



Journal of Food Science and Technology (Iran)

Homepage: www.fsct.modares.ir

Scientific Research

Preparation of Structured Low-Saturated Water-in-Oil (W/O) Emulsion Based on Canola Oil and Lipidic Oleogelators as Butter Substitute

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ARTICLE INFO

Article History:

Received: 2024/9/7

Accepted: 2025/1/22

Keywords:

Canola oil,

Emulsion,

Palm kernel,

Glycerol,

Sorbitan,

Oleogel

DOI: 10.22034/FSCT.22.162.199.

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ABSTRACT

This study investigates the production and evaluation of low-saturated, trans-fat-free water-in-oil (W/O) structured emulsions based on canola oil and lipidic oleogelators as a butter substitute. This research aims to create emulsions by utilizing canola oil, which is low in saturated fatty acids and high in unsaturated fatty acids such as linolenic and oleic acid, that are nutritionally and functionally comparable to or superior to commercial butter. In this study, palm kernel stearin used as the hard component, along with two types of emulsifiers: glycerol monostearate and sorbitan monostearate. Their properties were evaluated, including fatty acid composition, thermal stability, physical stability, and textural and sensory characteristics. The results showed that increasing the percentage of palm kernel stearin led to increasing for hardness and thermal stability of emulsions, while the choice of emulsifier type had a significant effect on physical and oxidative stability. Additionally, samples containing sorbitan monostearate showed higher physical stability compared to those with glycerol monostearate. The findings from this study suggests that the produced structured emulsions could serve as a suitable substitute for butter in the food applications without compromising the sensory and functional quality of the final product. This research highlights the high potential of modified vegetable oils for producing healthy and high-quality food products.

1-Introduction

Butter is one of the dairy products that has various uses. However, in the field of butter production, two issues are very important: 1) the existence of limitations in its production and packaging and 2) the presence of a large amount of saturated fatty acids in it. [2,1]. Therefore, due to the fact that cheap resources with suitable nutritional value for the production of substitutes for butter are abundantly available, it is necessary to pay more attention to the production of substitutes for butter. Usually, margarine (vegetable butter) - in its preparation, vegetable sources are used instead of milk fat - replaces butter. [4,3]. In the past decades, partially hydrogenated oils with a higher amount of trans fatty acids (more than 20%) have been used in the preparation and production of margarines. [5]. Today, according to the existing standards, the maximum allowed trans fatty acids in margarine for home consumption is 1-2% and in industrial confectionery margarine is 5%. [6,3]. In addition, these products can contain a maximum of 35% (in the case of spreads), 37% (in the case of cooking margarine), 48% (in the case of table margarine) or 65% (in the case of confectionery margarine) of saturated fatty acids. It is clear that although appropriate steps have been taken to remove trans fatty acids from oil and fat products, these products still contain more saturated fatty acids. Therefore, reducing the amount of saturated fatty acids is still one of the challenges in the field of margarine production [6,5].

In the past, various methods have been used to change the physical characteristics of oils/fats and make them suitable for different uses, including hydrogenation, interesterification.¹, component by component, mixing and

oleogelation/structuring. Among the above methods, oleogelation/structuring is a newer method that allows changing the state of oil from liquid to solid with minimal (or even no) manipulation of the fatty acid composition of the base oil. Oleogelation is actually a method in which liquid oils are trapped in a network created by oleogelators and finally a gel-like structure is created. [8,7]. In general, structured systems can be divided into two groups: single-phase systems - which contain only an oily phase and are known as oleogel or structured oil, and two-phase systems - which contain oily and aqueous phases and are known as structured emulsions. Oil-water biphasic systems can be broadly classified into three main groups: aqueous continuous-phase emulsions structured with biopolymers (such as proteins and polysaccharides) that act as both emulsifiers and thickening/gelling agents; Emulsions with a very thick aqueous continuous phase in which structuring occurs as a result of the approach of very large dispersed droplets; and emulsions with a continuous oily phase structured by a crystalline network of fat particles [9]. Among these three groups, products based on oil-based emulsions can benefit the most from oil structuring methods, because solid fat plays a significant role in the texture of these products.

Various researches have been conducted on the use of oleogel in the preparation of butter substitutes. Hwang et al. (2013) They prepared margarine based on wax and soy oil; The results of this research have shown that the type of oleogelator is effective in creating the properties of margarine; So that the samples containing sunflower wax had the highest hardness compared to other samples [10]. In the research conducted by Yılmaz and Ögütçü

1- Interesterification

(2015), using two types of wax and also two types of oil sources, butter substitute products were prepared; The results have shown that both prepared groups had similar results, especially in the field of sensory properties, compared to commercial butter and margarine samples. [11]. In the research conducted by Gaudino et al. (2019) for the use of two types of gelators in the preparation of semi-solid products, the researchers came to the conclusion that the interaction of two types of hydrogelators (soy lecithin and stearic acid) can lead to more hardness in the sample. [12]. Silva et al. (2021) prepared margarine based on oleogels containing different fat percentages (35 and 60%), the results showed that the samples containing 65% fat had a higher hardness, lower spreadability and more thermal stability than the control sample (60% fat margarine). [13]. In the research conducted by Naeli et al. (2022) in the field of preparing low-saturated shortenings based on oleogel using two types of oleogelators (ethyl cellulose and hydroxypropyl methyl cellulose), sunflower oil and palm stearin, by using the response surface optimization method, they succeeded in reducing the percentage of saturated fatty acids to 15.19% in shortening, which is much lower than the saturation of commercial samples. (58.47-65.87 percent). However, although some properties of the unsaturated shortening (melting point, hardness and rheological) were slightly higher than the control samples, the solid fat content² And also their oxidative stability was less [14].

This research was conducted with the aim of designing a low-saturated structured emulsion of canola oil as a base oil for making emulsion. Among vegetable oils, canola oil has significant characteristics, such as the presence of a low amount of saturated fatty acids (less than 12%), a higher amount of linolenic acid (about 8%)

and a higher amount of oleic acid (60%), which indicates its nutritional and consumption value. In addition, canola oil is reasonably priced and abundantly available [15,4]. Therefore, according to the mentioned cases, canola oil is a suitable source for making margarine. In this article, also the effect of formulation variables on the characteristics of structured emulsion, the effect of the amount of hard component³ (palm kernel stearin), the type of emulsifier and the oil phase ratio have been investigated.

2- Materials and methods

1-2- Materials

Refined canola oil and commercial butter samples were purchased from a store in Sari, Iran. Palm kernel stearin (PKS) was obtained from PT Wilmar, Indonesia. Glycerol monostearate emulsifier was obtained from Kia Shimi Yasouj Cosmetics Company, Iran. Sorbitan monostearate emulsifier was obtained from Danesh Banyan Products and Creative Industries, Vitfa, Iran.

2-2- Research plan

The emulsions prepared in this research were structured water-in-oil emulsions. The components used in this type of emulsions include: 1) canola oil (base oil), 2) Palm kernel stearin (hard component), 3) glycerol monostearate and sorbitan monostearate (emulsifier) and 4) water (the role of the aqueous phase). In this type of emulsion, a fixed percentage of 7% emulsifier and two levels of 7 and 10% Palm kernel stearin was used. In addition, the percentage of the total oily phase (canola oil+ Palm kernel stearin) was determined at 3 levels of 60, 70 and 80%. In this research, the complete factorial design was used to examine the individual effect of each factor alone, the double effect

2- Solid fat content (SFC)

3- Hardstock

and the overall effect of the factors for each type of test.

