The Influence of Thickeners on the Rheological and Sensory Properties of Cosmetic Lotions

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Abstract: Two empirical models were proposed for a description of rheological characteristics of four eye creams, differing only in the thickener component that preserves the chemical structure of these cosmetic lotions. Coupling between selected sensory variables (such as softness when removing cream from the pot and the "spreadability" on the back of the hand) and rheological parameters was carried out for both models. A close coupling (and hence mutual substitution) between the rheological and sensory parameters enabled evaluation of the sensory parameters by the rheological ones and thus, saving time and money consuming sensory assessment by fast instrumental rheological analysis. It was shown that a proper choice of an empirical model substantially broadens the range of these substitutions.

Keywords: cosmetic lotion; eye cream; empirical rheological modelling; sensory analysis

1 Introduction

Cosmetic lotions are the emulsions formed in principle by two immiscible liquids. They are prone to various instabilities such as creaming, sedimentation, flocculation, Ostwald ripening, coalescence and phase inversion summarized in Tadros [1]. To prevent emulsion from the appearance of the instabilities, various admixtures (in very limited volumes), namely emulsifiers and thickeners are added into the emulsions. Emulsifiers exhibit two favorable properties - a decrease in interfacial tension between both liquids and a stabilization of the dispersed phase against coalescence. Thickeners, on the other hand, partially inhibit the reaction between the chemicals contained in the emulsion and simultaneously modify, to a higher extent, than emulsifiers, the rheological characteristics.

The principal aim of sensory analysis is to differentiate between consumer-friendly and negative attributes of the materials such as cosmetic lotions. No wonder that sensory analysis dominates in the process of their production (see Lukic et al. [2]). This methodology of sensory evaluation of cosmetic products follows three principal points: suitable choice of evaluated variables, suitable choice of the corresponding absolute or universal scales, and suitable choice of a professional panel (expensive). Gilbert et al. [3, 4] have presented a method of Spectrum Descriptive Analysis reflecting an accurate sensory description of products by rating each attribute on chosen scales. This method allows for comparison of the relative intensities within a product or among additional products.

However, sensory analysis has several drawbacks. The evaluation is subjective and very time and money consuming; since, it requires the service of a professional panel. The current discussion revolves around substituting the sensory analysis by rheological measurements that would provide a model flow curve approximating the relation shear stress τ vs. shear rate $\dot{\gamma}$, where shear viscosity η represents a related factor

$$\tau = \eta \cdot \dot{\gamma} \tag{1}$$

The number of parameters in such empirical models usually range from two (the power-law model) to five (the Carreau-Yasuda model), see Macosco [5]. However, the cosmetic lotions quite often exhibit viscoplastic behavior, i.e. the so called yield stress is present, a value of which is necessary to exceed for passage from the static form of cosmetic lotion to its spreadable phase. In the case of yield stress, the number of adjustable parameters in the empirical models is raised by one in respect to the plasticity of the studied material. Yield stress τ_0 can be expressed either explicitly (as e.g. in the three-parameter Herschel-Bulkley model) or implicitly. If there are found tight relations between the individual sensory parameters (pouring from the bottle, softness when removing cream from the pot, ease of spreading, or thickness) and adjustable parameters appearing in the empirical rheological models, then an evaluation of the sensory parameters by their rheological, adjustable counter-parts, can represent a time and money saving approach for improving the final product. Scott Blair [6] was the first who applied this approach in 1939.

There are a series of empirical models that describe the behavior of emulsions or suspensions, including the well-known, Einstein's theoretically based model, for dilute suspensions. However, their applicability is often restricted either to low percentage participation of one component with respect to the other, or the proposed models are directly tailored for the final material. This is caused by complexity of the emulsions viscosity and depends on a number of factors. Pal [7] that summarize ten entry factors: shear rate, time, viscosity of continuous and dispersed phase, density of continuous and dispersed phase, particle (droplet) radius, concentration of particles, thermal energy and interfacial tension. In addition, there is an influence of other factors. Danov [8] proposed an analytical expression for the viscosity of dilute emulsions in the presence of emulsifiers. Experimental determination of emulsion viscosity is very well elaborated and its measurement is very accurate to a fraction of a percent.

