

## COMPARISON OF OLEOGELS PROPERTIES OBTAINED WITH DIFFERENT STRUCTURE- FORMING SUBSTANCES

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### Abstract

Evaluation of selected quality parameters of oleogels made with one type of lipid solvent – rapeseed oil was done. The effect of two gelling agents: ethyl cellulose (EC) and monoacylglycerol (MAG) on the hardness, lubricity and stability of organogels was determined. Oleogels containing 7% and 8% w/w of single EC or MAG were prepared, as well as mixed variants with 3.5% MAG & 4.0% EC and EC 3.5% & 4.0% MAG in rapeseed oil. It has been shown that both: ethyl cellulose and monoacylglycerol had structural-forming properties. The greatest hardness and the least spreadability was found in the oleogel with an 8% polysaccharide addition. EC showed good ability of gelling rapeseed oil but organogels with EC were less stable in time compared to the single-monoacylglycerol oleogels. Mixed variants had the lowest stability compared to oleogels with the addition of a single gelling substance.

### Introduction

Vegetable oils containing essential unsaturated fatty acids are a desirable ingredient in the daily diet. Due to the presence of acids from the group of n-3, n-6, n-9, antioxidants and the lack of cholesterol are recommended for consumption by both food technologists and dieticians (LIN et al. 2013). Confectionery or bakery products require the presence of solid

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lipids in order to obtain the appropriate sensory and physical quality (ŻBIKOWSKA 2010, ŻBIKOWSKA et al. 2015). In technological terms, liquid oils are not, therefore, recommended substitutes for shortening or other solid bakery fats, which contain nutritional undesirable fatty acids isomers in trans configuration (JANG et al. 2015, HWANK et al. 2016, DOAN et al. 2017). The search for an alternative to these lipid food ingredients has become one of the reasons for the formation of oleogelation (MARANGONI and GARTI 2015, PATEL 2015). It is a process of forming semi-solid consistency of liquid oil with the use of a gelling substance (MARANGONI 2012). Oleogelation is a physical transformation, based on the dissolution of gelators in a lipid medium whose chemical properties do not change during process (PATEL and DEWETTINCK 2016). Gelling substances that are currently used in the production of oleogels are, among others, polysaccharides (e.g., ethyl cellulose, hydroxypropyl methyl cellulose) monoacylglycerol, natural waxes, or low molecular weight gelators (LMWGs) (WRIGHT and MARANGONI 2007, HUGHES et al. 2009, HWANK et al. 2016, SAGIRI et al. 2017, MENG et al. 2018).

The most commonly described compound in the literature, having the ability to gel vegetable oils is ethyl cellulose (EC). It consists of 1,4-D-glucose molecules linked to the ethyl groups at 2,3 and 6 carbon atoms (ROGERS et al. 2014). It is the only cellulose derivative that has the ability to be directly dispersed in liquid oil (PATEL and DEWETTINCK 2016). The non-smooth, rough structure of the network formed by ethyl cellulose ensures the maintenance of oil particles (ROGERS et al. 2014). This biopolymer is one of the most effective gelling agent used in the food industry (DAVIDOVICH-PINHAS et al. 2016). It is generally permitted for use in food in accordance with the principle of *quantum satis* as an additional substance (Regulation of the Minister of Health... 2010). According to STORTZ et al. (2013), ethyl cellulose is one of the gelling agents with the ability to create a network that maintains fat molecules, e.g. in chocolate or nut butter. In the form of oleogel, EC could be used as a lipid component of frankfurters (ZETZL et al. 2012).

Another substance that has the ability to form a gel in a lipid solvent is monoacylglycerol (MAG). It is a single chain of fatty acid (most commonly palmitic or stearic acid), connected by an ester bond with a glycerol molecule (EICHMANN and KNITTELFELDER 2015, CHEN and TERENTJEV 2015). According to GOLDSTEIN et al. (2012), monoacylglycerols exist in two crystalline forms:  $\alpha$  and  $\beta$ . The first of these is used to produce baked products, e.g. cakes, because it facilitates the insertion of air into the fat phase. The crystalline form  $\beta$  is in turn more suitable for harder products, such as biscuits, due to its greater hardness.