2-3-Preparation of a structured water-in-oil (W/O) emulsion sample

The preparation of structured water-in-oil emulsions was performed using the method presented by Garcia-Ortega (2021). [16]. The samples were weighed with an electric scale. First, the oil phase was weighed and then heated to 70°C using a mixer heater. Of course, at the same time as the entire oily phase, the aqueous phase was also subjected to the same thermal conditions separately. The emulsifier was added to the total oil phase in the desired fixed amount (7 grams) and was placed under the temperature of 300 rpm for 15 minutes under the temperature of 70 degrees Celsius. In the following, after fulfilling the mentioned conditions, 40% of the total oil phase - emulsifier was separated from the container, the water phase was added to it and it was placed under the mentioned temperature-stirring conditions. Of course, 60% of the total oily phase - emulsifier was kept. Next, mix 40% of the total oily phase – Emulsifier + aqueous phase was placed in a suitable cylindrical container for homogenization with an Ultrathorax device (Heidolph Instruments GmbH & Co., KG, Germany). The power used by the ultrathorax for homogenization was 20,000 rpm for 30 seconds. After homogenization, 60% of the total oil-emulsifier phase mixture was added to the homogenized sample, and it was stirred using a digital stirrer in an ice-water bath. The stirring conditions in this part were 190 rpm for 10 minutes to reduce the temperature of the sample to 20 degrees Celsius. After reaching a temperature of 20 °C (Completing the crystallization of the sample), the sample was removed from the water and ice bath, and then the sample was subjected to the mentioned stirring conditions (rpm190 for 10 minutes).

4-Shimadzu

Finally, the container containing the sample was kept in the freezer until the relevant tests were performed.

2-4- Test methods of structured emulsions of water in oil (W/O)

1-4-2-Analysis of fatty acid composition of structured water-in-oil (W/O) emulsions

In order to check the composition of fatty acids, a gas chromatography device was used according to the AOCS standard with numbers Ce 2-66 (1996) and Ce 1-91 (1996). [17]. Gas chromatography device (Shimadzu⁴, 2014 ECD model, Japan) was equipped with a column with certain specifications (30 m × 0.25 mm ID × 0.25 µm) and a capillary type called RTX-WAX. The sample was injected in the amount of 1 microliter with a split ratio of 150. The temperature of the injector part °C250 and detector temperature at °C 280 was set. Nitrogen was injected as a carrier gas at the rate of 1.26 ml/min. Temperature program for sample analysis includes: start from temperature °C155 and keeping at said temperature for 3 minutes; Increase the temperature up to °C220 with rates °20 C/min and finally kept at the final temperature for 60 minutes. Finally, the device software reported the peaks and percentages of fatty acids.

2-4-2-Determining the thermal properties of structured water-in-oil emulsions (W/O)

To check the thermal analysis of the samples by the differential scanning calorimetry method⁵ (model 400, SANAF Electronic Industries, Tehran, Iran) was used. 15-20 mg of the sample was placed in the container of the weighing machine and in the chamber of the machine. Next, the samples were analyzed in the

5- Differential scanning calorimetry (DSC)

temperature range of 25-95°C with a heating/cooling rate of 10°C/min. Finally, the thermal characteristics as 4 T characteristics T_{onset} , T_{peak} , T_{offset} and ΔH were reported [18]. Determination of sliding melting point was done using open capillary tube method and AOCS standard No. Cc 3-25 [17].

3-4-2- Textural and oxidative properties of structured water-in-oil emulsions (W/O)

1-3-4-2-Measuring the hardness of water-in-oil structured emulsions (W/O)

The texture of emulsions (hardness property) was measured using TA-XT2i texture tester (Stable Microsystems, Godalming, UK) and penetration force. [11]. The measurements were taken at ambient temperature (25°C) and the probe used was a glass type with specific dimensions (4×4×4 cm) was The probe speed of the device to penetrate the sample was 3 mm/s. The probe penetrated 23 mm into the sample and the speed of the probe separation was 10 mm/s. Finally, the maximum penetration force was considered as hardness (g force).

2-3-4-2-oxidative stability-oxytest⁶ Structured water-in-oil (W/O) emulsions

Oxidative stability was determined using the oxytest method according to the AOCS standard, No. Cd 12c-16 (1996) and the Oximeter device (Velp Scientifica, Usmate, Italy). [17]. 10 grams of the sample was placed in the container of the weighing machine and in the chamber of the machine. The samples were exposed to a temperature of 90 degrees Celsius and an oxygen pressure of 6 bar. induction period⁷ It was presented by the software of the device and reported as the amount of oxidative stability (in hours).

4-4-2-Physical stabilities of structured water-in-oil emulsions (W/O)

1-4-4-2-Centrifugation stability of structured water-in-oil emulsions (W/O)

A centrifuge (Hermle Laboratechnik, GmbH, type: Z 366, Germany) was used to check the centrifugation stability of the samples. In order to check the stability against the centrifuge, first, 5 grams of sample (W_A) was weighed inside a plastic tube with a specified volume (50 ml). Then the tubes containing the samples were subjected to specific centrifugation conditions (3600 rpm, 30 minutes and 25 °C). [19]. After the mentioned conditions, remove the separated phase part, weigh the remaining part of the sample (W_B) and finally the stability of centrifugation was determined based on the following equation (Equation 1).

$$CS \quad (\%) = (W_B / W_A) \times 100 \quad (1)$$

2-4-4-2-Oil drop of structured water-in-oil emulsions (W/O)

Filter paper weighing method was used to check the oil loss index [20]. 10 grams of each sample (W_s) separately on filter paper (Whatman grade 4) pre-weighed (W_{before}), was weighed. After 4 hours of storage at ambient temperature (25°C), the sample was separated from the filter paper and the filter paper was weighed (W_{after}). Based on the following equation (Equation 2), the amount of oil loss was calculated for each sample.

$$\text{Oil loss } (\%) = (W_{\text{after}} - W_{\text{before}}) / W_s \times 100 \% \quad (2)$$

3-4-4-2-Refrigeration stability of structured water-in-oil emulsions (W/O)

In order to check the refrigeration stability (saltification index), the method of storing the samples in refrigerated conditions (4 degrees Celsius) and the changes in the height of the samples in storage containers were used. [21]. In order to check the refrigerator stability, the samples were

6- Oxitest

7 -Induction period (IP)

placed in plastic tubes with a specific volume (15 ml), weighed at the rate of 10 grams, and then sealed with parafilm (Neenah, WI 54956, Bemis Flexible Packaging). The samples were stored in a refrigerator (4°C) and in a tube for 90 days. Refrigerative stability finally using the following equation (Equation 3) and according to S (Sodiumization index), CS (refrigerated stability), H (height of separated oil phase in the upper part of the pipe), H_0 (the initial height of the emulsion in the tube) was calculated.

$$S \text{ or } CS (\%) = (H/H_0) * 100 \quad (3)$$

5-4-2- Investigating sensory properties of structured water-in-oil emulsions (W/O)

The scoring method was used to check the sensory characteristics. 7 sensory characteristics of the investigation, the score of 0 was considered as the lowest and 10 as the highest. Sensory characteristics were carried out in ambient conditions (25°C) with the help of people with commercial butter samples, apple slices and a glass of water (to clean the sample). [11].

3-Statistical analysis

All treatments in this research were done in three replications. Investigating the effect of single, double and triple factors of this research was done using full factorial design and Minitab16 software (Minitab Inc., State College, PA, USA). The significance level was 95% (0.05) and the results were averaged $\pm$ Standard deviation was reported.

