MICROSTRUCTURE AND RHEOLOGICAL BEHAVOR OF EMULSIONS WITH IMPROVED NUTRITIONAL VALUE

Capcanari Tatiana, Popovici Cristina, Paladi Daniela, Deseatnicova Olga

Technical University of Moldova, Chisinau, Republic of Moldova

Capcanari Tatiana: tatiana.capcanari@toap.utm.md

Abstract: Food emulsions occupy a special place in the diet and are characterized by high taste and nutritional qualities, which are determined by a specific structure of emulsions. In the paper are studied sunflower and walnut oils with lipid fraction content in a balanced ratio of ω-3 and ω-6 polyunsaturated fatty acids and natural extracts of leaves and green nut shells (*Juglans regia* L.). Experimental data on microstructure of emulsions have shown that natural extracts positively influence the structure, size and arrangement of fat cells, increasing the degree of dispersion of vegetable oils in the aqueous phase. The analysis of rheological behavior shows that balanced ratio emulsions of polyunsaturated fatty acids and natural extracts have effective viscosity values and better Power Law parameters compared with the control sample. These results offer new interesting expectations to continue with this research line and demand the application of oil mixtures and natural extracts to provide improved nutritional value and better quality of food emulsions, being the main challenge to be faced in future studies.

Key words: walnut oil, natural extracts, emulsion, microstructure, rheology

Introduction

The knowledge of the microstructure and rheological properties of food emulsions is important because of many reasons. Sensory attributes and shelf-life of emulsions are directly related to their properties, and also, the information about the microstructure and rheology is necessary to design more rational technological processing operations [1].

Microstructure and rheological measurements are frequently used as an analytical tool to provide fundamental insights about the structural organization and interactions of the components within emulsions, for example, measurements of viscosity versus shear rate can be used to provide information about the strength of the colloidal interactions between droplets [2].

Food emulsions of "mayonnaise" type are "oil-in-water" finely dispersed emulsions, prepared from vegetable oil with the addition of emulsifiers, stabilizers, thickeners, flavorings and spices [5]. Modeling the mayonnaise recipe by introducing nutritionally valuable supplements is a perspective direction. A precious lipid product is walnut oil *Juglans regia* L. Walnut oil is rich in antioxidants (tocopherols, polyphenols), but also in polyunsaturated fatty acids ω-3 and ω-6 [6]. Partial substitution of sunflower oil with nut oil in mayonnaise will allow balancing of fatty acids, increasing of the biological and taste qualities, and the diversification of the raw material base for the production of improved nutritional value mayonnaise.

The objective of this study was to investigate the microstructure and rheological properties of food emulsions of "mayonnaise" type with improved nutritional value by using the lipid fraction (sunflower and walnut oil) with a balanced ratio of ω-3 and ω-6 polyunsaturated fatty acids. Natural extracts of leaves and green nuts have served as a stabilizing component of possible oxidation processes.

Materials and methods

Materials

The following raw vegetable oil was used for experimental research: double-refined and deodorized sunflower oil "Floris" (HGM434 / 2010) and extra virgin Greek walnut oil. Primary raw material harvested in the years 2012-2013 was also used: leaves and green walnut shell *Juglans regia* L.

Chemicals and reagents

Ethanol (99.9%), chloroform, glacial acetic acid, potassium hydroxide, phenolphthalein, potassium iodide, sodium thiosulfate (Na2S2O3 × 5H2O) and starch were supplied by Eco-Chimie Ltd. (Chisinau, Moldova). All used chemicals were of HPLC or analytical grade. Distilled water was used throughout.

Microstructure and particle size distribution

The microstructure of food emulsions was determined using an optical digital microscope of advanced series, model “Motic DMB” (China). For this purpose a drop of the investigated sample of food emulsion was placed on subject glass, covered with its integumentary glass and then established in a microscope. Photos of food emulsion samples were obtained by digital camera connected to a microscope. Obtained photos of food emulsions were analyzed and particle size distributions were calculated.

