PHYSICAL CHARACTERISATION OF COMMERCIAL MAYONNAISES AND SALAD DRESSINGS

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Nomenclature: G´- storage modulus
G´´ - loss modulus
G^o_N – plateau modulus
η_0 – zero shear rate limiting viscosity
γ - shear rate
γ_C - critical shear rate
s - constant of the Carreau Model
d_{32} – Sauter mean diameter

Abstract: A specific methodology was applied to define the rheological and textural properties for the development of new food emulsions with plant proteins in lieu of egg yolk. Physical properties including rheological properties (η_0 and G^o_N), textural properties (firmness and adhesiveness), Sauter diameter (d_{32}) and physical stability (% oil removed by centrifugation) were evaluated for eleven mayonnaises and seven salad dressings. Principal Component Analysis (PCA) was applied to the results and three different groups with different physical properties were obtained - traditional mayonnaises, light mayonnaises and salad dressings. Three mayonnaises, from the traditional and light mayonnaise groups were subjected to sensory evaluation and one of these was found to be 42% preferred in a consumer panel hedonic test and its properties to be a good standard to be used as a guidance to develop new food emulsions with physical properties close to those of commercial mayonnaise.

1. INTRODUCTION

Mayonnaise and salad dressings are consumer goods still showing a positive market trend in several countries. The importance of these products on human diet implies a better knowledge and development on the ingredients involved in their manufacture. The legal requirements for the composition of these products vary from country to country since there is no European directive for these products. In several countries, like Switzerland, "mayonnaise" means an o/w food emulsion with an oil content higher than 75%, using egg yolk as emulsifier, with no addition of thickening agents. In Spain, a mayonnaise must have a minimum oil content of 65% (w/w), over 5% (w/w) of egg yolk, an acid index of at least 0.2% in acetic acid and a pH of less than 4.2 and the term "salad dressing" refers to an o/w emulsion with 30% of oil and 3% of egg yolk [1]. However, in 1993 the Spanish restricted the use of the denomination "mayonnaise" to products with at least 80% of oil content. Dickinson and Stainsby [2] defined mayonnaise as an o/w emulsion with an 80% minimum oil content, containing egg or egg yolk, vinegar, salt and flavoring, coloring and thickening materials, and salad cream as a similar product but with only 25 to 60% of oil content.

The oil and the emulsifier are the most important components to consider for the production of the mayonnaise and salad dressings. These products are o/w emulsions and their high oil content causes stability problems [3, 4] which must be overcome with the help of an emulsifier. Regarding the oil, its importance comes from its high content and its specific nature, as far as the quality is kept high, plays a secondary role. Vegetable oils, namely sunflower and soybean oil are the most commonly used oils on the production of commercial mayonnaise and salad dressings. The emulsifier has the important role of reducing the interfacial tension between the oil and water phases [5]. Nevertheless, its content has to be controlled so that it is enough to cover the oil droplet and to develop an entanglement network between droplets. Traditionally, egg yolk is used as an emulsifier, but other low or no cholesterol emulsifiers such as milk and soy protein have been used in the industry.

Due to the growing interest on low fat low energy products, a tendency to a decrease of the oil content of food products and ingredients is currently observed. Lowering the oil content and changing from egg yolk as main emulsifier, to something else, means that one must use an appropriate thickening agent to help stabilize the oil droplets against coalescence and to obtain an emulsion with physical properties close to those of traditional mayonnaise. The thickening agents that were used for this purpose are xanthan gum, galactomannans, intact or modified starches, propylene glycol alginate and pectin.

According to the previously described tendency to develop new mayonnaise and salad dressing products with low cholesterol and low fat content, it is important to characterise products which are marketed nowadays, in order to define a target and to optimize the composition and processing conditions of the non traditional food emulsions. The knowledge of the physical behavior of these products is also important for quality control, storage stability, design of the unit operations and to the control of processing variables [6-10].

Mayonnaise and salad dressings are viscoelastic materials which can be characterised with small amplitude oscillatory or creep/relaxation compliance experiments [11].

