

Utilization of Nanotechnology in Improving the Properties of Prepared Table Margarine

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ABSTRACT

In recent years nanotechnology-based products have been developed for use in many applications including food. Nanoemulsions are one of the most important applications because they have positive effects on the physical and chemical properties of various fatty products. In this study, table margarine was prepared using palm oil, palm stearin in addition of soybean and sunflower oils at the ratio of (15% soybean oil: 15% sunflower oil : 70% palm oil) and (15%soybean oil : 15%sunflower oil : 70% palm stearin) . Nanotechnology was used to modify the emulsifying properties of table margarine and to study the effect of these properties on its stability during storage period up to 11 weeks under cooling conditions at (4°C). Chemical, physical and emulsion characteristics of table margarine blends processed by nanoemulsion technique were determined and compared with the control samples. Nanoparticles of water phase which used in preparing of table margarine by nanoemulsion technique were examined using Transmission Electron Microscope and Zeta Potential Analyzer. Results showed that the margarine blends processed using this technique led to an improvement in emulsification properties and increased storage stability under refrigeration conditions. obtained results of chemical properties namely acid and peroxide values for margarine blends contained (15% soybean oil:15% sunflower oil : 70% palm oil) and (15%soybean oil : 15%sunflower oil : 70% palm stearin) were determined and being 0.666 and 0.688mg KOH/gm oil and 3.998 and 3.990 ml.eqv/kg oil at the end of storage period in compared with the control samples which were 0.731 and 0.745 mg KOH/gm oil and 5.281 and 5.333 ml.eqv/kg oil. Results of physical properties namely colour and refractive index were also determined and indicated that all prepared margarine blends using nanoemulsion technique were more stable during storage than the others, while the results of emulsion stability indicated that the consistency of the creaming stability were nearly similar to those of control samples.Finally, it could concluded that using of nanoemulsion technique in preparing of table margarine could be prolonged stability and extend storage period.

Keywords: Nanoemulsion-Table margarine- Transmission Electron Microscope- Zeta Potential Analyzer- Emulsion stability

INTRODUCTION

As a challenge towards the food crises, the world is seeking for a food product that can fulfill all health, safety, low price and satisfaction demands of consumers. fats and oils are one of the most important food constituents as it is the main source of energy and at the same time it has an important role in improving the palatability of foods especially the highly spread fast foods(Badawy *et al.*, 2015).

Margarine is a water in fat emulsion in which water droplets are kept separated by the fat crystals. It was categorized according to demand by different consumers and based on melting points and hardness Dian and Sahri(2011).

Table margarine is a type which spreadable at room temperature and maintain its shape at this temperature for a certain time. Most table margarines have very similar consistency to butter and that gives the same functionality, but butter is not spreadable straight from the refrigerator. The solid fat content should decrease dramatically to create a cooling effect and at body temperature it provides information about the mouth feel and flavor release (Dewettinck *et al.*,2011).

One of the major concerns for emulsion is keeping its droplets uniformly distributed during storage and consumption (Boye *et al.*,2012).Nanoemulsions are emulsions with droplet size on the order of 100 nm. A typical nanoemulsion contains oil, water and an emulsifier. The addition of an emulsifier is critical for the creation of small sized droplets as it decreases the interfacial tension i.e., the surface energy per unit area, between the oil and water phases of the emulsion (Doly *et al.*,2016).

Our research was aimed to process a new type of table margarine by using some blends of palm fractions namely palm oil and palm stearin in addition of soybean and sunflower oils and increasing the stability of prepared margarine using nanoemulsion technique under refrigeration storage condition .

MATERIALS AND METHODS

Materials:

Vegetable fats and oils

Palm stearin, palm oil, soybean and sunflower oils (Refined, Bleached and Deodorized) were obtained from Arma For Food Industries Company, 10th Ramadan city, Egypt.

Emulsifiers

Monoglycerides and Lecithin were obtained from Sigma Chemical Company, Cairo,Egypt.

Coloring agent

Beta carotene as colouring matter was secured from Shehab Company for Dairy Pro. , El-Mansoura city, Egypt.

Flavouring agent

Ghee commercial essence used as flavoring agent was obtained from Misr for Oil and Soap Company, El-Mansoura city, Egypt.

Other ingredients:

Potassium sorbate, Citric acid and Sodium chloride were purchased from El-Gomhoria Pharmaceutical and Chemicals Company,El- Mansoura city, Egypt and skim milk was secured from Shehab Company for Dairy products , El-Mansoura city, Egypt.

Essential oil:

Commercial essential oil (Thyme) was obtained from local Fathalla market , El-Mansoura city, Egypt.

Commercial margarine:

Table margarine was obtained from supermarket Hayber One, Cairo,Egypt.

Methods:

Preparation of fat phase blends:

Soybean oil "SBO" and sunflower oil "SFO" were added to palm stearin oil "PSO " and palm oil "PO" with different ratios as mentioned in Table(1) .All fat blends were melted at 50°C for 20 min. Then cooled quickly and stored in domestic refrigerator at 4°C until further

chemical and physical analysis were carried out as reported by (Mirhosseini *et al.*, 2008a).

Table 1. Different vegetable fats and oils blends used in fat phase preparation:

Vegetable fats and oils Fat blends	SBO	SFO	PO	PS
Blend(1)	15	15	70	-----
Blend(2)	15	15	-----	70

Water phase:

Water phase was presented as 12% of emulsion contained adequate amount of water and other ingredients were mentioned in Table (2) water phase was prepared by two methods as follow :

First for regular type, all ingredients were dissolved in distilled water and then mixed gradually for 5 min by MPW-120 homogenizer, 1000rpm. The other part used in nanoemulsion type all ingredients were also dissolved gradually in distilled water but mixed using Omni International 17106 Variable-Speed Homogenizer, 18,000 rpm; 220V to obtain nanoemulsion particles.