Rheological properties

Rheology measurements were performed with a rheometer TA Instruments AR-2000 ex UK. The flow properties of food emulsion samples at 20°C were determined by using a cone-plate geometry having a diameter of 40 mm. The increase of the thixotropy area was initially achieved by increasing the shear rate speed from 0 to 300 s^{-1} and then decreasing the shear rate speed from 300 to 0 s^{-1}. A mathematical model based on the experimental data and suitable for shear flow for food emulsion samples was established to quantify the samples. The power law was used as a consecutive shear flow model that establishes the relationship between shear stress and shear rate $\left(\gamma^{-n}\right)$. The power law equation is indicated below:

$$\tau = K\left(\gamma^{-t} \cdot n\right) \qquad (1)$$

Where:
τ – the shear stress,
K – the consistency index ($Pa.s^n$),
n – flow index.

The oscillatory tests were performed in the frequency range 0-100 Hz, using strain values comprised in linear viscoelasticity (0.5%). Data was collected and rheological parameters had been calculated using a TA software program tool. The collected data included the storage module (G’) and the relaxation module (G "). Delta components and complex viscosity were, also, measured. The curves G”, G, and delta were plotted according to frequency. All rheology measurements were performed at 20°C using a 1000 μm gap [7, 8].

Statistical analysis

Variance analysis of the results was carried out by least square method with the application of Microsoft Office Excel program. The differences were considered statistically significant, because the probability was greater than 95% ($q < 5\%$). All assays were performed at room temperature, $20 \pm 1\ ^0C$. The experimental results are represented according to standard rules.

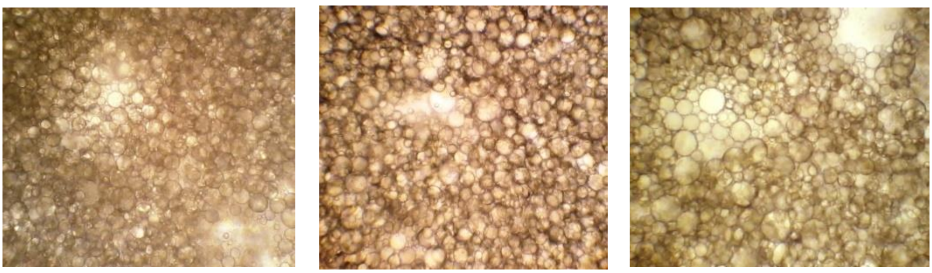
Results and discussions

Microstructure of food emulsions

A current trend in the development of the food lipid industry is the production of food emulsions based on the mixture of vegetable oils of various types, taking into account their fatty acid content. This direction is a priority because none of the individual vegetable oils provide the correlation of ω-3 and ω-6 fatty acids recommended by specialists, so for the production of food emulsions with improved nutritional value, it is necessary in the first line, to create a balanced product in terms of fatty acid content [1, 2, 5].

The quality of any finished food product is closely related to its structural properties. The study of the influence of incorporated natural extracts on the quality of food emulsions can not be completed without analyzing the influence of these factors on the emulsion structure, the parameters of the fat globules dispersed in the aqueous phase. This index shows the dispersion degree of fat, which is the dominant factor in determining the degree of assimilation of finished product, its structural, oxidative and rheological stability.

The microstructure of food emulsion samples was studied by microscopic analysis using the digital optical microscope. The microstructure images of the investigated samples are shown in figure 1.



Control emulsion 100% sunflower oil | Emulsion with 25% extra virgin walnut oil *Juglans regia* L. | Emulsion with 25% extra virgin walnut oil *Juglans regia* L. and BHT 0,1%

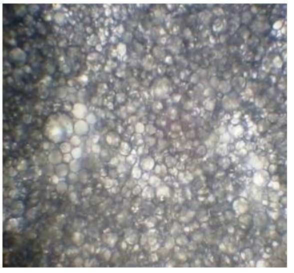
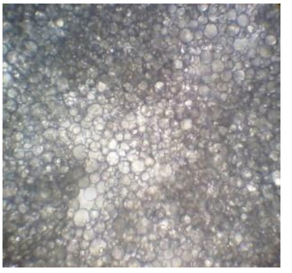
	
