water etc. Each type of constituents in a product has its own physicochemical properties, what causes the thermal phenomena occurring in the whole product, which are more noticeable, when the amount of some constituent in this product are greater [1]. Differential scanning calorimetry can observe changes occurring in food, such as crystallization, melting, evaporation, vitrification, denaturation, sublimation, polymorphic transformation [3]. The main thermal phenomena occurring in carbohydrates are the release of crystallization water, melting, starch gelling or retrogradation and crystallization. In the fats are occurring mainly crystallized, melted, oxidized and the formation of polymorphic forms of fat. In proteins are for example denaturation, vitrification (when the proteins are in solution) and oxidation (when the proteins are in powder form). In addition to analysis of phase transformations, differential scanning calorimetry can be used, for example to determine the addition of emulsifiers [1]. The reactions occurring in food often show a very small change of energy, so they are difficult to detect, so the measuring equipment must comply with high demands, especially with the measuring system and software that is used to evaluate the occurring phase transitions. Differential scanning calorimetry fulfills these standards, and as a result, this method is increasingly used in the food industry for routine quality control, analysis and also for testing products to evaluation [4] and improve their quality [2, 3]. This method in the food processing has a very wide application. It is mainly used to evaluate falsified products, for example the addition of vegetable oils [5-7], the different animals fats, than the milk fat [8-10], or water [11] to butter, honey [12], oils [13], including olive oil [14, 15], cacoa fat [16] and also used in the study of the thermal stability of biological materials such as meat [17, 18].

The tvarogs are the kind of fresh cheese and one of the most important dairy products in Poland, what causes interest in optimizing their production and storage. Although the market of dairy products in Poland is more and more diversified, the volume of tvarog production is not decreasing, and moreover, a constant increase in their consumption is observed [19]. The average consumption of this kind of cheese in Poland is much higher than the level of consumption of ripened and processed cheeses, where for many years exceeds 6 kg per person. In 2010 the consumption of white fresh cheeses in Poland was 6.60 kg per person, which was 58.5% of total cheese consumption [20]. Tvarogs are products with a complex chemical composition, whose technological process requires a lot of individual operations related to temperature changes. There are for example pasteurization, cooling, centrifugation and homogenization of milk and heating and drying of curd. All these processes are performed at a different temperature that is characteristic of the process. Differential scanning calorimetry can be an easy, quick and accurate measuring method for tvarog testing, due to their complex composition and the complex production process where the temperature changes many times.

2. EXPERIMENTATION

The research material was three skimmed, three half-fat and three full-fat tvarogs, made in three different dairy plants located in north-eastern Poland. The tvarogs were labeled with letters A, B and C denoting dairy plant and then denoted by a numerical symbol for full-fat – 1, half-fat – 2, skimmed – 3. The samples from the second test were labeled with double letter symbols. The chemical composition of tvarogs was determined using the FOSS FoodScan™Lab. Three repetitions of chemical composition analysis were performed for each cheese. Average values and standard deviation were calculated, and the results are presented in Table 1. All nine cheeses were frozen to -80°C and then freeze-dried using the CHRIST Alpha 1-2 LD plus with freeze-drying parameters 0.006 mbar and -64°C. The moisture analyzer METTLER TOLEDO MJ33 was used to determine dry matter content, and then the chemical composition of freeze-dried tvarogs was calculated on the basis of the obtained dry matter concentration (Tab. 2). All freeze-dried cheeses were weighed, and then to conduct an experiment by the DSC sequences Heating/Cooling/Heating. The measurements were conducted in an atmosphere of nitrogen with the sample mass in the range of 2 to 3 mg. The TA Instruments DSC Q10 with closed RCS cooling system was calibrated using only one standard, which was indium. The analysis was performed in two tests, using a wider range of temperatures in the second test, which consisting of the following stages – heating, cooling and heating. Both test were

starting by setting the initial temperature to 20°C. The first heating was increasing the temperature by 5°C/min to 60°C in the first test (in the second test to 80°C). The cooling was decreasing the temperature by 5°C/min to -30°C in the first test (in the second test to -40°C). The second heating was increasing the temperature by 5°C/min to 20°C in the both tests. After every stage there was a stage of holding for 6 minutes. The analysis was repeated for each tvarog twice.