4-Results and discussion

1-3- Composition of fatty acids in structured water-in-oil emulsions (W/O)

Factors such as the type of oily base, the type of structuring/emulsifying agents, and

the amount of components used can affect the composition of fatty acids. [22,3]. According to Table 1, the highest degree of saturation was related to the sample containing 10% palm kernel stearin; While the highest amount of monounsaturations, polyunsaturations and total unsaturations is related to the sample containing 7% Palm kernel stearin. According to Table 1, the amount of trans fatty acids is the lowest for Palm kernel stearin (0.03 percent) and the highest amount was related to commercial butter (0.97 percent). Comparison of fatty acid composition of commercial butter samples and samples based on 7 and 10% Palm kernel stearin. It showed that the prepared samples had less saturation, more total unsaturation, and less trans fatty acids than the commercial butter sample (Table 1).

The use of vegetable oil sources with low saturation level, high level of unsaturation and at the right level (according to the desired type and amount of fatty acids) for the preparation of substitutes for Korean products are very important in terms of health and nutrition. [13]. The amount of saturated fatty acids in the samples presented in this research was much lower than the samples presented as 24% by Lumor et al. (2007) and also the range of 20.17-24.93% by Silva et al. [22 and 13].

Table 1 Fatty acid composition of canola oil (CO), palm kernel stearin (PKS), commercial butter (CB) and blends of CO and PKS

Fatty acids	CB	PKS	CO	WHAT: PKS (93:7)	WHAT: PKS (90:10)
C6:0	1.75±0.00	-	-	-	-
C8:0	1.10±0.01	1.88±0.00	-	0.13	0.19
C10:0	2.64±0.01	2.73±0.00	-	0.19	0.27
C12:0	3.38±0.01	54.33±0.00	-	3.80	5.43
C14:0	11.09±0.01	21.51±0.00	-	1.51	2.15
C14:1	0.14±0.00	-	-	-	-
C15:0	0.99±0.01	-	-	-	-
C15:1	0.19±0.00	-	-	-	-
C16:0	38.19±0.01	9.55±0.00	3.92±0.01	4.31	4.48
C16:1	1.68±0.00	-	-	-	-
C17:0	0.63±0.01	-	-	-	-
C17:1	0.20±0.00	-	-	-	-
C18:0	9.73±0.00	9.36±0.00	1.75±0.00	2.28	2.51
C18:1	24.74±0.02	0.60±0.00	56.71±0.00	52.78	51.10
C18:2	2.63±0.00	-	31.77±0.00	29.55	28.59
18:3	-	-	4.91±0.00	4.57	4.42
C22:0	-	-	0.29±0.01	0.27	0.26
SFA	69.43±0.13	99.37±0.01	5.96±0.00	12.50	15.30
jack	26.97±0.01	0.60±0.00	56.71±0.00	52.78	51.10
PUFA	2.63±0.00	-	36.68±0.00	34.11	33.01
DIE	29.60±0.00	0.60±0.00	93.39±0.00	86.89	84.11
TFA	0.97±0.00	0.03±0.00	0.65±0.00	0.61±0.00	0.60±0.00

Data are shown as means ± standard deviation of three replicates. SFA: sum of saturated fatty acids; MUFA: sum of monounsaturated fatty acids; PUFA: sum of polyunsaturated fatty acids; UFA: sum of unsaturated fatty acids; TFA: Trans fatty acids.

2-3-Thermal properties of structured water-in-oil emulsions (W/O)

1-2-3- thermal analysis of the samples - differential scanning calorimetry method of structured water-in-oil (W/O) emulsions

The results of thermal analysis are shown in Table 2. Statistical analysis of the data of T_{onset} and also T_{peak} It indicated the existence of a significant difference between the samples caused by the factors and their interaction (binary and overall) ($p < 0.05$). However, the statistical analysis of the data of T_{offset} It did not show any significant difference ($p > 0.05$). In terms of ΔH , the effect of some interactions (incl Palm kernel stearin x type of emulsifier; Palm kernel stearin × type of emulsifier × percentage of oily phase) was not significant ($p > 0.05$), while the effect of

other factors on interactions and the effect of single factors were significant ($p < 0.05$).

The lowest and highest amount of T_{onset} respectively as $^{\circ}C 20/19$ (sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with sorbitan monostearate) and $^{\circ}C 46/29$ (the sample contains 10 percent Palm kernel stearin, with the ratio of oil phase to water 80% to 20% and with sorbitan monostearate); The lowest and highest amount of T_{peak} respectively as $^{\circ}C 74/28$ (sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with sorbitan monostearate) and $^{\circ}C 17/36$ (the sample contains 10% Palm kernel stearin, with the ratio of oil to water phase 70 to 30% and with glycerol monostearate); The lowest and highest amount of T_{offset} respectively as $^{\circ}C 28/38$ (the sample contains 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with sorbitan

monostearate) and °C 26/41 (sample containing 10 percent Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with glycerol monostearate); The lowest amount of ΔH is 7.86 J/kg (the sample contains 7% Palm kernel stearin with an oil ratio of 60:40 and with glycerol monostearate and a sample containing 7% Palm kernel stearin with the ratio of oil to water phase 60 to 40% and with sorbitan monostearate) and the highest amount of ΔH of 9.68 J/kg (the sample containing 10% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with glycerol monostearate) was recorded (Table 2).

In other words, the results of thermal analysis showed that consumption Palm kernel stearin At the rate of 7%, the emulsifier sorbitan monostearate and the ratio of oil to water phase of 60 to 40% led to the creation of thermal properties in the minimum amount (Table 2). In contrast, consumption of 10 percent Palm kernel stearin, ratio of oil to water phase 80 to 20% and with glycerol monostearate, led to strengthening of thermal properties (Table 2). In terms of comparing the thermal properties of samples prepared with commercial butter, the results show that the thermal properties of emulsion samples were lower than commercial butter (Table 2). The comparison of thermal properties in terms of emulsifier generally showed that the respective results were close in terms of amount, although in some cases there were slight differences (Table 2).

The thermal properties of oleogels can be variable according to the type and amount of main components and especially

oleogelatory/emulsifying agents.] 25,24[. It has been reported that oleogelatory agents (including waxes) had different effects on thermal properties according to the type and percentage of use.] 26,24 [. It has been reported that the samples made with ethyl cellulose oleogelator had lower ΔH , but more thermal stability than the oleogel made with wax oleogelator.]27[. The degree of saturation of alternative fat/oil sources as well as structuring factors also affect the thermal properties of oleogels]13[. In the research conducted by Silva et al. (2021), they reported that samples with equal amounts of structuring factors had different thermal properties.]13[. Silva et al. (2021) also reported that if equal amounts of structuring agents were used, the margarine sample containing 60% oil phase compared to the sample containing 35% oil phase, had a characteristic T_{peak} It was less]13[.

Consuming more water in the samples can lead to the improvement of the solid structure in the sample and finally create melting resistance in the samples.]13[. Oleogels have a similar thermal behavior to Korean products]28[. Some oleogels had lower thermal properties, although they had a higher amount of aqueous phase]13[. In some cases, emulsifying agents have a great effect compared to oleogelatory agents in the occurrence of differences in the thermal properties of oleogel.]13[. It has been reported that the two characteristics of thermal and sensory analysis can be considered in the suitability of oleogels as substitutes for fatty products.]11[.

