Comparison of Physical and Functional Properties of Whipping Cream and Whipping Cream Analogue

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ABSTRACT
Replacement of milk fat with vegetable counterpart brings up possibilities of engineering new characteristics of dairy emulsions – e.g. desired rheological properties, better stability, enhanced whipping ability. In this paper, laser diffraction, differential scanning calorimetry, rheometry, density analysis, pH and zeta potential measurement were used to compare physical characteristics of whipping cream and whipping cream analogue. In addition, changes in functional properties were assessed for both emulsions being stored at two different cooling temperatures for two weeks.

Introduction
Production of dairy imitations, like whipping cream analogue, is a dynamically developing trend. This is due to the fact, that replacement of milk fat with vegetable substitutes lowers products' prices. Furthermore, usage of different fats or oils brings up possibilities of engineering features in order to obtain more stable, easy to use, functional or texturally interesting products.

Growing market's demand calls for scientific development. Researchers formulate methods enabling comparison of the products (especially considering stability, functionality and consumers' perception).

Material and Methods
Whipping cream
Material investigated in the experiment was a commercial UHT treated whipping cream of 36% fat content. The cream's fat phase was the milk fat only, without any additives.

Whipping cream analogue
For comparison, a whipping cream analogue was manufactured on a pilot scale. The fat phase was made of 2/3 vegetable oil: Akotop P70 (AAK AB) batch number: 0001772226, and 1/3 milk fat – accounting for 34.2% fat altogether. The whipping cream analogue was stabilized with additives, UHT treated and homogenized. The whipping cream analogue contained also: emulsifier RRH Tate & Lyle, buttermilk powder, colorant β – carotene BC-200WS, aroma Carotex SM 4/3 and sorbitol.

Particle size analysis
Particles' size distribution was done using laser light scattering method with Mastersizer 3000 Malvern Instruments equipped with Hydrosight. Measurements were done at a room temperature. Samples were diluted with distilled water. Obscuration level was kept between 3 and 8%. Measurements were performed under moderate stirring (1400 rpm). Optical parameters chosen for the investigated system were as follows: absorption factor 0.001, dispersant's refractive index 1.33, sample's refractive index 1.458. Measurement mode was adjusted for spherical particles.

Fat thermal profile examination
In order to examine crystallization and melting behavior of the samples, Differential Scanning Calorimetry (DSC Mettler Toledo) was used. Measurements were performed after system's calibration on indium (Mettler Toledo, ME – 119442). For the examination, the samples (about 10 mg) were weighted in aluminum pans and sealed, leaving micro pinhole in the lid. The reference sample was an empty pan. Measurement mode was set to be as follows:

heating up to 65°C (heating rate: 5°C/ min), holding time 5 min, cooling from 65°C to -65°C (cooling rate -5°C/ min), holding time 5 min, heating from -65°C to 65°C (heating rate 5°C/min). Heating prior to cooling was needed in order to erase thermal memory of the sample.

Viscosity measurement
Viscosity was measured using Brookfield DV III Ultra rheometer with RV3 or RV4 spindle depending on thickness of the sample. Viscosity assessment was done under constant shear rate 120 rpm, 30 measuring steps.

pH
pH was measured using Mettler Toledo Seven Multi pH-meter. Calibration was performed using two buffers (pH 4 and pH 7). Before each measurement, accuracy of pH reading was checked using buffer pH 5.

Density
Density measurement was preceded by conditioning samples at 20°C for 24h. Measurement itself was done using aerometer laboratory kit 801/16/POIG.

Zeta Potential
Zeta potential was measured using dynamic light scattering method. Measuring device was Zetasizer ZS (Malvern Instruments).

The samples required dilution down to 0.01% with distilled water prior to examination, which was dictated by optical requirements of the method. Introduced parameters' values (viscosity and dielectric constant) were equal to those of water. Electrophoretic mobility was converted into zeta potential using the Smoluchowski equation.

