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METHODS OF RESEARCH INTO HAIR CONDITIONERS STABILITY

METODY BADANIA STABILNOŚCI KONDYCJONERÓW DO WŁOSÓW

Abstract

The aim of this work was to produce emulsion hair conditioners, and then to study their stability and rheological properties. For preparing emulsions two recipes with different oil phases and various emulsifiers were used. The emulsification process was performed using a homogenizer. Obtained samples were analyzed to determine their stability. Under the microscope the size of dispersed phase droplets was identified. The samples were also subjected to visual observation. At the same time rheological tests were carried out, which aimed at observing changes in rheological properties of emulsions.

Keywords: *emulsion*, *emulsion stability*, *yield stress*

Streszczenie

Celem niniejszego artykułu było wytworzenie emulsyjnych odżywek do włosów, a następnie zbadanie ich stabilności i własności reologicznych. Do sporządzenia emulsji wykorzystano dwie receptury z różnymi fazami olejowymi oraz emulgatorami. Proces emulgowania wykonano przy użyciu homogenizatora. Stosując techniki mikroskopowe, analizowano strukturę wytworzonych układów. Badania stabilności prowadzono dwoma metodami, tj. metodą wizualną oraz metodą zmiany rozkładu wielkości kropel fazy rozproszonej podczas przechowywania.

Słowa kluczowe: *emulsje*, *stabilność emulsji*, *granica płynięcia*

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Notation

$\dot{\gamma}$ – shear rate [1/s]
τ – shear stress [Pa]
τ_0 – yield stress [Pa]
η – fluid viscosity [Pa·s]
d – droplet diameter [μm]

1. Introduction

The cosmetics industry is dominated by products which are multi-component heterophasic systems. The most valued form because of their properties are emulsions. Emulsions are defined as a heterogeneous system consisting of at least two mutually immiscible liquid phases, one of which is dispersed in the other in the form of droplets. The liquid that forms droplets is called a dispersed phase – internal, the liquid over which the droplets are scattered is a continuous phase – outer. Emulsions can be divided according to the number of phases into simple oil-in-water (O/W) emulsions and water-in-oil (W/O) emulsions, as well as into complex ones of the types O/W/O and W/O/W. The most popular in cosmetics are simple emulsions, in which additional components such as liposomes, antioxidants, fragrances or preservatives are dissolved in particular phases. For producing emulsions later used for hair cosmetics such as shampoos and conditioners mainly emulsions O/W are used because of their nutritional values, where the dispersed phase content is 10–30%.

One of the factors affecting consumers' assessment are application properties and the consistency of a product. Due to viscosity emulsions are divided into creams, lotions or milks. A type and quantity of ingredients of the oil phase as well as the presence of components affecting consistency all have a significant influence on rheological properties of emulsions.

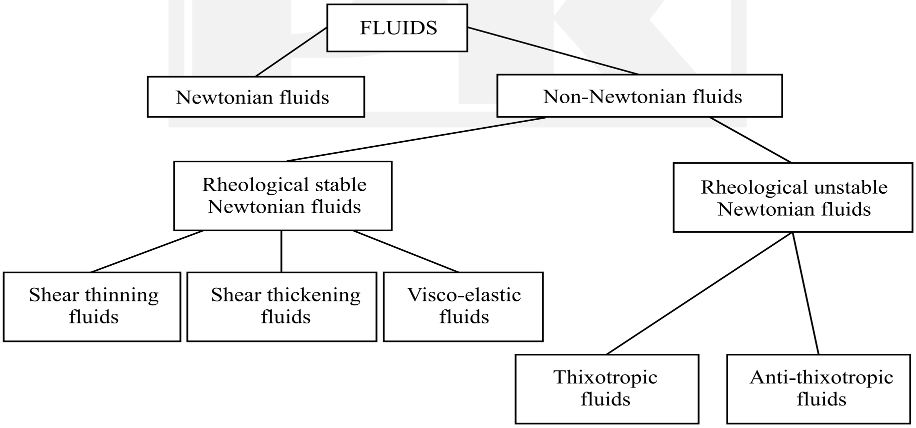


Chart 1. Fluids division due to their rheological properties

Schemat 1. Podział płynów ze względu na ich właściwości reologiczne

Rheology deals with issues related to the deformation and flow of materials. These phenomena are described by presenting the relationship between the occurring stresses and deformations or the rate of deformation formation. The basic rheological properties are viscosity, plasticity and elasticity.