Monoacylglycerol-contained organogels may be produced using one of the two methods: as an oil solutions or water-lipid mixtures. However, those that have water in their structure are four times less durable (GOLDSTEIN et al. 2012). According to CHEN and TARENTJEV (2015), monoacylglycerol organogels, in particular, could be used in the production of ice cream, as ingredients that create their creamy consistency.

This paper compares two additional substances, belonging to different groups of chemical compounds: ethyl cellulose (polysaccharide) and monoacylglycerol (lipid), as single and mixed gelators of rapeseed oil. Their impact on selected qualities of oleogels (hardness, spreadability, as well as centrifugal and filtration stability) were evaluated.

## Materials and Methods

### Raw materials and preparation of organogels

Ethyl cellulose (EC) and monoacylglycerol oleogels (MAG) were made in two variants. The first one contained 7%, the second 8% of a single gelling substance. The organogels, being a mixture of the mentioned gelators, consisted of 3.5% EC (EC45 Std Premium – a gift from Dow Chemical Company, Germany) and 4.0% MAG (Lasenor, Spain), or 4.0% EC and 3.5% MAG (two variants). In all oil gels, rapeseed oil (ZT “Kruszwica” S.A., Poland) was used as a lipid solvent.

Preparation of organogels consisted in dissolving a gelling substance of a specified concentration in rapeseed oil at a temperature allowing the dissolving of gelators, i.e. 90°C for monoacylglycerol lipid gels and 140–160°C for ethyl cellulose and mixed oleogels. Prior to qualitative determinations, the oleogels were allowed to solidify for 24 hours at a temperature of  $20 \pm 1^\circ\text{C}$ .

### Analysis of fats

The rapeseed oil was subjected to derivatization into fatty acid methyl esters (*Animal and vegetable... ISO 5509:2001*) to the content analysis of FA by the GC method in gas-liquid partition, according to recommendations in the ISO standards (*Animal and vegetable... ISO 15304:2003*, *Animal and vegetable... ISO 5508:1996*). The analysis was carried out using the gas chromatograph Agilent Technologies 6890 II with the software ChemStation with an FID detector, equipped with an SGE BPX 70 capillary column. The temperature during the analysis was maintained between

140 to 220°C. Identification of peaks of fatty acids was carried out by comparing them with the retention time of samples of fatty acid methyl esters (Supelco 37, Sigma Aldrich, St. Louis, MO, USA) – Table 1.

Table 1

The fatty acids composition of rapeseed oil (g FA/100 g FA)

Fatty acids									
C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C22:0	C20:1	C22:1	another
3.6±0.02	2.4±0.01	57.9±1.02	21.1±0.05	9.8±0.01	2.1±0.01	0.6±0.02	1.0±0.02	1.1±0.03	0.4±0.02

### Hardness of oleogel

The hardness of oleogels were shown using penetration test. Samples were tested using a TX.AT plus device (Micro Stable Systems, UK). It consisted of dipping the cylinder shape tip (P/0.5R), with a diameter of 1 cm in the sample to a depth of 5 mm. Samples were poured into glass weighing dishes (diameter 3.5 cm) to a height (H) of approx. 2.5 cm. The speed at which the rod moved was 1 mm s<sup>-1</sup>. Results were obtained in the form of curves on the graph, illustrating the force (y-axis) in time (x-axis). The highest penetration value obtained, expressed in Newton, was the hardness of the gel. The measurements were realized executed at room temperature. A total of twelve determinations were carried out for each type of oleogel.

### Spreadability of olegel

The spreadability determination was based on the penetration test, which consists in submerging the tip of the measuring apparatus in the shape of a cone (spreadability ring) with a diameter of 45 mm, in a special container perfectly suited to it. The speed at which the upper working element was lowered (until 1 mm gap obtained between the two measuring parts) was 3 mm s<sup>-1</sup>. The test was performed using a TX.AT plus device (Micro Stable Systems, UK) at room temperature. Spreadability was determined as a total value of twelve for each type of oleogel in the N mm unit, as the area under the curves on the graph illustrating the force (y-axis) in time (x-axis).