Coupling between rheological and sensory properties was recently studied by Karsheva et al. [9], Nakagawa and Ueda [10], Reeve and Amigoni [11], Ibanescu et al. [12], Moravkova and Stern [13]. The study of influence of a solid ingredient on both rheological and sensory properties is relatively rare. Danov [8] proposed an analytical expression for the viscosity of dilute emulsions in the presence of emulsifiers as already mentioned above. Lukic et al. [2] studied four water-in-oil creams differing in only one emollient component. The samples were submitted to rheological, sensory and textural characterization. The results indicated that certain alteration restricted to the oil phase induced a change in all investigated characteristics. Obtained correlation between physical measurements and certain sensory attributes confirmed that textural analysis, as a fairly simple measurement, can be used as a surrogate for rheological measurements. Abu-Jdayil et al. [14] analyzed the influence of the Dead Sea salt content in cosmetic emulsions to its rheological properties and stability. Karsheva and Georgieva [15] studied an effect of plant extracts and thickeners on flow properties of phytocosmetic formulation comparing two oily cosmetics gels (with different gelling components) to a cosmetic cream. For a description of its consistency they applied the power law model, specifically behavior of the consistency index K.

The objective of this study is to specify the influence of a small change in the composition of a cosmetic emulsion (eye creams) to its rheological and textural properties. The composition of four eye creams differ only in the thickener used, all other components are identical. For the rheological description there were proposed two empirical models and for each of them an analysis relating the adjustable and sensory parameters was carried out. It was shown that coupling between these groups of parameters strongly subject to a choice of an empirical model. This indicates that a suitable model should be carefully selected either from the existing ones or tailored with respect to a type of studied emulsion.

2 Experimental

2.1 Materials

Four samples of eye creams, labeled cr1, cr2, cr3, and cr4, were prepared using the laboratory homogenizer SilentCrusher M (Heidolph, Schwabach, Germany). This homogenizer enables individual adjustment of speed from 5000 to 26000 rpm and is suitable for quantities from 0.8 to 2000 ml.

The composition of the samples and suppliers is contained in Table 1 (without thickeners). Total amount of each sample was 2 kg and afterwards filled in 50 ml containers. All four samples differed only in a type of the thickener (mostly 0.3 wt.%), only cr3 deviates negligibly in other components, see Table 2.

Table 1
Ingredients of the samples

Ingredients (INCI name - International Nomenclature of Cosmetic Ingredients)	Ingredient	Supplier	Content [wt.%] cr1-4
details in Table 2	Thickener	details in Table 2	
Polyglyceryl -3-Methylglucose Distearate	Tego care 450	Degussa	3
Glyceryl Stearate	Cutina GMS V	Cognis	2
Cetearyl Alcohol	Lanette O	Cognis	1
Caprylic/Capric Triglyceride	ACE CCT	ACE Trade	7
Cetyl Ricinoleate	Tegosoft CR	Evonik-Goldschmidt	4
Persea Gratissima (Avocado) Oil	Avocado oil	M&H	4
Macadamia Ternifolia Seed Oil	Macadamia oil	M&H	6
Panthenol	Panthenol 75 L	Roche Vitamins	0.5
Tocopheryl Acetate	Vitamin E acetat	Roche Vitamins	1
2-Bromo-2-Nitropropane-1,3-Diol, Methylchloroisothia-zolinone, Methylisothia-zolinone	Euxyl K 145	Schülke&Mayr	0.15
Sodium Lactate, Sodium PCA, Glycine, Fructose, Urea, Niacinamide, Inositol, Sodium Benzoate, Lactic Acid	Lactil GDS	Evonik-Goldschmidt	0.5
Parfum	Fragrance	Charabot	0.1
Aqua	Water, distilled		cr1,2,4 70.45 cr3 70.39

While xanthan gum and carrageenan are of natural origin, polyacrylamide and carbomer represent synthetic thickeners. The usage of the thickeners is almost identical, only carbomer is presented in lower concentration because neutralization by triethanolamine is required.

Table 2
Thickeners contained in the samples

Sample	Thickener	Thickener (trade name)	Supplier	Content [wt.%]
cr 1	polyacrylamide	Sepigel 305	Seppic	0.3
cr 2	xanthan gum	Keltrol CG-SFT	CP Kelco	0.3
cr 3	carbomer with	Carbopol Ultrez 20	Lubrizol	0.12
	triethanolamine	TEA		0.24
cr 4	carrageenan	Genuvisco CI 123	CP Kelco	0.3

2.2 Devices

Rheological measurements were carried out with a rotational rheometer RheoStress 300 (Thermo Scientific, Karlsruhe, Germany). A cone-and-plate system with Sensor: C35/1° Ti (cone diameter 35 mm, cone angle 1°) was used. In contrast to a plate-and-plate arrangement, the chosen cone-and-plate arrangement respects non-Newtonian course of measured characteristics, and hence provides more responsible data. All measurements were carried out at 25°C.

