

A Approach to the Assessing of the Physical Stability of the Emulsion-Based Foods: A Mayonnaises [†]

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[†] Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: <https://asec2023.sciforum.net/>.

Abstract: A significant number of foods are manufactured in the form of emulsions. A typical example of such a product are mayonnaises, which vary in oil content. However, as a macroemulsion, they are a thermodynamically unstable system. Therefore, physical instability associated with processes such as flocculation, coalescence and Ostwald ripening leads to separation of the oil and water phases over time. This is especially typical for low-fat mayonnaises. As the oil content in the sauce decreases, it is necessary to add various biopolymers to ensure its stability over time. Physical instability predicting is important for food technology development purposes and especially for reduced oil systems as the most challenging task in terms of system stabilization. In the first approximation according to the Stoke's model, the stability of an emulsion is affected by such a microstructural characteristic as the droplet size and the rheological properties of the emulsions. The combination of this approximation with the generalized Casson's rheological model for structured liquid systems allows us to propose an approach for estimating the rate of emulsion cremation. The parameters used for calculations are determined from rheology and laser diffraction data for mayonnaise samples. The approach is devoid of empirical variables, since all parameters have a physical meaning on the basis of the kinetic model of destruction-recovery of the structural aggregates of the system. Calculations were carried out for a series of commercial mayonnaises (CM) and developed low-fat mayonnaise (LFM). The results make it possible to evaluate the physical stability of emulsions, as well as the influence of rheological and microstructural characteristics on the texture of the final product during its shelf life.

Citation: Gubsky, S.; Sachko, A. A Approach to the Assessing of the Physical Stability of the Emulsion-Based Foods: A Mayonnaises. *Eng. Proc.* **2023**, *52*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor: Santosh Kumar

Published: date



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Keywords: emulsion; physical stability; creaming; drop size; viscosity; Casson's model

1. Introduction

Emulsion is a very popular and widely available form of food. Their typical representatives are traditional food products such as ketchups, mayonnaise, ice cream, sauces and others. The trend of modern healthy eating is associated with reducing the calorie content of foods. For emulsion-based foods this means a reduction in oil content. However, it can significantly impair their physical stability. Colloidal particles of emulsions can be very different, both charged and neutral, with or without developed adsorption layers, aggregated into flocs, etc. The size of particles can vary widely: from several nanometers (protein and polysaccharide molecules) to several millimeters (textured vegetable proteins) [1]. In the case of low-fat emulsion a significant role in their stabilization is played by the formation of an intermolecular associate-complex between protein and polysaccharides. Proteins, which are natural surfactants, can be adsorbed on the surface of oil droplets, and polysaccharides, in turn, are water-soluble and mostly remain in the

aqueous phase, changing its rheology due to the gel formation [2,3]. A big problem in the application of emulsion systems is their potential thermodynamic instability. In the process of long-term storage, a slow process of particles coarsening begins. It is accompanied by a decrease in the system viscosity, a change in the main rheological parameters, and sometimes—a complete delamination of the system. The reason for this is destabilization processes such as creaming, flocculation, coalescing and Ostwald ripening, which leads to the oil and water phases separation [4]. Desorption of the emulsifier from the drop surface can be an additional destabilizing factor during storage. The probability of desorption and ripening according to Ostwald decreases in the case of systems stabilized by a protein-polysaccharide complex, however, this complex behaves as a “soft” polymer, so ripening can be avoided only by creating a so-called Pickering emulsion, i.e., by adding insoluble particles to the system [5].

Emulsion stability is a critical factor in ensuring the effectiveness and quality of all types of food products. In this regard, issues related not only to ensuring, but monitoring the long-term stability of emulsion food systems is very relevant. This paper proposes an approach to assessing the physical stability of emulsion-based foods as non-Newtonian systems, based on the incorporation of a theoretically based generalized Casson’s model into Stokes’ law for predicting the rate of creaming.

2. Materials and Methods

2.1. Materials and Samples

The object of this study was a series of samples of commercial mayonnaises and developed low-fat mayonnaise). More detailed information about CM is presented in [6], and about the formulation for the LFM in [7].