Table 2. Fat and water phases used in margarine processing:

Ingredients	Function	%
1-Fat phase:(88%)		
Fat blends		87%
Lecithin	Emulsifier	0.1%
Monoglycerides	Emulsifier	0.1%
Beta carotene	Coloring agent	0.003%
Essence	Flavoring matter	0.3%
2-Water phase(12%)		
Water		11%
Potassium sorbate	Preservative	0.1%
Citric acid	Preservative	0.1%
Sodium chloride	Preservative	0.1%
Thyme extract	antioxidants	0.01%
Skim milk	stabilizer	0.8%

As stated by (ESS,2007)

Margarine processing:

Table margarine with types (with nanoemulsion and regular emulsion) were formulated by dissolving emulsifiers (lecithin"0.1%" and monoglycerides"0.1%" and other soluble fat ingredients(beta carotene"0.003%" and essence"0.3%") in fat blends at 70°C then added to water phase using MPW-120 homogenizer, 1000rpm for 30min. The prepared margarine was finally cooled to 4±1°C at domestic refrigerator and stored at this temperature for different analysis .

Characterization of nanoemulsion particles:

(a)Transmission electron Microscope Measurement (TEM):

Size of nanoemulsion particles was characterized using Transmission Electron Microscopy, TEM (JEOL TEM-2100) connected to CCD camera at an accelerating voltage of 200 KV. Measurements were recorded at the Central Laboratory, Electron Microscope Unit, Faculty of Agriculture, Mansoura University, Mansoura city, Egypt.

(b)Zeta potential measurements:

It was measured by Zeta Potential Analyzer Malvern Zeta size Nano-zs90 . Measurements were recorded at the Central Laboratory, Electron Microscope

Unit, Faculty of Agriculture, Mansoura University, Mansoura city, Egypt.

Physical properties of different fat blends used in table margarine preparing:

Refractive Index(RI) , Melting Point(MP) and Colour as described by (A.O.A.C.,2000)

Solid Fat Content(SFC):

It was determined for different fats blends used in table margarine preparing by Nuclear Magnetic Resonance(NMR) in temperature ranged between 10-40°C according to (A.O.A.C.,2000).at Food Quality Central Laboratory of Arma Food Industries, 10th Ramadan city, Egypt .

Chemical properties:

Acid value (A.V) and Free fatty acids%(F.F.A%)

Acid value and FFA% were determined according to method that described by (A.O.A.C.,2000) .

Peroxide value(P.V) and Iodine value(I.V)

Peroxide value was determined according to (A.O.A.C.,2000) .While Iodine value was determined according to MPOB Test Method(2004) .

Fatty acids profile:

Fatty acids methyl esters were determined by gas chromatography (GC) according to the method described by (Radwan.,1978) at Food Tech. Res. Institute, Agric. Res. Center, El-Giza, Egypt.

Emulsion properties:

Some properties were used to determine emulsion state of prepared table margarine after processing and prolonged storage namely (Lower phase%, separated layers and creaming stability)as follow:

Lower phase % :

Lower phase % was determined and calculated according to the method that described by (Mirhosseini *et al.*, 2009)using the following equation :

$$\text{The Lower phase \%} = (\text{lower phase height} / \text{initial emulsion} \times 100)$$

Separated layers%:

Separated layers % was determined and calculated according to method that illustrated by (Mirhosseini *et al.*, 2008a) using the following equation :

$$\text{Separated layers \%} = (\text{the height of the separated layer} / \text{the total height of the emulsion}) \times 100$$

Creaming stability:

Emulsion stability was measured by the change in the height of the bottom serum phase(Hs) within time and was compared with total height of emulsion(HE) (Klinkersorn *et al.*, 2004).

The creaming index (CI) was determined according to Eq.:

$$CI = 100 \times (HE/Hs)$$

RESULTS AND DISCUSSION

Chemical and physical properties of soybean oil (Refined, Bleached and Deodorized), sunflower oil(RBD), palm stearin oil(RBD) and palm oil(RBD) used in table margarine preparing:

In this study, there were four types of vegetable oils and fats used in table margarine processing namely soybean, sunflower oils, palm stearin and palm oil. Chemical and physical properties of these vegetable oils and fats were determined and the results were tabulated in Table (3).

It noticeable from results of chemical properties that Acid value (A.V) and Free Fatty Acids(FFA%) value were used as a measure of the formation of acidic compounds and secondary products that were formed during oxidation Khalaf(2015).

From data presented in Table (3) it could be observed that AV and FFA% of (RBD)soybean and sunflower oils were (0.351,0.266 mg KOH/gm oil and 0.42 ,0.51%)respectively while palm stearin and palm oil being (0.471, 0.373 mg KOH/gm oil and 0.03,0.04%) respectively. These results may be due to that the formation of fatty acids composition of vegetable oils and fats.

These results were nearly in accordance with those found by(El-Ghonamy *et al.* ,2015) who reported that AV of soybean and sunflower oils were (0.290 and 0.170 mg KOH/gm oil)respectively , while (Oladiji *et al.*, 2010) reported that FFA% of soybean was ranged from (0.3:1.01%). El-Gammal (2007)reported that FFA% of palm stearin and palm oil were (0.251 and 0.216%) respectively.