### Stability of oleogels – centrifugal separation method

The stability of the oleogels was determined on the modified method of DA PIEVE et al. (2010). The oil-gel samples were transferred to empty tubes (mt) at 3.00 g weight. The whole samples were centrifuged at 3500 rpm. in the MPW-340 centrifuge (MPW Med. Instruments, Poland). The duration

of the process was 20 minutes, after which the mass of the gel and the centrifuged oil (mgo) was determined. The liquid collected at the top of the test tube was drained. The residue was weighed with the tube [mg]. Each variant was subjected to nine determinations.

The stability of the oleogel determined by the centrifugal method (ST) was calculated from the modified YILMAZ and ÖĞÜTCÜ (2014) formula:

$$ST = \frac{(mg - mt)}{(mgo - mt)} \cdot 100\%$$

### Oil binding capacity

The oil-binding measurements were managed using modified BLAKE et al. (2014) method. It consisted in measuring mass (gram) of rapeseed oil leakage, filtered through a 150 mm diameter filter paper (Munktell-Ahlstrom, Germany) at  $20 \pm 1^\circ\text{C}$ . Thirty-gram samples of all the oleogels were placed on glass funnels with filter paper located in pre-weighed conical flasks. After 15, 30, 45, 60, 90, 120, 180, 240, 300, 360 minutes, and after 24, 48 and 72 hours, rapeseed oil leakage was weighed. The oil binding capacity of gelling agents was determined as the percentage loss of the initial weight of organogel. It was measured in sixuplicate.

### Statistical analysis

Statistical preparation was carried out using the software Statgraphics Plus 4.1. Analysis of the obtained results of physical parameters of oleogel was performed using one-way analysis of variance and regression. The assessment of the significance of differences between the means was performed using Tukey Test ( $p \leq 0.05$ ). The regression method was used for model determination. Based on the experimental data for each dependent variable ( $y$  – mass of liquid fraction – the size of mass loss) equations were formulated ( $y = a_0 + a_1 + \dots + a_k x$ ) in which  $a_{0,1}, \dots, a_k$  are appropriate coefficients determining intercepts, and  $x$  is the time of measurement.

## Results and Discussion

### The effect of gelling agents on the textural parameters of oleogels

Hardness is a mechanical texture feature, expressing the force that causes a specific deformation. The results showed that the highest hardness was characterized by oleogels with the highest percentage of single

gelling ingredient, i.e. 8% polymers (EC) and 8% monoacylglycerol (MAG). The maximum force causing their deformation in the penetration test was 1.8 N and 1.7 N (Figure 1). This proves that the higher the concentration of a single gelling substance in rapeseed oil, the harder the oleogel structure. Organogels, being a mixture of two gelling substances, were characterized by lower hardness (more than twice) in the case of lower EC content (for the variant 3.5% MAG & 4.0% EC – 0.7 N and for 3.5% EC & 4.0% MAG – 0.3 N). This results suggesting that polysaccharide gelator causes an increase in the hardness of the organogels.

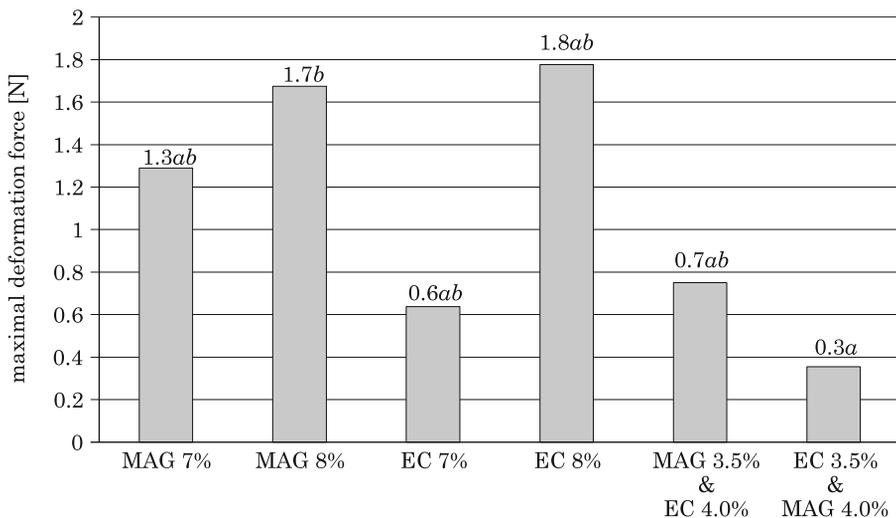


Fig. 1. Hardness of oleogels [N]; \*a, b – different letters indicate mean values being statistically significant,  $p \leq 0.05$