Accelerated stability test
Accelerated stability test was performed by subjecting the system to centrifugal force. NIZO procedure was used [1]. The NIZO procedure allows to examine homogeneity of the sample before and after centrifugation (350g, 40°C).
Equation (1)

$$NIZO = \frac{\text{fat content in a lower (20 cm3) fraction of a homogenization pippete after centrifugation}}{\text{fat content in a starting material}} \cdot 100\%$$

Whipping properties
Whipping was done with Braun Multiquick 450 Wat MR 4050 HC mixer with a beater of 6 cm diameter, using lower power mode. The conditioning was done at 4°C and 10°C for 24 hours. The whipping time was examined visually after reaching the biggest volume expansion and appropriate system's consistency. Calculation of the difference between the volume of the sample before and after whipping allowed to determine the amount of incorporated air.

Properties of whipped cream
Whipped cream (foam) was examined for its texture (firmness and stickiness factor), drainage and freeze-thaw stability.

Texture was measured with Texture analyzer TA.XT Plus (Stable Micro Systems) exploiting PS1 element. Before the analysis, the whipped cream was held for at least 5 hours under appropriate cooling conditions (4°C or 10°C) to regain storing temperature. Measurement mode was as follows: distance between the measuring ball PS1 and the surface of whipped material 18 mm, force 0.05 N, measuring speed 1 mm/s.

Drainage stability was examined right after whipping. About 50 g of the foam was left for an hour on a sieve of 1,25 mm mesh at a room temperature. After that time, the leaked serum was weighted and drainage was calculated as a fraction of serum leaked divided by mass of the foam.

Freeze-thaw stability examination comprised of whipping the system and its immediate freezing at -20°C. The foam was kept in cups under this conditions overnight. On the next day, the cups with the foam were put into chamber at 20°C (up-side-down). When the thawing started cups were removed and the sample was left at 20°C for additional 2 hours. After this time, the leakage was measured and freeze thaw stability was calculated as a mass of leaked serum divided by a mass of foam in the cup.

Statistical analysis
Statistical analysis was performed using Statistica 13 and Excel for Office 365 MSO. Measurements were performed using completely randomized model. Significance level was assumed to be $\alpha = 0.05$, unless stated otherwise.

Results were characterized with use of descriptive analysis. Within appropriate groups normal distribution was analyzed with Shapiro Wilk Test and then equality of variances was checked with Levene's Test. Depending on the verdict, parametric analysis of variance (ANOVA/ Main Effects ANOVA) or non-parametric (U-Mann Whitney, separately for material and temperature groups) analysis of variance was performed.

Results and Discussion
Particle size analysis
Results of particles' size analysis are presented in Table 1. Investigated parameters with the exception of vol. below 100 μm exhibited normal distribution. Variances met requirement of equality in case of: Uniformity, D_{32}, D_{53}, $Dv(10)$, as well as $Dv(50)$. Results of ANOVA performed with appropriate tests are presented in Table 2.

The investigated whipping cream (Figure 1, WC) was a polydisperse system, consisting of 4 classes of droplets sizes (0.137 μm – 0.818 μm; 0.929 μm – 10.508 μm; 11.939 μm – 55.239 μm; 62.761 μm – 255.584 μm) (Figure 1). Sauter mean diameter (mean diameter of spheres of the same surface as measured particles, D_{32} for examined whipping cream was equal to 2.7 μm (Table 1). Most dairy type whipable emulsions should have an average particle size between 0.5 μm and 1.0 μm [2], which is far less than in the examined material. What is more, the average particle size was higher than a terminal diameter used for microscopic evaluation

of homogenization efficiency [3], which in the standard is defined as 2 µm. This suggests that the investigated emulsion might not be stable during the long-term storage and the whipping properties might be affected as well.