Table 2 Thermal characteristics of the structured W/O emulsion samples

Sample code	Thermal characteristics				
	T_{onset} (°C)	T_{peak} (°C)	T_{offset} (°C)	ΔH (J/kg)	JUNIOR HIGH SCHOOL (°C)
P7GO60	19.23±0.00	28.77±0.00	38.32±0.00	7.86±0.00	38.35±0.01

P7SO60	19.20±0.00	28.74±0.00	38.28±0.00	7.86±0.00	38.33±0.00
P7GO70	19.32±0.00	28.86±0.00	38.40±0.01	7.89±0.00	38.39±0.00
P7SO70	19.26±0.00	28.80±0.00	38.34±0.00	7.87±0.00	38.37±0.00
P7GO80	19.45±0.00	29.01±0.00	38.56±0.00	7.94±0.01	38.45±0.00
P7SO80	19.40±0.00	28.90±0.00	38.41±0.00	7.90±0.00	38.43±0.00
P10GO60	28.12±0.00	34.61±0.00	41.13±0.00	9.46±0.00	41.17±0.01
P10SO60	28.12±0.00	34.61±0.00	41.13±0.00	9.46±0.00	41.16±0.01
P10GO70	28.40±0.00	36.17±2.31	41.20±0.00	9.52±0.00	41.23±0.01
P10SO70	28.36±0.00	34.77±0.00	41.19±0.00	9.51±0.00	41.21±0.00
P10GO80	28.53±0.00	35.44±0.00	41.26±0.00	9.68±0.00	41.28±0.00
P10SO80	29.46±0.00	35.34±0.00	41.23±0.01	9.66±0.00	41.26±0.00
CB	36.64±0.00	49.53±0.00	60.42±0.00	166.82±0.00	35.89±0.00

Data are shown as means $\pm$ standard deviation of three replicates. T_{onset} = Initial temperature of melting; T_{peak} = Peak temperature; T_{offset} = Final temperature of melting; ΔH = Enthalpy of the peak; SMP = Slip melting point; PG/SO = Palm kernel stearin, Glycerol monostearate/Sorbitan monostearate, Oil ratio (P7&10% and O 60, 70&80%); CB = Commercial butter.

2-2-3-Sliding melting point of structured water-in-oil emulsions (W/O)

The results related to sliding melting point are shown in Table 2. In the statistical analysis related to the melting point, the results show that there is a significant effect ($p < 0.05$) for the factors (Palm kernel stearin, emulsifier type and oil phase ratio). The statistical analysis of the melting point also showed that their interaction (binary and overall) had no significant effect on the melting point ($p > 0.05$). The lowest and highest amount of sliding melting point in terms of the percentage of oily components (Palm kernel stearin - Canola oil), respectively $^{\circ}\text{C}$ 33/38 (sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with sorbitan monostearate) and $^{\circ}\text{C}$ 28/41 (sample containing 10% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with glycerol monostearate) (Table 2).

The sliding melting point in the samples prepared with the help of glycerol monostearate emulsifier is at the lowest level as $^{\circ}\text{C}$ 35/38 (the sample contains 7% Palm kernel stearin, the ratio of oil to water phase is 60 to 40% and with glycerol monostearate) and the highest amount as $^{\circ}\text{C}$ 28/41 (sample containing 10% Palm kernel

stearin, with the ratio of oil to water phase 80 to 20% and with glycerol monostearate) (Table 2). Also, the sliding melting point of samples made with sorbitan monostearate emulsifier is at the lowest level as $^{\circ}\text{C}$ 33/38 (sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with sorbitan monostearate) and the maximum amount as $^{\circ}\text{C}$ 26/41 (sample containing 10% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with sorbitan monostearate) (Table 2).

In the investigation of the sliding melting point according to the ratio of oil to aqueous phase, it was found that the samples containing the ratio of oil to water phase 60:40% had a lower sliding melting point compared to the sample of 80:20% (Table 2). According to Table 2, the sliding melting point of samples based on glycerol monostearate for both ratios Palm kernel stearin (7 and 10%) and also all three ratios of oily to water phase (60 to 40, 70 to 30 and 80 to 20%) were in a higher amount. The amount of sliding melting point depends on various factors, the reason for the difference between the results of the sliding melting point of the current research samples and commercial samples can be due to the type and amount of components

used in preparing the final samples. [29, 30, 31 and 32].

Higher melting point can be due to lower level of unsaturation and saturated fatty acids with longer carbon chain length [31]. Melting point is actually an important indicator in determining suitable products as substitutes for Korean products [29]. The melting point indicates the possibility of melting with the help of the heat of the mouth during consumption [31, 32]. The range of the standard melting point of spread margarine is 33-37 degrees Celsius and it begins to spread and melt at the temperature of the mouth when consumed without any mechanical work. [29, 30]. Bentayeb Ait Lounis et al. (2018) compared different types of Algerian margarine and found that they have different sliding melting points (range 35-46 degrees Celsius) based on type and consumption. [32].

3-3- Textural and oxidation properties Structured water-in-oil (W/O) emulsions

1-3-3- Texture hardness of structured water-in-oil emulsions (W/O)

The results related to hardness (textural property) are shown in Table 3. The results of the statistical analysis showed that the factors (Palm kernel stearin ; The type of emulsifier and the percentage of oily phase), as well as interactions (binary and total), had a significant effect on hardness ($p < 0.05$). Based on this, the results related to tissue hardness show that increasing the amount Palm kernel stearin (from 7 to 10 percent) has led to an increase in hardness. Hardness results generally showed that the lowest hardness is related to the sample containing 7% Palm kernel stearin, glycerol monostearate and the ratio of oily to water phase is 60 to 40% and the highest hardness is related to the sample containing 10% Palm kernel stearin, sorbitan monostearate and the ratio of oil to water phase was 80% to 20% (Table 3). The hardness results in terms of the effect of the type of emulsifier showed that the highest hardness in the

samples prepared from glycerol monostearate emulsifier is related to the ratio of the oily phase to the water phase of 60 to 40% and the sample containing 10% Palm kernel stearin was; If for the sorbitan monostearate emulsifier, the highest hardness is related to the ratio of the oil phase to the water phase of 80% to 20% and the sample containing 10% Palm kernel stearin was (Table 3). The structured emulsions prepared in the present study were different from commercial samples in terms of texture hardness (Table 3).

Texture hardness index is actually one of the important indicators in the field of acceptance of Korean products by consumers [33]. Based on past research, there is a textural difference in hardness between butter and margarine samples; Some margarines are harder than butter [10]. The texture hardness of oleogel samples can be similar to butter and margarine and even different [33]. The components of oleogels have different effects on the hardness of oleogel samples depending on the type and amount of components [33]. Bascuas et al. (2019) prepared a chocolate spread based on oleogel, they reported that if the spreads are prepared using a combination of coconut oil, olive oil and sunflower, they have more hardness. [33]. Also, the hardness of the oleogel samples based on coconut oil - olive oil was higher than the coconut oil - sunflower oil sample ($N_{23.168} > N_{71.140}$ in Newton). [33].

It has been reported that samples of replacement products based on oleogel based on a type of base oil/fat + replaced oil/fat (according to the replacement percentage and type of source) have a higher texture hardness. [33]. The samples with higher hardness in the preparation of chocolate spread based on oleogel conducted by Bascuas et al. (2019) were similar to the samples with higher hardness in the present study. [33]. Kupiec et al. (2020) prepared an oleogel containing

pumpkin seed oil and reported that the oleogels based on beeswax were weaker, while the samples based on carnauba wax had stronger viscoelastic properties, more oil retention and more stiffness. [34]. According to Table 3, there was a direct relationship between the increase in the components used (separate examination based on the type of emulsifier and the

increase in oily components) and the hardness index of the sample. In the research conducted by Dadalı and Elmacı (2019) in the study of the effect of fat and emulsifier on margarine, they found that increasing the ratio of the oily part in margarine leads to an increase in the hardness of the samples. [35].