Peroxide value(PV) used as an index for the early stage of oxidation process and degree of lipid oxidative rancidity and the formation of hydro-peroxides compounds (Karoui *et al.*,2011).

Also in Table (3),results indicated that values of PV were 2.630, 1.872, 3.310 and 2.923 ml.eqv\kg oil for soybean, sunflower, palm stearin and palm oil respectively. Our obtained results were nearly in accordance with those of (El-Ghonamy *et al.* ,2015). They found that PV of soybean and sunflower were 1.57 and 1.39 ml.eqv\kg oil respectively, while El-Gammal (2007) reported that values of PV for palm stearin and palm oil were 2.650 and 3.310 ml.eqv/kg oil respectively.

Iodine value(IV) is a quantitative measure of unsaturation percent in a lipids. The principle of the assessment is based on the fact that halogens add to the

double bonds of unsaturated fatty acids. It can be seen from Table (3) that iodine values as follow soybean oil, sunflower oil, palm stearin and palm oil were 122.32,103.11, 45.77 and 57.98 gm\100gm oil respectively. These results were nearly accordance with those found by (Zaliha *et al.*,2014) whose reported that values of IV for soybean oil ,palm stearin and palm oil were 134.20, 41.90 and 52.69 gm\100gm oil, while (Hashem *et al.*,2016) found that IV of sunflower oil was 131.60 gm\100gm oil.

Results of some physical properties were also presented in Table(3).Refractive index values were 1.022,1.218, 1.441 and 1.428 of SBO,SFO,PS and PO respectively .

Colour is one of the main factors for determining quality of oils. Vegetable oils have minimum values of colour index are more suitable for edible purposes Askar(2017).

In Table(3), it could be observed that the light yellow colour was observed in palm stearin and palm oil, it is primarily due to B-carotene content, it was higher in palm oil(1.367) compared with palm stearin(1.095),this may be due to the effect of temperature which was used in different steps of processing steps for palm oil El-Gammal (2007). Also results in Table(3) indicated that colour were(1.222 and1.412 at 440 mm)respectively for soybean oil and sunflower oil. These values are nearly close to Saafan(2014).

Melting point of fats is used to characterize oils and fats and is related to their physical properties, such as hardness and thermal behavior .

Results in Table (3) also, indicated that melting point in palm stearin and palm oil was 45 and 26°C respectively. These results were nearly in accordance with those found by El-Waseif and Hashem(2017) whose reported that melting point of palm stearin and palm oil was 38.5 and 27.5°C respectively.

Table 3. Chemical and physical properties of soybean oil(RBD), sunflower oil(RBD), palm stearin oil(RBD) and palm oil(RBD) used in table margarine preparing:

Vegetable fats and oils	SBO	SFO	PS	PO
Chemical and physical properties				
Acid value(AV) mg KOH/gm oil	0.351	0.266	0.471	0.373
Free fatty acid (FFA%)(as oleic acid%)	0.228	0.208	0.354	0.291
Peroxide value(PV) (ml.eqv\kg oil)	2.630	1.872	3.310	2.923
Iodine value(IV) (gm\100gm oil)	122.32	103.11	45.77	57.98
Refractive index(RI) (at40°C)	1.022	1.218	1.441	1.428
Colour(at 440 mm)	1.222	1.412	1.095	1.167
Melting point ^o 40C(MP)	NA	NA	45	26

NA: Not analyzed

SBO:soybean oil , SFO:sunflower oil, PS:Palm stearin, PO:Palm oil

Fatty acids profile of soybean oil(RBD), sunflower oil(RBD), palm stearin oil(RBD) and palm oil(RBD) used in table margarine preparing:

Most studies on lipids for health and nutrition have focused on their fatty acid composition. However, the distribution of these fatty acids in the triacylglycerol molecule is specific for the native fats and oils (Ract *et al.*,2015).

Results of the gas chromatography analysis of methyl esters of saturated and unsaturated fatty acids of soybean, sunflower, palm stearin and palm oil are mentioned in Table (4).

From these results saturated and unsaturated fatty acids could be specified in all investigated samples. From

our obtained results in Table(4) it could be observed that the amount of saturated and unsaturated fatty acids were approximately equal in palm oil, Palmatic acid(C16:0) was the predominate saturated fatty acid in both of palm stearin and palm oil. On the other hand the epidemic unsaturated fatty acid in all samples was linoleic acid(C18:2). Data also showed that linoleic acid(C18:2"ω6")were (55.41, 52.44, 18.24 and 30.54%) for soybean, sunflower, palm stearin and palm oil respectively.

From these mentioned data, it could be concluded that palm stearin and palm oil were convenient to hard stock fat processing according to their fatty acids profile in the processing of diverse fat spreads and restrain stable against oxidation.

Table 4. Fatty acids profile of soybean oil(RBD), sunflower oil(RBD), palm stearin oil(RBD) and palm oil(RBD) used in table margarine preparing:

Fatty acids%	Vegetable fats and oils			
	SFO	SBO	PS	PO
Saturated fatty acids(SFA)				
Caproic acid(C _{6:0})	0.04	0.02	ND	ND
Caprylic acid(C _{8:0})	0.34	0.06	ND	ND
Capric acid(C _{10:0})	ND	ND	ND	ND
Lauric acid(C _{12:0})	0.23	0.10	0.28	0.19
Myristic acid(C _{14:0})	0.07	0.07	1.16	1.32
Palmitic acid(C _{16:0})	7.56	10.49	55.22	44.93
Margaric acid(C _{17:0})	0.04	0.09	0.16	0.10
Stearic acid(C _{18:0})	3.42	3.93	11.27	5.11
Arachidic acid(C _{20:0})	0.33	0.37	0.36	0.32
Behenic acid(C _{22:0})	0.66	0.45	ND	ND
Total(SFA)	12.69	15.58	68.45	51.97
Unsaturated fatty acids(USFA)				
Palmitoleic acid(C _{16:1})	0.11	0.09	0.20	0.06
Heptadecenoic acid(C _{17:1})	0.02	0.04	0.02	0.21
Oleic acid(C _{18:1})	28.22	25.62	13.39	15.47
Linoleic acid(C _{18:2} "ω6")	55.41	52.44	18.24	30.54
Linolenic acid(C _{18:3} "ω3")	4.07	6.18	1.17	1.11
Eicosenoic acid(C _{20:1})	0.15	0.23	0.03	0.12
Total(USFA)	87.98	84.60	33.05	47.51
Total(FA)	100.67	100.18	100.50	99.48

ND: Not detected

Solid fat content(SFC)of fat blends used in table margarine preparing:

The quality of margarine for various categories of usage depends on their crystallizing and melting behavior Sahri and Dian(2011). Solid Fat Content (SFC) is a measure (in percentage) of the amount of solid fat presented in samples at temperature (Zaliha *et al.*,2014). Results in Table(5) showed the solid fat contents of blend(1) and blend(2).

Table 5. Solid fat content(SFC)of fat blends used in table margarine preparing:

Fat blends Temperature(°C)	Blend (1)	Blend (2)
10°C	33.01	45.69
20°C	18.04	33.39
25°C	12.60	27.94
30°C	9.31	22.27
35°C	6.41	17.87
40°C	4.67	13.93

It could be observed that the blend(2) had the highest SFC being (45.69%)in compared with blend(1)(33.01%). This may be due to the presence of higher amounts of Palmitic acid. Obtained results showed that these different amount of SFC could be suitable in table margarine processing.

Transmission Electron Microscopy(TEM) of nanoparticles of water phase used in prepared table margarine by nanoemulsion::

Morphology and structure of nanoemulsion were studied using TEM. Combination of bright field imaging at increasing magnification and of diffraction modes was used to reveal the forms and sizes of nanoemulsion droplets Savardekar and Bajaj (2016).

Figure1(a and b)showed that regular water phase of emulsion particle size was 244:297nm while our obtained results from TEM indicated that particles size of water phase processed by nanoemulsion technology were smaller than the origin emulsion type and ranged from 30.69 to 94.33nm . Also, the particles seemed to be a smooth, spherical and tetragonal shapes which resulted to the stability and consistency of the prepared products.

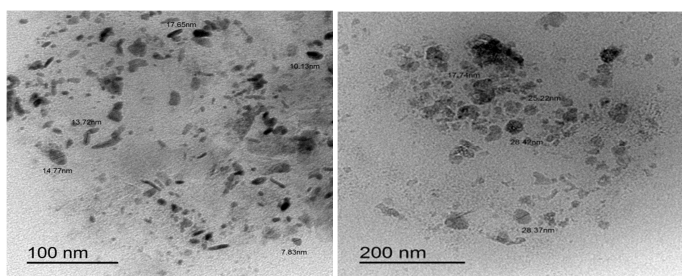


Fig. 1a. Water phase by nanotechnology Fig. 1b. Regular water phase
Figure (1a,b). TEM micrographs characterization illustrating the size and morphology of the particles of water phases used in prepared table margarine at 200nm and which by nanotechnology at 100nm

Zeta potential measurements of water phase used in prepared table margarine by nanoemulsion:

Zeta potential is related to interactions between particles and biomolecules and is thought to be an important factor for formation of aggregates Horie and Fujita (2011). Assessment of zeta potential (ZP) is a part of standard procedure frequently employed for thorough characterization of developed nanoemulsion systems Isailović and Savić (2017).

Measurements of zeta potential were also carried out in order to study the stability of nanoparticles as this extremely important for many applications. Figure 2(a and b) are summarizing the zeta potential measurements of samples in a solution form at different values of PH ranges.

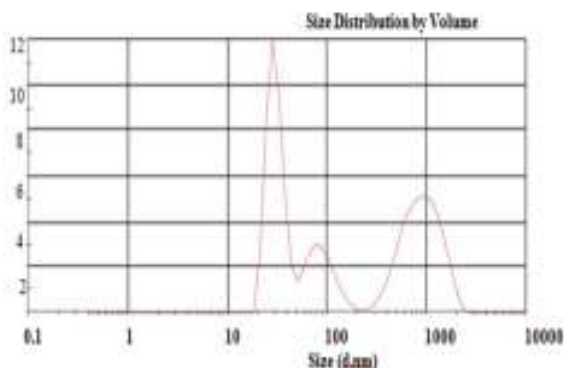


Fig. 2a. Water phase by nanotechnology

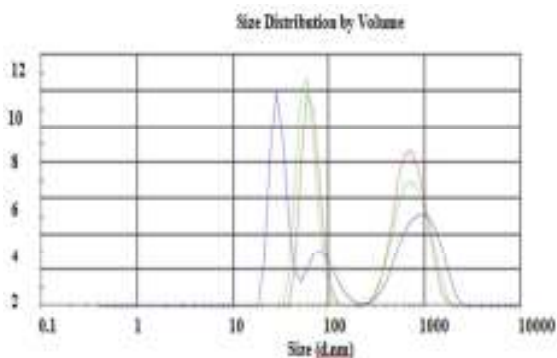


Fig. 2b. Regular water phase

Figure. 2 a and b. Zeta potential measurements water of water phases used in prepared table margarine and which by nanotechnology

Changes of chemical properties of table margarine blends during storage (4°C):

Changes of Acid value (A.V)

Results in Table (6) illustrated that acid value of stored prepared table margarine blends by nanoemulsion used to evaluate the stability during cold storage at (4°C) for 11 weeks.