2.3 Methodology

Both rheological and sensory approaches were applied to characterize the samples. These two approaches are not mutually independent, but coupled. As already mentioned above, sensory analysis is time and cost demanding, in addition, there is a certain influence of evaluation panel subjectivity. Evaluation from the sensory analysis can be, to some extent, replaced by the rheological characterization, which represents a substantially cheaper and effective solution. To verify the possibility for an acceptable replacement of selected sensory parameters by rheological means, for the problem (thickener alteration), the following steps were carried out:

- Rheological measurement determining a relation between shear stress and shear rate (flow curve) in the range of shear rate 10^{-2} - $600 s^{-1}$. Such experiments range among classical routine measurements, when using any standard rotational rheometer. In contrast, to sensory analysis requiring skilled and qualified panelists, staff using a rotational reometer can be acquainted with the mentioned type of measurements in a short span of time (hours)

- Sensory evaluation was carried out under standard conditions, as specified by the ISO standards (ISO 8589, ISO 8586.1, ISO 6658). Nineteen trained panelists completed a special questionnaire concerning 14 parameters (including color, shine, appearance of the surface, feeling during rub in, fragrance, frequency of the use of eye creams etc.). Each parameter was rated on a category scale with pre-defined descriptive terms. The four most important parameters (softness when removing cream from the container, ease of spreading on the face and on the back of the hand, and feeling on the skin after absorption) were rated on a graphical unstructured scale as well. For these four sensory parameters there were adjusted their counter-equivalent rheological qualities measured by the rotational rheometer.

The following section presents data processing of both rheological and sensory measurements and the possibilities of their coupling.

3 Results

3.1 Rheological Analysis

The experiments relating shear stress τ and shear rate $\dot{\gamma}$ for eye creams cr1-4 were carried out, see Figs. 1-4. It is apparent that the small change in the compositions of eye creams cr1, cr2, cr3, and cr4 results in substantially different behavior of flow curves. This confirms a non-negligible impact of the thickeners used on the overall manifestation of the individual products.