3. RESULTS AND DISCUSSION

The highest level of dry matter, fat and protein content and acidity in fresh tvarogs was determined in tvarogs from B dairy plant, but the lowest level of these factors was in tvarogs from A dairy plant (Tab. 1). After freeze-drying similar results were obtained (Tab. 2).

The results of the DSC analysis were obtained in the form of graphs showing the relationship of heat flow (W/g) to temperature (°C). The DSC curve with the characteristic points of temperature were shown, where sudden changes in heat flow were observed. The graphs showed separate shades of DSC analysis cycles, based on the first and second DSC analysis sequence. Graphs of tvarogs produced at dairy plant A were presented, because they showed the largest changes in heat flow. The DSC graphs of tvarogs from the other dairy plants did not differ significantly from the tvarogs produced at dairy plant A, so they were not presented.

The analysis of A1 and AA1 tvarogs (Fig. 1) showed that at the end of cycle 1, the sample temperature of tvarog A1 was 20.08°C and the heat flow was 0.01051 W/g, and in the sample AA1 was 19.98°C and 0.02854 W/g. At the end of cycle 2 in the sample of A1 the heat flow was -0.12340 W/g, when the sample temperature was 59.05°C, and in the sample AA1 the heat flow was -0.26060 W/g, when the sample temperature was 78.64°C. The heat flow difference between the beginning and the end of the cycle 2 in the case of A1 was 0.13391 W/g, while in the case of AA1 was 0.28914 W/g. At the end of cycle 3 in the sample of A1 the heat flow was 0.00648 W/g, when the sample temperature was

Table 1 The mean chemical composition of fresh tvarogs

-	Component			
Tvarog	**pH**	**Fat (%)**	**Protein (%)**	**Dry matter (%)**
A1	4.60 ± 0.03	8.06 ± 0.03	15.42 ± 0.02	26.50 ± 0.06
A2	4.62 ± 0.00	3.85 ± 0.03	17.35 ± 0.05	25.13 ± 0.06
A3	4.62 ± 0.01	0.11 ± 0.01	17.11 ± 0.04	23.81 ± 0.08
B1	4.76 ± 0.01	8.16 ± 0.08	17.25 ± 0.04	27.84 ± 0.06
B2	4.72 ± 0.00	4.08 ± 0.00	18.07 ± 0.10	26.51 ± 0.12
B3	4.77 ± 0.01	0.14 ± 0.02	18.52 ± 0.16	23.88 ± 0.02
C1	4.72 ± 0.01	7.65 ± 0.09	16.60 ± 0.05	27.58 ± 0.14
C2	4.74 ± 0.01	3.96 ± 0.03	17.24 ± 0.06	26.02 ± 0.18
C3	4.70 ± 0.01	0.10 ± 0.01	17.60 ± 0.12	24.15 ± 0.02

Table 2 The mean chemical composition of freeze-dried tvarogs

-	Component		
Tvarog	**Fat (%)**	**Protein (%)**	**Dry matter (%)**
A1	7.89	15.09	25.93
A2	3.78	17.02	24.66
A3	0.11	16.69	23.23
B1	7.98	16.88	27.24
B2	4.00	17.71	25.98
B3	0.14	18.00	23.21
C1	7.41	16.07	26.70
C2	3.84	16.71	25.22
C3	0.10	17.09	23.45

59.93°C, and in the sample of AA1 the heat flow was -0.02381 W/g, when the temperature was 79.53°C. In the cycle 4 the two peaks in sample A1 occurred at the temperature of 14.2°C (0.15580 W/g) and 6.05°C (0.20040 W/g), while in sample AA1 the only one peak occurred at the temperature of 3,68°C with the heat flow of 0.35380 W/g. At the end of cycle 4 in the sample of A1 the heat flow was 0.10550 W/g, when the sample temperature was -29.82°C, and in the sample of AA1 the heat flow was -0.19170 W/g, when the temperature was -28.86°C. The heat flow difference between the beginning and the end of the cycle 4 in the case of A1 was 0.11198 W/g, while in the case of AA1 0.21551 W/g. At the end of cycle 5 in the sample of A1 the heat flow was 0.00512 W/g, when the sample temperature was -30.10°C, and in the sample of AA1 the heat flow was -0.04836 W/g, when the temperature was 39.48°C. At the end of cycle 6 in the sample of A1 the heat flow was -0.14880 W/g, when the sample temperature was 18.31°C, and in the sample of AA1 the heat flow was -0.29180 W/g, when the temperature was 16.79°C. In the sample of A1 the peak occurred at the temperature of 11.74°C and the heat flow of -0,13090 W/g. The heat flow difference between the beginning and the end of the cycle 6 in the case of A1 was 0.15392 W/g, while in the case of AA1 0.34016 W/g.

