Proceeding Paper

Rheological and Microstructural Characteristics of Commercial Mayonnaise-Type Emulsions: A Chemometric Analysis [†]

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Abstract: Mayonnaise is a widely used emulsion-like food that is popular for its flavor properties. However, the modern trend of healthy eating requires a reduction in the calorie content of this product, which means an oil content decrease. Such emulsion systems require the solution of increased problems associated with the stabilization of their spatial structure. It is known that the size of droplets as a microstructural characteristic depends on the stability of the emulsion and correlates with the rheological properties of emulsions. Thus, the study of these characteristics becomes one of the important factors in predicting the properties of emulsions being developed with different natures of the main ingredients. The purpose of this study was a preliminary chemometric analysis of data on acidity, rheological and microstructural characteristics of commercial mayonnaises containing from 25 to 76% oils (sunflower, rapeseed and olive) in order to predict the effect of the main ingredients of the recipe on textural characteristics. Rheological data were analyzed within the framework of a structural representation based on the generalized Casson's model. The nine standardized parameters were grouped using multivariate statistical methodology techniques such as principal component analysis and hierarchical cluster analysis. The experimental flow curves demonstrated pseudoplastic behavior, which is typical for such emulsion systems. The three factors of multivariate factor analysis can explain 72.5% of the variability. In the first factor, the most important variables (with the highest loads) were the Casson's model coefficient of the aggregation degree, the static yield stress and the average droplet size. In the second factor, the highest loadings were the oil content and the Casson's model coefficient, which indicates a tendency to form an infinitely large droplet aggregate. The pattern captured by PCA is confirmed by HCA analysis data. Rheology combined with microstructural characteristics can be used as a tool to evaluate the effect of ingredients in mayonnaise and mayonnaise sauces on textural properties. This information is important for formulation in case using alternative ingredients.

Keywords: rheology; pseudoplastic behavior; Casson's model; yield stress; viscosity; shear stress; shear rate

1. Introduction

Mayonnaise is one of the most widely used oil-in-water emulsion-based foods which typically contains high amounts of fat and a mixture of egg yolk, vinegar, spices and some optional ingredients [1]. The modern trend of healthy nutrition with the use of low-fat foods stimulates efforts to change their recipes while maintaining all the organoleptic characteristics of the original formulation. Substitution of ingredients in the formulation can dramatically change the microstructure of the product, which can greatly impair its stability. The solution of this problem lies in understanding the principles of particle

interactions with the food matrix and the influence of the functional and technological properties of main ingredients on the end-product characteristics [2]. The droplet size as a microstructural characteristic directly affects the stability of the emulsion and correlates with the rheological properties of the emulsions [3]. Thus, the research of these characteristics becomes one of the important factors in predicting properties of emulsion-based food products with main ingredients different in nature. In summary, the purpose of this study is to apply classification procedures of multivariate statistical analysis to study the influence of ingredients on the rheological and microstructural characteristics of commercial mayonnaises with different formulations (Figure 1).

Commercial samples	Main functional ingredients	Properties	Chemometric analysis
•11 samples with an oil content from 25 to 76%	•Oil •Water •Emulsifier •Stabilizer •Thickener •Acidity agents	•Oil content •Casson's model coefficients τ_c, χ, η_c •Static yield stress •SPAN •D[4,3] •pH •TA	•Principial component analysis •Hierarchcal clusters analysis
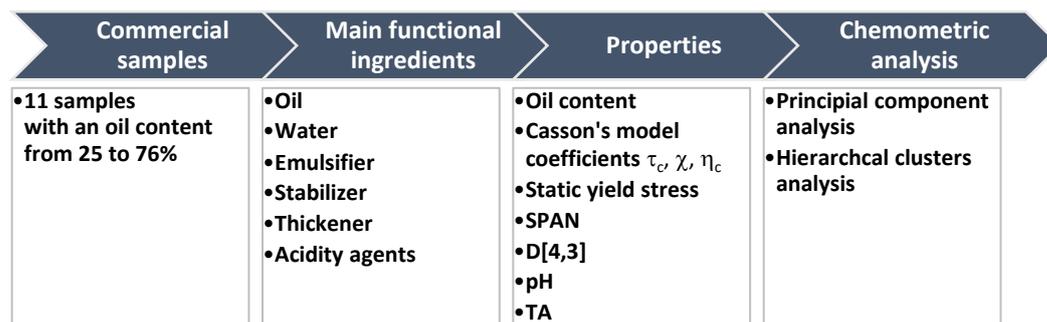
Figure 1. Chart flow of the purpose of this study.