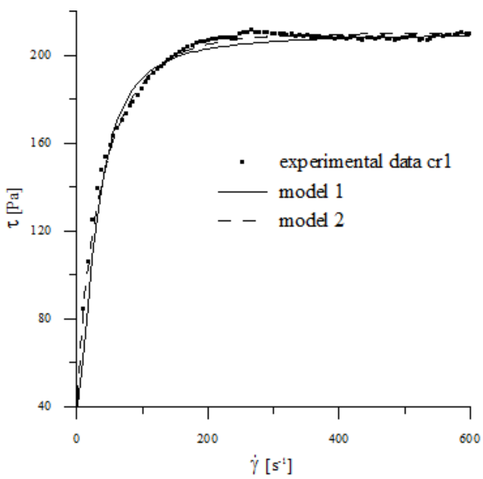

Figure 1
Approximation of the flow curve of cr1 by models 1 and 2

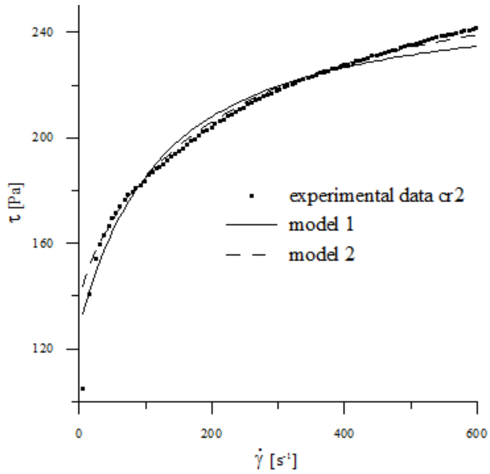

Figure 2
Approximation of the flow curve of cr2 by models 1 and 2

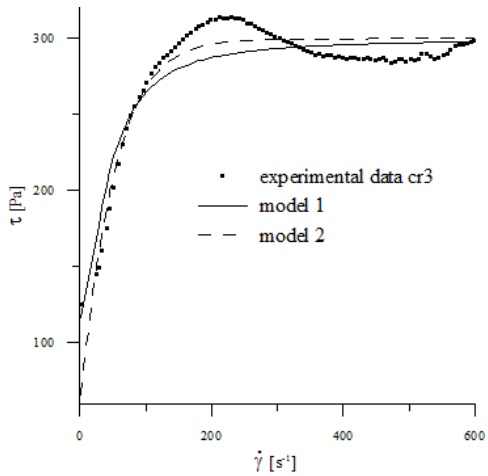

Figure 3
Approximation of the flow curve of cr3 by models 1 and 2

Two empirical models were proposed for a description of flow behavior of the individual eye creams. The two models differ not only in their algebraic forms but also in a number of adjustable parameters. Naturally, emphasis is paid to the relatively simple algebraic structure of both models, usage of well-known monotonous functions (powers, hyperbolic functions), unambiguous determination of the entry parameters, and overall simplicity of evaluation of the individual parameters. The required attributes of newly proposed empirical models are presented in more detail for example in David and Filip [16].

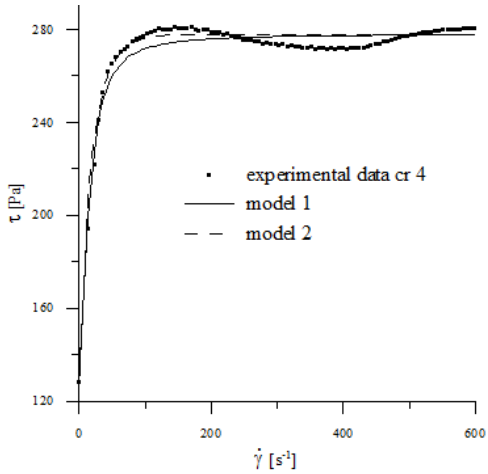

Figure 4

Approximation of the flow curve of cr4 by models 1 and 2

The 5-parameter model 1 is of the form

$$\tau = a_1 - \frac{b_1}{c_1 + d_1 \dot{\gamma}^{e_1}} \tag{2}$$

and the 4-parameter model 2 is of the form

$$\tau = a_2 \cdot \tanh\left(b_2 \dot{\gamma}^{c_2} + d_2\right) \quad . \tag{3}$$

Optimization of the parameters with respect to the individual eye creams is summarized numerically in Table 3 and graphically in Figs. 1-4. As can be seen, the average deviations of both model curves from the experimental points are quite similar.

Table 3

The parameters of the models 1and 2

Eye cream	Parameters of model 1					Parameters of model 2			
	a_1	b_1	c_1	d_1	e_1	a_2	b_2	c_2	d_2
cr 1	210	340	2.0	0.007	1.66	210	0.050	0.70	0.18
cr 2	254	400	3.2	0.020	1.06	254	0.013	0.70	0.60
cr 3	300	550	3.0	0.005	1.70	300	0.016	0.94	0.22
cr 4	278	300	2.0	0.022	1.66	278	0.060	0.80	0.48

3.2 Sensory Analysis

The results of the sensory analysis involving all assessed parameters evaluated at category scales are presented in Table 4. Each category contained descriptive terms, and the trained evaluators marked one or more category on a scale. The most frequent descriptions are introduced in the last column of Table 4.

Table 4
Results of the sensory analysis

Assessed property	Descriptive terms	Most frequent descriptions
frequency of the use of eye cream	daily, very often, often, sometimes, rarely, never	daily, often
surface of the cream	smooth, grainy, bubbles, separated oil/water, other in-homogeneity	smooth, bubbles
shine of the cream	very shiny, shiny, matt, uneven	very shiny, shiny
color of the cream	bright white, white, blue-ish, greenish, ivory, grey, brownish, uneven, spots	white, bright white
fragrance	extremely nice, very nice, nice, neutral, unpleasant, unsavory	nice, neutral
softness when removing cream from the pot	very hard, hard, adequately hard, soft, too soft, sticky	adequately hard, soft, hard
spreadability on the back of the hand	optimal, satisfactory, bad, very bad	bad, satisfactory
fragrance during spreading	extremely nice, very nice, nice, neutral, unpleasant, unsavory	neutral, nice
intensity of the fragrance	light, optimal, intensive, too intensive	optimal, light
spreadability on the face	optimal, satisfactory, bad, very bad	satisfactory, bad
feelings during rub in	cooling, smooth, warm, rough, scratchy, burning, drying out	cooling, smooth
absorption	very quick, good, difficult, very difficult	difficult, very difficult
feeling on the skin after absorption	extremely nice, very nice, nice, neutral, unpleasant, unsavory	neutral, nice, unpleasant
interest in using the sample	daily, very often, often, sometimes, rarely, never	often, daily

Spreadability of the cream is evaluated at two places – on the face and on the back of the hand due to different body temperature. This dual assessment of spreadability was proved to be useful (see Moravkova and Stern [13]).

