Assessment of Physical Properties of Structured Oils and Palm Fat

SYLWIA ONACIK GUR[1], ANNA ZBIKOWSKA[1], MARZENA PRZYBYSZ[1], MALGORZATA KOWALSKA[2*]
[1]Department of Food Technology, Warsaw University of Life Sciences, Nowoursynowska 159c, 02-766 Warszawa, Poland
[2] Department of Chemistry, Faculty of Materials Science, Technology and Design, Kazimierz Pulaski University of Technology and Humanities in Radom, Poland

Oleogels are structured liquid oils with applications in food, cosmetic, and pharmaceutical industries. Structured oils may become alternatives to the commonly used solid fats, such as palm fat or hydrogenated fats. Properties of oleogels are primarily dependent on the structuring agent applied. This paper was intended as an examination of structuring properties and oleogel oil binding capacities of various monomer ingredients (plant and beeswaxes, monoacylglycerol) and comparison of the oleogels produced with palm fat. An oleogel produced with candelilla wax (CLX) exhibited a structure most similar to that of palm fat. These products showed statistically significant differences of colour from palm fat. In addition, textures of the oleogels differed from one another and from palm fat. Oleogel containing rice bran wax (RBX) had the most similar viscosity properties. Oleogels including candelilla wax and yellow bees wax displayed best oil binding structures (assayed by centrifugal and LumiSizer methods). When filtered (at 40°C), on the other hand, minimum oil loss after 24h was demonstrated by the oleogels containing CLX and RBX, possible evidence that these structure-forming substances roduce oleogels that could be used in products exposed to more elevated temperatures. Oleogels may become alternatives to the commonly used solid fats. Thanks to the use of oil structuring agent at the level of 3% liquid oil becomes solid. Using these innovative fat products can stabilize oil in the product, and also it can improve the nutritional value of food products by replacing a popular palm fat rich in saturated fatty acids, which exert an adverse influence on humans' cardiovascular system, by oils rich in unsaturated fatty acids.

Keywords: oleogels, waxes, monoacylglycerols, high-oleic sunflower oil, rheology

High content of saturated fatty acids (SFA) and often also presence of trans fatty acid (TFA) isomers account for solid consistency of typical hard fats. Solid fats provide desirable sensory properties to products made involving them [1].

International food and nutrition organisations (EFSA and WHO) recommend maximum reduction of SFA and TFA consumption [2]. It is therefore necessary to develop new fat products based on vegetable oils rich in non-saturated fatty acids. However, application of liquid oils to a number of products adversely affects their sensory properties and may cause their loss [3]. Oil structuring substances must be added to prevent this.

Problems of binding liquid fats in products are known in food technology, with the process of emulsification to produce stable emulsions or suspensions being an instance of oil stabilisation (binding) in products. In emulsions like mayonnaise, two different phases – hydrophobic and hydrophilic -are dispersed [4]. Liquid and solid phases are also combined, for example, in the case of peanut butter, where the peanut mass is suspended in oil. However, very considerable additions (ca. 50%) of structuring agents (other than oil) are added to these products to obtain their solid consistency [1].

Oil can be bound as gel by application of the so-called oleogel generating compounds, polymers (cellulose ethers) or monomers (monoacylglycerols, plant and animal waxes, lecithin) [5]. These ingredients form molecular networks. Gelling of monomers consists in formation of microcrystalline plates that agglomerate to build complexes of three-dimensional networks and thereby bind liquid oils [6]. Compared to cellulose ethers [Rogers et al., 2014], monomer substances dissolve at lower temperatures and over shorter time periods [7], owing to which oxidative changes of structured oil are substantially more limited at the time of production [8].

Waxes are by-products of oil manufacturing or are derived from plant or animal secretions [9]. Waxes may consist of a range of chemical substances: wax esters, long-chain alcohols, long-chain fatty acids, ketones [10].

Our project was designed to analyse selected properties of a fat product based on vegetable oil by addition of structuring substances.

Experimental part

Materials and methods

Structured fats (oleogels) derived from high-oleic sunflower oil (Bunge Poland) including 3% of oleogel-forming substances: monoacylglycerols (MAG), candellila wax - CLX, carnauba wax - CRX, white beeswax - WBX, yellow beeswax - YBX, and rice bran wax - RBX (Strahl & Pitsch, Inc., USA) as well as palm fat (Bunge, Poland) were the study materials.