	Variable	$\bar{x}$	min	max	s	CV [%]
Whipping cream	Uniformity	5.87	5.54	6.16	0.31	5.33
	Spec. surf. area [m²/kg]	2229.33	2187.00	2275.00	44.09	1.98
	D_{32} [µm]	2.71	2.65	2.76	0.06	2.03
	D_{43} [µm]	30.87	29.60	32.90	1.78	5.76
	D_{53} [µm]	55.10	52.90	57.10	2.11	3.82
	Dv(10) [µm]	1.35	1.33	1.36	0.02	1.13
	Dv(50) [µm]	4.84	4.50	5.13	0.32	6.58
	Dv(90) [µm]	109.67	105.00	112.00	4.04	3.69
	Vol. below 100 µm [%]	87.77	87.18	88.93	1.00	1.14
Analogue	Uniformity	1.34	1.32	1.35	0.01	1.06
	Spec. surf. Area [m²/kg]	36506.67	35940.00	36900.00	502.92	1.38
	D_{32} [µm]	0.17	0.16	0.17	0.00	1.60
	D_{43} [µm]	3.99	3.91	4.06	0.08	1.89
	D_{53} [µm]	6.04	5.88	6.16	0.14	2.37
	Dv(10) [µm]	0.05	0.05	0.05	0.00	1.82
	Dv(50) [µm]	2.59	2.55	2.65	0.05	2.04
	Dv(90) [µm]	10.43	10.20	10.60	0.21	2.00
	Vol. below 100 µm [%]	100.00	100.00	100.00	0.00	0.00

Table 1: Results of particles size distribution analysis.

Symbols explanation:

- Uniformity – a measure of absolute deviation from median [22]:

$$Uniformity = \frac{\sum v_i |d(v,0.5) - d_i|}{d(v,0.5) \sum v_i}$$ Equation (2)

where

d(v, 0.5) – median size of the distribution, d_i – mean diameter of class i, v_i – size class i

- Spec. surf. area– surface area of particles divided by mass [22]:

$$S_e = \frac{6 \sum \frac{V_i}{d_i}}{\rho \sum V_i} = \frac{6}{\rho D_{32}}$$ Equation (3)

where

V_i – relative volume in class i, d_i - mean diameter of class i, ρ – density, D_{32} – Sauter mean diameter

- D_{32} – surface weighted mean diameter (Sauter diameter) [23]

$$D_{32} = \frac{\sum_1^n d_i^3 v_i}{\sum_1^n d_i^2 v_i}$$ Equation (4)

where

d_i – mean diameter of class i, v_i – size class i

- D_{43} – volume weighted mean diameter [23],

$$D_{43} = \frac{\sum_1^n d_i^4 v_i}{\sum_1^n d v_i}$$ Equation (5)

where

d_i – mean diameter of class i, v_i – size class i

- D_{53} – size parameter characterized by Walstra as H [1]
- Dv(10), Dv(50), Dv(90) – percentage of particles at respective cut-off levels (10%, 50%, 90%) [22],
- Vol. below 100 (µm) – percentage of particles smaller than 100µm [22].

	Uniformity	Spec. surf. area [m²/kg]	D_{32} [µm]	D_{43} [µm]	D_{53} [µm]	Dv(10) [µm]	Dv(50) [µm]	Dv(90) [µm]	Vol below 100 µm [%]
Material	**	**	**	ns	**	**	**	ns	ns

Table 2: Results of ANOVA: particles' size distribution.

where:

**: p≤ 0.01; ns: not significant.

As far as stability of the cream is concerned, two main phenomena have to be taken into account: creaming and coalescence. According to the Stokes law, creaming rate is proportional to the square diameter of a droplet. Hence, the bigger are the droplets, the more rapid is the process [4]. On the other hand, coalescence may result from insufficient fat globules stabilization [5]. One can consider solving these problems by homogenization in case of creaming, or by addition of stabilizers, in case of insufficient electric stabilization of fat globules. However, whipping cream subjected to high homogenization pressures, loses its whipping properties. Thus, it is suggested to use two stage homogenizations with following lower pressures: I stage 3MPa, II stage 1MPa [6]. On the other hand, addition of stabilizers may cause depletion attraction which eventually leads to phase separation. To avoid this phenomenon, it is advised for particles of additives to exceed size of 0.65 µm. Then the stabilizer remains mixed with the oil droplets, forming a stable network [5].