GRAVELLE et al. (2014) proved that as the percentage of EC in rapeseed oil increases, the hardness of the gel increases. Similar relationships were found in the tested ethyl cellulose oleogels, produced with the participation of rapeseed oil (Figure 1). SI et al. (2016) also obtained such a link, but for two variants of monoacylglycerol oleogels, containing 3% and 6% MAG. The solvent for mentioned gelling agent was soybean oil. The hardness of oleogels tested by SI et al. (2016), increased with increasing MAG concentration and was successively: 0.1 N and 0.4 N. These values are lower than obtained in organogels containing rapeseed oil as a solvent, which additionally confirms the dependence of force from monoacylglycerol concentration in the penetration test.

The Figure 2 presents the value of area, under the force-time penetration curve, interpreted as the spreadability. It is a parameter that charac-

terizes the texture of food e.x. margarines, creams, peanut butter. The greater its value, the worse the possibility of spreading them (JAKUBCZYK et al. 2014). The obtained data indicate an upward trend in the spreadability values of oleogels containing a single gelling substance (MAG or EC), along with their increasing percentage in organogels.

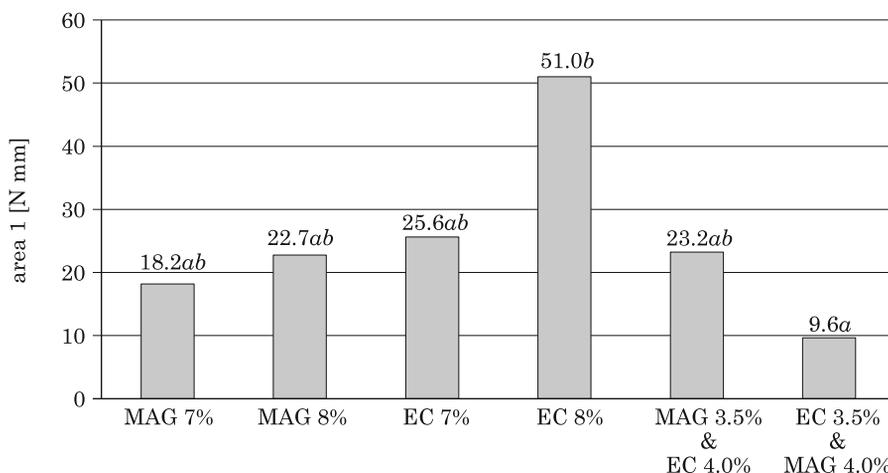


Fig. 2. Spreadability of oleogels [N mm]; \**a*, *b* – different letters indicate mean values being statistically significant,  $p \leq 0.05$

The highest value of the tested parameter – 51.0 N mm, was obtained by the variant containing 8% concentration of ethyl cellulose in rapeseed oil. Oleogel with an 8% addition of the lipid gelator MAG had more than twice the lower spreadability value (22.7 N mm). The results indicate the effect of ethyl cellulose on the increase in the value of this parameter. Among mixed oleogels, the variant with higher concentration of ethyl cellulose – 3.5% MAG & 4.0% EC obtained a more-than-twice-higher spreadability value, which also confirms a stronger structural effect of the polysaccharide gelling agent (EC).

### Stability of the tested oleogels

For examination the oil binding capacity of gelling agents, a stability test was carried out using the centrifuge method. The results present a relatively high durability of the structure of the all organogels (Figure 3). The mean values did not differ significantly and ranged from 97.9% for the variant containing 8% ethyl cellulose to 96.7%, for the oleogel with 3.5% MAG & 4.0% EC. This proves that both mentioned gelators created a stable oleogel network, resistant to centrifugal force.