Table 3 Physicochemical properties, physical stability and oxidative stability of structured W/O emulsion samples

Sample code	Textural properties-Hardness (g force)	Oxidation stability-Oxitest (h)	Physical Stabilities		
			CS (%)	OL (%)	RS (%)
P7GO60	59.96±0.15	1.12±0.00	100.00±0.00	0.91±0.01	0.00±0.00
P7SO60	84.02±0.09	4.23±0.00	100.00±0.00	2.03±0.06	0.00±0.00
P7GO70	38.03±0.06	8.29±0.00	100.00±0.00	1.04±0.13	0.00±0.00
P7SO70	130.86±0.41	11.04±0.00	98.80±0.01	1.22±0.08	4.37±0.00
P7GO80	35.10±0.10	12.30±0.00	100.00±0.00	2.44±0.04	0.00±0.00
P7SO80	153.01±0.08	13.17±0.00	100.00±0.00	2.68±0.04	0.00±0.00
P10GO60	84.70±0.01	3.15±0.00	100.00±0.00	0.93±0.06	0.00±0.00
P10SO60	100.99±0.00	5.32±0.00	100.00±0.00	2.12±0.02	2.50±0.10
P10GO70	53.50±0.00	11.58±0.00	100.00±0.00	1.12±0.11	0.00±0.00
P10SO70	158.06±0.05	12.05±0.00	100.00±0.00	1.15±0.01	3.75±0.01
P10GO80	49.80±0.00	12.31±0.06	100.00±0.00	2.10±0.11	0.00±0.00
P10SO80	185.02±0.59	15.18±0.00	98.00±1.00	2.65±0.05	5.00±1.00
CB	193.45±0.00	41.61±0.00	100.00±0.00	0.00±0.00	0.00±0.00

Data are shown as means ± standard deviation of three replicates. CS=Centrifugal stability; OL=Oil loss; RS=Refrigerator stability; PG/SO=Palm kernel stearin+ Glycerol monostearate/Sorbitan monostearate+ Oil ratio (P7&10% and O 60, 70&80%); CB=Commercial butter.

2-3-3- Oxidative stability based on oxytest of structured water-in-oil emulsions (W/O)

The results related to oxidative stability based on the oxytest method are shown in Table 3. Statistical analysis related to oxytest showed that all factors and their interaction (binary and overall) had a significant effect ($p<0.05$). Oxidation stability with increasing ratio Palm kernel stearin increased (Table 3). Based on this, the lowest amount of oxidative stability is related to the sample containing 7% palm kernel stearin, with the ratio Oil to blue phase 60 to 40% and with glycerol monostearate and the highest oxidative stability related to the sample containing

10% palm kernel stearin, with a ratio of Oil to blue phase 80 to 20 and with sorbitan monostearate.

The results of oxidative stability generally showed that if more and appropriate amount of hard component is used (Palm kernel stearin) and sorbitan monostearate emulsifier, better and more appropriate oxidation stability will be observed in the samples. According to Table 3, the oxidative stability of the commercial butter sample was higher than the prepared samples. More oxidative stability can be due to more saturation in fatty acid composition [32]. Oxidative stability index can also be affected by the chemical structure of oleogelators in the preparation

of samples]34[. In comparing the properties related to fatty acid composition and oxidative stability of several Algerian margarine samples conducted by Bentayeb Ait Lounis et al. (2018), the results generally showed that the highest oxidative stability was related to samples with the highest degree of saturation]32[. Kupiec et al. (2020) in investigating the effect of the type of wax compound on the oxidative stability of oleogels containing rapeseed oil, found that the sample of oleogel containing sunflower wax had the highest oxidative stability (6.8 hours) compared to others, and therefore showed that the type of oleogelator can affect the oxidative stability.]34[.

4-3-Physical stabilities of structured water-in-oil emulsions (W/O)

1-4-3-Centrifugation stability of structured water-in-oil emulsions (W/O)

The results related to the stability of the samples against the centrifuge are shown in Table 3. The results of the statistical analysis of centrifugation stability showed that the factor Palm kernel stearin and interaction Palm kernel stearin $\times$ type of emulsifier had no significant difference ($p>0.05$); While other factors and their interaction had a significant effect on centrifugation stability ($p<0.05$). According to Table 3, the lowest centrifugation stability is 98.80% (the sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 70 to 30% and with sorbitan monostearate) and 98% (the sample containing 10% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with sorbitan monostearate) was recorded. However, other samples had good centrifugation stability (100%). In other words, samples with less centrifugation stability were related to samples containing sorbitan monostearate emulsifier.

In terms of centrifugation stability, there was a similarity between the stable samples in the present study and the commercial

butter sample (Table 3). The oleogels prepared from canola oil containing candelilla wax by Kupiec et al. (2020) had the same centrifugal stability as the samples containing monoacylglycerol related to the present study.]34[. The type of oleogelator can have a different effect on centrifugation stability]34[. In the preparation of oleogels based on rapeseed oil, centrifugation stability based on waxes was Candelilla wax (99.67%), beeswax (97.80%) and yellow beeswax (89.30%), respectively.]34[. One of the reasons for the difference between the results of the samples with lower centrifugation stability related to the current research and other studies can be due to the method used to determine the centrifugation stability (10000 rpm for 5 minutes and also the amount of oleogel components. According to the results of some researches, the type of gelator, the type of oil and the amount of components are effective on the centrifugation stability]34, 36[.

In the research conducted in the field of preparation of gel-filled emulsion based on olive oil-inulin and ultrasound treatment by Nourbehesht et al. (2016), unlike the present study, no stable sample was observed.]36[. In the research on the preparation of oil-in-water (O/W) emulsion based on canola oil and xanthan gum by Putra et al. (2020), the results showed that the centrifugation stability of all samples was less than 100%, which was similar to the samples with less stability in the present study.]37[. In the study of preparation of frankfurter sausage based on fat substitute by Wolfer et al. (2018), the centrifugation stability results were similar to the less stable samples in the present study.]38[. The reasons for the difference in centrifugation stability results can be influenced by various factors such as the type of emulsion/oleogel, centrifugation conditions (power, time and temperature), the method of calculating centrifugation stability, and the type and amount of components. Cellulose derivatives

(including ethyl cellulose) as oleogelators have a good effect on the stability of oleogels. Some oleogelators have a negative effect on centrifugation stability. In general, it can be said that there is a direct relationship between the length of carbon chains and centrifugation stability [39].

2-4-3-Oil drop of structured water-in-oil (W/O) emulsions

The results related to the oil loss of the samples are shown in Table 3. The results of statistical analysis related to oil loss showed that the factor Palm kernel stearin And also on interaction Palm kernel stearin $\times$ type of emulsifier had no significant effect ($p > 0.05$). If other factors as well as other interactions had a significant effect on oil loss ($p < 0.05$). The amount of oil loss related to the samples of this research was below 3%. According to Table 3, the lowest oil loss index is 0.91% (the sample contains 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with glycerol monostearate) and the most 2.68% (the sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with sorbitan monostearate). The amount of oil loss index based on glycerol monostearate emulsifier, at least 0.91% (the sample contains 7% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and with glycerol monostearate) and a maximum of 2.44% (the sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with glycerol monostearate) (Table 3). Also, the oil loss index for sorbitan monostearate emulsifier is as low as 1.15% (sample containing 10% Palm kernel stearin, with the ratio of oily to water phase 70 to 30% and with sorbitan monostearate) and the highest amount is 2.68% (the sample containing 7% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and with sorbitan monostearate) (Table 3). The results of the oil loss index showed that the use of an oil-to-water phase ratio of 80% to 20% led to an increase in oil loss (in the presence of

both emulsifiers); If the ratio of oil to water phase is 70% to 30% for sorbitan monostearate emulsifier and also the ratio of oil to water phase is 60% to 40% for glycerol monostearate emulsifier, the oil loss index is at a minimum (Table 3). The amount of oil drop index for samples based on sorbitan monostearate compared to glycerol monostearate was higher according to the comparison of each oil ratio (Table 3). Of course, despite consumption Palm kernel stearin In two separate percentages (7 and 10%), the results related to the drop index were close in terms of the amount, considering the type of emulsifier as well as the ratio of oily to aqueous phase (Table 3). The amount of oil loss index in commercial butter samples was different from the samples of the present study (Table 3).