The analysis of A2 and AA2 tvarogs (Fig. 2) showed that at the end of cycle 1, the sample temperature of tvarog A2 was 20.04°C and the heat flow was 0.01997 W/g, and in the sample AA2 was 19.98°C and 0.01531 W/g. At the end of cycle 2 in the sample of A2 the heat flow was -0.14480 W/g, when the sample temperature was 59.35°C, and in the sample AA2 the heat flow was -0.32170 W/g, when the sample temperature was 79.09°C. The heat flow difference between the beginning and the end of the cycle 2 in the case of A2 was 0.34450 W/g, while in the case of AA2 was 0.33701 W/g. At the end of cycle 3 in the sample of A2 the heat flow was 0.00424 W/g, when the sample temperature was 59.85°C, and in the sample of AA2 the heat flow was -0.01938 W/g, when the temperature was 79.80°C. In the sample of A2 the peak in that cycle occurred at the temperature of 5,99°C (0.16950 W/g). At the end of cycle 4 in the sample of A2 the heat flow was 0.11570 W/g, when the sample temperature was -29.77°C, and in the sample of AA2 the heat flow was 0.22850 W/g, when the temperature was -38.77°C. In the sample AA2 the peak occurred at the temperature of 6.51°C (0.33690 W/g). At the end of cycle 5 in the sample of A2 the heat flow was 0.00835 W/g, when the sample temperature was -30.10°C, and in the sample of AA2 the heat flow was 0.01062 W/g, when the temperature was -40.10°C. At the end of cycle 6 in the sample of A2 the heat flow was -0.14430 W/g, when the sample temperature was 16.24°C, and in the sample of AA2 the heat flow was -0.29240 W/g, when the temperature was 16.70°C. The heat flow difference between the beginning and the end of the cycle 6 in the case of A2 was 0.15265 W/g, while in the case of AA2 was 0.30302 W/g.

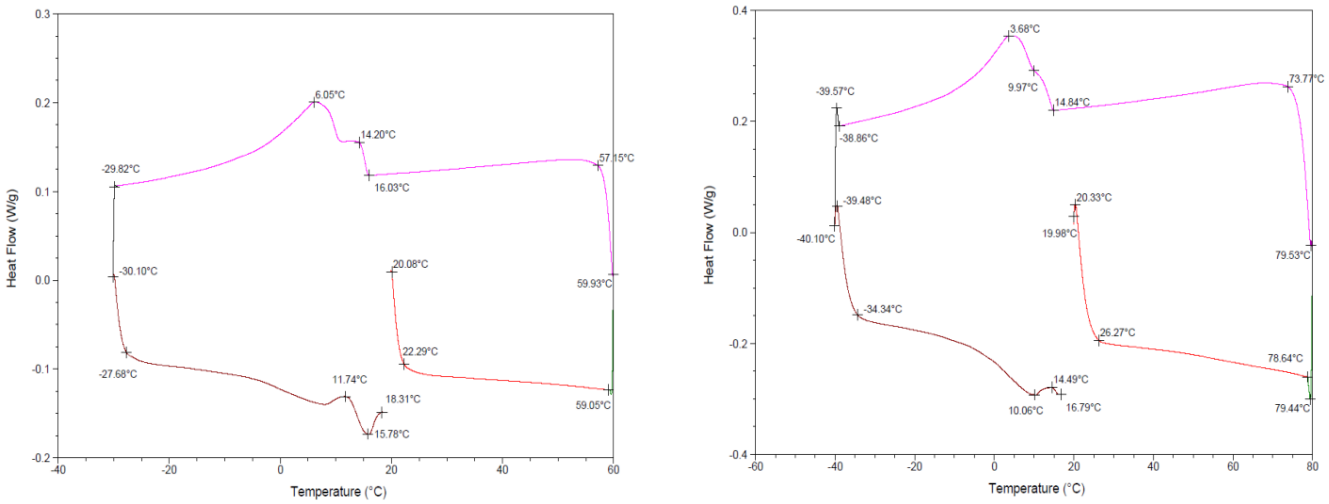

Figure 1 DSC curve of tvarogs A1 and AA1 – heat flow (W/g) depending on the temperature (°C)