2. Materials and Methods

2.1. Materials and Samples

The object of the study was a series of 11 mayonnaise samples with a typical low- and full-fat mayonnaises with oil content from 25 to 76% and different types of oil [1]. Varying these characteristics is important to study their influence on the final results of chemometric analysis (Table S1). The samples used in this study obtained from local stores in city Kharkiv, Ukraine and Wien, Austria. The main ingredients of mayonnaises have been identified according to the information on the sample label. No further information is available on the ingredient content and its characteristics.

2.2. Methods

The pH and total titratable acidity (TTA) in acetic acid equivalent (%) of the samples were measured by 692 pH/Ion meter (Metrohm, Herisau, Switzerland) with combined glass electrode Unitrode (Metrohm, Herisau, Switzerland) according [4].

The apparent viscosity and the yield shear stress τ_s of samples measurements were performed on a rotation viscometer Visco QC 300R (Anton Paar, Graz, Austria) with concentric cylinder CC12 geometry and a series of vane spindles (V73, V74 and V75), respectively, 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 0.2 to 5.0 s^{-1} over the period of 120 s. The generalized flow of the Casson's rheological model [5] [6]was used to fit the viscosity curves as in [7]:

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

where τ_c, χ and η_c are integral characteristics of a structured emulsions. Thus, this equation is based on a physical model with non-empirical coefficients. The coefficients τ_c characterize the degree of aggregation of the emulsion, and coefficient χ indicates the tendency to form an infinitely large aggregate of droplets. When χ is equal to zero, the emulsion has plastic behavior during flow, and the τ_c coefficient in this case is equivalent to the yield shear stress. Under the condition $\chi > 0$, the structured emulsion exhibits pseudoplastic behavior. The Casson's viscosity coefficient η_c can be considered as the apparent viscosity of the emulsion with a destroyed structure (absence of associates) [6]. The presence of non-

empirical coefficients in Equation (1) distinguishes it favorably from alternative equations with empirical constants such as power-law, Herschel-Bulkley and other models commonly used in calculations.

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 droplet sizes are volume mean diameter as D_{43}. The SPAN index was calculated as SPAN = $(D_{90} - D_{10})/D_{50}$, where D_{10}, D_{50}, and D_{90} are the particle diameters at 10%, 50%, and 90% in the cumulative size distribution, respectively.

2.3. Chemometric and Statistics Analysis

Nine parameters were used as inputs in the sample variable matrices (Figure 1). Prior to multivariate analysis, all matrix elements were scaled by centering and divided by their standard deviation to ensure the same weight of elements in the results. As grouping methods of multivariate statistics methodology such as principal components analysis (PCA) and hierarchical cluster analysis (HCA) are used. The HCA used the Ward's linkage method with Euclidean distance to select objects.

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. Results and Discussion

3.1. Reological and Microstructural Data

The apparent viscosity of all mayonnaises decreased with a shear rate increasing, demonstrating typical for mayonnaise-like emulsion non-Newtonian and shear-thinning behavior with pseudoplastic flow (Figure 2a). The obtained viscosity curves were fitted by expression (1) and calculated coefficients τ_c, χ and η_c for samples presented in Table 1. It was noted above that τ_c, χ and η_c are integral characteristics of a structured emulsions, while the coefficient τ_c characterizes the degree of aggregation of the emulsion and the coefficient χ indicates a tendency towards the formation of an infinitely large aggregate of drops. According to the Table 1 there is no strong correlation between the magnitude of this coefficient and oil content. Biopolymers such as guar gum and xanthan gum were used as a partial replacement for oil in samples to preserve the texture and rheology of low-fat mayonnaise. Dissolved in low concentrations they could form networks that lead to an increase in the viscosity of food [8]. For most samples, this substitution results in similar rheological and shear behavior. Therefore, τ_c magnitudes are observed in the range of 50–80 Pa. The anomalous values for the samples S50, T50 and L67 are apparently related to the increased concentration of biopolymers, and for the K50 sample, their absence.

The emulsion-base structure of mayonnaises contains a mixture of aggregates of spherical oil droplets of various sizes, their associates in the form of flocs, as well as biopolymer particles of various sizes within the distribution width with SPAN equal to 1.5–2.9 (Table 1). At the same time, there are differences in the position of the maximum for mayonnaises with different types of oil, and a predominantly larger average droplet size is observed for mayonnaises with olive and rapeseed oil compared to sunflower oil (Figure 2b).

