



*Dedicated to the memory of  
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

## STABILITY OF DISPERSE SYSTEMS ESTIMATED USING RHEOLOGICAL OSCILLATORY SHEAR TESTS

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Three oil/water cosmetic emulsions systems have been studied using simple and oscillatory shear rheological tests. Rheological parameters controlling processing, storage stability and application of these products have been determined. All the studied systems exhibited gel-like behavior, with different consistencies and degrees of structural stability. A good correlation between rheological parameters and sensory perception of the consumer was found.

### INTRODUCTION

Rheology – the science of flow and deformation of matter – has deep implication in an extremely large number of processing operations. Moreover, the rheological characteristics influence storage stability and end-use properties for a large variety of products in different industrial fields.<sup>1,2</sup>

Most of the processing operations require a rigorous control of the rheological properties due to the strong relationship between flow and deformation characteristics of materials and their structure. Polymeric materials – multiphase systems having a very complex structure – are characterized by different flow behaviors depending on the type and time of sollicitation. Knowledge of the rheological and mechanical properties of different cosmetic systems is important in the design of flow processes, for quality control, in predicting storage and stability

behavior, and in understanding and designing, their texture. Many shear thinning liquids (emulsions, suspensions or dispersions of any kind) are essentially affected by shear, their structure being significantly modified. Irregular shape particles, liquid drops dispersed in another liquid, densely coiled macromolecules or particle agglomerates exhibit considerable resistance to flow, hence a high viscosity. Under continuously increased shear rates the rearrangement and orientation of these flow elements induce a decrease in the viscosity of the system.<sup>1-3</sup>

To obtain products with desired properties for the consumer's satisfaction (aspect, consistency, texture, ease of manipulation) rheological additives are often used. These additives play an important role in improving storage stability, products processing and the synergy among different components of the system. However, this is not always the case. By simply mixing two or more

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polymers, due to their mutual influence and interaction, systems with completely modified rheological properties may be obtained.<sup>4</sup>

Sensory properties of cosmetics are of outstanding importance for the consumer and almost all of them are directly associated with the rheological behavior of the systems. The aspect of the product, spreadability, skin feel and texture have to meet the requirements of the consumer. For example, the consistency plays an important role in the feeling of a product. The consumer expects a higher consistency (viscosity) for a hand cream as compared to a body lotion. The latter has to present a better spreadability on larger surfaces. For manipulation and production phases, as well as for energy savings purposes, consistency is also very important.<sup>5,6</sup>

Rheological measurements proved to be a very important tool in replacing time consuming sensory methods in the evaluation of cosmetics properties. Surprisingly, not too many literature references are dealing with the relationship between rheology and sensory perception for cosmetic products.<sup>4-12</sup>

Oscillatory tests are used to examine all kinds of viscoelastic materials, from low-viscosity liquids to polymer solutions and melts, pastes, gels, elastomers, and even rigid solids<sup>2</sup>.

This paper aims to evaluate the rheological properties of some cosmetic systems based on oil/water emulsions and to clarify the way these properties can predict their stability and correlate with sensory attributes important for consumers.

## RESULTS AND DISCUSSION

Emulsions are widely used in the cosmetic industry as the base for many formulations for skin creams and lotions. Rheological characteristics controlling most of the sensory properties may be determined by simple or oscillatory shear measurements.<sup>4</sup>

Comparative rheological studies have been carried out for three cosmetics systems (skin creams) based on oil/water emulsions. The names conventionally attributed to the studied samples are correlated with the exhibited sensory attributes. Three systems with different consistencies, denoted as hard cream (HC), gel cream (GC) and mousse cream (MC), were analyzed. The differences in the formulation of these systems and the correlation emulsions structure–rheological

properties–sensory properties were discussed elsewhere.<sup>13</sup>

Rheological oscillatory tests are widely used to characterize and quantify the rigidity and integrity of multiphase viscoelastic polymeric systems as well as their internal structure. Typical measured parameters are the storage modulus  $G'$  (a measure of the deformation energy stored by the sample during the shear process, representing the elastic behavior of the material), loss modulus  $G''$  (a measure of the deformation energy used by the sample during the shear process, representing the viscous behavior of the material), phase angle  $\delta$ , damping or loss factor:  $\tan \delta = G''/G'$  (revealing the ratio of the viscous and the elastic portion of the viscoelastic deformation behavior) and complex viscosity  $\eta$ .<sup>1-3</sup>

Three types of dynamic measurements were carried out: (a) amplitude sweep; (b) frequency sweep; (c) creep and creep-recovery tests.