Technology of oleogel production

High-oleic sunflower oil was mixed with oleogel-forming substances and then heated at 90°C for 30 min in a combi steam oven (UNOX, Italy). On removal from the oven, the samples were stirred thoroughly once again.

Testing of texture

Texture of the samples was analysed with TX.AT plus (Micro Stable Systems, UK), by means of penetration testing. A cylindrical tip with a diameter of 1cm (P/0.5R) was used for the purposes of measurements, dipped 5mm into a sample, with the working component moving at a rate of 1mm/s. The test was carried out at room temperature. The resulting curves (of penetration force

---

email: mkowalska7@vp.pl; Phone:48 483617547

over time) served to determine hardness and viscosity of the samples (fig. 1). The maximum measured force was defined as hardness and the minimum force as stickiness [11]. The data were expressed in Newton [N].

Testing of apparent viscosity

Viscosity of the gels was measured with Brookfield HA (USA) device by means of DIN-87 spindle. The measurement proceeded over 25 stages, with the initial rotational speed of 10 rpm to rise by 10 rpm with every stage. The measurements were carried out at 25°C by placing the test samples in the thermostat (Brookfield TC-550).

Colour measurement

Colours were measured as part of CIELab system using the reflection method by means of Konika-Minolta 200 device. To compare colour differences between the palm fat and the gels produced, the total colour differences (ΔE) were calculated according to:

$$\Delta E = [(L_p^* - L_x^*)^2 + (a_p^* - a_x^*)^2 + (b_p^* - b_x^*)^2]^{0,5}$$

where: L_p- L parameter of palm fat; L_x- L parameter of tested oleogel; a_p -a parameter of palm fat; a_x -parameter a of tested oleogel; b_p- parameter b of palm fat; b_x - parameter b of tested oleogel.

Crystallisation time

The oleogels and palm fat were heated in a water bath at 90° C for 120 min. All the samples were then removed from the bath at the same time and their crystallisation time was defined as the time from the removal to gel solidification in min. A gel was solid when it was not observed to flow after a test tube was tipped by 90° [6].

Oil binding capacity (centrifugal method)

Test tubes containing 3g of a sample were whirled for 15 min in a centrifuge MPW-340 (Poland) set at 4000 revolutions per minute. In effect, unstable oleogels separated into two phases, with the upper phase constituted by the separated oil. The centrifuged test tubes were placed upside down on a paper towel to remove the separated oil. The remaining layer was weighed after 5 min.

Oil binding capacity (ZWO) was calculated from [11]:

$$ZWO\% = (M_{st} - M_t)/(M_g - M_t) \times 100\%$$

where:

M_{st}- weight of sample and test tube on centrifugation (g),

M_g- weight of gel and test tube (g),

M_t- weight of test tube (g).

Oil binding capacity determined by the dryer method at 40°C

The test was undertaken a day after production of oleogels using a modified method of Blake et al., [9]. 30g of a gel was transferred to a funnel with Munktell #3 paper placed in a flask. Weight of gel oil loss was measured at intervals of 0.25, 0.5, 0.75, 1, 1, 5, 2, 3, 4, 5, 6, 24 h. The test was carried out in a laboratory drier at 40°C (±2°C). The results were illustrated as a diagram of dependence between % oil loss and duration of the experiment. The data were analysed in Prim 6.0 software and substituted to the kinetic formula of natural disintegration:

$$Y = Y_{MAX} \cdot (1 - e^{-kt})$$

Microscope photographs of oleogels

The gel samples were analysed, magnified x600 times, 24 h after production, under an optical microscope linked with OPTA-Tech MB 300 camera. Crystal lengths were measured using Opta View 7.0 software.

Stability assay by means of dispersion analyser

Stability, transmission and back reflection profiles of the particular oleogels were assayed with the method of laser diffraction by means of dispersion analyser LumiSizer 612. Oleogel samples (ca. 0.2 mL) of initial concentrations (undiluted) were placed in measurement chambers and analysed. The following parameters of analysis were applied: centrifugal force (4000 RPM), light coefficient (1.0), wavelength (870 nm), temperature (25°C), interval - recording time of transmission profiles (10s), total duration of the analysis (50 min). The analysis produced coefficients of sample instability and distribution of passing light intensity as a function of time and location all along a sample, which also helped to determine a type of destabilisation processes in a given sample. There were two runs of the assays.

Statistical analysis

The results were analysed statistically using Statistica 10.0 and applying one-way analysis of variance -Tukey's t-test.