(**a**)

(**b**)

(**c**)

(**d**)
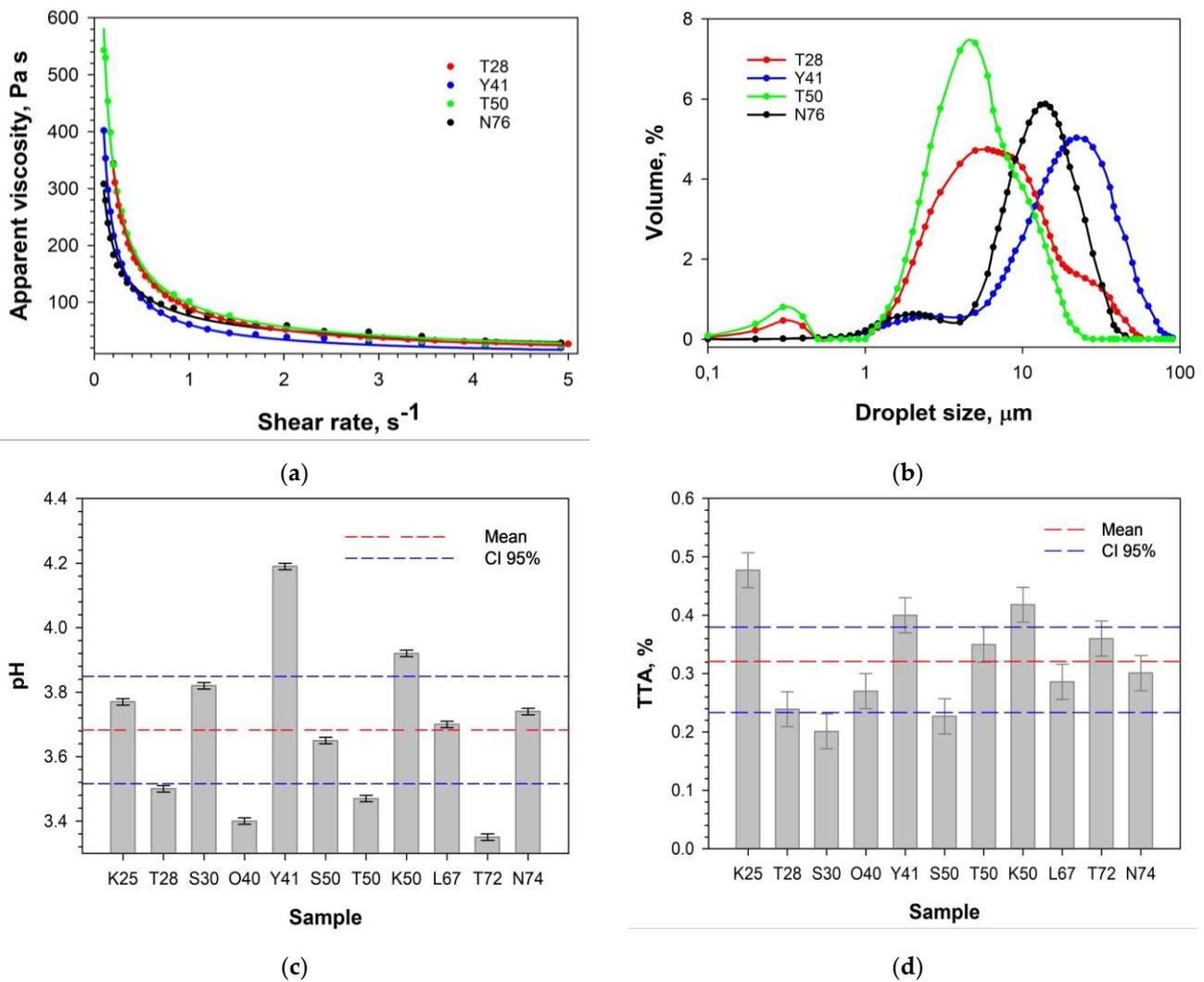
Figure 2. Experimental data for some samples of the commercial mayonnaises: (**a**) Viscosity curves; (**b**) Volume droplets size distribution; (**c**) pH; (**d**) Total titratable acidity.

In all mayonnaises, almost the same ingredients were used as acidity an regulator that is why the active and titratable acidity of samples was kept in a narrow range of pH and TTA values (Figure 2c,d).