In the present work, eleven commercial mayonnaise and seven salad dressings sold in Portugal, were physically characterised in order to define a standard to use as a target to develop new o/w food emulsions using vegetable proteins to replace egg yolk and lowering the oil content.

2. MATERIALS AND METHODS

Eleven commercial mayonnaises and seven commercial salad dressings were used. The stated label compositions are shown in Tables 1 and 2.

Dynamic viscoelasticity and steady-state flow measurements were carried out in a controlled-stress rheometer (RS-75) from Haake (Germany). Oscillatory tests were performed using a cone and plate sensor system (35 mm, 2º) in a frequency range of 10^{-2} to 10^{2} rad/s using stresses within the linear region. Steady-state flow curves were obtained with a serrated plate-plate sensor system (20 mm) to overcome the slip effect as recommended by Barnes [12] and Franco *et al.* [13] with shear rates ranging from 10^{-5} to 10^{3} s^{-1}. Each rheological test was conducted at 20±1ºC and performed at least three times.

Table 1: Label composition of the commercial mayonnaises studied.

Code	Composition
M_1 (Light)	Water, vegetable oil, vinegar, starch, sugar, mustard, milk protein, preservative (potassium chloride).
M_2	Sunflower oil, water, egg yolk, wine vinegar, sugar, salt, starch, lemon juice, spices.
M_3 (Soya)	Sunflower oil, water, vinegar, lemon juice, soya protein, maize starch, lemon, salt, mustard.
M_4	Vegetable oil, water, olive-oil, egg yolk, salt, sugar, flavor, lemon juice, non-oxidizing agents (EDTACaNa2, butyl-hidroxyanisol), color (β-carotene).
M_5	Vegetable oil, egg yolk and egg white, water, vinegar, sugar, salt, flavor, lemon juice, non-oxidizing agents (EDTACaNa2, butyl-hidroxyanisol), spices.
M_6 (Light)	Water, vegetable oil, starch, egg yolk, wine vinegar, sugar, salt, color (β-carotene), preservative (potassium sorbate), natural flavors.
M_7 (Soya)	Sunflower oil, water, soya protein, apple vinegar, salt, apple juice, lemon juice, thickeners (guar gum, xanthan gum).
M_8	Vegetable oil, water, egg yolk, glucose syrup, mustard, vinegar, salt, preservative (potassium sorbate, citric acid), spices, non-oxidizing agent (EDTACaNa2), color (β-carotene).
M_9	Vegetable oil, egg yolk, water, glucose syrup, vinegar, mustard, salt, preservative (potassium sorbate, citric acid), spices, thickener (guar gum), flavor, color (β-carotene).
M_{10}	Sunflower oil, olive-oil, water, egg, wine vinegar, sugar, salt, lemon juice, spices, preservatives (potassium sorbate, sodium benzoate).
M_{11} (Light)	Water, vegetable oil, sugar, starch, egg yolk, mustard, vinegar, salt, thickener (guar gum), preservative (potassium sorbate), non-oxidizing agent ($EDTACaNa_2$), spices, flavours, color (β-carotene).

Table 2: Label composition of the commercial salad dressings studied.

Code	Composition
S_1	Vegetable oil, water, tomato sauce, vinegar, sugar, mustard, egg yolk, starch, whisky, salt, spices, preservatives (citric acid), flavors, non-oxidizing agent ($EDTACaNa_2$).
S_2	Vinegar, vegetable oil, sugar, water, mustard, salt, egg yolk, maize starch, thickeners (xanthan gum, guar gum), color (riboflavine).
S_3	Water, vegetable oil, vinegar, sugar, salt, egg yolk, garlic, thickeners (propylene glycol, alginate, carragenan, xanthan gum), preservative (potassium sorbate).
S_4	Water, vegetable oil, sugar, vinegar, mustard flour, salt, egg yolk, maize starch, thickeners (xanthan gum, agar-agar), color (riboflavine).
S_5	Water, vegetable oil, vinegar, glucose syrup, starch, salt, mustard, egg yolk, thickener (guar gum), preservatives (citric acid, potassium sorbate), spices, flavors, color (β-carotene).
S_6	Water, cream, coagulum, vegetable oil, sugar, vinegar, egg yolk, salt, starch, lemon juice, spices.
S_7	Water, vegetable oil, vinegar, glucose chirrup, starch, sugar, salt, mustard, egg yolk, thickener (guar gum), preservatives (potassium sorbate, citric acid), spices, flavor, color (β-carotene).