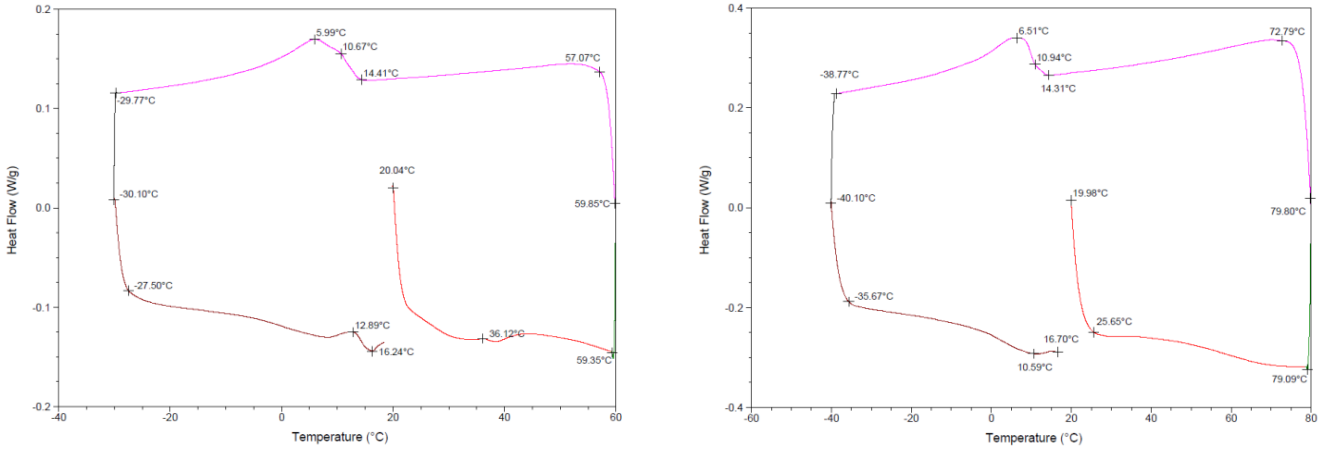

Figure 2 DSC curve of tvarogs A2 and AA2 – heat flow (W/g) depending on the temperature (°C)

The analysis of A3 and AA3 tvarogs (Fig. 3) showed that at the end of cycle 1, the sample temperature of tvarog A3 was 19.98°C and the heat flow was 0.01043 W/g, and in the sample AA3 was 20.07°C and 0.01247 W/g. At the end of cycle 2 in the sample of A3 the heat flow was -0.14240 W/g, when the sample temperature was 59.35°C, and in the sample AA3 the heat flow was -0.30360 W/g, when the sample temperature was 78.64°C. The heat flow difference between the beginning and the end of the cycle 2 in the case of A3 was 0.15283 W/g, while in the case of AA3 was 0.31607 W/g. At the end of cycle 3 in the sample of A3 the heat flow was -0.14240 W/g, when the sample temperature was 59.85°C, and in the sample of AA3 the heat flow was -0.16810 W/g, when the temperature was 79.80°C. At the end of cycle 4 in the sample of A3 the heat flow was 0.08021 W/g, when the sample temperature was -29.71°C, and in the sample of AA3 the heat flow was 0.15310 W/g, when the temperature was -38.95°C. The heat flow difference between the beginning and the end of the cycle 4 in the case of A3 was 0.09535 W/g, while in the case of AA3 was 0.21290 W/g. At the end of cycle 5 in the sample of A3 the heat flow was 0.00515 W/g, when the sample temperature was -30.10°C, and in the sample of AA3 the heat flow was 0.00691 W/g, when the temperature was -40.10°C. At the end of cycle 6 in the sample of A3 the heat flow was -0.08141 W/g, when the sample temperature was 18.39°C, and in the sample of AA3 the heat flow was -0.16820 W/g, when the temperature was 16.87°C. The heat flow difference between the beginning and the end of the cycle 6 in the case of A3 was 0.08656 W/g, while in the case of AA3 was 0.17511 W/g.