The examined whipping cream analogue (Figure 1 WCA) had 3 classes of droplets (0.011 µm – 0.201µm; 0.228 µm – 1.759 µm; 1.999 µm – 25.680 µm), which makes it more homogeneous than the investigated whipping cream. The droplets of this emulsion were substantially smaller as well. Their Sauter mean diameter was 0.17 µm (fulfilling restriction of droplets size [2]. What follows, specific surface area of the whipping cream analogue was 16.4 times higher than that of the whipping cream. All this suggests that the whipping cream analogue should be more stable.
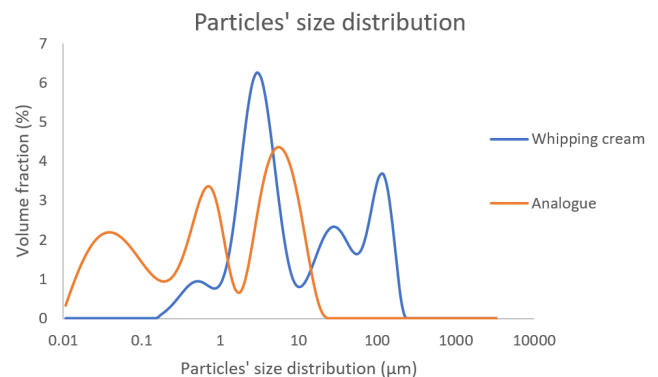

Figure 1: Diagram of particles' size distribution: WC – whipping cream, WCA – whipping cream analogue.

Whipping cream analogue owes its finer droplets due to:
- Higher homogenization pressures [7,8],
- Stabilizers addition, that facilitated emulsification,
- Lower fat content [7].

Thermal profile

Thermal profile of milk fat resembles that in the diagrams obtained by Mulder [9]. Two crystallization (Figure 2) and two melting (Figure 3) peaks can be observed. Each of them is assigned to a group of different triglycerides' classes. Crystallization of the investigated milk fat began at 16.5°C and ended at 2.78°C. It exhibited two crystals' fractions, the first one was formed in a temperature range of 16.5°C – 14.29°C and the second one between 12.51°C and 2.78°C. Melting started at 11.19°C and ended around 36.27°C. The first fraction melted at temperature range 11.19 – 18.85°C, while the second one started to melt at 28.29°C and ended at 36.27°C.
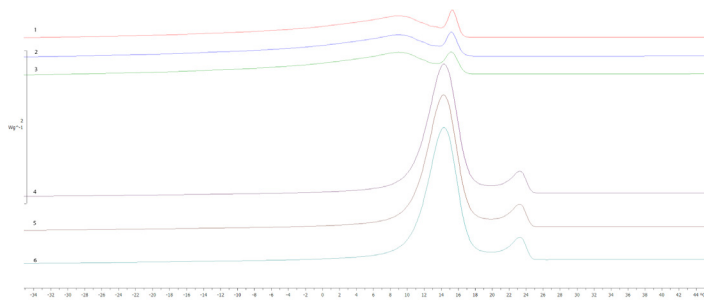

Figure 2: Crystallization profile: 1, 2, 3 – milk fat, 4, 5, 6 – vegetable fat (Akotop).
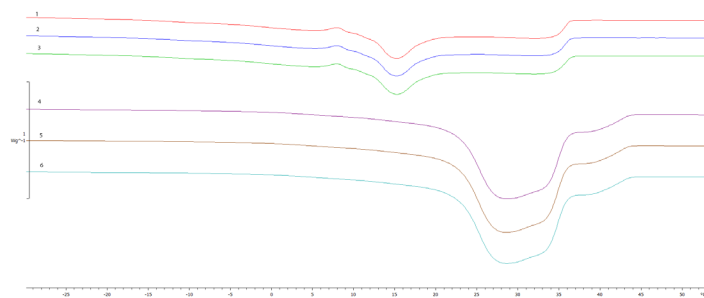

Figure 3: Melting profile: 1, 2, 3 - milk fat, 4, 5, 6 - vegetable fat (Akotop).