Emulsion with 25% extra virgin walnut oil *Juglans regia* L. and natural extract of green walnut leaves	Emulsion with 25% extra virgin walnut oil *Juglans regia* L. and natural extract of green walnut shell

Fig. 1. *Food emulsion microstructure with improved nutritional value*

As can be seen from the presented images, the microstructure of the emulsions with the addition of natural extracts differs considerably from the structure of the control emulsions. The radius of fat cells is characterized by much smaller dimensions, which is significantly highlighted in the microscopic images of the investigated samples.

It should be noted, that in most samples of emulsions with extracts, the radius of fat cells is much smaller than in other samples. The structure of these emulsions is characterized by the dense and compact arrangement of fat globules. The dispersion degree of vegetable oils is maximal for such emulsions, which ensures homogeneity and fineness of the product. It should be noted, that emulsions with natural extracts showed more stable values compared to the sample with added 0.1% BHT synthetic antioxidant [4, 5].

Analyzing the experimental data on the microstructure of the investigated emulsions, one can say that natural extracts have a significant influence on the structure, size and arrangement of fat globules, increasing the dispersion degree of vegetable oils in the aqueous phase, stabilizing the structure for a long time.

Rheological behavior of food emulsions

A particularly important problem is that of making the emulsions, of their correct formulation, so as to obtain the desired viscosity under specified working conditions. Rheological knowledge of emulsions represents a number of difficulties that are related to the greater complexity of these systems.

Highlighting the factors which are influencing the viscosity of emulsions and knowing their mode of action are important for emulsion formation. Rheological studies performed with emulsions have shown that their viscosity depends not only on the shape and size of the particles, but also on the distribution of their size. It was shown, that the mean particle size exerts a considerable effect on the viscosity of the emulsions.

The flow curves of the food emulsion samples are shown in figure 2. All food emulsion samples have been subjected to shear-flow behavior of immersion, characterized by increased shear stress and decreased apparent viscosity by increasing the shear rate speed in the ascending rate shear speed 0-300 s^{-1}. The data for the initial samples of the food emulsion samples is shown in the investigated rheorgrams.

The dipping characteristics were dependent both on shear speed and time, and on the type of food emulsion samples. These characteristics are specific to non-Newtonian pseudoplastic fluids.

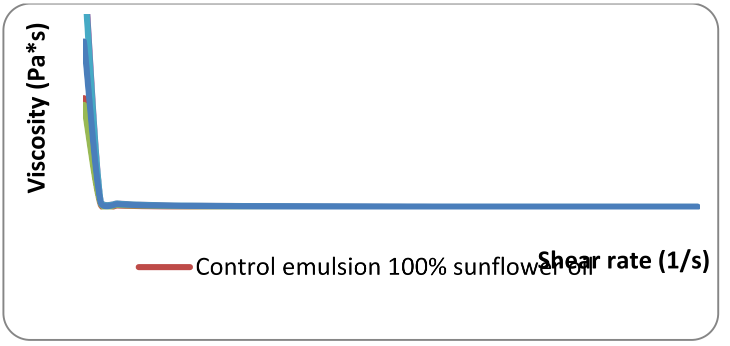


Fig. 2. *Viscosity change of food emulsion samples depending on shear rate*

It has been observed that the actual viscosity is directly dependent on the nature and composition of the investigated food emulsions.

Analyzing the obtained rheograms, it has been found that the viscosity of the emulsions decreases significantly at the shear rate, which can be explained by the destruction of their structure.

It is necessary to mention that, on the downward branch of shear velocity between 300 – 0s^{-1}, the emulsion behavior was inversed. The samples of the tested food emulsions showed thixotropic characteristics, thixotropy being dependent on the type food emulsion samples. All fresh samples returned to their original point. Table 1 lists the flow emulsion parameters (Power Law) for food emulsion samples.