DSC curves, which showed the relationship between heat flow and temperature, allow to determine and compare thermal properties of tvarogs with different fat content. In the skimmed tvarogs no major differences were found between individual samples from different dairy plants. Similarly, DSC curves of half-fat tvarogs did not differ significantly from each other, however, there were peaks in them, which showed

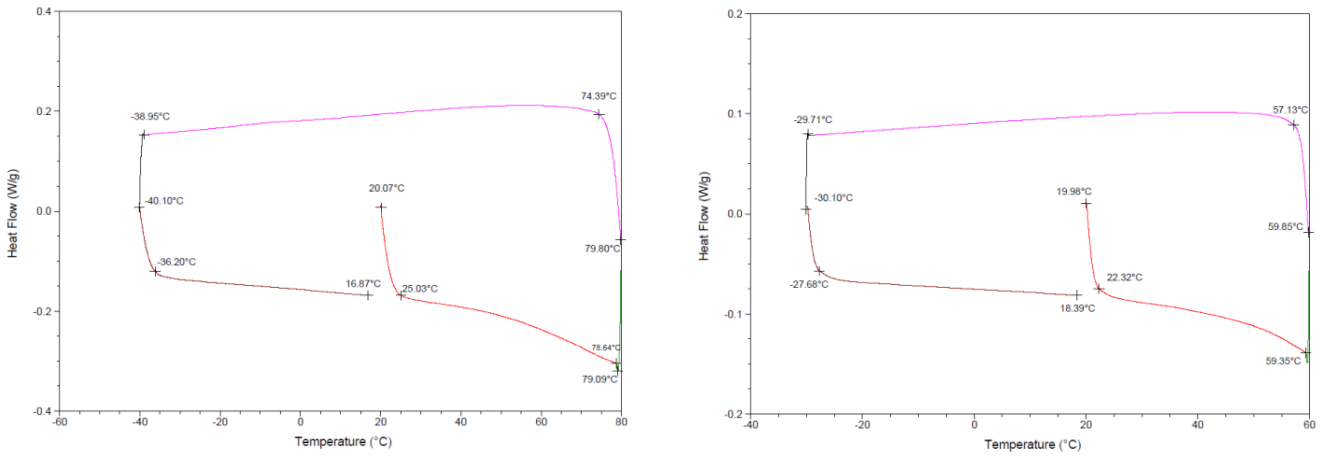

Figure 3 DSC curve of tvarogs A3 and AA3 – heat flow (W/g) depending on the temperature (°C)

the occurrence of phase transitions. The most noticeable differences occurred between DSC curves in full-fat tvarogs, where the phase transitions during DSC analysis occurred in a larger quantity than in half-fat and skimmed tvarogs. Therefore, differential scanning calorimetry can be used to analyze fat in tvarogs, because the phase transitions occurred in a different temperature range for each type of tvarogs, depending on the content of fat. The peaks of phase transitions of full-fat and half-fat tvarogs were observed in the temperature range from 3.68 to 18.33°C, while in the skimmed tvarogs them were not observed. More exothermic reactions than endothermic were observed in the full-fat tvarogs, and these exothermic reactions showed higher heat flow than endothermic reactions. The protein content of the tvarogs did not affect the result of the DSC analysis in the used temperature range. It may be related to a similar content of protein in the tvarogs (from 15 to 18%). The temperature range of the tests influenced the DSC curves. In the limited temperature range (from -30 to 60°C) the peaks were more pronounced than in the wider range (from -40 to 80°C). This indicates that the test temperature range has a significant impact on the result of the analysis. Differential scanning calorimetry as a method of thermal analysis allows for quantitative and qualitative characterization of heat flow changes as a function of time and temperature, which takes place during physicochemical transformations under heating or cooling conditions of the sample. DSC is characterized by many advantages, which include the ease of sample preparation, small sample amount for analysis, a short time of analysis compared to other analytical methods, for example gas chromatography, as well as the possibility of using a wide range of temperatures to determine phase transitions. The possibilities of using differential scanning calorimetry in the evaluation of tvarogs require further research.

4. CONCLUSIONS

Differential scanning calorimetry allows to determine and compare thermal properties of tvarogs depending on the fat content. The most noticeable differences were observed between the DSC curves of full-fat tvarogs, where the phase transitions peaks during DSC analysis occurred more frequently than in half-fat and skimmed tvarogs. The cheeses from different dairy plants differed from each other, and the most characteristic peaks were observed in tvarogs from dairy plant A. The results obtained in both tests were different. In the first test the peaks were more marked than in second test. The optimization of measurement parameters requires further research.

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