(a) The amplitude sweep (Fig. 1) is generally used to determine the linear-viscoelastic (LVE) range. Here, the oscillation frequency was kept constant ( $\omega = 10$  rad/s), while the oscillation amplitude ( $\gamma$ ) was varied (between 0.01 and 100%). All experiments were carried out at 37°C.

The limit of the LVE region indicates the maximum deformation tolerated by the sample before the internal super-structure is destroyed<sup>2</sup>. Based on the plots in Figure 1, the deformation  $\gamma_L$  and shear stress  $\tau_0$  limiting values of the linear viscoelastic range of the samples were estimated and listed in Table 1. As expected, the mousse cream containing carbomer as a rheology modifier exhibits the highest limiting value of the shear strain. This extension of the linear viscoelastic domain is due to the crosslinked acrylic polymer (carbopol), being well known that polymer solution characterized by strong intermolecular associations (e.g., containing biopolymers) have longer viscoelastic zones. Such a structure confers higher mechanical stability to the formulation and thus the LVE domain is enlarged. The HC (containing xantan gum) with an increased rigidity (higher  $G'$ ) is characterized by the lowest limit values of LVE. The HC sample has an increased consistency, but the structure is unstable and sensitive to mechanical deformation. The presence of starch in the formulation (GC) increases the limits of LVE with no significant influence on consistency.