Results of acid value was used to asses oil degradation and is related to food quality Khalaf (2015). The initial acid values of prepared table margarine blends by nanoemulsion were (0.512 and 0.515 mg KOH/kg oil) in compared with (0.520 and 0.522 mg KOH/kg oil) for control prepared table margarine blends at zero time.

All values of AV in prepared table margarine were increased gradually prolonged storage period, the

increment was around (0.666 to 0.745 mg KOH/kg oil).Also, all values of AV were below (1%) and these indicated that these prepared margarine blends were safety for human consumption.

Table 6. Changes of Acid value of table margarine blends during storage at 4°C for 11 weeks:

Storage Period (weeks)	Commercial table margarine	Control prepared table margarine blends		prepared table margarine blends by nanoemulsion	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
		Zero time	0.501	0.520	0.522
(1)	0.520	0.525	0.528	0.512	0.525
(2)	0.528	0.533	0.538	0.523	0.525
(3)	0.528	0.542	0.542	0.533	0.525
(4)	0.532	0.548	0.555	0.533	0.529
(5)	0.633	0.599	0.569	0.533	0.544
(6)	0.650	0.655	0.590	0.576	0.547
(7)	0.658	0.676	0.638	0.598	0.588
(8)	0.676	0.688	0.698	0.608	0.643
(9)	0.690	0.690	0.705	0.611	0.654
(10)	0.712	0.698	0.732	0.643	0.678
(11)	0.720	0.731	0.745	0.666	0.688

Changes of Peroxide value (P.V):

Peroxide value can give an idea about the early stages of lipid oxidation Ali and El-Anany(2012). From data presented in Table (7) it could be noticed that peroxide values of prepared table margarine blends by nanoemulsion technique were gradually increased during storage period and reached to 3.998 and 3.990 ml.eqv /kg oil for blend (1) and blend (2) up to 11 weeks of storage, while peroxide value of control prepared table margarine being 5.281and 5.333 ml.eqv/ kg oil for blend (1) and blend (2) prepared with traditional methods. These obtained results may be due to that addition of palm oil and palm stearin which contained high amount of palmitic acid which increase resistance of prepared table margarine blends to oxidation steps.

Table7. changes in peroxide value of table margarine blends during storage at 4°C for 11 weeks:

Storage period (weeks)	Commercial table margarine	Control prepared table margarine blends		prepared table margarine blends by nanoemulsion	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
		Zero time	2.430	2.520	2.466
(1)	2.444	2.588	2.503	2.430	2.433
(2)	2.586	2.679	2.644	2.430	2.433
(3)	2.654	2.788	2.902	2.550	2.655
(4)	2.748	2.932	3.111	2.601	2.732
(5)	2.788	3.110	3.244	2.622	2.755
(6)	2.980	3.222	3.654	2.690	2.900
(7)	3.011	3.298	3.900	2.881	3.012
(8)	3.210	3.343	4.012	2.905	3.105
(9)	3.543	3.890	4.765	3.033	3.332
(10)	3.876	4.611	4.998	3.133	3.678
(11)	4.098	5.281	5.333	3.998	3.990

The results also showed the stability of these blends which processed with nanoemulsion technology were also more stable than commercial sample.

Changes of Iodine value(IV) :

Iodine value is a measurement of degree of unsaturation and is used to characterize fats and oils quality (Hazirah et al.,2014) . From Table(8), it could be observed that iodine values of all margarine blends were decreased during storage (at 4°C).

The decrement of iodine values of prepared table margarine using nanoemulsion technique was less than those of control prepared table margarine and the values of IV were nearly to commercial table margarine. IV for blend (1) and blend (2) of prepared table margarine by nanoemulsion were reached 100.888 and 99.807 gm /100gm oil respectively while for blend (1) and blend (2) of processed table margarine were 95.342 and 95.010 gm/100gm oil respectively.

Iodine values of all prepared table margarine blends were changed during storage and were in the recommended range which it was less than 90 gm /100gm oil.

It could be concluded from data tabulated in Table (8) that nanoemulsion technique can be used as advisable method to formulate new and stable blends of table margarine.

Table 8. changes in Iodine value of table margarine blends during storage at 4°C for 11 weeks:

Storage period (weeks)	Commercial table margarine	Control prepared table margarine blends		prepared table margarine blends by nanoemulsion	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
		Zero time	105.342	101.320	101.330
(1)	105.002	101.002	101.009	104.222	104.033
(2)	104.221	100.023	100.908	104.001	103.222
(3)	104.001	99.551	100.022	103.432	103.043
(4)	103.775	99.010	99.843	103.400	102.702
(5)	103.201	98.601	98.770	102.952	102.004
(6)	102.443	98.043	97.922	102.444	101.996
(7)	101.332	97.980	97.221	102.377	101.322
(8)	101.220	97.021	96.605	102.007	101.012
(9)	100.554	96.880	96.011	101.534	100.823
(10)	99.754	95.993	95.888	101.220	100.103
(11)	99.011	95.342	95.010	100.888	99.807

Changes of physical properties of table margarine blends during storage at 4°C for 11 weeks:

Changes of Refractive index (RI)

Refractive index is physical criteria used to estimate the degree of unsaturation and identifies the molecules present in lipids El-Gammal (2007). It could be observed from presented data in Table (9) that refractive index values were slightly decreased during storage for all prepared table margarine blends. From data in Table(9) it could be renowned that it is relevance between RI and IV which two parameters of fats and oils effect with amount of saturated and unsaturated fatty acids.