Liquids having a complex internal structure, such as pastes, disperse systems, suspensions, polymers, emulsions, mortar and cement slurries exhibit non-Newtonian characteristics. Their structure is characterized by the presence of suspended particles or dispersed molecules that are larger than typical fluid particles. This results in the formation of long-range interactions between movements of these elements.

Depending on the reported rheological properties fluids can be classified according to Chart 1.

2. Emulsion stability

Emulsion systems are thermodynamically unstable. They embrace various processes that lead to the binding of particles and the violation of dispersed phase balance and ultimately to the destruction of the entire system. Their durability depends on many factors, such as the presence of substances lowering interfacial tension, emulsion particle size, viscosity, sphericity of droplets in dispersed phase, Brownian motion and temperature. Emulsion stability is highly influenced by an applied emulsifier which is absorbed on the interfacial surface, which lowers surface tension. It causes a decrease in cohesion forces between the dispersed liquid particles, which increases the degree of dispersion of one phase in the other.

Emulsion stability is a basic and very important property. The phenomenon of instability may relate to processes occurring simultaneously or sequentially, depending on conditions. Physicochemical mechanisms responsible for emulsion instability are the Stokes' law, Van der Waals forces, the phenomenon of Ostwald ripening and Brownian motion.

Instability phenomena can be divided into two groups – reversible and irreversible instabilities. There are two types of reversible instability, namely creaming and sedimentation. In both cases mixing causes restoration of the primary emulsion. Creaming is a process in which the dispersed phase particles migrate to the sample surface without changes in the droplets distribution. However, the sedimentation process involves movement of the dispersed phase drops under the influence of gravity force to the bottom of a vessel without changing their sizes.

Another type of reversible instability is flocculation. The mechanism of this phenomenon consists in concentrating the dispersed phase particles into larger aggregates with no tendency to accumulation at the top or bottom of the vessel. However, merging of these into larger droplets often occurs, which is the essence of the phenomenon of coalescence, i.e. irreversible instability. The coalescence process often leads to emulsion breaking, which is the process of complete phase separation into the organic phase and water phase. This effect is also irreversible.

3. Experimental part

Tested hair conditioner emulsions are silk and protein. They differ in the oil phase and an emulsifier used. In the cases of both silk and protein conditioner the oil phase was 11% whereas aqueous phase 89%. The composition is shown in Table 1.

Table 1

The composition of examined hair conditioners

PROTEIN CONDITIONER – B	
OIL PHASE 11%	AQUEOUS PHASE 89%
Avocado Oil	Keratin
Cottonseed oil	D-panthenol
SPL, HLB 11	Silk hydrolyzate
	FEOG
	Hydrolate – sweet almond water
SILK CONDITIONER – A	
OIL PHASE 11%	AQUEOUS PHASE 89%
Avocado Oil	Sorbitol
Refined coconut oil	D-panthenol
GSC, HLB 12	Silk hydrolyzate
	FEOG
	Hydrolate –Ylang Ylang flower water

3.1. Emulsion preparation

In industry emulsions are obtained with methods which are based mainly on mechanical stirring, homogenizing, ultrasonic energy, or shaking. Emulsion systems consist of two mutually immiscible liquids. After mixing they form drops, one of them becomes a continuous phase, the other one – a dispersed phase. The intensity and duration of the mixing process should be individualized for each emulsion. In order to receive the studied emulsions the homogenization method was used with a homogenizer MICCRA D-9. After initial tests the following parameters were established for the studied emulsion systems: emulsification time 480 seconds, revolutions frequency 350 s^{-1}.