Results and discussions

Analysis of microscope photographs

Addition of waxes and monoacyloglycerols to high-oleic sunflower oil caused its gelation. A solid oleogel was produced not only upon addition of carnauba wax CRX (fig. 1). The resulting samples differed in appearance. Surfaces of the palm fat and oleogels including rice bran wax (RBX) and monoacylglycerols (MAG) was not shiny, whereas the oleogel containing candelilla wax (CLX) was the most light reflective (fig. 1).

The gelation mechanism of waxes and mono-acylglycerols involves formation of microcrystalline plates that agglomerate into a three-dimensional network, thereby binding liquid fat [9]. The shape of carnauba wax crystals was markedly different from that of the remaining crystals, namely, more rounded. The remaining oleogel-forming substances had the shape of needles, sometimes branching. CLX oleogel contained the smallest crystals (fig 2). The different appearances of crystals are caused by

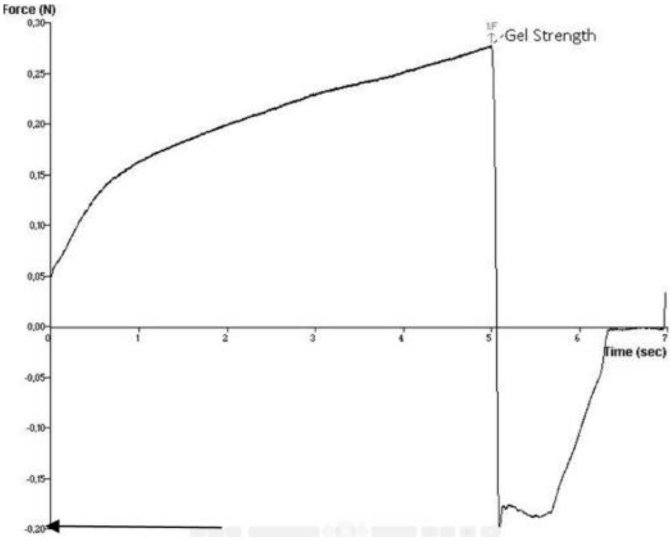


Fig.1. A sample diagram derived from oleogel penetration testing.

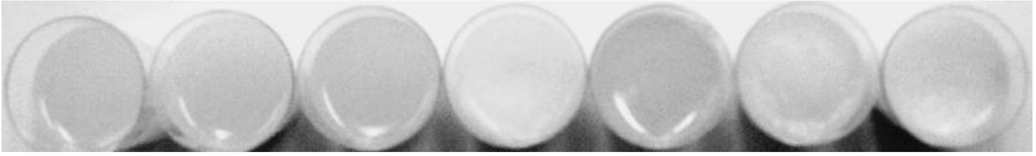


Fig.2. Appearance of the oleogels and palm fat produced. Left to right: white beeswax (WBX), carnauba (CRX), yellow bees wax (YBX), rice bran wax (RBX), candelilla wax (CLX), monoacylglycerol (MAG), palm fat

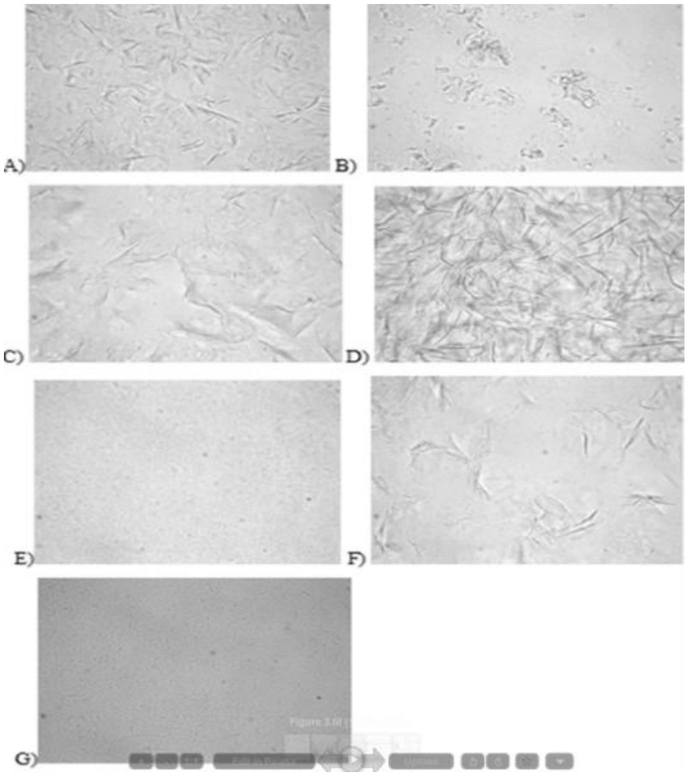


Fig. 3. Microscopic photos of the following oleogel structures: A - WBX, B- CRX, C-YBX, D-RBX, E-CLX, F- MAG, G- palm fat

the diverse origins and chemical compositions of the waxes [10].