Changes of Colour:

Colour is one of the criteria which responsible for fat spreads stability during storage periods. Obtained results tabulated in Table (10) showed that margarine blends prepared with nanoemulsion technique were more

stable in colour prolong storage periods under cooling conditions in compared with commercial sample and other prepared blends. This may be due to small size of nanoemulsion particles which increase the surface area of distribution of colour.

Table9. changes in refractive index of table margarine blends during storage at 4°C for 11 weeks:

Storage period (weeks)	Commercial table margarine	Control prepared table margarine blends		prepared table margarine blends by nanoemulsion	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
		Zero time	1.022	1.021	1.019
(1)	1.022	1.021	1.019	1.022	1.021
(2)	1.020	1.020	1.017	1.022	1.021
(3)	1.019	1.018	1.016	1.020	1.021
(4)	1.019	1.018	1.016	1.020	1.020
(5)	1.019	1.018	1.016	1.020	1.019
(6)	1.018	1.016	1.015	1.020	1.019
(7)	1.017	1.016	1.014	1.019	1.018
(8)	1.015	1.015	1.014	1.019	1.018
(9)	1.015	1.015	1.012	1.018	1.018
(10)	1.015	1.014	1.012	1.017	1.018
(11)	1.014	1.012	1.010	1.017	1.017

Table10. changes in colour of table margarine blends during storage at 4°C for 11 weeks:

Storage period (weeks)	Commercial table margarine	Control prepared table margarine blends		prepared table margarine blends by nanoemulsion	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
		Zero time	1.330	1.311	1.300
(1)	1.330	1.300	1.300	1.298	1.313
(2)	1.330	1.243	1.265	1.298	1.300
(3)	1.222	1.201	1.222	1.268	1.278
(4)	1.220	1.201	1.201	1.265	1.264
(5)	1.220	1.195	1.198	1.255	1.252
(6)	1.201	1.133	1.198	1.212	1.252
(7)	1.110	1.111	1.133	1.212	1.200
(8)	1.110	1.111	1.101	1.116	1.118
(9)	1.110	1.032	1.044	1.111	1.117
(10)	1.022	1.032	1.023	1.109	1.102
(11)	1.017	1.014	1.015	1.033	1.032

Emulsion stability of fresh and stored table margarine blends :

The stability of the emulsion was determined by three methods namely Lower phase%, Separated layer% and creaming stability. Emulsion stability of formulated table margarine from different blends at zero time and after storage at (4°C) for 11weeks was specified in Tables (11,12and 13).

Data in Table (11) illustrated that the lower phase(%)increased in prepared table margarine by nanoemulsion more than those of prepared table margarine which increases the emulsion stability. From this data in Table(11) it is clear that blends of prepared table by nanoemulsion were stable more than others so, that could be due to using the suitable emulsifiers and small size and diffusion of water phase molecules .

The lower phase (%) was ranged from 0.4 to 0.8 that means all blends were processed were stable.

The small droplet size gives nanoemulsions unique rheological and textural properties which render them

transparent and pleasant to the touch; both of these unique features can be desirable in processing of margarine Singh(2015).

Table11. Lower phase % of fresh table margarine:

	Commercial table margarine	Control prepared table margarine blends by nanoemulsion			
		Blend (1)		Blend (2)	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
Lower phase %	0.8	0.5	0.4	0.8	0.7

Results in Table (12) showed that emulsion in prepared table margarine by nanoemulsion technique in blend (1) was stable during first three weeks of storage and the changes were observed during last 4 weeks of storage at (4°C).

Table12. Separated layer % of table margarine blends during storage at 4°C for 11 weeks:

Storage period (weeks)	Commercial table margarine	Control prepared table margarine blends by nanoemulsion			
		Blend (1)		Blend (2)	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
Zero time	1.1	1.2	1.2	1.1	1.1
(1)	1.1	1.2	1.3	1.1	1.2
(2)	1.1	1.3	1.4	1.1	1.3
(3)	1.2	1.3	1.4	1.1	1.3
(4)	1.3	1.3	1.4	1.2	1.3
(5)	1.3	1.4	1.5	1.2	1.4
(6)	1.3	1.4	1.6	1.3	1.5
(7)	1.5	1.5	1.6	1.3	1.5
(8)	1.6	1.7	1.7	1.6	1.6
(9)	1.6	1.7	1.8	1.6	1.7
(10)	1.6	1.8	1.8	1.7	1.7
(11)	1.7	1.9	1.9	1.7	1.7

Creaming index can be appears due to gravity separation. Upward movement of droplets on the fact that their density is less than the density of their environment is called creaming. Flocculation is result of the aggregating of two or more droplet at conditions that each droplet has maintained its entirety Esmaelian(2016).The results in Table(13) revealed that creaming index was increased at a lower rate for blends (1 and 2) of prepared table margarine by nanoemulsion compared with prepared table margarine.

Data in Table (13) showed that creaming of table margarine prepared by nanoemulsion technique is prevented by the faster diffusion rate of smaller droplets.

The changes in all emulsion stability parameters in prepared table margarine were different than those of processed margarine by nanoemulsion and commercial margarine.

Using nanotechnology in table margarine processing protect the emulsion from oiling off and watering off and increased it's stability during storage period.