The textural variables were obtained from the texture profile analysis (T.P.A.) carried out in a texturometer TA-XT2 (Stable Micro Systems, U.K.). The samples were placed in cylindrical glass vessels (60x53 mm). Penetration tests were performed using a cylindrical probe of 38 mm diameter (5 mm penetration and 2 mm/s crosshead speed). Firmness and adhesiveness were calculated from the force *versus* time texturograms. Firmness was taken as the maximum resistance to the penetration of the probe in the glass flask filled with emulsion up to 5 cm height. Adhesiveness is a characteristic of sticky materials and can be defined as the

resistance of the material when the probe is recessing. This parameter is recorded as a negative area and is evaluated as the work necessary to take the probe out of the material [14]. Results for each sample were determined at least five times.
Droplet size distribution (DSD) of emulsions was measured using a laser light scattering instrument (Malvern Mastersizer-X, U.K.). Values of the Sauter mean diameter [15], which is inversely proportional to the specific surface area of droplets, were obtained using the following expression:

$$d32 = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \qquad (1)$$

Each value is a mean of three or more determinations. Emulsions must be diluted in distilled water to a droplet concentration of less than 0.04% (to eliminate multiple scattering effects) and stirred (to ensure they are homogeneous) prior to measurement. Dilution and stirring could disrupt any weak flocculated droplets, but leave strongly flocculated droplets intact [16].
The stability of emulsions was analyzed using a centrifuge (Sorval) and measuring the oil separated during this operation (expressed in percentage of oil by weight). Samples of emulsions (2 g) were centrifuged at 38000xg for 30 minutes. The oil droplets have a lower density than surrounding aqueous phase and therefore move upwards when the centrifugal force is applied. Four replicates were made of each emulsion.
A Principal Component Analysis (PCA) was applied to the above results using the software STATISTICA Version 5 Statsoft.
Sensory evaluation was performed to three commercial mayonnaises studied using a consumer triangular preferences test. An university population of 120 male and female students and staff was considered. Mayonnaises were taste randomly. The question asked was: "Which is the mayonnaise that you like most?". The percentage of preference for each mayonnaise tested was calculated.

3. RESULTS AND DISCUSSION

Linear viscoelasticity

Figures 1a, b and c show the evolution of storage (G´) and loss (G´´) moduli with frequency, for the emulsions studied. Generally, the viscoelastic moduli are higher in commercial mayonnaises than in commercial salad dressings. This higher viscoelasticity of mayonnaises is due to the larger oil phase in the former, and this suggests more complexity of the emulsion structure as previously stated by Gallegos *et al.* [17].
The existence of a minimum or, at least, a plateau region in the G´´ *versus* frequency plots is due to the formation of an entanglement network by an extended bridging flocculation, involving both macromolecules which are adsorbed to the interface and no adsorbed macromolecules [18, 19]. A characteristic parameter of this plateau region is the plateau modulus, G^o_N, which may be calculated from the value of G´ for which the loss tangent $\left(\frac{G''}{G'}\right)$ shows a minimum in the frequency range studied [20]:

$$G^o_N = [G']_{\tan\sigma \to \text{minimum}} \qquad (2)$$

This parameter was considered to be a measure of the density of the aforementioned entanglements [11]. Absence of a plateau region has been observed in non-flocculated or weakly flocculated dispersions [21]. As a result of the entanglement enhancement, the emulsions that show a plateau region and higher G^o_N values are considered more stable.