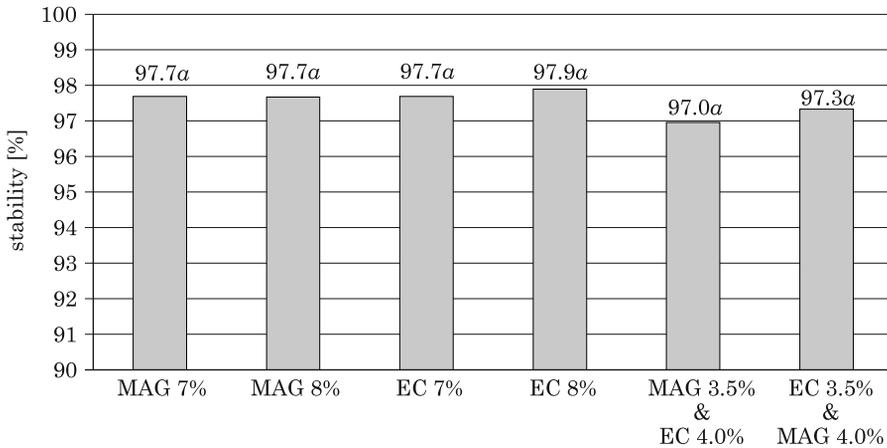


Fig. 3. Stability of oleogels; <sup>a</sup> – homogeneity group

YILMAZ and ÖĞÜTCÜ (2014) received 99.8% stability for oleogel with a 7% share of monoacylglycerol in hazelnut oil. This is a 2.1% higher parameter value, compared to an organogel with the same content of gelling substance in rapeseed oil (Figure 3). The difference in the stability of the mentioned oleogels indicates a more stable bonding of hazelnut oil by monoacylglycerol. This also presents, that the oil binding capacity is affected not only by the concentration of the gelling substance (MAG), but also by the type of lipid solvent.

Determination of stability by filtration was aimed to present the durability of the structure of oleogels at room temperature depending on time. The weight of the oil phase was measured. The stability of the systems was expressed as a percentage of the effluent relative to the initial weight of the filtered oleogel.

All organogels have retained their structure within 1 hour (Figure 4). The first spills were observed after 1.5 hours in variant with MAG 3.5% & EC 4.0%, which proved to be the least stable system. Oleogels with the most stable structure turned out to be those of variants that contained only monoacylglycerol – the first leakage was recorded in MAG 7% conical flasks after 24 hours and after 48 hours in MAG 8% (Figure 4). Also the variant with an 8% concentration of the polysaccharide gelator obtained a longer time of the first drop of oil and a smaller loss of mass throughout the entire test. These results show the dependence that the higher the concentration of a single gelling substance, the longer the separation time of the oleogels and thus their greater durability.