Table13. Creaming stability of the table margarine blends during storage at 4°C for 11 weeks :

Storage period (weeks)	Commercial table margarine	Control prepared table margarine blends by nanoparticles			
		Blend (1)		Blend (2)	
		Blend (1)	Blend (2)	Blend (1)	Blend (2)
Zero time	1.2	1.4	1.4	1.3	1.3
(1)	1.2	1.4	1.4	1.3	1.3
(2)	1.2	1.4	1.5	1.3	1.4
(3)	1.4	1.5	1.5	1.3	1.4
(4)	1.4	1.5	1.6	1.3	1.4
(5)	1.4	1.6	1.6	1.3	1.4
(6)	1.4	1.6	1.6	1.5	1.5
(7)	1.5	1.6	1.7	1.5	1.6
(8)	1.5	1.7	1.8	1.6	1.6
(9)	1.6	1.7	1.8	1.7	1.7
(10)	1.7	1.8	1.9	1.7	1.7
(11)	1.7	1.9	1.9	1.7	1.7

CONCLUSION

Finally, it could be concluded that the properties of processed table margarine were improved by using nanoemulsion technology. It is could be considered as new technique to produce new fat spread product in Egyptian markets.

REFERENCES

- Ali, F.M. and El-Anany, A.M. (2012). Pysicochemical Studies on sunflower oil blended with cold pressed tiger nut oil during deep frying process. *Journal food technology* 318.
- A.O.A.C. (2000). Association of official Analytical Chemists. *Official Methods of Analysis*. 17th Ed. Vol. (11) Washington DC. USA.
- Asker, Mohamed A.A. (2017). Utilization of phytosterols in Functional Foods. PHD. Thesis, Fac. Of Agric. Mansoura, univ. Mansoura, Egypt.
- Badawy, I.H.; Amany, E.; Seham, S.K.; Saadia, M.A.; Ghada, A.A. and El-Shattory, Y.(2015).Nutritional Studies On Nano-Fortified Zero Trans Vegetable Butter from Palm Olein and Starin Interesterified Fat blend. *International Journal of Chem. Tech. Research*.vol.7,No.01,pp1-19.
- Boye, J.I.; Zamani, Y. and Achouri, A. (2012). Stability and physical properties of Emulsion prepared with and without soy proteins. *Journal of Food Research*. Vol. 1, P.254-267.
- Dian, N.L.H.M., and Sahri, M.M. (2011). Formulation of Trans-free and low saturated margarine. *Journal of oil palm Research* vol.23 P. 958-967.
- Doyle, P.S.; Hatton, T.A.; Eral., B.H. and Gupta, A. (2016). Nanoemulsions: formation, properties and applications. *The Royal society of chemistry Journal*.
- Egyptian Standard Specification for manufacture of margarine No.6374/2007.
- El-Gammal, Rania E. (2007). Studies on stability of oils and fats. Ph.D. Thesis, Mansoura, Univ. Fac. Of Agric. Food Indust. Dept. Mansoura, Egypt.

- El-Ghonamy, Marwa A.; El-Kalyoubi, M.H.; Khalaf, M.M. and El-Ogamy, M.A.(2015). Improving the Oxidative Stability of Sunflower and Soybean Oils during Frying. Middle East Journal of Applied Sciences. Vol. 5 . P 335-343.
- El-Waseif , M.A. and Hashem , H.A.(2017). Utilization of Palm Oils in Improving Nutritional Value, Quality Properties and Shelf-Life of Infant Formula . Middle East Journal of Agriculture Research . Vol. 06 P.:274-281.
- Esmaelian, M. (2016). Formulation and fuzzy modeling of emulsion stability of Neroli essential oil, gum Arabic and maltodextrin. BIOSCIENCE BIOTECHNOLOGY RESEARCH COMMUNICATIONS . 9(2): 189-194 .
- Hashem, H.A. and El-Wasief, M.A. (2016). Using palm oils in improving oxidative stability and covering lipid requirements of oil blends used in manufacturing infant formula. Journal of oil palm, Environment and Health. 7:34-42.
- Hazirah, M.F.; Norizzah, A.R.; Norsyamimi, M.; Zaliha, O. and Nur, A.K. (2014). Physicochemical properties of palm oil and palmkernel oil blend fraction after intersterification. International Food Reseach Journal. 22(4) : 1390-1395.
- Horie, M. and Fujita, K. (2011). Chapter 4: Toxicity of metal oxides nanoparticles. In: Advances in molecular 978 toxicology. Vol. 5. Elsevier B.V.
- Isailović, M. N.T.,and Savić, D. S. (2017). Natural Surfactants-Based Micro/Nanoemulsion Systems for NSAIDs—Practical Formulation Approach, Physicochemical and Biopharmaceutical Characteristics/Performances ,Chapter 7, Pages 179-217.
- Karoui, I.J.; Dhifi, W.; Jemia, M.B. and Marzouk, B.(2011). Thermal stability of corn oil flavoured with Thymus Capitatus under heating and deep frying conditions. J.Sci. Food Agr. 91(5):927-933.
- Khalaf, Y.A. (2015). Effect of blending and Natural Antioxidants on stability of sunflower oil. M.S.C. Thesis, Fac. Of Agric. Mansoura, Univ. Mansoura, Egypt.
- Klinkesorn, U.; Sophanodora, P.; Chinachoti, P. and McClements, D.J. (2004). Stability and rheology of corn oil- in -water emulsions containing maltodextrin. Food Res. Int., 37, 851-859.
- Mirhosseini, H. C.P.; Tan, N.S.A.; Hamid, S. Y. and B.H. Chern,(2008a). Effect of Arabic gum, xanthan gum and orange oil on flavor release from diluted orange beverage emulsion. Food Chem., 107:1161-1172.
- Mirhosseini, H., C.P.; Tan, N.S.A.; Hamid, S. Y. and B.H. Chern,(2009). Characterization of the influence of main emulsion components on the physicochemical properties of orange beverage emulsion using responsesurface methodology. Food Hydrocolloids, 23: 271-280.
- MPOB Test Methods(2004). A Compendium of Tests on Palm Oil Product, Palm Kernel Products and Fatty Acids. Food –Related Products and Others.
- Oladiji, A.T. ; Yakubu, M.T.; Idoko, A.S.; Adeyemi, O. and Salawu, M.O. (2010).Studies on the physicochemical properties and fatty acid composition of the oil from ripe plantain peel(*Musa paradisiacal*).
- Ract, J.N.R.; Soares, F.A.S.D.; Rodrigues, H.G.; Bortolon, R.J.; Murata, M.G.; Gonclaves, A.I.M.; Hatanaka, E.; Curi, R. and Gioielli, L.A. (2015). Production of vegetable oil blends and structural lipids and their effect on wound healing. Brazilian Journal of Pharmaceutical Science vol. 51(12) P.415-427.
- Radwan, S.S. (1978). Coupling of two dimensional thin layer chromatography with G.C for quantitative analysis of lipid classes and their constituents fatty acids. J. Chrom. Science 16:538-542.
- Saafan, Eman E. (2014). Studies on stability of oils M.S.C. Thesis, Fac. Of Agric. Mansoura, Univ. Mansoura, Egypt.
- Singh, N.(2015). An overview of prospective application of nanoemulsions in food stuffs and food packaging. ASIO journal of Microbiology, Food science and Biotechnological Innovations vol.1,20-25.
- Savardekar, P. and Bajaj, A.(2016).Nanoemulsion –A Review. International Journal of Research in Pharmacy and Chemistry 6(2):312-322.
- Zaliha, O.; Norizzah, A.R.; Siti, H.M.F. and Zaizuhana, S.; (2014). Effect of blending on physic-chemical properties of palm oil and palm oil products with soyabean oil. Journal of oil palm Research. Vol. 26(4) p.332-339.