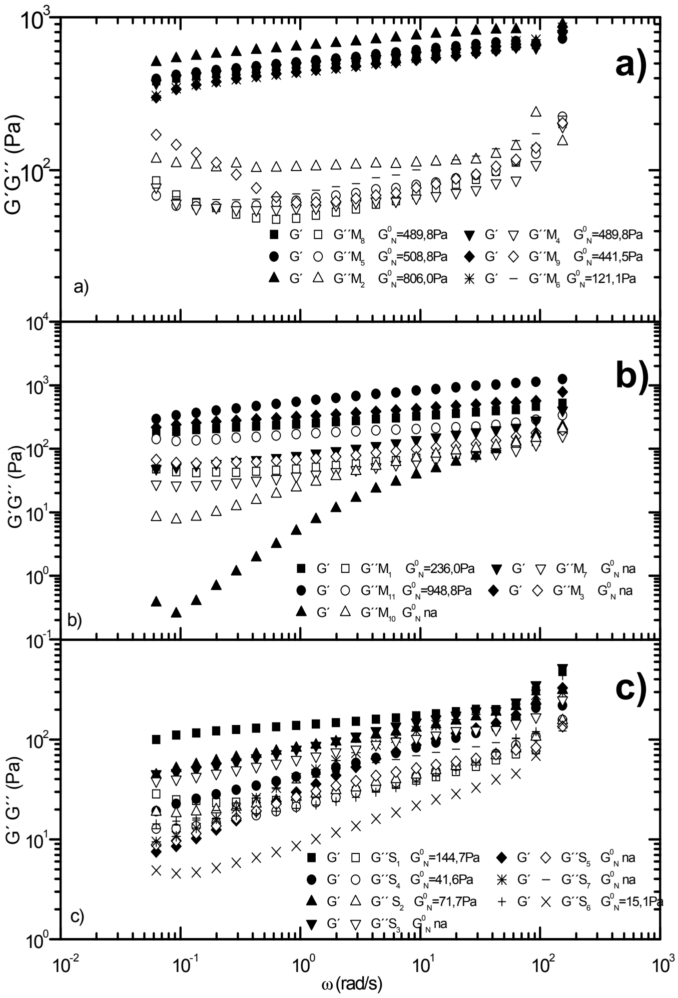

Figure 1. Evolution of G´ and G´´ for mayonnaises a) M_2, M_4, M_5, M_6, M_8 and M_9; b) M_1, M_3, M_7, M_{10} and M_{11}, and for c) salad dressings ("na" means not available experimental data).

For most of the emulsions studied the storage moduli were higher than the loss moduli in the frequency range considered. However, for mayonnaise M_{10} and for salad dressings S_5 and S_7 the loss moduli were higher than the storage moduli at low frequencies, yielding a crossover between viscoelastic functions, and S_3 has a tendency to show very similar values of both viscoelastic functions. G^o_N for these four emulsions was not calculated since tanδ had no minimum. Consequently, these emulsions were considered to be less stable, especially M_{10} due to the crossover of the viscoelastic functions at a very high frequency suggesting that the material has a very week structure, if any.

In the mayonnaises that show G´>G´´ in the frequency range studied a plateau region can be observed, except for M_7, which can be considered less stable. This is also the case for the salad dressings studied for which a plateau region could not be found, except for S_1, S_2, S_4 and S_6. The calculated G^o_N (Figure 1c) for these emulsions were lower than those of mayonnaise. As expected, salad dressings were generally less structured and hence physically more unstable than mayonnaise.

Flow behavior

All the emulsions studied under steady-state conditions show a strong shear-thinning behavior. The viscosity *versus* shear stress plots (Figures 2a, b and c) show high values of viscosity at very low shear and fall suddenly many orders of magnitude over a narrow range of shear stress, a type of flow that was recently well described by Barnes [22]. Considering the Newtonian plateau zone, we concluded the existence of two different groups of mayonnaises. The first group, formed by traditional mayonnaises, shows an extended plateau and the structure breaks at about 20-50 Pa of applied stress. The second group, formed by light and soybean mayonnaises, and the salad dressings, show a small plateau region and the structure breaks at about 10 Pa.