In the experiment two melting peaks have been found, however, three peaks should be present corresponding to fractions of low, middle and high melting triglycerides [10,11]. Probably the third peak would have emerged on the readings if the cooling/heating rates were lower [11-13] or it was not registered due to other (overlapping) thermal changes [11]. Fractionation of fat into classes that crystallize/melt at different temperatures results from different composition of fatty acids incorporated into triacylglycerol – for example: the longer carbon chain, the higher is its crystallization temperature.

Since milk fat is a mixture of various triacylglycerols with identified about 400 fatty acids' types, it has a wide melting temperature range: from -40°C to 40°C. Nevertheless, it has been proven that the highest share of milk fat melts between 10°C and 20°C [6]. This seems to be convergent with results depicted in the Figure 3, where the biggest melting peak fits within 11.19°C and 18.85°C (average values from all repetitions).

Akotop exhibited two crystallization (Figure 2) and two melting

(Figure 3) peaks as well. Crystallization took place at temperatures between 24.62°C and 10.84°C. First crystallization peak began at 24.62°C and ended at 21.52°C. The second one started at 17.26°C and ended at 10.85°C. Melting, on the other hand, started at temperature around 23.14°C and ended about 43.81°C. First melting peak was situated at temperatures between 23.14°C and 36.39°C, the second one between 38.22°C and 43.81°C.

One can consider temperature 20°C as a temperature significant for milk fat, since it was stated before that at this temperature most of the fat crystals are melted [6]. Under the same conditions Akotop did not even start to melt. What is more, crystallization peaks of Akotop were higher and narrower than that of milk fat, which suggests higher intensity of a thermal change.

Physical properties

Results of physical properties analysis are presented in Table 3. Investigated parameters with the exception of Z exhibited normal distribution. Variances met requirement of equality in case of: η^4, ρ^{20}, pH as well as Homog. Eff. Results of ANOVA performed with appropriate tests are presented in Table 4. Physical properties are closely related to the systems' structure, thus they should be considered together.

Viscosity of the analogue measured at 4°C was substantially higher than that of the whipping cream. It is possible that there were more fat crystals in the examined whipping analogue than in case of the whipping cream since crystallization of Akotop began earlier (at a higher temperature) than in case of the investigated milk fat (Figure 2). What is more, crystallization of the vegetable fat in the analogue was more intensive, thus it might had affected ability to control thermization process. It seems to be convergent with a fact that increase in viscosity was higher for the analogue (75%) than for the whipping cream (46%), during temperature decrease from 10 to 4°C. The examined analogue was also denser than the whipping cream.

As far as pH is concerned, it was the same for the both examined samples, and corresponded to a regular creams pH. Zeta potential of both systems was similar too. Its value was lower than -25mV, which suggests that they should be electrically stable [14].

Homogenization efficiency measured with NIZO procedure was significantly higher for analogue than for the whipping cream. This was because the analogue:
- was subjected to higher homogenization pressures [15],
- contained stabilizers [16],
- had higher density, thus it was more difficult for fat droplets to move within continuous system [16].

Whipping properties

Analyzed parameters of whipping, as well as the whipped creams properties are presented in Table 5. Investigated parameters with the exception of Vair at 4°C and twhipping at 10°C exhibited normal distribution. Variances analyzed for main effects of temperature and material met requirement of equality in case of: Vair, S*, as

well as F*. Results of ANOVA performed with appropriate tests are presented in Table 6.

Although not significantly different, it seems that whipping time was shorter when higher storing temperatures had been used. This stands in agreement with findings of Ihara et al. [17]. Though the analogue and the whipping cream had similar whipping times when kept at 10°C, lowering it down to 4°C, caused extension of the process – especially in case of the analogue.