2.2. Methods

The apparent viscosity measurements were performed on a rotation viscometer Visco QC 300R (Anton Paar, Graz, Austria) with concentric cylinder CC12 geometry according [3] and thermostat Peltier PTD 175 temperature device (Anton Paar, Graz, Austria) at temperature 20 °C. Steady-state measurements were obtained for each sample with shear rates ranging from 0.1 to 5 s⁻¹ over the period of 120 s. The apparent viscosity of sample O40 (mayonnaise with oil content 40% (Olis, Dnipro, Ukraine) was performed at 20 °C using an Anton Paar rotational MCR 302e rheometer (Anton Paar, Graz, Austria) and the cone-plate geometry CP50-1 device. The measurements were obtained at shear rates ranging from 0.01 to 300 s⁻¹ and collected using Anton Paar RheoCompass 1.21 software (Anton Paar, Graz, Austria). The generalized flow of the Casson’s rheological model [8] was used to fit the viscosity curves as in [9,10].

The particle and droplet size of samples was measured by laser diffraction on a PSA 1190 particle size analyzer (Anton Paar, Austria) in the range of 0.1–2500 µm. To measure the size of the drops, the emulsion was diluted in warm water (~30 °C) in a ratio of approximately 1/100 of their initial concentration to prevent potential multi-scattering effects and added to the measuring cell in portions to obtain the required degree of field of vision filling. All measurements were carried out at speeds of the stirrer from 150 to 450 rpm. The reported droplet sizes are volume-moment mean diameter as of $D_{43} = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3}$, where n_i is the number of particles in emulsion with diameter d_i . Particle size measurements were conducted within 24 h of sample preparation.

2.3. Statistics Analysis

All experiments were performed in triplicate and results were presented as mean ± standard deviation. One-way ANOVA with Tukey’s multiple comparison post-hoc test was performed to assess differences between groups. Differences were considered significant at $p < 0.05$. Statistical data were processed using the Minitab ver. 19 (Minitab Inc., State College, PA, USA).

3. Result and Discussion

3.1. The Theoretical Approach

To a first approximation according [11], the rate v_{st} at which the droplets move due to gravitational forces in a dilute emulsion is given by Stokes' Law:

$$v_{st} = g(\rho_a - \rho_o)d^2/18\eta, \quad (1)$$

where g is the gravitational acceleration constant (9.81 ms^{-2}), d is the droplet diameter, ρ_a and ρ_o are density of the continuous (aqueous) and dispersed phases (oily), respectively.

The generalized flow [12] of the Casson rheological model [8] was used to equation for apparent viscosity:

$$\eta^{1/2} = \tau_c^{1/2}/(\chi + \gamma^{1/2}) + \eta_c^{1/2}, \quad (2)$$

where τ is shear stress (Pa), τ_c , χ and η_c are integral characteristics of a structured emulsions. The coefficient τ_c characterizes the degree of aggregation of the emulsion. The coefficient χ indicates a tendency towards the formation of an infinitely large aggregate of drops and it determines the plastic ($\chi = 0$) or pseudoplastic ($\chi > 0$) behavior of a structured emulsion. Casson's viscosity coefficient η_c can be considered as the total viscosity of the system with the complete destruction of the associates of the dispersed system [13]. This model allows you to calculate the non-empirical integral characteristics of structured emulsion-based food products from rheological data, for example [9].

It is known that the rate of sedimentation or cremation corresponds to shear rates of the order of $0.001\text{--}0.01 \text{ s}^{-1}$. In this of shear rates range, the generalized flow Equation (2) of the Casson's rheological model is transformed into the equation for apparent viscosity at rest (zero-shear viscosity):

$$\eta_o^{1/2} \cong \tau_c^{1/2}/\chi + \eta_c^{1/2} \text{ at } \gamma \rightarrow 0 \quad (3)$$