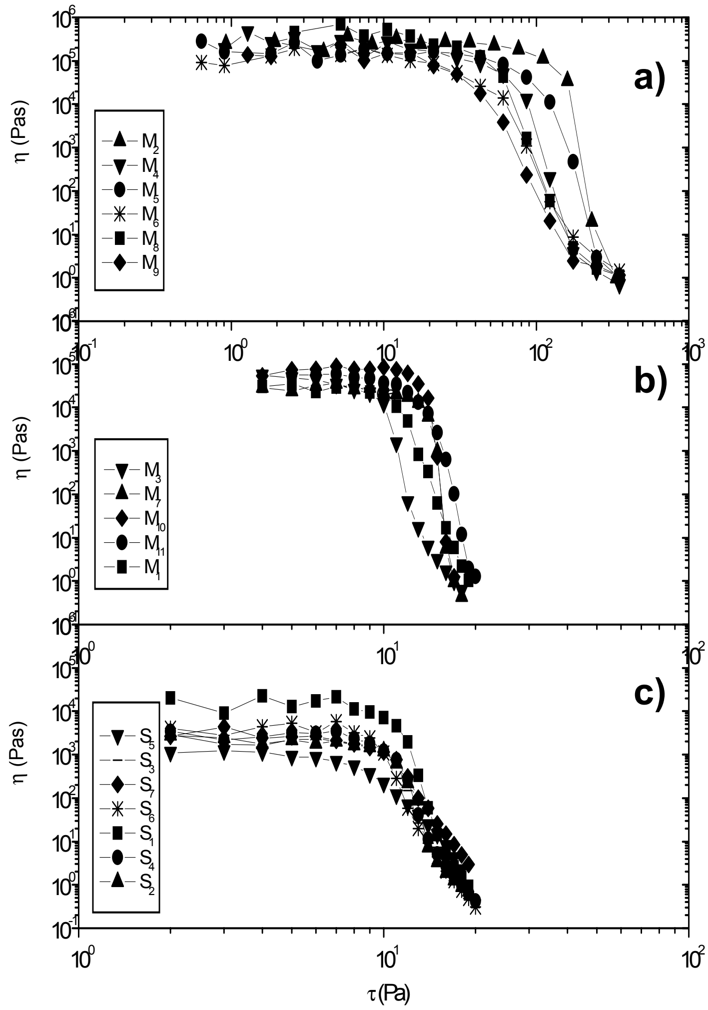

Figure 2. Steady-state flow curves for mayonnaises a) M_2, M_4, M_5, M_6, M_8 and M_9; b) M_1, M_3, M_7, M_{10} and M_{11} and for c) salad dressings.

The flow curves can be fitted with fairly good agreement by the Carreau model [23]:

$$\eta = \eta_0 / [1 + (\gamma/\gamma_c)^2]^s \quad (3)$$

where η is the apparent viscosity measured at the shear rate γ, η_0 is the limiting viscosity of the initial Newtonian plateau, γ_C is the critical shear rate for the onset of the shear thinning region and s is a parameter related to the slope of the shear thinning zone. The values of these fitting parameters, obtained with the "Origin 3.2" software, are shown in Table 3. The relevant characteristic is η_0 but s and γ_C may be of interest it one needs to consider the simplification to the power law. For this reason and for a complete description of the flow curve the three parameters are given.
The group of traditional mayonnaises has η_0 values of the order of 10^5 Pa s and the group of light and soybean mayonnaises has η_0 values of the order of 10^4 Pa s. However, the light mayonnaise M_6 also belongs to first group. The salad dressings have lower η_0 values compared to mayonnaises, of about 10^3 Pa s, with exception of S_1 for which a η_0 value of 10^4 Pa s was found, similar to the values showed by the second mayonnaises group.

Table 3: Parameters of the Carreau model, η_0, γ_c and s values fitted for the flow curves of the emulsions studied.