The microscopic image of the samples showed the densest crystal distribution in CLX and RBX oleogels. The CLX oleogel was closest to palm fat in respect of microscopic structure, dense arrangement and size of the crystals (fig. 3). The average size of palm fat crystals was 3.87 um, while that of CLX 2.30 um. The largest crystals occurred in structured fats produced using rice wax (RBX-28.02 um) and MAG (24.27 um) (table 1).

Crystallisation time

The structured fat including RBX exhibited the shortest crystallisation time, the oleogel becoming solid after 251 seconds. Palm fat arrived at this condition after 650.3 seconds, with CLX oleogel coming closest with the time of 608 seconds. On the other hand, oleogel containing 3% of monoacylglycerol, MAG, solidified the longest (table 1). The structured fat including CRX was not solid at room temperature, therefore, it is not addressed in this analysis. Yilmaz and Ogutcu [11] produced oleogels containing 7% of structuring substances and their sample including monoacylglycerol crystallised faster than the one with beeswax.

Colour of the oleogels

Colours of all the products were clearly different from that of palm fat as the total colour difference (ΔE) was considerably greater than 3. Palm fat was the brightest, with the parameter L* of 73.62, followed by the oleogel RBX (L*=46.65). The test samples also differed in respect of the remaining colour parameters (table 2).

Table 1

CHARACTERISTICS OF OLEOGELS AND PALM FAT

		WBX	CRX	YBX	RBX	CLX	MAG	palm fat
Crystal size [um]	Min	2.53	4.84	4.6	5.63	1.49	5.99	1.92
	Max	24.73	37.86	41.96	48.22	3.08	39.65	10.73
	Average	12.05	16.71	21.95	28.02	2.30	24.27	3.87
Crystallisation time [s]		1001.7	-	727.0	251.2	608.0	2165.0	650.3

„-„ liquid at room temperature

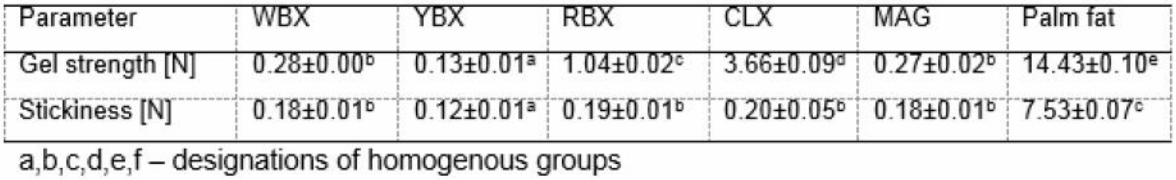
Table 2

COLOUR PARAMETERS OF THE OLEOGELS

Samples	Colour parameters			Total colour difference
	L*	a*	b*	ΔE
WBX	38.61 ± 0.66^{b}	0.27 ± 0.58^{e}	-4.44 ± 0.05^{b}	35.33
CRX	43.59 ± 0.52^{d}	-1.95 ± 0.34^{b}	-2.01 ± 0.27^{d}	30.30
YBX	37.91 ± 0.63^{b}	-0.41 ± 0.32^{d}	-1.34 ± 0.16^{e}	36.14
RBX	46.65 ± 0.79^{e}	-0.22 ± 0.23^{de}	0.77 ± 0.21^{f}	19.60
CLX	35.90 ± 0.08^{a}	0.72 ± 0.54^{ef}	-3.56 ± 0.23^{c}	38.10
MAG	42.65 ± 0.06^{c}	-0.81 ± 0.07^{c}	-3.44 ± 0.02^{c}	31.22
T palm	73.62 ± 0.81^{f}	-4.43 ± 0.52^{a}	-5.16 ± 0.44^{a}	0