Oil loss is one of the methods of checking the stability of fatty products, including butter [20]. The sample with more stability in terms of oil loss index is the sample that has the minimum amount of the desired index [20]. The existence of differences in the loss of oils in the samples can be affected by the type of samples and the measurement method [40]. Important and influential factors on oil loss include oleogel components (type and amount), oleogel preparation method, and storage conditions (temperature and time). [41]. In the research conducted on the preparation of edible oleogels based on 3 types of edible oil (olive, sunflower and linseed) and two structuring agents (hydroxypropyl methyl cellulose and xanthan gum) by Bascuas et al. was present). [33]. Some studies reported that less oil loss was related to samples that had less glycerol monostearate and more oleogelator. [25, 40]. In the research on the preparation of oleogel based on grape seed oil, candelilla wax and glycerol monostearate emulsifier by Choi et al (2020), it was found that the amount of oleogel components used was effective on the oil loss index, so that the lowest oil loss index was related to the sample containing

more wax (75%) and less emulsifier (25%).]40[.

In the research conducted in the field of preparation of alternative shortening for filling cream based on canola oil, candelilla wax and glycerol monostearate.]41[The obtained results showed that if the samples were prepared based on an oleogelator (condelilla wax or glycerol monostearate), the amount of oil loss index was higher. The results of the research on the preparation of oleogel containing grape seed oil-condelilla wax-glycerol monostearate]40[and research on the preparation of alternative shortening for filling cream]41[, were similar to the results of the present study, especially in the field of samples based on glycerol monostearate for oil loss index. A research was conducted in order to prepare a fat product using rapeseed oil, monoglyceride, completely hydrogenated rapeseed oil, lecithin and sound treatment, the results showed that the type, percentage of consumption and the composition of the components together led to the creation of an oil loss index at an appropriate level.]42[.

da Silva and Danthine (2022) reported that the oil loss index for oleogels containing a triple gelator combination (monoglyceride + fully hydrogenated rapeseed oil + lecithin) was lower than samples containing a double gelator combination (monoglyceride + lecithin; monoglyceride + fully hydrogenated rapeseed oil; fully hydrogenated rapeseed oil + lecithin).]42[. The results related to the research on the preparation of oleogels containing one, two and three types of gelators]42[, had similar results, especially in the field of samples based on the binary combination of lecithin - fully hydrogenated rapeseed oil and the triple combination (monoglyceride + fully hydrogenated rapeseed oil + lecithin) with stable samples in terms of oil loss related to the present research. The use of sound treatment to increase oil loss index in monoglyceride binary combination –

lecithin compared to the other composition and it showed that in addition to the percentage of oleogelator, the type of composition of the components together is also effective in creating the results of the oil loss index.]42[.

In the research conducted with the aim of preparing margarine based on oleogel containing low and high fat, the results showed that the oil loss index of the samples was influenced by the oleogelator (type and percentage used), the amount of fat phase (35 and 60%) and the test method (storage 0-180 days at 5°C).]13[. The reason for the difference between the results of the drop index in the present study and the study on the preparation of margarine containing low-fat and high-fat oleogel]13[, can be due to the use of different components and also the type of oil drop index measurement method in the mentioned research]20[. It is expected that there is a direct relationship between the amount of oily phase and the numerical amount of the drop index; In the case of the research conducted on the preparation of 4 types of margarine with two levels of fat content (35 and 60%) based on oleogel, it showed a different relationship.]13[. In the research on the preparation of margarine based on oleogels containing 35 and 60% fat, the oil loss index for the samples in terms of quantity was 60% fat - low structuring components > 35% fat samples - medium structuring components > 60% fat sample - more structuring components.]13[. The results related to the oil loss index related to the research of margarine based on oleogel]13[, shows that the type of components, the percentage of components consumed, as well as the combination of components lead to the difference in the results related to the oil loss index.

3-4-3-Refrigeration stability of structured water-in-oil (W/O) emulsions

The results related to glacial stability are shown in Table 3. Statistical analysis

showed that all factors and their interactions (binary and overall) had a significant effect ($p < 0.05$) on glacier stability. Refrigerative stability of stable samples is reported as zero and samples with less stability are numerically greater than zero (Table 3). Accordingly, only samples containing 7% Palm kernel stearin, with oil-to-water phase ratios of 60 to 40 and 80 to 20%, along with sorbitan monostearate and also all samples based on glycerol monostearate had good refrigeration stability (zero number). In the current research, two sample groups include: 1) with glycerol monostearate emulsifier + 7 or 10 percent Palm kernel stearin + ratio of oily to water phase 60 to 40, 70 to 30 and 80 to 20% and 2) with emulsifier sorbitan monostearate + 7% Palm kernel stearin + Oil to water phase ratio of 60 to 40 and 80 to 20% had good refrigeration stability (Table 3). Samples with moderate stability (about 2.50%) include: sample containing 10% Palm kernel stearin, with the ratio of oil to water phase 60 to 40% and sorbitan monostearate emulsifier and samples with poor/minimum stability (around 5.00%) including: sample containing 10% Palm kernel stearin, with the ratio of oil to water phase 80 to 20% and the emulsifier was sorbitan monostearate (Table 3). In this way, the results of the stability of the refrigerator showed that if using different ratios of oily to water phase (60 to 40, 70 to 30 and 80 to 20%), Palm kernel stearin (7 and 10%) and glycerol monostearate emulsifier, a stable state will be observed in all samples (Table 3). On the other hand, the results of the refrigeration stability related to the sorbitan monostearate emulsifier showed that only the use of oil-water phase ratios of 60 to 40 and 80 to 20 along with 7% Palm kernel stearin, will lead to a steady state in the samples (Table 3). The results of the glacial stability of the samples of the present study were similar to the samples of commercial

butter (Table 3). Of course, there has been an exception related to the refrigerator stability of the sample containing 10% Palm kernel stearin and sorbitan monostearate, with an oil-to-water ratio of 70 to 30% (3.75%) and it could be due to the fact that the use of an oil-to-water phase ratio of 70 to 30% has led to instability unlike other ratios (60 to 40 and 80 to 20%). Unlike the samples with refrigerator stability, especially based on glycerol monostearate, the results related to the unstable samples showed that the use of the ratio of oil to water phase (60 to 40, 70 to 30 and 80 to 20%) along with the use of 10% Palm kernel stearin, in an increasing trend leads to an increase in instability (in terms of storage index in refrigerated conditions).

In the research conducted by Sun et al. (2007) on the effect of xanthan gum and whey protein isolate on the stabilization of oil in water (O/W) emulsion, the results showed that there is an inverse relationship between the concentration of xanthan hydrogelator used and the degree of instability (clotting).⁸⁾ is present in the sample [43]. A research has divided the gel emulsion samples into stable states (absence of xanthan), medium stability (0.15-0.02% by weight of xanthan), unstable (0.2% by weight of xanthan) and partial coagulation/no coagulation (0.5% by weight of xanthan). [43]. Some emulsions have good stability, but increasing the storage time has led to their instability [21]. It has been reported that the type of hydrogelator, the percentage of its use and the type of production sample have an effect on the stability of the final sample, and according to the amount of hydrogelator agent used, various states such as the absence of clotted state (proper stability), the weak and limited clotted state (beginning of instability) and the occurrence of obvious clotted state (unstable state) appear in the emulsion

sample. [43]. In terms of the effect of the type and appropriate concentration of the substance used in the preparation of oleogel, there is a similarity between the results of the refrigerator stability related to the use of xanthan along with whey protein isolate for oil-in-water (O/W) emulsion with the present study. [42]. In the case of water-in-oil (W/O) emulsions containing polyglycerol polyricinoleate, the stability has decreased due to storage; But if casein gels were used in the preparation of emulsion, the level of stability obtained was higher than before [21].