Emulsion	η_0 (Pa s)	γ_c (s^{-1})	s (Pa s^2)
M_1	3.03×10^4	5.43×10^{-4}	0.39
M_2	2.37×10^5	4.02×10^{-4}	0.47
M_3	5.56×10^4	2.24×10^{-4}	0.40
M_4	2.02×10^5	9.55×10^{-4}	0.43
M_5	1.48×10^5	2.19×10^{-4}	0.45
M_6	1.26×10^5	2.07×10^{-4}	0.41
M_7	2.72×10^4	1.00×10^{-3}	0.42
M_8	4.19×10^5	6.98×10^{-5}	0.43
M_9	1.60×10^5	1.63×10^{-4}	0.42
M_{10}	7.37×10^4	5.94×10^{-4}	0.43
M_{11}	5.29×10^4	5.15×10^{-4}	0.38
S_1	2.14×10^4	3.19×10^{-4}	0.40
S_2	1.93×10^3	4.70×10^{-3}	0.40
S_3	1.85×10^3	3.60×10^{-3}	0.40
S_4	2.88×10^3	2.49×10^{-3}	0.39
S_5	1.34×10^3	4.33×10^{-3}	0.34
S_6	5.41×10^3	3.95×10^{-4}	0.39
S_7	2.42×10^3	2.22×10^{-3}	0.35

Textural parameters

The firmness and adhesiveness values of the emulsions studied are shown in Table 4. Comparing these results with the zero shear rate limiting viscosity values (Table 3), a close relationship between rheological and textural parameters can be observed namely on Figure 4a it can be seen that they are all at a similar distance from the second axis.

Table 4: Textural parameters, firmness and adhesiveness values for the emulsions studied.

Emulsion	Firmness (g)	Adhesiveness (-g s)
M_1	96.8	86.5
M_2	161.0	182.3
M_3	50.5	72.6
M_4	126.5	181.5
M_5	155.4	182.3
M_6	90.1	126.1
M_7	101.5	63.7
M_8	115.6	177.6
M_9	105.9	150.2
M_{10}	128.2	129.6
M_{11}	129.7	174.4
S_1	41.0	43.2
S_2	44.2	19.5
S_3	33.7	17.1
S_4	49.9	32.5
S_5	49.7	47.3
S_6	28.7	15.7
S_7	46.6	49.7

Droplet size distribution (DSD)

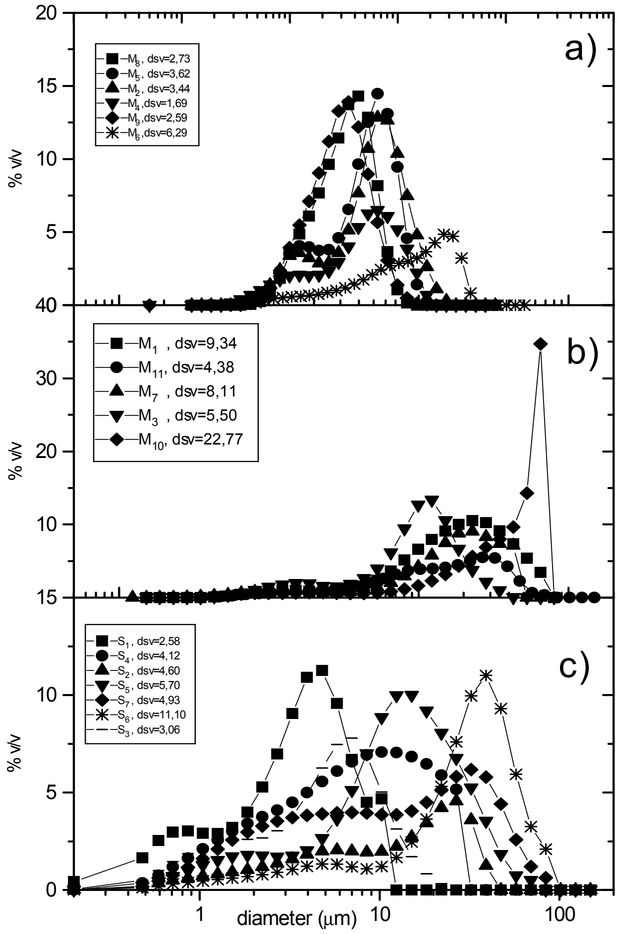

Figure 3. Droplet size distributions for mayonnaises a) M_2, M_4, M_5, M_6, M_8 and M_9; b) M_1, M_3, M_7, M_{10} and M_{11} and for c) salad dressings.