Table 1. *Power Law parameters and the thixotropy of food emulsions with improved nutritional value*

Nr.	Sample name	Viscosity, Pa·s	Power index	Standard error, %	Thixotropy, Pa/s
1.	Control emulsion 100% sunflower oil	14.85	0.1377	31.91	413.4
2.	Emulsion with 25% extra virgin walnut oil *Juglans regia* L.	13.39	0.4203	8.671	2567.0
3.	Emulsion with 25% extra virgin walnut oil *Juglans regia* L. and BHT 0,1%	10.4	0.3135	22.23	1727.0
4.	Emulsion with 25% extra virgin walnut oil *Juglans regia* L. and natural extract of green walnut leaves	9.75	0.2942	24.13	1783.0
5.	Emulsion with 25% extra virgin walnut oil *Juglans regia* L. and natural extract of green walnut shell	8.09	0.3512	25.24	-193.3

The analysis of the experimental data has shown that the observations made are in line with those previously found by [7]. In concentrated emulsions, like mayonnaise, oil droplets, proteins and emulsifiers interact, which leads to the formation of a three-dimensional cluster of droplets. If shear rate increases, the hydrodynamic forces cause the deformation of aggregates and, eventually, ruptures, which leads to reduced viscosity [8]. The hysteresis loop was obtained for each sample by successive growth and decreasing the shear speed. The surface area between the two curves, known as the hysteresis loop, differs depending on the type of mayonnaise and the storage period. It is worth mentioning, that the value of this index is minimal, for some samples practically equals "0".

According to the data presented in table 1, the control sample with 100% sunflower oil, as well as the samples with natural extracts, showed a much lower thixotropy than food emulsion with the addition of walnut oil and those with no antioxidant added. As thixotropy growth corresponds to a progressive degradation of the product's structure during high shear [1], it results that the given samples underwent the smallest structural changes during application of the shear stress.

Conclusions

In the paper, it was justified the opportunity of using the walnut oil Juglans regia L. as a lipid component for obtaining food with improved nutritional value due to its important content of polyunsaturated fatty acids (ω-3, ω-6), tocopherols and polyphenols, which exhibit enhanced antioxidant activity.

The research of the microstructure of the investigated emulsions has shown, that natural extracts have a significant influence on the structure, size and arrangement of fat globules, increasing the dispersion degree of vegetable oils in the aqueous phase, stabilizing the structure for a long time.

The analysis of the influence of incorporated natural extracts on rheological characteristics (effective viscosity and Power Law parameters) proves that food emulsions with natural extracts manifest better rheological characteristics.

Acknowledgements

This work was done in the framework of Project 15.817.02.30A, "*Development of methods and techniques for modernization of nuts (Juglans Regia L.) processing technology using their biologically active constituents in the functional foods*", cofounded by the Academy of Science and by the Technical University of Moldova.

References

1. Abu-Jdayil B., Modelling the time-dependent rheological behavior of semisolid foodstuffs. In: *Journal of Food Engineering*. 2003. nr.57, pp. 97-102.

2. Tadros T.F., Application of rheology for assessment and prediction of the long-term physical stability of emulsions. In: *Advances in Colloid and Interface Science*. 2004. pp. 108-258.

3. Heird W.C., Food insecurity, hunger, and under nutrition. In: *Nelson Textbook of Pediatrics*. 18th ed. Philadelphia, Pa: Saunders Elsevier. 2007.

4. Enig M.G., Know your Fats. In: *Maryland*, USA: Bethesda Press. 2005. pp. 249.

5. Leal-Calderon F., Schmitt V., Bibette J., Emulsion science basic principles. In: *Springer*, New-York, USA. 2007. pp.227.

6. Akoh C., Min D.B., Food lipids: chemistry, nutrition, and biotechnology. In: *Taylor & Francis Group*, CRC Press. 2008. pp.914.

7. Smith J., Functional Food Product Development. In: *John Wiley and Sons*. 2010. pp. 528.

8. Tadros T.F., Rheology of Dispersions: Principles and Applications. In: *John Wiley & Sons.* 2011. pp. 232.