Assuming approximation Exp. (3), then Exp. (1) is transformed into the following expression:

$$v_{st} = g(\rho_a - \rho_o)d^2/18\eta \cong g/18 \cdot (\rho_a - \rho_o) \cdot \eta_o^{-1} \cdot d^2 \quad (4)$$

It is known that in a wide range of shear rates (several orders of magnitude), the viscosity η_∞ magnitude at high shear rates is less than $1 \text{ mPa}\cdot\text{s}$ and the relation $\eta_o \geq \eta_\infty$ is observed [14]. This fact allows us to simplify expression (4) by reducing the value of $\eta_c^{1/2}$ in it, since at $\gamma \rightarrow 0$ expression (3) takes the form $\eta_o^{1/2} \cong \tau_c^{1/2}$. In this assumption, from Exp. (4) follows Exp. (5):

$$v_{st} \cong C \cdot [\rho_a - \rho_o] \cdot [\chi^2/\tau_c] \cdot d^2 = C \cdot F_\eta(t) \cdot F_d(t) \quad (5)$$

where C is constant, the value of which depends on the dispersed phase and the dispersion medium nature, $F_\eta(t)$ and $F_d(t)$ are time functions of rheological parameters (τ_c and χ) and droplet sizes d of the dispersed phase, respectively. These values can change over time due to emulsion instability, which is shown as a function of time t .

3.2. The Assessing of the Physical Stability of the Emulsion-Based Foods

Assessment of the physical stability of real food systems using Equations (4) and (5) was carried out on rheological and microstructural measurements of commercial mayonnaise samples and developed low-fat mayonnaise based on aquafaba canned beans. When processing the data, it was noted that the samples viscosity was measured in a narrow range of shear rates from 0.1 to 5 s^{-1} due to the hardware limitations of the rotational viscometer used. In a previous study [10], it was shown that for some systems, the calculated parameters of the rheological model strongly depend on the interval of the shear rate range used in the calculation. The range of shear rates used is sufficiently adequate for calculating the τ_c coefficient, but may overestimate the value of η_c .

This remark is important for assessing the relationship between viscosities η_0 and η_c , and hence replacing Equation (4) with Equation (5). To test this hypothesis on one of the samples of commercial mayonnaise called O40, additional measurements were carried out on a rheometer in a wider range of shear rates from 0.01 to 300 s⁻¹. The results obtained indicated good repeatability of experimental viscosity values measured on different instruments. The calculated coefficients of the Casson's rheological model (Equation (2)) for this sample in a comparison of two data sets are given in Table 1. The comparison shows a significant difference in all considered coefficients ($p > 0.05$). This also determines the difference in the value of v_{st} by approximately 40%, which confirms the above remark about the influence of the experimental range of shear rates on the final result.

Table 1. Coefficients the generalized flow equation of the Casson rheological model and the creaming rate v_{st} for sample O40 [6].

Shear Rate Range	Number of Measurements	τ_c , Pa	χ	η_c , Pa·s	R ²	Standard Error of Estimate	η_0 , Pa·s	$v_{st} \cdot 10^{15}$
0.1–5	22	66.5 ± 0.1	0.030 ± 0.004	0.67 ± 0.06	0.9999	0.063	74335	134
0.01–300	27	64.6 ± 0.1	0.025 ± 0.002	0.56 ± 0.09	0.9997	0.320	103842	96

A similar comparison of the values of parameters η_0 and η_c was carried out for samples of commercial mayonnaise (Table 2). For almost all samples except two, the η_0/η_c ratio is at 0.01%. This makes it possible to use expression (5) for v_{st} calculations (Table 2 and Figure 1a).

The data in Table 2 shows the difference in the rate of creaming and, accordingly, in the physical stability of mayonnaise-like emulsions, depending on the content of oil and thickener, type of oil, etc. To maintain the texture and rheological properties of low-oil mayonnaises as oil substitutes, biopolymers such as guar gum and xanthan gum are used as stabilizers. Their hydration in water allows the formation of networks, which significantly increases the viscosity of the final product, as evidenced by the higher η_0 value and greater stability compared to the same value for medium- and high-oil mayonnaises. The values of the zero-shear viscosity of the samples calculated using Exp. (5) correlate well with the rate of creaming (Figure 1b), which confirms the conclusions given in [15,16]. This fact indicates the adequacy of the approximations used in this approach and the correctness of calculations using expressions (3) and (5).