The instability of emulsions can be affected by the ratio of water and oil phases [44]. research In order to stabilize the emulsions, liquid wax (jojoba oil), vegetable solid wax (carnauba wax), two types of mineral solid wax (paraffin wax and cressin) and paraffin oil were used; The results showed that the state of stability (absence of coagulation and phase separation) was observed only if the appropriate amount of different waxes were consumed along with the appropriate ratio of water to oil. [45]. It has been reported that solid mineral waxes lead to the creation of water-in-oil emulsions; If triple emulsions of oil– Water-oils are created by solid plant wax [45]. It has been reported that phase separation is observed in emulsions containing jojoba oil-carnauba wax (affecting the stability of the emulsion), and the reason for this phenomenon can be due to the high wettability of the surfaces related to carnauba wax to jojoba oil, which leads to the instability of the wax surfaces and ultimately causes the instability of the emulsion. [45]. In the research conducted on the preparation of double (W/O) and triple (O/W/O) emulsions based on different percentages of wax (5-30%) and 3 water-oil ratios (70:30, 80:20 and 90:10) by Szumala and Luty (2016), the results showed that the type and amount of wax used, as well as the ratio of the water phase to the oil phase, have a definite effect on the amount of glacial stability. So the stability

results were different according to the type of wax, percentage of wax and ratio of water phase to oil phase [45]. The higher ratio of oil, the appropriate selection of the type and percentage of gelator components lead to the creation of a suitable stability state in oleogel samples.] 21, 29 and 45[. Research showed that the wax (type and percentage used) and the ratio of aqueous and oily phases had an effect on the stability of emulsions, so that the results related to stable emulsions with a ratio of aqueous to oily phase of 10 to 90% were related to paraffin wax (10 to 30%), cressin wax (15, 25 and 30%) and carnauba wax (10, 15 and 20%). [45]. The results of the research conducted in the field of investigating the stability of double (W/O) and triple (O/W/O) emulsions based on several types of wax [45], has similarity with the current research in the field of stable samples in terms of refrigeration, including: 1) based on glycerol monostearate + 7 and 10% Palm kernel stearin and all three ratios of oily to blue phase 60 to 40, 70 to 30 and 80 to 20%; 2) based on sorbitan monostearate + 7% Palm kernel stearin And the ratios of the oily to water phase were 60 to 40 and 80 to 20 percent. In the study of the preparation of double (W/O) and triple (O/W/O) emulsions based on wax, the results related to the glacial stability were reported as confirmation (+) and non-confirmation (-). [45]. In the double and triple emulsion research, there was an inverse relationship between the stability of the samples and the amount of aqueous phase used in the preparation of emulsions. [45].

It has been reported that there is a direct relationship between the stability of the emulsion and the appropriate percentage of xanthan hydrogelator, but if the appropriate amount of xanthan is exceeded, it leads to instability. [43]. Some researches reported that the consumption of a larger amount of gelator/emulsifier leads to instability in the produced emulsions.] 21, 29 and 45[. In the research conducted based on margarine

containing low-fat and high-fat oleo gels, the results showed that wax oleogelators create barriers around the emulsion particles and lead to proper stability.]13[.

5-3-Sensory properties of structured emulsions of water in oil (W/O)

The results related to sensory characteristics are shown in Table 4. Statistical analysis of playability results, melting rate, acidity and mouth coating showed a significant effect ($p < 0.05$) for all factors and their interactions (binary and overall). In the case of milkiness, the statistical analysis of non-significance ($p > 0.05$) of the interaction Palm kernel stearin $\times$ type of emulsifier $\times$ showed the percentage of oily phase. In addition, statistical analysis showed no significant difference ($p > 0.05$) for the factor Palm kernel stearin and also on interaction Palm kernel stearin $\times$ type of emulsifier $\times$ percentage of the oily phase showed the hardness characteristic. Regarding the fat-like characteristic, statistical analysis of the significant effect ($p < 0.05$) of two factors Palm kernel stearin and the type of emulsifier as well as the interaction Palm kernel stearin $\times$ showed the percentage of the oily phase.

Examining the results of the sensory analysis showed that the lowest and the highest amount of hardness respectively correspond to the sample containing 7% Palm kernel stearin and sorbitan monostearate emulsifier with a ratio of 60 to 40 oil to water phase and a sample containing 10% Palm kernel stearin and sorbitan monostearate emulsifier with oil to water phase ratios of 60 to 40, 70 to 30 and 80 to 20. The sample contains 7% Palm kernel stearin and glycerol monostearate emulsifier with the ratio of oil to water phase 60 to 40 is the weakest and the sample contains 10% Palm kernel stearin, and glycerol monostearate emulsifier with an oil-to-water phase ratio of 80:20 showed the strongest spreading property. Regarding the characteristic of the melting rate, the

lowest rate corresponds to the sample containing 7% Palm kernel stearin, and glycerol monostearate emulsifier with a 60 to 40 oil to water phase ratio and the highest amount related to the sample containing 10% Palm kernel stearin, and the emulsifier was sorbitan monostearate with a ratio of oil to water phase of 60:40. The weakest characteristic of milk in the sample containing 10% Palm kernel stearin and sorbitan monostearate emulsifier with a ratio of 70 to 30 oil to water phase and the strongest in the sample containing 7% Palm kernel stearin, and sorbitan monostearate emulsifier was observed with an oil-to-water phase ratio of 70:30. Acidity characteristic in the sample containing 7% Palm kernel stearin and glycerol monostearate emulsifier with 70 to 30 oil-to-water phase ratio, the lowest score and in the sample containing 10% Palm kernel stearin, and glycerol monostearate emulsifier with an oil-water phase ratio of 70 to 30 scored the highest. Fat-like feature in the sample containing 7% Palm kernel stearin, and glycerol monostearate emulsifier with the oil-to-water phase ratio of 60 to 40 is the weakest and contains 7% in the sample. Palm kernel stearin, and glycerol monostearate emulsifier with an oil to water phase ratio of 80:20 was the strongest. Finally, the sample contains 10% Palm kernel stearin and sorbitan monostearate emulsifier with the ratio of oil to water phase of 80 to 20 is the lowest and the sample contains 10% Palm kernel stearin, and sorbitan monostearate emulsifier with 60 to 40 oil-to-water phase ratio obtained the highest score in terms of oral coating characteristics (Table 4). In terms of comparison, the sensory characteristics of the commercial butter obtained more points than the samples of the present study (Table 4).

Two of the important indicators in the field of Korean products and spreads are hardness and spreadability, which are more important than other indicators (especially consumer acceptance).]28[. Examining the

sensory properties of butter substitutes can have different results depending on the type and amount of components used (fat/oil substitute, emulsifying/oleogelatory agents). [46]. Yılmaz and Ögütçü (2015) reported a reciprocal relationship between hardness and spreadability properties, which is similar to the present study. [11]. In the research conducted by Yılmaz and Ögütçü (2014) in the field of preparing oleogel based on virgin olive oil, carnauba wax and monoglyceride as a spreadable product and stored at two different temperatures (4 and 20°C), the results showed that increasing the amount of oleogelator led to an increase in the hardness index (similar to the present study), so that the samples based on 10% carnauba wax had more hardness than the 3% samples. [28]. in linseed oil-based butter enrichment as well as linseed oil-whey protein concentrate combination, Nasirpour-Tabrizi et al. (2020) found that using more components leads to a decrease in playability [47].