الاستفادة من تكنولوجيا النانو في تحسين خصائص مارجرين المائدة المصنعة

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في السنوات الأخيرة تم تطوير المنتجات القائمة على تكنولوجيا النانو لاستخدامها في العديد من التطبيقات بما في ذلك الغذاء وتعتبر تكنولوجيا المستحلبات النانوية من أهم التطبيقات لما لها من تأثيرات إيجابية على الخواص الفيزيائية والكيميائية لمختلف المنتجات الدهنية. في هذه الدراسة تم تصنيع مارجرين المائدة باستخدام خليط زيت النخيل وإستياريين النخيل وزيت فول الصويا وزيت عباد الشمس بنسبة (١٥٪ زيت فول الصويا: ١٥٪ زيت عباد الشمس: ٧٠٪ زيت النخيل) و (١٥٪ زيت فول الصويا: ١٥٪ زيت عباد الشمس: ٧٠٪ زيت النخيل). ثم استخدام تقنية النانو لتعديل خصائص الاستحلاب لمارجرين المائدة ودراسة تأثير ذلك على ثباتها خلال فترة التخزين حتى ١١ أسبوعاً تحت ظروف التبريد عند درجة حرارة (٥-٣ درجة مئوية) وتم تحديد الخواص الكيميائية والفيزيائية لمستحلبات خلطات مارجرين المائدة التي تم تصنيعها بواسطة تقنية النانو ومقارنتها بعينات التحكم. تم فحص جزيئات الطور المائي المستخدم في معالجة مارجرين المائدة بطريقة تقنية النانو باستخدام جهاز Transmission Electron Microscope و Zeta Potential Analyzer أظهرت النتائج أن خلطات المارجرين المجهزة باستخدام هذه التقنية أدى إلى تحسن في خصائص الاستحلاب وزيادة ثباته أثناء التخزين في ظل ظروف التبريد. وكانت نتائج الاختبارات الكيميائية (رقم الحموضة والبيروكسيد) للخلطات المصنعة من (١٥٪ زيت فول الصويا: ١٥٪ زيت عباد الشمس: ٧٠٪ زيت النخيل) و (١٥٪ زيت فول الصويا: ١٥٪ زيت عباد الشمس: ٧٠٪ نخيل استياريين) ٠.٦٦٦ و ٠.٦٨٨ مجم أيدروكسيد بوتاسيوم/جم زيت و ٣.٩٩٨ و ٣.٩٩٠ ملك/كجم زيت في نهاية فترة التخزين (١١ أسبوعاً) مقارنة بعينات التحكم التي كانت ٠.٧٣١ و ٠.٧٤٥ مجم أيدروكسيد بوتاسيوم/جم زيت و ٥.٢٨١ و ٥.٣٣٣ ملك/كجم زيت. تم تقدير بعض الخواص الفيزيائية وهي اللون و معامل الانكسار وأشارت النتائج إلى أن جميع خلطات المارجرين التي تمت تصنيعها باستخدام تقنية المستحلبات النانوية كانت أكثر ثباتاً أثناء التخزين مقارنة بالخلطات الأخرى. وتشير الدراسة إلى أهمية استخدام تقنية المستحلبات النانوية لإطالة فترة الثبات والتخزين في مختلف المنتجات الدهنية مثل المارجرين.