Table 2. Rheological and microstructural parameters for commercial mayonnaise samples [6] and calculation results using expression (4).

Sample	τ_c , Pa	χ	η_c , Pa·s	η_0 , Pa·s	η_0/η_c , %	D_{43} , μm	$v_{st} \cdot 10^{15}$
K25	50.6 ± 0.2 ^h	0.011 ± 0.006 ^f	4.57 ± 0.10 ^b	420951	0.001	5.98	3.72
T28	74.3 ± 0.1 ^e	0.065 ± 0.005 ^c	1.88 ± 0.04 ^f	17951	0.010	8.89	196
S30	59.5 ± 0.1 ^g	0.025 ± 0.005 ^e	2.00 ± 0.04 ^e	96075	0.002	8.50	33.1
O40	66.5 ± 0.1 ^f	0.030 ± 0.004 ^e	0.67 ± 0.06 ^h	74335	0.001	15.1	134
Y41	35.8 ± 0.1 ⁱ	0.013 ± 0.007 ^h	3.84 ± 0.10 ^c	213642	0.002	24.0	118
S50	140 ± 0.1 ^a	0.048 ± 0.005 ^d	0.01 ± 0.01 ^j	60813	0.000	5.44	21.2
T50	106 ± 0.6 ^c	0.124 ± 0.021 ^a	0.31 ± 0.10 ⁱ	6987	0.004	6.13	237
K50	44.1 ± 0.4 ^h	0.119 ± 0.024 ^a	2.85 ± 0.24 ^d	3305	0.086	5.17	374
L67	124 ± 0.6 ^b	0.099 ± 0.008 ^b	0.62 ± 0.02 ^h	12830	0.005	5.61	108
T72	83.7 ± 0.2 ^d	0.066 ± 0.002 ^c	1.01 ± 0.01 ^g	19495	0.005	7.81	138
N76	33.8 ± 0.6 ^j	0.105 ± 0.038 ^a	12.0 ± 0.10 ^a	3461	0.347	13.8	2706

^{a-k} Means within each column with different superscripts are significantly ($p < 0.05$) different