In the case of emulsification with a homogenizer emulsions with almost the same dispersion degree may be obtained. In the initial phase of emulsification the decomposition of oil and water phases occurs; large droplets of one phase dispersed in the other are formed then. In subsequent stages these droplets are broken down into smaller ones. This phenomenon is dependent on two interacting forces: disintegration force generated by the homogenizer and surface tension forces that make drops stick together. Such obtained emulsions are more stable than emulsion systems which are not homogenized.

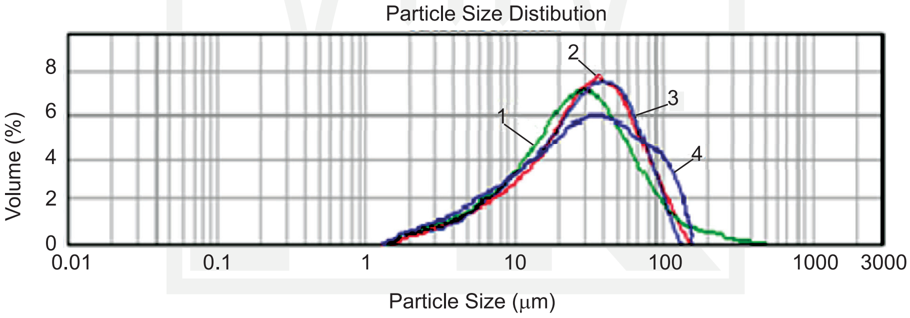
3.2. Emulsion preparation

The samples obtained in this way were subjected to stability tests. The tests were conducted at the following time intervals: immediately after preparing a sample, a day after, 7 days after, one month and 3 months after making the emulsion they were subjected to rheological testing with a rotational rheometer HAAKE RS 75 using a cone-plate system with a diameter of 35 mm and an angle of 1°. The research was carried out at a temperature of 293 K. Then emulsion stability tests were performed using a Mastersizer 2000 apparatus which measured particle size distribution. Photographs of the samples were taken using a microscope Morphologi G3.

4. Tests results

One of the factors affecting the stability of emulsion is the size of dispersed phase droplets. The formation of droplets in the emulsification process is static. Sizes of droplets depend on the method of emulsion preparation, when a homogenizer is applied particles of a relatively small size and of an approximate size are formed. The narrower size distribution of emulsion droplets the greater emulsion stability.

Figures 1 and 2 as well as Tables 2 and 3 show the droplet size distribution, the corresponding diameters d_{32}, d_{43}, d_{10}, d_{50}, $d_{90,}$ and microscopic images (Fig. 3) on the basis of which histograms of quantitative droplets distribution of dispersed phase were made.



1 - protein conditioner - after 1 hours
2 - protein conditioner - after 1 day
3 - protein conditioner - after 7 days
4 - protein conditioner - after 1 month

Fig. 1. Comparison chart of particle size distribution of protein conditioner dispersed phase after a specified time

Rys. 1. Wykres porównawczy rozkładu wielkości cząstek fazy rozproszonej odżywki proteinowej po określonym czasie

Table 2

Change in average diameter sizes compared to the time of protein emulsion aging

Time of conducted study	Average diameters of dispersed phase droplets [μm]					SPAN
	d_{10}	d_{32}	d_{50}	d_{90}	d_{43}	
after 1hour	8.930	11.776	31.133	70.876	33.175	1.975
after 1 day	7.708	16.836	28.152	72.192	35.642	2.139
after 7 days	7.759	17.287	30.809	75.17	37.067	2.199
after 30 days	6.931	18.327	26.703	78.138	38.667	2.667