Table 1. Rheological, microstructural and acid properties of commercial mayonnaises samples.

Sample	Cluster	τ_c, Pa	χ	η_c, Pa·s	τ_s, Pa	D_{43}, μm	SPAN, μm	pH	TTA, %
K25	1	50.6 ± 0.1 [h]	0.011 ± 0.002 [h]	4.57 ± 0.04 [b]	68.5 ± 4.1 [f]	5.98	2.68	3.77 ± 0.01	0.477 ± 0.003
T28	1	74.3 ± 0.1 [e]	0.065 ± 0.002 [d]	1.88 ± 0.04 [f]	160 ± 6 [b]	8.89	2.91	3.50 ± 0.01	0.239 ± 0.004
S30	1	59.5 ± 0.1 [g]	0.025 ± 0.002 [g]	2.00 ± 0.04 [e]	142 ± 5 [c]	8.50	2.50	3.82 ± 0.01	0.201 ± 0.005
O40	3	66.5 ± 0.1 [f]	0.030 ± 0.002 [f]	0.67 ± 0.05 [h]	67.6 ± 6.1 [f]	15.1	1.78	3.40 ± 0.01	0.270 ± 0.003
Y41	4	35.8 ± 0.1	0.013 ± 0.002 [h]	3.84 ± 0.04 [c]	106 ± 7 [e]	24.0	1.96	4.19 ± 0.01	0.400 ± 0.006
S50	2	140 ± 0.1 [a]	0.048 ± 0.002 [e]	0.01 ± 0.04 [j]	146 ± 5 [c]	5.44	1.94	3.65 ± 0.01	0.227 ± 0.008
T50	3	106 ± 0.1 [c]	0.124 ± 0.002 [a]	0.31 ± 0.04 [i]	60.7 ± 6.5 [g]	6.13	2.26	3.47 ± 0.01	0.350 ± 0.009
K50	3	44.1 ± 0.1 [i]	0.119 ± 0.002 [b]	2.85 ± 0.04 [d]	60.9 ± 5.1 [g]	5.17	1.94	3.92 ± 0.01	0.418 ± 0.003
L67	2	124 ± 0.1 [b]	0.099 ± 0.002 [a]	0.62 ± 0.05 [h]	202 ± 8 [a]	5.61	2.46	3.70 ± 0.01	0.286 ± 0.007
T72	3	83.7 ± 0.1 [d]	0.066 ± 0.002 [d]	1.01 ± 0.04 [g]	59.6 ± 6.1 [g]	7.81	2.31	3.35 ± 0.01	0.360 ± 0.004
N76	5	33.8 ± 0.1 [j]	0.105 ± 0.002 [c]	12.0 ± 0.04 [a]	122 ± 8 [d]	13.8	1.57	3.74 ± 0.01	0.301 ± 0.002

[a–j] Means within each column with different superscripts are significantly ($p < 0.05$) different.

3.2. Chemometric Analysis

The PCA has been used as a factor analysis method to extract the most important factors from a large number of the original variables (Figure 3a). This information is encoded in coefficient loadings, a high absolute value of which indicates that a given original variable has an important contribution (Table S2). The first factor mainly correlated (factor loading magnitude > 0.7) with the content of τ_c (0.888) and there is a negative correlation with volume mean size (-0.709). Second factor was mainly correlated with the oil content (0.899) and coefficient χ (0.796). The third factor mainly correlated with the static yield stress (0.804). Three principal factors accounted for 72.5% of the total variation.

These results correspond to the concept of mayonnaises as structured emulsions that exhibit both fluid (viscous) and solid (elastic) behavior. For such systems, an important parameter is the yield point. Its value is important both for various technological processes, including the final product stability, and for its perception by consumers [9]. In addition, according to the authors [10], this value is more useful as a predictor of the sensory characteristics of mayonnaise than the apparent viscosity. Note that the coefficient τ_c is the equivalent to the dynamic yield shear stress for systems with plastic behavior ($\chi = 0$). Thus, both characteristics (dynamic and static) of the yield stress are the main differentiating factors in the rheological behavior of samples with different oil content. Obviously, this is primarily due to the stabilizing effect of the biopolymers included in the formulation. The latter play an important role in the second factor as well, changing the structure of traditional mayonnaises from densely packed individual oil droplets [8] to a looser one compared to a biopolymer network. This results in a change in the χ coefficient, which is smaller for low fat mayonnaises.