Lower values of the Sauter diameter and monodisperse distributions imply higher stability of the emulsions [16]. The oil droplet size distribution plots obtained for the emulsions and the d_{32} calculated from these plots (Figure 3a, b and c) gives some indication to help predicting their stability.
Mayonnaises M_2, M_3, M_4, M_5, M_8 and M_9 should be more stable because they have lower values of the Sauter diameter, although some of them present a slight scatter of results. Mayonnaises M_6 and M_{11} have high size dispersion plots and are therefore considered to be less stables. Mayonnaises M_1 and M_7 present droplet size distributions with little dispersion but higher values of Sauter diameter. Consequently, they should be less stable. According to this criterium, M_{10} should be the most unstable mayonnaise due to its high value of Sauter diameter.
The major part of salad dressings studied present more dispersed droplet size distributions when compared to mayonnaises. S_1 is expected to be the most stable salad dressing, followed by S_5. The salad dressings S_2, S_3, S_4 and S_7 would be less stable due to their high oil droplet size dispersion and S_6 should have the lower stability due to its high Sauter diameter value.

Stability evaluation
The use of the centrifugal force represents a direct method of stability evaluation. The oil portion that is separated depends on several factors such as the viscosity of continuous phase, droplet size distribution and the surface viscoelasticity of the adsorbed layer [24]. Percentage values of separated oil obtained for the emulsions studied are shown in Table 5.

Table 5: Percentage of oil separated during the centrifugation of the emulsions studied.

Emulsion	% w/w of oil
M_1	2.219
M_2	0.000
M_3	0.000
M_4	0.000
M_5	4.931
M_6	10.495
M_7	15.611
M_8	2.039
M_9	0.000
M_{10}	61.583
M_{11}	0.000
S_1	9.992
S_2	21.194
S_3	12.894
S_4	0.000
S_5	0.460
S_6	Not avaible
S_7	0.000

According to these results mayonnaise M_{10} is the least stable emulsion tested and this is in agreement with the prediction based on d_{32} and G^0_N values. Nevertheless, in several cases, the prediction of the emulsion stability based on d_{32} values is not totally in agreement with the prediction based on G^0_N. This can be explained by the existence of two different phenomena involved on the emulsion stability - small size oil droplets and entanglement between oil droplets forming a network measured as G^0_N. Examples of this are the mayonnaises M_{11} and M_4. The former, presents the higher value of G^0_N but not the lower value of d_{32} and is a very stable mayonnaise (0% oil removed). In this case, the development of the entanglement network between oil droplets was the most important effect responsible for emulsion stability.

On the other hand, mayonnaise M_4 shows the lower value of d_{32} but not the higher value of G^0_N and is also a very stable emulsion (0% oil removed). In this case, the d_{32} factor was predominant for stability. According to these results, the prediction of the stability of food emulsions should take in account both data for Sauter diameter (d_{32}) and plateau modulus (G^0_N).

Principal Component Analysis (PCA)

PCA methodology was applied to group the emulsions studied and to determine the relationship between the variables used in this work (η_0, d_{32}, firmness, adhesiveness, % of separated oil). The variable G^0_N was not used in this statistical approach because there are five emulsions for which no plateau modulus was determined. According to Figure 4a there is a close relationship between d_{32} and fraction of separated oil and also between textural parameters and η_0. An analysis of Figure 4b suggests two different groups of mayonnaises: a central group that is formed by light and soybean mayonnaises (M_1, M_3, M_6, M_7 and M_{10}) and an other group formed by traditional mayonnaises (M_2, M_4, M_5, M_8 and M_9) and the light mayonnaise M_{11}. On the other hand, there is one group of salad dressings only. The existence of two distinct groups of mayonnaises is due to the lower textural parameters and η_0 values of soy and light mayonnaises. The fact that M_{10} is apart relatively to central group is due to its high d_{32} and fraction of separated oil values.