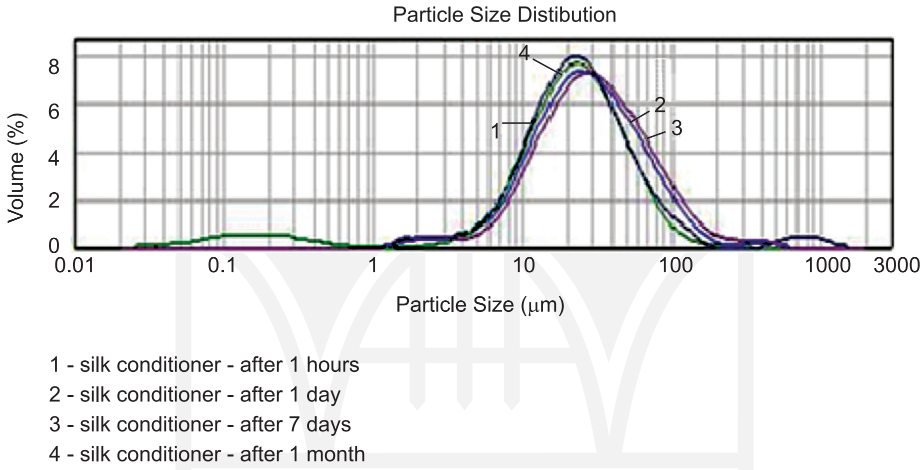


Fig. 2. Comparison chart of particle size distribution of silk conditioner dispersed phase after a specified time

Rys. 2. Wykres rozkładu wielkości cząstek fazy rozproszonej odżywki jedwabnej po określonym czasie

Table 3

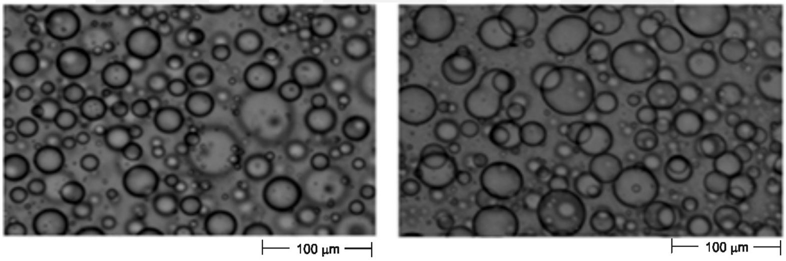
Change in average diameter sizes compared to the time of silk emulsion aging

Time of conducted study	Average diameters of dispersed phase droplets [μm]					SPAN
	d_{10}	d_{32}	d_{50}	d_{90}	d_{43}	
after 1 hour	0.261	0.903	16.356	38.539	18.442	2.339
after 1 day	4.224	1.173	21.417	56.780	27.701	2.454
after 7 days	9.044	17.095	26.673	78.679	38.248	2.611
after 30 days	10.456	19.926	29.980	91.140	44.697	2.691

Both charts present a shift towards larger droplets of the dispersed phase, which is associated with aging of the emulsion. Changes in the sample were observed 7 and 30 days after the emulsion was made.

Basing on the results from Table 1 and Table 2 it may be noted that the diameters of dispersed phase droplets d_{10}, d_{32}, d_{50}, d_{90}, d_{43} grow during the aging of the emulsion. The size of the diameter d_{32} of dispersed phase droplets of silk conditioner is 0.903 µm on the day when it is made. However, the measurement made after 30 days shows that the diameter increased and amounts to 19.926 µm for the same sample, which shows that there has been a reduction in the interface. For the protein emulsion the values were 11.776 µm on the day of sample obtaining and 18.327 µm after 30 days.

Using the visual method it was observed that the silk conditioner sample on the day of obtaining was a homogeneous emulsion. However, after 30 days a clear phase separation was observed. In the case of samples with protein conditioner changes could be observed as early as after 14 days. The phase separation gradually increased. Photomicrographs taken with Morphologi G3 also allow to observe changes taking place in the system. One may also observe how droplets diameters change.