Four properties boldfaced in Table 4 (softness when removing cream from the pot - SRE, spreadability on the face - SprFa, spreadability on the back of the hand - SprH, and feeling on the skin after absorption - Feel) range to the most important features studied in the creams. Their more detailed evaluation is presented in Table 5. Only these properties will be discussed in the following. All other properties introduced in Tab. 4 serve only for more complete sensory characterization of the creams studied.

Table 5
Results of the sensory analysis, selected parameters (mean values, evaluated at scale 0-100)

	SRE – softness when removing cream from the pot	SprFa – spreadability on the face	SprH – spreadability on the back of the hand	Feel – feeling on the skin after absorption
100 responds to	very soft	optimal	optimal	very pleasant
cr1	37	79	80	69
cr2	43	81	80	63
cr3	73	61	53	63
cr4	65	55	52	58

The results of the sensory analysis confirmed the influence of the thickeners on the important sensory characteristics. Considering the spreadability (on both places), the samples cr1 and cr2 received more positive assessment than cr3 and cr4. The opposite distribution occurs in the SRE (softness when removing cream from the pot) category, where creams cr3 and cr4 were evaluated as softer compared to cr1 and cr2. The assessment of the feeling on the skin (Feel) gives similar values for all the four eye creams.

3.3 Correlation between Rheological and Sensory Measurements

Table 6
Correlation coefficients among the rheological (model 1) and sensory parameters
(significant relations are bold)

	a_1	b_1	c_1	d_1	e_1
SRE – softness when removing cream from the pot	**0.9397**	0.4895	0.1420	-0.0642	0.4810
SprFa –spreadability on the face	-0.7631	-0.0938	0.2570	- 0.1119	-0.6294
SprH –spreadability on the back of the hand	**-0.8473**	-0.2656	0.1065	-0.0204	-0.5998
Feel – Feeling on the skin after absorption	-0.7503	0.0963	-0.0636	-0.6910	0.0338

The linear relations between the sensory variables and the rheological parameters were determined. The individual correlation coefficients for all relations are summarized in Tables 6 and 7. The selected linear approximations for which the correlation coefficients indicate statistically significant coupling between the sensory and rheological analyses are depicted in Figs. 5-7 for the eye creams cr1, cr2, cr3, and cr4. It follows that the tightest relations are for the following couples: (a_1, softness when removing cream from the pot), (a_2, softness when removing cream from the pot), (c_2, softness when removing cream from the pot).

Table 7

Correlation coefficients among the rheological (model 2) and sensory parameters

(Significant relations are bold)

	a_2	b_2	c_2	d_2
SRE – softness when removing cream from the pot	**0.9397**	-0.0802	**0.9349**	-0.0896
SprFa – spreadibility on the face	-0.7631	- 0.3376	-0.7517	0.0659
SprH – spreadibility on the back of the hand	**-0.8473**	-0.1773	**-0.8509**	0.1003
Feel – Feeling on the skin after absorption	-0.7503	-0.1083	-0.3815	-0.6167

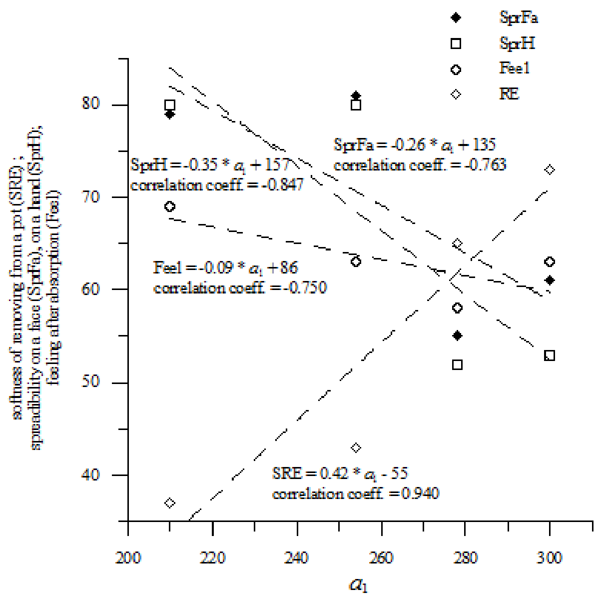

Figure 5

Relationships between sensory parameters and parameter a_1

Thus, the parameters a_1, a_2 and c_2 provide an alternative to subjective sensory analysis because they can directly estimate two sensory variables from the rheological measurements, namely the softness when removing cream from the pot and the spreadability on the back of the hand.