a,b,c,d,e,f – designations of homogenous groups

Table 3
TEXTURAL PROPERTIES OF THE OLEOGELS



Parameter	WBX	YBX	RBX	CLX	MAG	Palm fat
Gel strength [N]	0.28±0.00^b	0.13±0.01^a	1.04±0.02^c	3.66±0.09^d	0.27±0.02^b	14.43±0.10^e
Stickiness [N]	0.18±0.01^b	0.12±0.01^a	0.19±0.01^b	0.20±0.05^b	0.18±0.01^b	7.53±0.07^c

a,b,c,d,e,f – designations of homogenous groups

Texture of the oleogels

Textures of the oleogels were distinctly different to that of palm fat, which was the hardest. CLX followed by RBX were hardest among the structured fats (table 3). Hardness of the CRX samples was not determined as it was liquid. Hardness of gels may be a result of density of crystal cross-linking. The ability of monomer substances to gelate oil depends on the ratio of crystal and oil surfaces and solubility of a given substance in oil. The greater the surface and solubility, the stronger the oleogel produced [9].

CLX was the stickiest oleogel. Stickiness rose as hardness grew, though the relation was not proportional (table 3).

Yilmaz and Ogutcu [11] observed firmness of oleogels containing MAG and beeswax was not statistically significant, whereas stickiness of fat structured with MAG was considerably higher.

Viscosity of the oleogels

As far as apparent viscosity at 25°C is concerned, the oleogel containing RBX (412.4 mPa s) proved the most similar to palm fat (379.4 mPa s). Viscosity of CRX was not tested as it was highly unstable: it was observed to break 24h after production of the oleogel. YBX displayed the minimum viscosity. The oleogels examined turned out to be non-Newtonian liquids, since viscosity of a liquid diminished as the shear rate grew [12], which was confirmed once the results were matched to Ostwald de-Waele relationship (Power-law) (table 4):

$$\tau = kD^n$$

where: τ is shear stress (Pa), *k* flow consistency [mPa×s], *D* shear rate [1/s], and *n* flow behaviour index.

Sagiri et al. [12] also demonstrated oleogels derived from soya or sesame oil, with stearic acid added as the structuring substance, are non-Newtonian liquids.

The oleogels produced showed n<1, proof they are pseudoplastic liquids, while high values of k (particularly for CLX, palm fat and RBX) suggest thicker consistency of an oleogel (table 4).

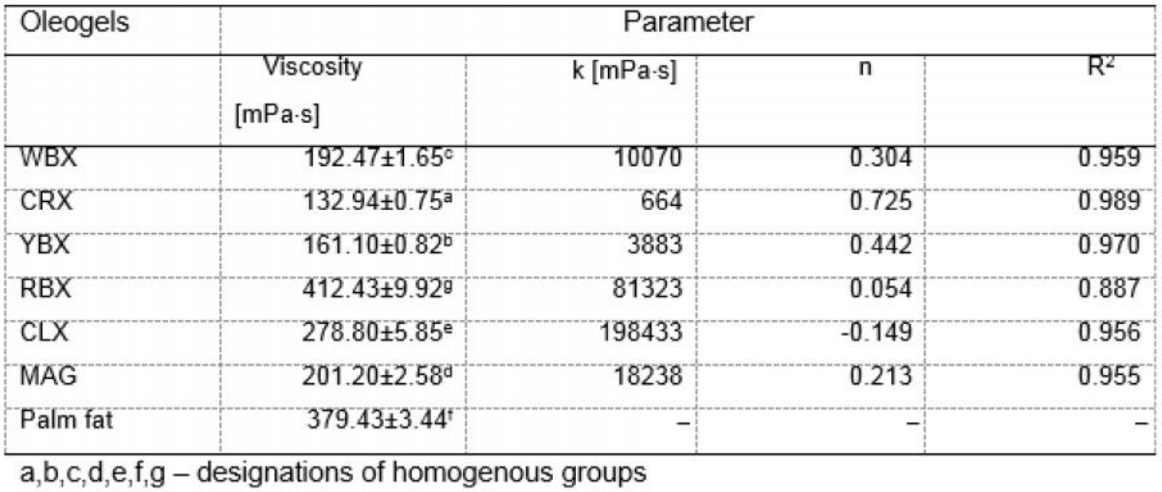
Oil binding capacity using centrifugal method

Oil binding capacity assayed by means of centrifugal method was maximum for CLX and YBX, amounting to 100%. CRX oleogel proved the least stable - 53.17% (table 5). Added to that, it was observed to delaminate after more than 24h of storage. The oil structured with 3% addition of monoacylglycerol (MAG) also showed relatively low stability of 69.02%. Similar results were arrived at by Yýlmaz and Ogutcu [11], who found the oleogel made of hazelnut oil with a 3% addition of monoacylglycerol was less stable than samples containing additions of beeswax.