The pattern captured by PCA is confirmed by the data of the HCA analysis with the selection of the appropriate clusters (Table 1, Figures S2 and 3b). It should be noted that chemometric analysis differentiates samples of mayonnaise with different types of oils, as well as separates traditional mayonnaise from low-fat ones, highlighting these samples into separate clusters.

(**a**)   (**b**)
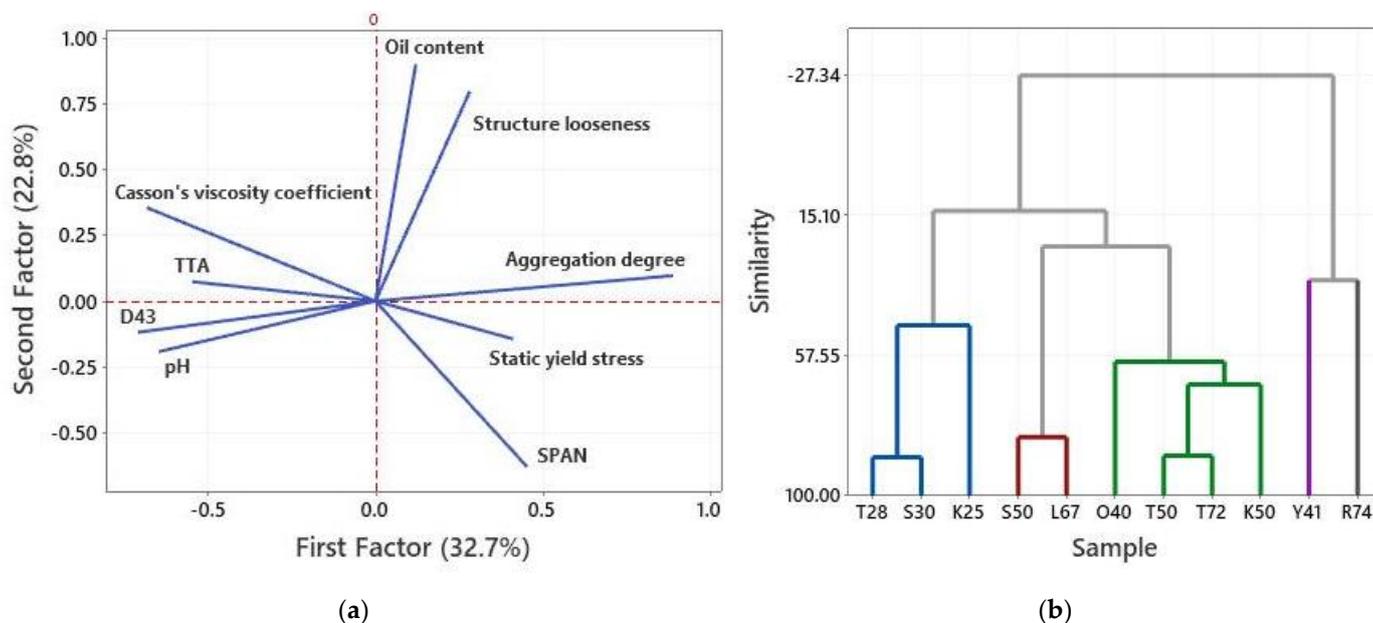
Figure 3. The multivariate analysis: (**a**) Factor loading plot of factor analysis, where τ_c, χ and η_c are aggregation degree, structure looseness and Casson's viscosity coefficient, respectively; (**b**) Dendrogram of HCA.

4. Conclusions

All samples of mayonnaise showed different rheological and structural characteristics. They demonstrated non-Newtonian pseudoplastic flow with a clear yield point. Partial replacement of oil in mayonnaise with biopolymers that have a stabilizing effect causes changes in rheological parameters: static and dynamic yield strength, as well as a parameter related to the compactness of the oil droplet structure. Greater rheological stability is shown by mayonnaises that contain thickeners and a stabilizer. Methods of multivariate analysis allowed identifying the main variables that determine the difference in the rheological and microstructural characteristics of mayonnaises. The data obtained require further verification on a larger number of different samples.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: Microphotograph of the structure of a sample of T28 mayonnaise with spherical drops of various sizes and flocculants as agglomeration of droplets; Figure S2: Principal component analysis: scope of samples; Table S1: Descriptive characteristics of samples; Table S2: Principal component factor analysis: factor loading.

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