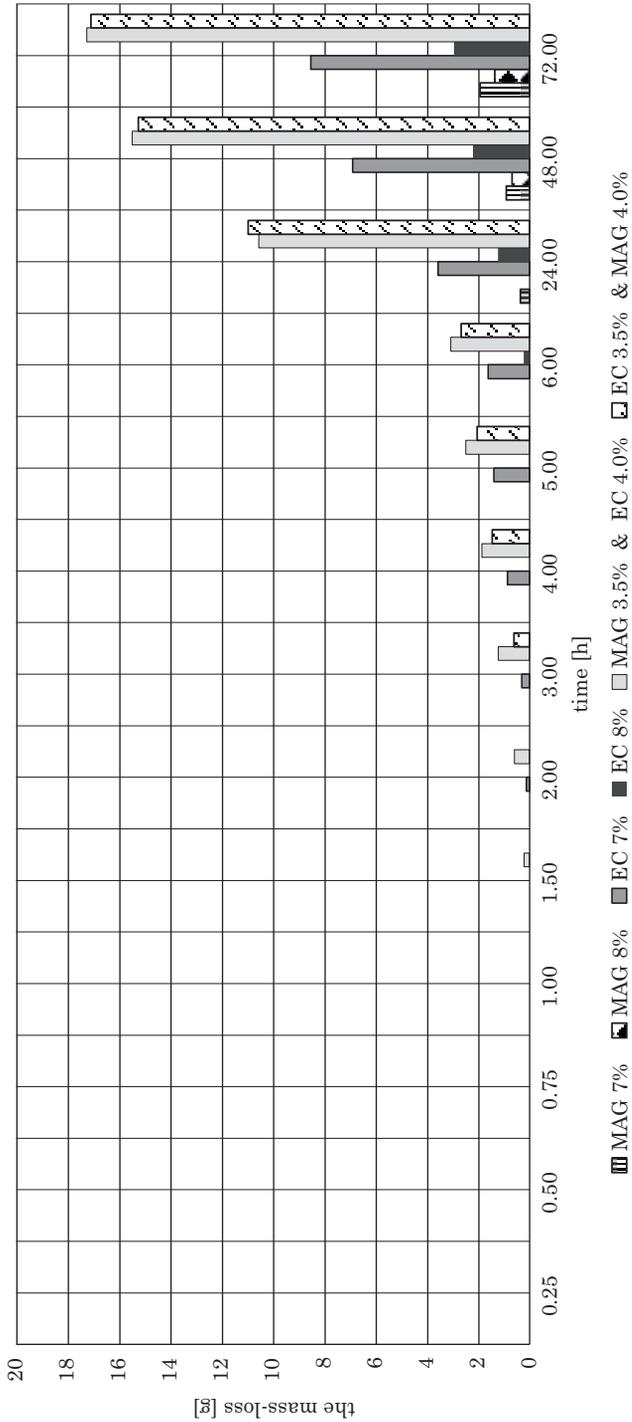


Fig. 4. Oil-binding capacity depending on time [h]

Both variants of ethyl cellulose-monoacylglycerol oleogels were characterized by very similar values of mass loss after 72 hours, higher, compared to organogels with a single gelling agent. However, the first filtrates were observed at an uneven time: after 1.5 h in MAG 3.5% & EC 4.0% flasks and after 3 h in EC 3.5% & 4.0% MAG variant (Figure 4). Determination of oleogels stability by filtration presents that lipid-type gelator had better binding capabilities of rapeseed oil than polysaccharide-type.

After the regression analysis, different models of the equation were obtained, depending on the type and amount of gelator additive – Table 2

Table 2

Correlation between loss mass (rapeseed oil leakage) and test duration

Gelator	Correlation	Model equation	$R^2$
MAG 7%	0.83	$Y = -0.92 + 0.44x$	68.4
MAG 8%	0.96	$Y = -0.11 + 0.02x$	91.6
EC 7%	0.99	$Y = 0.34 + 0.13x$	97.3
EC 8%	0.99	$Y = -0.08 + 0.04x$	98.6
MAG 3,5% & EC 4,0%	0.97	$Y = 1.14 + 0.26x$	93.4
EC 3,5% & MAG 4,0%	0.96	$Y + 0.75 + 0.26x$	92.2

( $R^2 = 68.4$  for MAG 7% to  $R^2 = 98.6$  for EC 8%). Stability of all oleogels, regardless of the variant, decreased statistically significantly over time (the mass of the liquid fraction in the oleogel increased statistically). The size of the leakage significantly increased ( $p < 0.05$ ). The weakest correlation was found between a lipid gelling substance (MAG 7% and MAG 8%) and the time of measurement (Table 2). The strong ( $R^2 > 0.9$ ) model was obtained during regression analysis: leakage mass =  $-0.11 + 0.02x$  (Table 2) – for oleogel with a 8% share of MAG. In the other variants, stronger models were obtained, i.e. the systems were less stable over time.

## Conclusion

Ethyl cellulose as a sample of polysaccharide gelator and monoacylglycerol as a lipid gelling agent are able to convert rapeseed oil into semi-solid oleogel structure, also as gelling mixtures. Increase in concentration of single mentioned gelling agents by 1% influenced the increase of hardness and spreadability of oleogels, as well as their stability in room temperature depending on time (especially variants with EC). The ethyl cellulose and monoacylglycerol belonging to different groups of chemicals do not show any synergy in the structuring of rapeseed oil.

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