Protein conditioner immediately after obtaining **Protein conditioner after 1 month**

Fig. 3. Photomicrographs of protein conditioner taken with Morphologi G3

Rys. 3. Zdjęcia mikroskopowe odżywki proteinowej wykonane przy użyciu Morphologi G3

Comparing these two pictures one can clearly observe changes that take place in the aging process of the emulsion. Droplets lost their spherical shape, some of them mingled together to form larger droplets. This can indicate that there is a correlation between changes affecting the conditioner structure and their rheological properties. Thickening of the emulsion structure is associated with a change in its viscosity. In this way the rheometric measurement gives the opportunity to evaluate the quality of the emulsion.

Emulsion systems are classified as non-Newtonian fluids. The nature of the emulsion rheological test using a rheometer allows to investigate the relationship between shear velocity and tangential stress.

Non-Newtonian fluids require a greater number of parameters characterizing their rheological properties. Data describing the nature of a fluid is, among others, viscosity coefficient and the relation between shear rate and tangential stress, called the flow curve. Therefore, while conducting rheological research the fundamental test was to determine the flow curves of both conditioners. This curve is not a straight line, it often shifts along the y-axis, so in order to determine its course approximations in the form of equations are used. The results obtained using HAAKE rheometer RS 75 were then elaborated by regression of experimental points with equations listed in Table 4. HAAKE ReoWin – rheometer software was used for this purpose.

Table 4

Equations describing flow curves for visco-elastic fluids

AUTHOR	FLOW CURVE EQUATION
Herschel, Bulkley	$\tau = K\dot{\gamma}^n + \tau_0$
Casson	$\tau^{1/2} = \tau_0^{1/2} + (\eta_p \dot{\gamma})^{1/2}$
Tscheuschner	$\tau = \gamma \left(\eta_\infty + \frac{\tau_0}{\dot{\gamma}} + \frac{\eta_b}{\left(\frac{\dot{\gamma}}{\dot{\gamma}_b} \right)^n} \right)$

In systems of two-or multi-phase, where one or more phases are dispersed in the form of particles the so called yield stress also occurs. When we deal with a sufficiently high concentration of dispersion the interaction between the dispersed particles can cause a three-dimensional structure, to some degree resistant to the impact of shear stress. Below the boundary point the system behaves as an elastic solid. By contrast, we assume that above this value, the structure is completely destroyed and begins to behave like a viscous liquid – it flows. This limit value is called the yield point. Under the conditions of tangential stress greater than yield stress the rheological properties can be explained as a result of the characteristics of the continuous phase. It may therefore be assumed that the dispersion of particles in a dilute sheared fluid will be Herschel-Bulkley fluid.

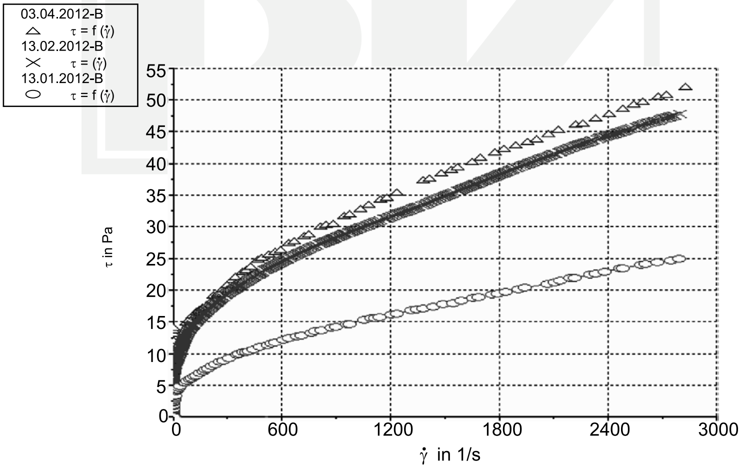


Fig. 4. Comparison chart of flow curves for protein conditioner

Rys. 4. Wykres porównawczy krzywych płynięcia dla odżywki proteinowej

The graph shows (Fig. 4) that with time the emulsion changes in viscosity, there is an increase in viscosity of the tested example, which results in a shift of flow curves. An increase in the yield point of both tested emulsions has been observed together with a decrease in quality.