Oil binding capacity assayed by means of filtration method at 40°C

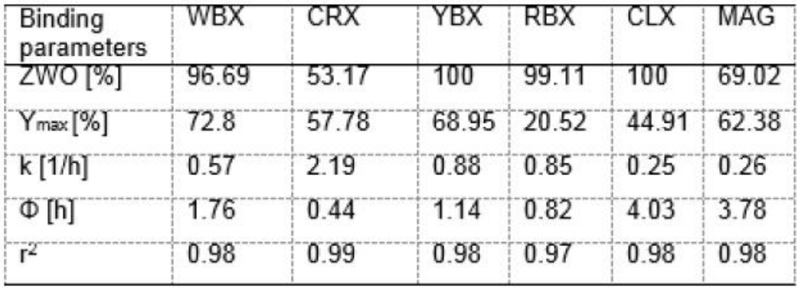
This method is applied to long-term storage of products. The oil loss is related to the capacity for its binding by networks of wax crystals.

Table 4
RHEOLOGICAL PROPERTIES OF OLEOGELS



Oleogels	Parameter			
	Viscosity [mPa·s]	k [mPa·s]	n	R^2
WBX	192.47±1.65^c	10070	0.304	0.959
CRX	132.94±0.75^a	664	0.725	0.989
YBX	161.10±0.82^b	3883	0.442	0.970
RBX	412.43±9.92^g	81323	0.054	0.887
CLX	278.80±5.85^e	198433	-0.149	0.956
MAG	201.20±2.58^d	18238	0.213	0.955
Palm fat	379.43±3.44^f	–	–	–

a,b,c,d,e,f,g – designations of homogenous groups



Binding parameters	WBX	CRX	YBX	RBX	CLX	MAG
ZWO [%]	96.69	53.17	100	99.11	100	69.02
Y_{max} [%]	72.8	57.78	68.95	20.52	44.91	62.38
k [1/h]	0.57	2.19	0.88	0.85	0.25	0.26
Φ [h]	1.76	0.44	1.14	0.82	4.03	3.78
r^2	0.98	0.99	0.98	0.97	0.98	0.98

Table 5
OIL BINDING CAPACITY OF OLEOGEL-FORMING SUBSTANCES

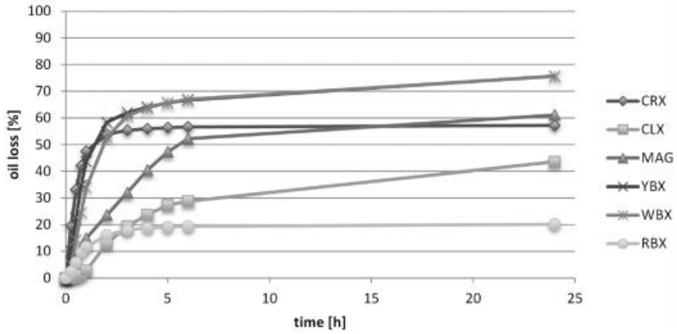


Fig. 4. Oil loss from the oleogels at 40°C
Key: CRX-carnauba, CLX - candelilla wax, MAG - monoacylglycerol, YBX - yellow bees wax, WBX-white bees wax, RBX - rice bran wax.