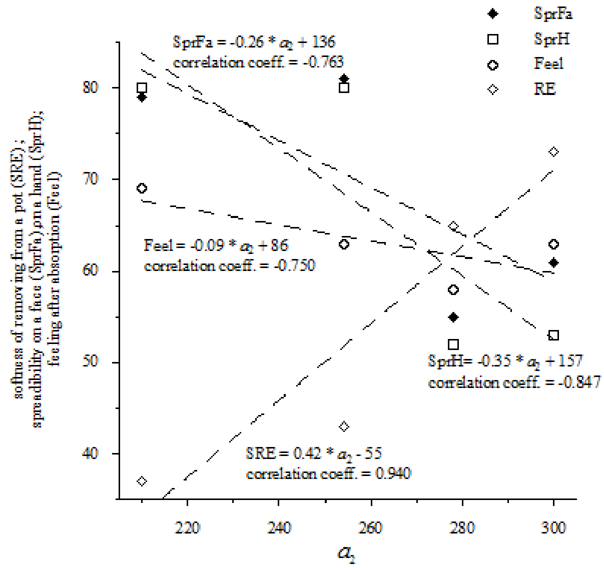

Figure 6

Relationships between sensory parameters and parameter a_2

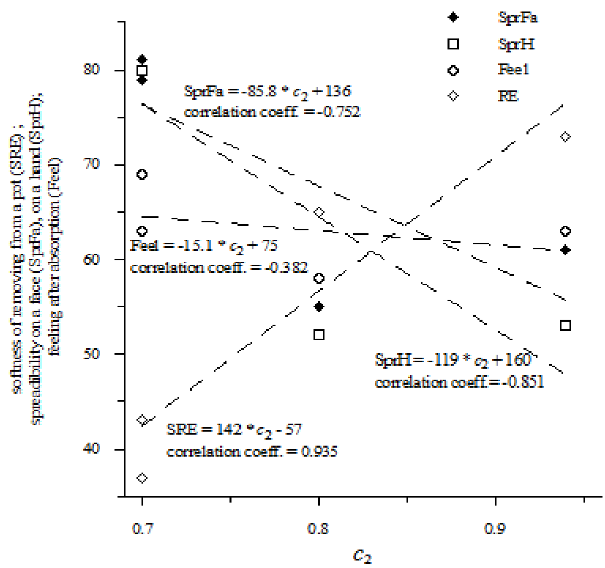

Figure 7

Relationships between sensory parameters and parameter c_2

Conclusions

A proper choice of a rheological model, can significantly help with a closer coupling of sensory variables and model parameters. An algebraic form of the rheological models belongs to a category of materials, to which the models are applied. A usage of standard empirical models (for example a classical power law model or viscoplastic Herschel-Bulkley one), represents a routine that makes it possible to proceed. However, if we want to obtain a closer coupling, a proposal of a new model with a better description of flow behavior of specific category of materials seems to be more promising.

This was confirmed in this present study of the characterization of four eye creams. In this case, two empirical models were proposed. Their rheological efficiency with respect to the description of the experimental data τ vs. $\dot{\gamma}$, is almost identical in spite of the different numbers of parameters (model 1: 5 parameters, model 2: 4 parameters). We found that the efficiency of model 2, concerning correlation of the rheological parameters, with the sensory variables is better. This is documented by the fact that softness, when removing cream from the container and spreadability on the back of the hand, can be checked independently, by two rheological parameters a_2 and c_2 in duplicated. Moreover, model 2 ensures easier evaluation because of the lower number of parameters being four.

However, either model under study, exhibits balanced efficiency from both the rheological and sensory point of view, and proves the possibility to substitute chosen sensory variables of four eye creams by their corresponding model parameters. It means that no panelists are required for the evaluation of sensory variables which are coupled with the rheological parameters. This significantly simplifies the procedure of the continuous checking of eye-cream production and reduces a pre-testing phase of new slightly modified recipes for new products.

The rheological experiments, as presented above, can be carried out using any standard rotational rheometer. These measurements can be classified as routine thus not requiring any special training of staff. As a result, evaluation of sensory variables by their rheological counter-parts, represents a remarkable time and money saving process.

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