The next step was to find an equation most accurately describing the obtained flow curves. Each of the equations presented in Table 4 allows to obtain the approximate correlation. It can be concluded that the rheological models by Tscheuschner and Herschel-Bulkley describe the flow accurately. Both give a very close approximation of the curve in the conformity test Ch2, however, the Herschel-Bulkley equation is easier to write, making it easier to grasp the sense of physical constants of the equation (Fig. 5).

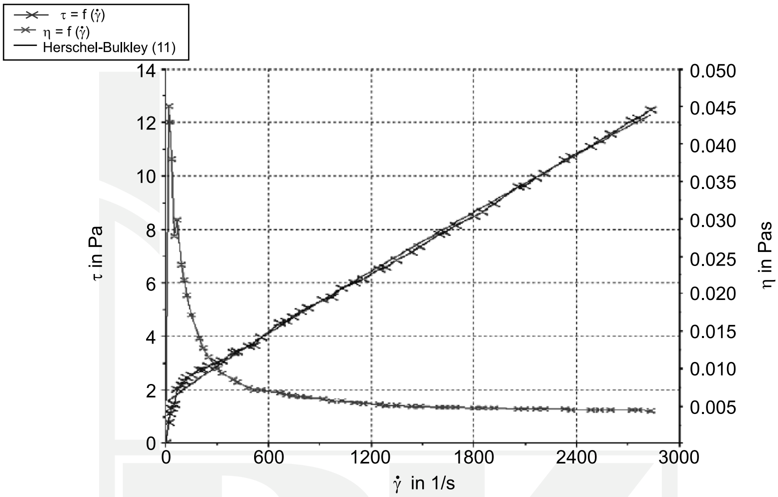


Fig. 5. Flow curve of silk conditioner at 293 K with tailored rheological model of Herschel-Bulkley

Rys. 5. Krzywa płynięcia odżywki jedwab w temperaturze 293 K z dopasowanym modelem reologicznym Herschel-Bulkley

5. Conclusions

In this study two types of conditioners were tested for their stability. The emulsion stability depends on numerous factors. The present research indicated that what matters is a method for obtaining the system, because the size of dispersed phase drops significantly affects the emulsion stability. The smaller the droplets the more stable the system. Emulsion systems, however, are thermodynamically unstable. After a longer period the system demonstrated merging of droplets, coalescence, which led to complete phase separation. The studies allowed to notice that there is a correlation between the values of rheological parameters, and sometimes the emulsion breakdown. The best description of experimental data allows to obtain the Herschel-Bulkey model.

References

[1] Sherman P., *Emulsion science*, Academic Press INC, LTD, London and New York 1968.

[2] Kiljański T., Dziubiński M., Sęk J., Antosik K., *Wykorzystanie parametrów właściwości reologicznych płynów w praktyce inżynierskiej*, EKMA Krzysztof Antosik, Warszawa 2009.

[3] Sherman P., *Rheology of emulsions*, Symposium Publications Division Pergamon Press, Oxford 1963.

[4] Ferguson J., Kembłowski Z., *Reologia stosowana płynów*, Wydawnictwo Marcus sc, Łódź 1995.

[5] Gilewicz J., *Emulsje*, Państwowe Wydawnictwo Naukowe, Warszawa 1957.

[6] McClements D.J., *Food Emulsions: Principles*, *Practice and Techniques*, CRC Press, London 2000.

[7] Myers D., *Surfaces Interfaces and Colloids*, Wilely-vch, Germany 1999.

[8] Binks B., *Modern aspects of emulsion science*, The Royal Society of Chemistry, UK 1998.

[9] Coussot P., *Rheometry of pastes, suspensions and granular materials*, Wiley, New Jersey 2005.

[10] Figiel W., Kwiecień M., *Właściwości reologiczne komponentów maści farmaceutycznych*, Czasopismo Techniczne, 10, 2010, 73-81.