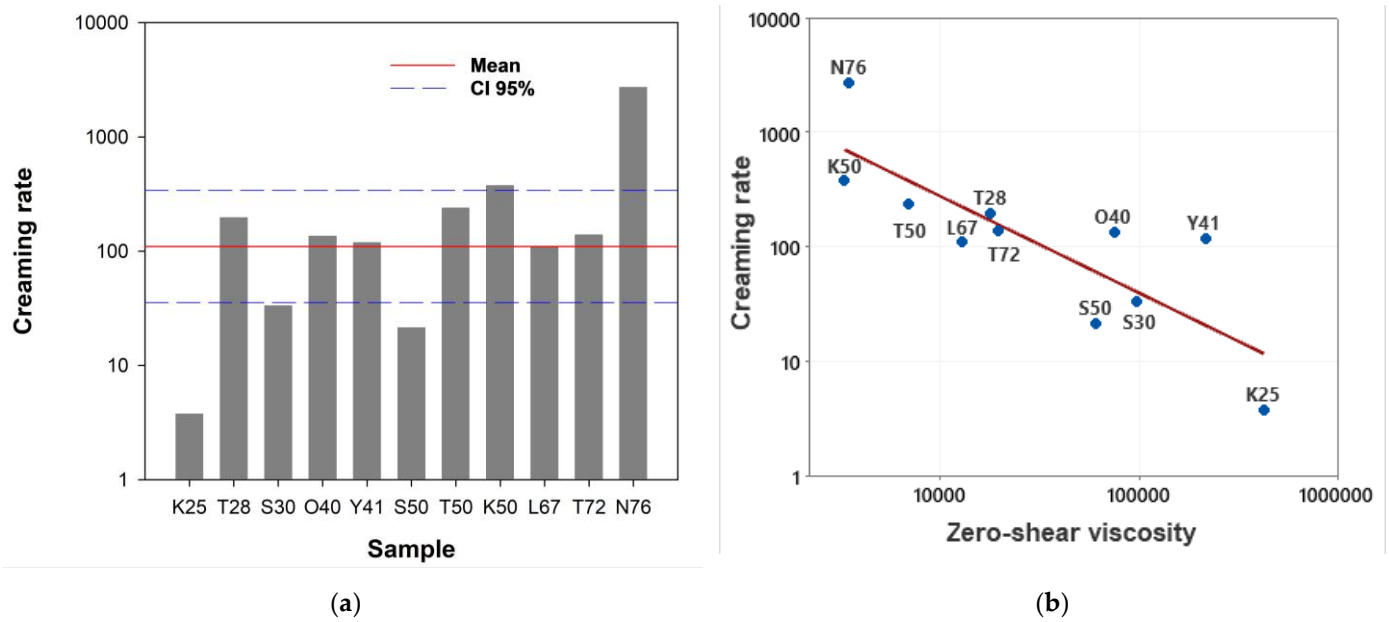


Figure 1. Characteristics of commercial mayonnaise samples in logarithmic coordinates: (a) The magnitude of creaming rate v_{st} ; (b) Dependence the creaming rate v_{st} on zero-shear viscosity η_0 .

Rheological data and particle size distribution for the LFM sample, measured on days 1 and 15 of storage, were used to estimate the time functions $F_\eta(t)$ and $F_d(t)$ in Equation (5) (Table 3).

Table 3. Rheological and microstructural parameters for LFM sample [7] and calculation results using expression (5).

Storage Time, days	τ_c , Pa	χ	η_c , Pa·s	$F_\eta(t) \cdot 10^{-4}$	η_0 , Pa·s	D_{43} , μm	$F_d(t) \cdot 10^{-12}$	$v_{st} \cdot 10^{15}$
1	50.6 ± 0.2^h	0.011 ± 0.006^f	4.57 ± 0.10^b	7.33	1400	8.40	70.6	2253
15	74.3 ± 0.1^e	0.065 ± 0.005^c	1.88 ± 0.04^f	4.28	2383	8.99	80.8	1506

These quantities have different temporal behavior. So the value of $F_d(t)$ increases while $F_\eta(t)$ increases. Above, for samples of commercial mayonnaise, it was noted that an increased η_0 value determines a lower creaming rate. For the LFM sample, a similar trend is observed and the predominance of the factor $F_\eta(t)$ over $F_d(t)$ ensures a decrease in the rate of cremation over time.

4. Conclusions

Physical instability due to creaming and eventual phase separation is one of the most important problems for emulsion-based food products. It is directly related to the shelf life and quality of the product. Therefore, the development of mathematical models is a very valuable tool for predicting the long-term behavior of emulsions when developing their composition. An important aspect of such developments is the use of real experimental rheological and microstructural data. Particle size as a microstructural characteristic has a significant impact on the physical stability of the emulsion and correlates with rheological parameters. Combining these quantities within the framework of Stokes' law made it possible to develop an approach for estimating the rate of cremation. An important point of this approach is the inclusion in Stokes' law of physically based coefficients of the generalized Caisson model for a non-Newtonian flow.

The calculations made for commercial mayonnaise as emulsion-base food products made it possible to estimate the rate of creaming in oil-water emulsions depending on the content and type of oil. The resulting estimate of the creaming rate within the framework of the proposed approach had a strong correlation with zero shear viscosity for samples

of different formulations, and a correct dependence in time with increasing zero shear viscosity for the developed sample of mayonnaise-like emulsion. Further research with an expansion of the range of objects will show the promise of this approach for predicting the physical stability of emulsion-based foods.

Author Contributions: Conceptualization, S.G.; Methodology, S.G. and A.S.; Formal analysis, S.G. and A.S.; Writing—original draft preparation, S.G. and A.S.; Writing—review and editing, S.G. and A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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