The research conducted by Nasirpour-Tabrizi et al. (2020) had different results from the current research in the field of the relationship between the amount of component consumption and the spreadability index. [47]. In the present study, with the increase of components in all samples (except the samples based on

sorbitan monostearate and 10% Palm kernel stearin), there is a direct relationship between the spreadability index and the percentage of components used (Table 6). In establishing the spreadability characteristic of glycerol monostearate emulsifier in both percentages of palm kernel stearin consumption (7 and 10%), it led to a direct relationship between the spreadability results and oil-to-water ratios (60 to 40, 70 to 30 and 80 to 20%) (Table 4). If the emulsifier sorbitan monostearate showed a direct relationship like glycerol monostearate in only 7% of palm kernel stearin (Table 4). The spreadability results related to sorbitan monostearate showed that if a low amount of palm kernel stearin (7%) was consumed, a suitable spreadability level was created in the samples; If the amount of hard and auxiliary component increased (palm kernel stearin from 7 to 10%), it led to a decrease in spreadability and an increase in stiffness of the samples (Table 4). Sensory characteristics related to Korean and spreadable products can be changed according to the type and amount of substitute source (fat / substitute oil), the type and percentage of constituents and auxiliary components (hydrogelator / oleogelator, emulsifier) as well as the effective concentration of components.

Table 4 Sensory evaluation of the structured W/O emulsion samples prepared in this study (means±SD)

Sample name	Sensory evaluation						
	H	S	L	M	R	F	MC
P7GO60	4.23±1.66	0.66±0.01	0.40±0.00	0.85±0.00	0.14±0.00	2.16±0.05	2.51±0.01
P7SO60	3.86±0.05	1.25±0.00	1.85±0.00	0.82±0.01	0.13±0.00	2.26±0.02	2.75±0.00
P7GO70	5.76±0.41	2.13±0.02	3.81±0.01	0.92±0.02	0.11±0.00	2.75±0.00	2.91±0.00
P7SO70	4.27±0.01	1.35±0.01	2.25±0.01	0.95±0.00	0.17±0.00	2.65±0.00	2.72±0.01
P7GO80	4.62±1.14	1.00±0.10	4.11±0.01	0.46±0.01	0.19±0.00	3.00±0.17	2.96±0.00
P7SO80	4.17±0.06	2.23±0.05	3.36±0.11	0.61±0.01	0.13±0.00	2.86±0.02	2.81±0.01
P10GO60	4.10±0.17	0.85±0.01	0.71±0.01	0.83±0.04	0.12±0.00	2.81±0.01	3.51±0.00
P10SO60	6.13±0.02	7.73±0.02	8.13±0.11	0.65±0.00	0.23±0.01	2.53±0.02	3.66±0.01
P10GO70	7.71±0.01	5.43±0.05	5.95±0.01	0.52±0.02	0.28±0.00	2.23±0.02	2.76±0.00
P10SO70	7.97±0.02	6.13±0.02	5.45±0.00	0.45±0.01	0.26±0.00	2.36±0.01	2.61±0.01
P10GO80	7.11±0.01	8.06±0.05	6.10±0.01	0.65±0.00	0.21±0.00	2.57±0.01	2.54±0.00
P10SO80	7.65±0.00	5.75±0.00	5.71±0.01	0.74±0.00	0.22±0.00	2.41±0.01	2.41±0.01
CB	3.71±0.00	7.94±0.00	5.41±0.00	2.09±0.00	1.49±0.00	7.28±0.00	2.91±0.00

Data are shown as means $\pm$ standard deviation of three replicates. H=Hardness; S=Spreadability; L=Liquefaction; M= Milky; R=Rancid; F= Fatty; MC= Mouth coating; PG/SO=Palm kernel stearin, Glycerol monostearate/Sorbitan monostearate, Oil ratio (P7&10% and O 60, 70&80%); CB= Commercial butter.

5-Conclusion

The results of this research showed that low-saturated water-in-oil (W/O) emulsions without trans fatty acids, prepared using canola oil and lipid oleogelators, have great potential to replace butter in various food products. Increasing the amount of palm kernel stearin in these emulsions has improved physical and thermal properties, including hardness and thermal stability. Also, choosing the type of emulsifier had a significant effect on the physical and oxidative stability of emulsions; In particular, samples containing sorbitan monostearate showed more physical and oxidative stability than samples containing glycerol monostearate. On the other hand, in addition to having proper physical and oxidation stability, these emulsions also had favorable sensory characteristics that could lead to consumer acceptance. In general, the findings of this research showed that by using vegetable oils such as canola oil and new structuring methods, it is possible to produce products with higher nutritional value and physical and sensory characteristics similar to or even better than butter. This issue can significantly help in reducing the consumption of saturated and trans fats in diets. Therefore, the production of these types of emulsions can be considered as an effective strategy in the food industry to produce healthy and nutritionally quality products.

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مقاله علمی-پژوهشی

تهیه امولسیون ساختار یافته آب در روغن (W/O) کم - اشباع بدون ترانس بر پایه روغن کانولا و اولئوژلانور های لیپیدی به عنوان جایگزین کره

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چکیده

اطلاعات مقاله

تاریخ های مقاله :

تاریخ دریافت: ۱۴۰۳/۶/۱۷

تاریخ پذیرش: ۱۴۰۳/۱۱/۳

کلمات کلیدی:

روغن کانولا،

امولسیون،

هسته پالم،

گلیسرول،

سوربیتان،

اولئوژل

این مطالعه به بررسی تولید و ارزیابی امولسیون های ساختار یافته آب در روغن (W/O) کم اشباع و بدون اسید چرب ترانس بر پایه روغن کانولا و اولئوژلانور های لیپیدی به عنوان جایگزین کره پرداخته است. این پژوهش تلاش نمود تا با بهره گیری از روغن کانولا، که دارای میزان کمتری اسید های چرب اشباع و میزان بیشتری اسید های چرب غیر اشباع نظیر اسید لینولنیک و اسید اولئیک است، امولسیون هایی را ایجاد کند که از نظر ارزش تغذیه ای و عملکردی، مشابه یا برتر از نمونه های تجاری کره باشند. در این پژوهش، از استئارین هسته پالم به عنوان جزء سخت و دو نوع امولسیفایر شامل گلیسرول مونو استئارات و سوربیتان مونو استئارات استفاده شده است. امولسیون های تهیه شده تحت تأثیر متغیر های مختلفی مانند میزان استئارین هسته پالم، نوع امولسیفایر و نسبت روغن به آب قرار گرفتند و خصوصیات آن ها از جمله ترکیب اسید های چرب، پایداری حرارتی، پایداری فیزیکی و خصوصیات بافتی و حسی مورد بررسی قرار گرفت. نتایج نشان داد که افزایش درصد استئارین هسته پالم منجر به افزایش سختی و پایداری حرارتی امولسیون ها شده، در حالی که انتخاب نوع امولسیفایر تأثیر بسزایی بر روی پایداری فیزیکی و اکسایشی داشت. همچنین، نمونه های حاوی سوربیتان مونو استئارات در مقایسه با گلیسرول مونو استئارات، پایداری فیزیکی بیشتری داشتند. نتایج حاصل از این مطالعه نشان می دهد که امولسیون های ساختار یافته تولید شده با این روش می توانند به عنوان جایگزین مناسبی برای کره در کاربردهای غذایی مورد استفاده قرار گیرند، بدون اینکه کیفیت حسی و عملکردی محصول نهایی تحت تأثیر قرار گیرد. این تحقیق نشان دهنده ظرفیت زیاد روغن های گیاهی اصلاح شده در تولید محصولات غذایی سالم و با کیفیت مناسب است.

DOI:10.22034/FSCT.22.162.199.

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