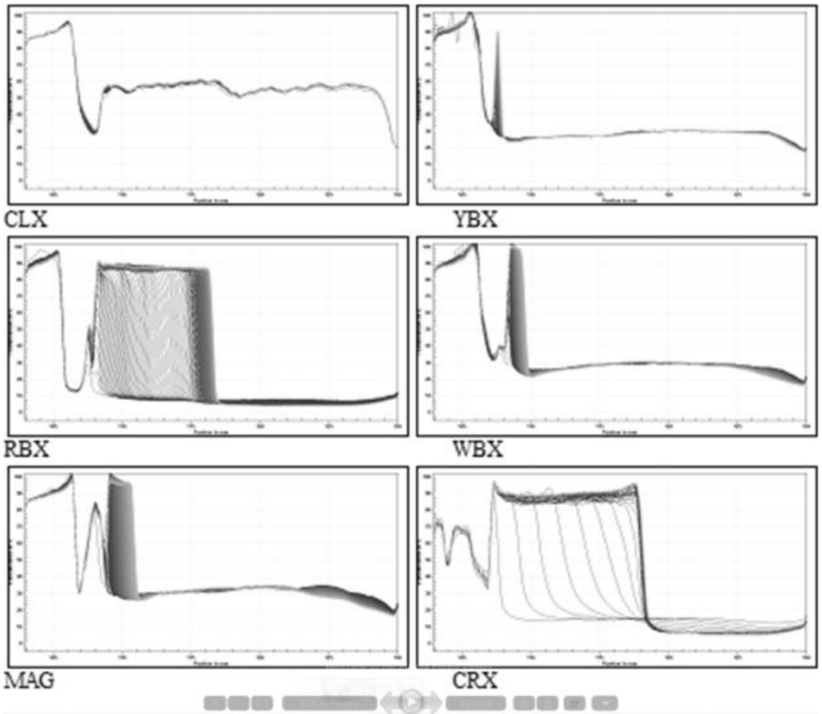


Fig. 5. Comparison of evolution of transmission profiles in the oleogels over 50 min, the first profile after 10 s – red, the last after 50 min-green

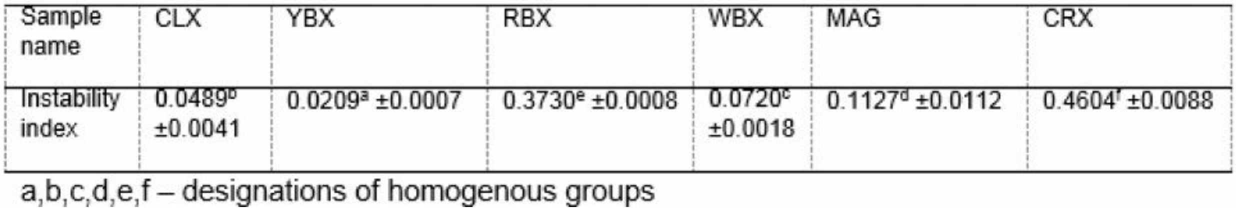
The results are presented as quantities of oil loss as a function of time. The dependence was then fitted to the kinetic formula $Y = Y_{MAX} \times (1\text{-}e^{-kt})$. The coefficient of determination (r^2) was more than 0.97 for all cases (table 3), evidence of the excellent fit between the formula and the data. It serves to compute such data as: Y_{MAX} - maximum oil loss of the system, k – the variable defining inclination angle of the curve, and Φ - the so-called 'golden mean', expressing the time after which half of the oil loss takes place. In light of the filtration method at 40°C, a minimum oil loss was exhibited by fat structured with RBX addition. The poorest binding properties were displayed by WBX and YBX waxes, for which Y_{MAX} reaches its maximum values (table 5, fig. 5).

A low k shows a low inclination angle of the curve and thus slow loss of oil. In the case of all oleogels except CLX, the loss grew rapidly to begin with and then declined dramatically - stabilising. CRX, delaminating 24h after production, exhibited a relatively stable structure (assayed by filtration at 40°C) and its Y_{MAX} was 57.78. On the other hand, this oleogel (CRX) displayed the highest value of k and the lowest Φ, proof its structure loses the most oil from among the remaining structured oils tested over short periods of storage. The curves illustrating the oil loss of CLX and MAG oleogels at the time of testing differed from the remaining curves as the oil loss increased very slowly in the initial phase (after about 2 h) (fig. 4). This is of particular importance, especially in the event of short-term storage.

Stability assay with dispersion analyser

No changes of transmission or back reflection were noted for CLX oleogel. The transmission signal and back reflection were found to change for the remaining samples, proof of their destabilisation. On the basis of the generated transmission profiles, the separation was determined to be the result of particle sedimentation (identified by the rising transmission across the meniscus, with the boundary between phases shifting towards the bottom of the chamber), most distinct in the sample containing RBX and CRX waxes and least noticeable in YBX oleogel. The sample including the addition of yellow beeswax (YBX) showed only minor signal changes in the region of the meniscus, evidence of incipient oil separation in the oleogel. For RBX and CRX oleogels, meanwhile, transmission profiles demonstrated a substantial region of light transmission in the top sample layer and, following centrifugation, two clearly separated phases (a limpid, transparent one on top and a turbid, bright towards the bottom) could be observed. This was corroborated by instability indices determined for these samples (for RBX-0.3730 and for CRX - 0.4604- the highest among those assayed). The lowest instability index characterised the YBX sample (0.0209). The index points to separation of a mixture under analysis. Values close to 1 indicate a total or nearly total sample separation, values close to 0 suggest absence of or a very slow separation of a mixture at the time of measurement recording. The transmission profile for CLX oleogel implies it should be more stable than YBX (the profiles overlap and no changes of the sample's appearance were noted on centrifugation) (fig. 5), whereas the instability index