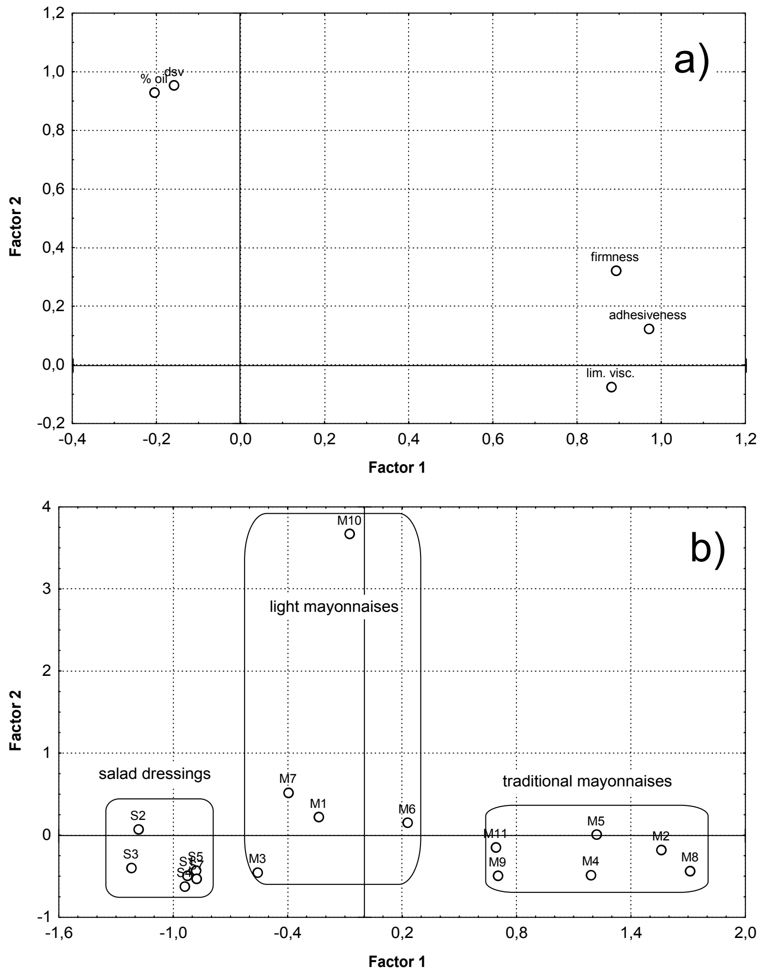

Figure 4. a) Variables distributions obtained by PCA and b) emulsions distributions obtained by PCA.

With the purpose of selecting a standard for the behavior of mayonnaise we selected three commercial mayonnaises (M_1, M_2 and M_6) to make a sensory preferential test. Mayonnaises M_2 and M_6 had 33% and 25% of preference and the mayonnaise M_1 achieved the highest score (42%). It may therefore be considered as a standard for commercial mayonnaise.
When a product is use as a standard for product development, is important to know its chemical composition. Thus, the protein, fat and carbohydrates content of the three mayonnaises selected for the hedonic test were supplied by the company that produce them (Table 6).

Table 6: Protein, fat and carbohydrates content of mayonnaises M_1, M_2 and M_6.

Emulsion	Protein (g/100g product)	Fat (g/100g product)	Carbohydrates (g/100g product)
M_1	0.7	34.3	6.2
M_2	0.6	76.0	1.3
M_6	0.6	35.0	7.1

4. CONCLUSIONS

From the above results, it can be concluded that Principal Component Analysis (PCA) methodology can be very useful in understanding the relationship between the physical variables used in this work to characterise the commercial mayonnaises and salad dressings and to group these emulsions. There is a close relationship between d_{32} and the oil fraction that is separated by centrifugation and between textural parameters and η_0. The direct method of stability evaluation used in this work showed that both d_{32} and G^0_N data should be considered to predict the stability of emulsions.
The hedonic sensory evaluation showed that one traditional mayonnaise achieved the highest score of the panel and could be selected as the commercial standard. Thus, the physical and chemical properties of this mayonnaise can be used as a guidance when developing new food emulsions alternative to mayonnaise.

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