At 4°C, the analogue's whipping time extended more than 3 times as compared to the whipping time at 10°C. This corresponds to previously mentioned, rapid increase in the analogue's viscosity. What is more, a lowering of temperature caused highly significant increase in air incorporation. One can draw a parallel between stabilization of air trapped within the system and increase of solid fat fraction, because fat surrounds and stabilizes air bubbles [18]. This explains higher volume of incorporated air both for materials stored at lower temperature, and in case of whipping the analogue, due to thermal behavior of Akotop (crystallization and melting shifted towards higher temperatures).

What is more, the analogue was enriched with buttermilk powder and stabilizers that play a significant role in whipping properties enhancement [18]. Stabilizers addition is thought to be a critical technological step. According to Krog [19], it should fit within a range between 1 and 2% of a total formula. Krog states that there is no other way than to establish precise concentration during technological trials [19]. Otherwise, too low addition may result in a poor whipability, whereas too high concentration (which may had happened in this case) increases the viscosity too much due to fat globule agglomeration. Higher viscosity (η^4) is evident in a liquid form, where globule agglomeration is developed during storage and transportation of the liquid cream (Tables 3 and 4), as well as firmness increase in a whipped cream analogue (F*, both temperatures), where agglomeration occurs as a consequence of whipping (Tables 5 and 6).

Material	Variable	$\bar{x}$	min	max	s	CV [%]
Whipping cream	η^4 [Pa·s]	0.1522	0.1492	0.1558	3.364	2.210
	η^{10} [Pa·s]	0.0705	0.0700	0.0708	0.427	0.606
	$\rho 20$ [g/m³]	0.995	0.995	0.996	0.001	0.058
	pH	6.69	6.68	6.70	0.01	0.149
	Z [mV]	-38.33	-40.40	-36.90	1.83	-4.78
	Homog. Eff. [%]	86.63	86.53	86.73	0.10	0.12
Analogue	η^4 [Pa·s]	1.1294	1.1133	1.1433	15.123	1.339
	η^{10} [Pa·s]	0.8467	0.8300	0.8717	22.050	2.604
	$\rho 20$ [g/m³]	1.027	1.026	1.027	0.001	0.056
	pH	6.71	6.70	6.72	0.01	0.149
	Z [mV]	-35.30	-35.50	-34.90	0.35	-0.98
	Homog. Eff. [%]	99.94	99.91	99.97	0.03	0.03

Table 3: Physical properties.
Symbols explanation: η: viscosity, Pa·s; ρ: density, g/m³; Z: zeta potential, mV; Homog. Eff.: homogenization efficiency, %. indexes: 10, 4, 20 – temperature, ˚C.

	η^4 [Pa·s]	η^{10} [Pa·s]	ρ^{20} [Pa·s]	pH	Z [mV]	Homog. Eff. [%]
Material	**	ns	**	ns	ns	**

Table 4: Results of ANOVA: physical properties.
where: **: p≤ 0.01, ns: not significant.

Material	Temp. [˚C]	Variable	$\bar{x}$	Min	Max	s	CV[%]
Whipping cream/ whipped cream*	4	Vair [mL]	203.333	200.000	210.000	5.774	2.840
		twhipping [s]	88.333	85.000	92.000	3.512	3.976
		S* [N]	-0.759	-0.816	-0.670	0.058	-7.628
		F* [N]	1.269	1.252	1.280	0.015	1.207
		Drainage* [%]	0.000	0.000	0.000	0.000	0.000
		FT* [%]	0.000	0.000	0.000	0.000	0.000
	10	Vair [mL]	113.333	100.000	125.000	12.583	11.103
		twhipping [s]	63.333	63.000	64.000	0.577	0.911
		S*[N]	-0.975	-1.014	-0.922	0.047	-4.860
		F* [N]	1.420	1.326	1.527	0.101	7.117
		Drainage* [%]	1.297	0.300	1.890	0.868	66.924
		FT* [%]	0.000	0.000	0.000	0.000	0.000
Whipping cream analogue/ whipped cream an-alogue*	4	Vair [mL]	236.667	230.000	250.000	11.547	4.879
		twhipping [s]	173.333	165.000	180.000	7.638	4.407
		S*[N]	-1.547	-1.643	-1.468	0.089	-5.751
		F* [N]	2.566	2.436	2.641	0.113	4.398
		Drainage* [%]	0.000	0.000	0.000	0.000	0.000
		FT* [%]	0.000	0.000	0.000	0.000	0.000
	10	Vair [mL]	130.000	130.000	130.000	0.000	0.000
		twhipping [s]	56.333	55.000	57.000	1.155	2.050
		S*[N]	-1.816	-2.056	-1.685	0.208	-11.449
		F* [N]	2.742	2.515	2.880	0.198	7.220
		Drainage* [%]	0.550	0.210	0.900	0.345	62.727
		FT* [%]	0.000	0.000	0.000	0.000	0.000