Table 6
INSTABILITY INDEX ASSAYED BY MEANS OF DISPERSION ANALYSER



Sample name	CLX	YBX	RBX	WBX	MAG	CRX
Instability index	0.0489^b ±0.0041	0.0209^a ±0.0007	0.3730^e ±0.0008	0.0720^c ±0.0018	0.1127^d ±0.0112	0.4604^f ±0.0088

a,b,c,d,e,f – designations of homogenous groups

determined for CLX was greater than for the oleogel including yellow beeswax (table 6), possibly due to the consistency of the oleogel wax, as shown by greater transmission values recorded for that sample containing candelilla.

Conclusions

The oleogels produced differed by their physical parameters, therefore, the type of oleogel-forming substance applied had substantial impact on properties of structured fats. Microscopic images showed structure of the oleogel with a 3% addition of candelilla wax (CLX) was the most similar to that of palm fat. Arrangment of plates of structuring substances in the remaining gels was asymmetrical.

The products displayed statistically significant differences of colours and were not similar to palm fat in this respect. Textures of the oleogels were also different from one another and from palm fat. There were greater differences of hardness and clearly smaller differences with regard to viscosity. Best oil retaining properties in the oleogel structure were exhibited by the samples including additions of CLX and yellow bees waxes - assayed with the centrifugal method. As part of testing using filtration (at 40°C), on the other hand, the oleogel produced with candelilla and rice waxes displayed the minimum oil loss after 24h, which may prove these structure-forming substances help to produce oleogels that could be used in products exposed to higher temperatures.

References

1.PERNETTI M., VAN MALSSEN KF., FLÇTER E., BOT A., Curr. Opin. Colloid In., **12,** 2007, p. 221-231

2.ZBIKOWSKA A., RUTKOWSKA J., KOWALSKA M., J. Am. Coll. Nutr., **34,** 2015, p. 507-514

3.ONACIK GUR S., ¯BIKOWSKA A., JAROSZEWSKA A., CYTA - J. Food. **13**, 2015, p. 621-628

4.KOWALSKA M., ZBIKOWSKA A., TARNOWSKA K., J. Am. Oil Chem. Soc., **92,** 2015, p. 993-1002

5.ROGERS A.M., STROBER T., BOT A., TORO-VAZQUEZ J., STORTZ T., MARANGONI, A.G., Int. J. Gastr. Food Sci., **2,** 2014, p. 22-31

6.DASSANAYAKE L.S.K., KODALI D.R., UENO S., SATO K., J. Am. Oil Chem. Soc., **86,** 2009, p. 1163-1173

7.DASSANAYAKE L.S.K., KODALI D.R., UENO S., Curr. Opin. Colloid In., **16,** 2011, p. 432-439

8.GRAVELLE A.J., BARBUT S., MARANGONI A.G.,. Food Res. Int. **48,** 2012, p. 578-583

9.BLAKE AI., CO E.D., MARANGONI A.G., J. Am. Oil Chem. Soc., **91,** 2014, p. 885-903

10.ROCHA J.C.B., LOPES J.D., MASCARENHAS M.C.N., ARELLANO D.B., GUERREIRO, L.M.R., DA CUNHA, R.L., Food Res. Int., **50,** 2013, p. 318-323

11.YILMAZ E., OGUTCU M., J. Am. Oil Chem. Soc., **91,** 2014. p. 1007-1017

12.SAGRIRI,S.S., SINGH V.K., PAL K., BANERJEE I., BASAK P., Mat. Sci. Eng. C., **48,** 2015, p. 688-699

Manuscript received: 15.03.2017

REVISTA DE CHIMIE
_SI_
REVISTA MATERIALE PLASTICE
POT FI ACCESATE GRATUIT
LA URMATOARELE ADRESE:

http://www.revistadechimie.ro/
http://www.revmaterialeplastice.ro/

FREE WEB ACCESS FOR
REVISTA DE CHIMIE
AND
MATERIALE PLASTICE

http://www.revistadechimie.ro/
http://www.revmaterialeplastice.ro/