Table 5: Whipping properties, properties of whipped creams.
Symbols explanation:
η: viscosity, Pa·s; Vair: volume of incorporated air, mL twhipping: whipping time, s; S: stickiness factor, N, F: firmness factor, N, Drainage: drainage stability, %; FT – freeze thaw stability, %.

	Vair [ml]	twhipping [s]	S*	F*	Drainage	FT*
Material	**	ns	**	**	ns	ns
Temp	ns	ns	**	**	ns	ns

Table 6: Results of ANOVA: whipping properties and whipped creams properties.

where: **: $p \leq 0.01$, ns: not significant.

As far as the fat is concerned, Dickinson, Murray, & Allen [20] performed an experiment where they compared rheological properties of whipped creams which had either only liquid, or only solid dispersed phase. They reached a conclusion that solid state of fat, causes whipped cream to be more rigid and brittle. This seems to be convergent with results obtained in this experiment, taking into account that a whipped cream analogue (which had higher content of fat in a solid state because its crystallization onset was at higher temperature) occurred to be more rigid than a whipped cream counterpart (Tables 5 and 6).

However, in the experiment it also turned out that both materials where more firm at higher temperature (Tables 5 and 6). This suggests that other factors than solid fat content should also be considered. Perhaps it was related to elevation of temperature while whipping and subsequent cooling to maintain original conditions. Such procedure induced tempering of foam, which influenced its texture. Tempering of whipped cream was studied by other scientists, including Nguyen, Duong, & Vu [21]. Nguyen et al. [21] investigated influence of different tempering temperatures (20, 30, 40°C) and subsequent cooling rate (fast/slow) on properties of whipped cream. They proved that there were significant differences in texture between examined samples (hardness was higher for samples tempered at 30°C than at 20°C and all fast-cooled samples had higher hardness compared to slow cooled counterparts). To prove the hypothesis that tempering was responsible for higher hardness in samples at higher storage temperature further experiments with temperature control during whipping would be necessary.

Stickiness is a measure of restraining forces of the material (otherwise called a force of adhesion). It is related to inner viscosity of the analyzed sample. In the conducted experiment stickiness was much higher at 10 than at 4°C irrespectively of the investigated material. What is more, the whipped analogue exhibited higher stickiness than the whipped cream (Tables 5 and 6).

In both cases, findings showed that decreased storing temperature (4°C) is favorable and completely prevents serum leakage. At 10°C, the examined materials also exhibited quite good drainage stability with serum loss max 0.03% (whipped analogue). These results are similar to findings of Lundin [18] who stands that it is favorable for foams stability if the solid fat content during storage is high.

During freeze-thaw leakage test, only one sample (whipped cream) exhibited leakage (Table 5). However, during two other repetitions there were no leakage in every sample. Thus, it can be assumed that both whipped systems are stable in respect to freezing and thawing procedure.

Conclusion
The whipping cream analogue, as well as whipped cream analogue proved to have characteristics superior to the whipping cream counterpart. Partial replacement of milk fat with vegetable fat, as well as addition of stabilizers, permitted employment of high-pressure homogenization, and in turn obtaining more uniform emulsion with smaller particles. Different thermal properties of vegetable fat favored air incorporation. However, whipped cream analogue might not be acceptable for confectionery due to high firmness of created foam.

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