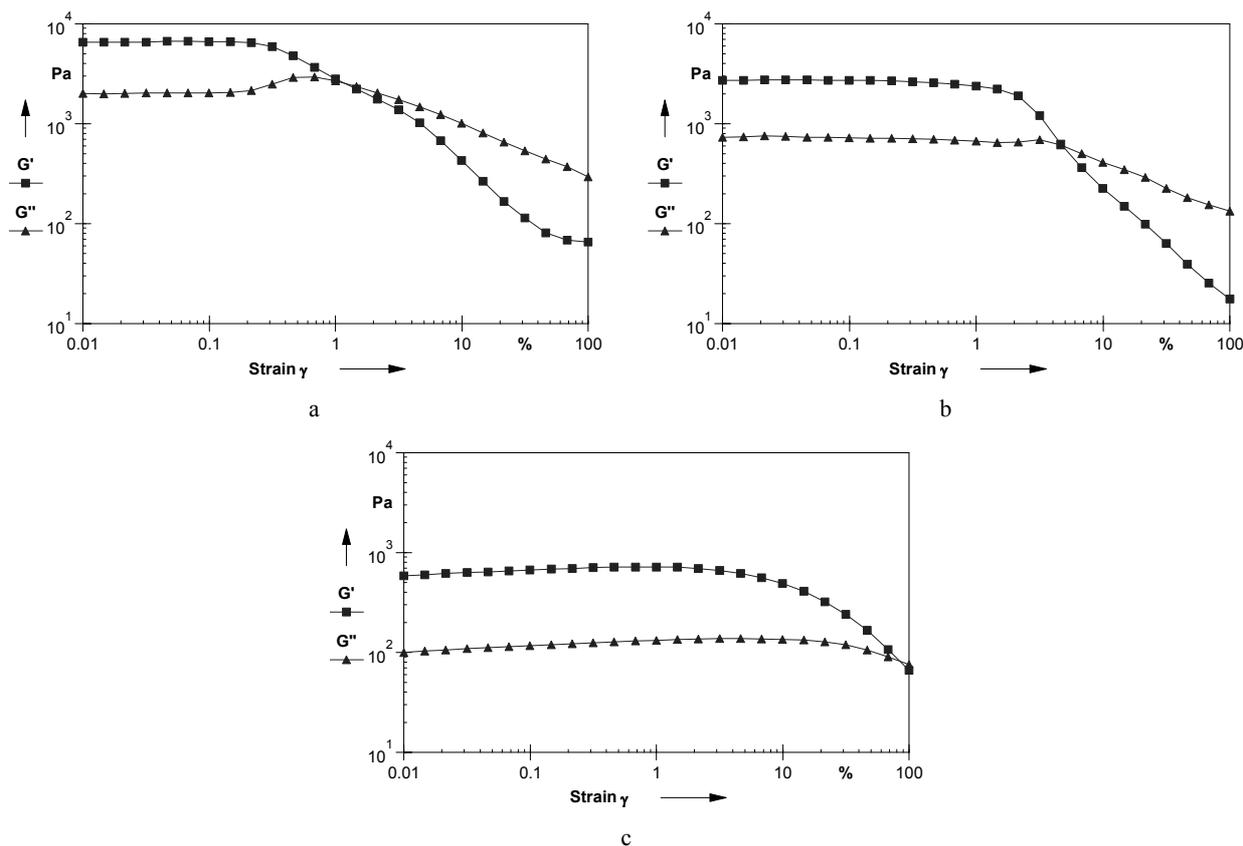


Fig. 1 – Amplitude sweep for: (a) HC; (b) GC and (c) MC at 37°C.

Table 1

Rheological parameters determined from amplitude sweeps for the investigated cosmetic systems

| Sample | The limiting value of the LVE range |                   | Flow point and cross over point |                   |                    |
|--------|-------------------------------------|-------------------|---------------------------------|-------------------|--------------------|
|        | $\tau_0$<br>(Pa)                    | $\gamma_L$<br>(%) | $\tau_c$<br>(Pa)                | $\gamma_c$<br>(%) | $G' = G''$<br>(Pa) |
| HC     | 6.96                                | 0.375             | 42.12                           | 1.160             | 2565.00            |
| GC     | 24.7                                | 1.52              | 40.83                           | 4.751             | 606.70             |
| MC     | 31.20                               | 9.56              | 98.60                           | 84.74             | 81.38              |

Starting with the crossover point of the curves  $G'(\gamma)$  and  $G''(\gamma)$ , hence for  $G' = G''$ , the gel character of a system turns into a liquid character and this point is referred to as “flow point”. Although the plots in Figure 1 are versus shear strain, the oscillatory tests on the three samples also afforded the functions  $G'(\tau)$  and  $G''(\tau)$  to be tracked, making possible the determination of the flow limit in terms of both deformation and stress, as shown in Table 1. The plots in Figure 1 and the data in Table 1 allow some considerations on the behavior of the three cosmetic systems under study.

Within the linear viscoelastic domain where essential modifications in the material internal structure do not happen the material show a reversible viscoelastic behavior. The domain

between the yield stress  $\tau_0$  ( $\gamma_L$ , respectively) and the flow limit  $\tau_c$  ( $\gamma_c$ , respectively) includes a region where  $G'$  is still higher than  $G''$  and the material shows a gel character. However, the domain of the reversible elastic deformations is often exceeded and an irreversible plastic deformation occurs. When the shearing process stops within this domain only a partial structure recovery occurs so that lower values of the elastic modulus are finally obtained in comparison with the corresponding values in the linear viscoelastic range.

The flow limit marked by the condition  $G' = G''$  is quite different within the three samples. The highest value of this limit corresponds to the “mousse” cream and the lowest to the “hard” cream, while the  $G' = G''$  values are in a reverse order, the differences between the three samples

being of two orders of magnitude. As a matter of fact, the values of the dynamic parameters of the samples obey the order  $HC > GC > MC$ , which would suggest a similar order of the stability of these cosmetic systems. But, taking into consideration the limits of the LVE domain and the difference in magnitude between  $G'$  and  $G''$  for the three samples, MC proved to be the most stable system. This observation is supported by the magnitude of the yield stress ( $\tau_c$ ), usually correlated to the strength of interparticle interaction in the three-dimensional network microstructure of creams. MC sample is characterized by a yield stress value two times higher than the two other samples, indicating more contact surfaces, stronger packing between

particles and a lower tendency for bridging flocculation.

(b) The frequency sweep (Fig. 2) is widely used as a standard test in polymer rheology. In this test a sinusoidal strain with a constant amplitude (depending on the LVE range limits for each sample,  $\gamma = 0.1\%$  for HC,  $\gamma = 1\%$  for GC and  $\gamma = 5\%$  for MC) was applied and the oscillation frequency was varied (between  $10^{-1}$  and  $10^3$  rad/s). All the measurements were carried out at  $37^\circ\text{C}$ . The oscillatory tests with frequency sweep were indicative of the preponderantly solid-like behavior of the three creams with  $G' > G''$  over the entire applied frequency domain. Figure 2 presents the variation of the dynamic parameters ( $G'$ ,  $G''$  and  $\eta^*$ ) with frequency for the three samples.

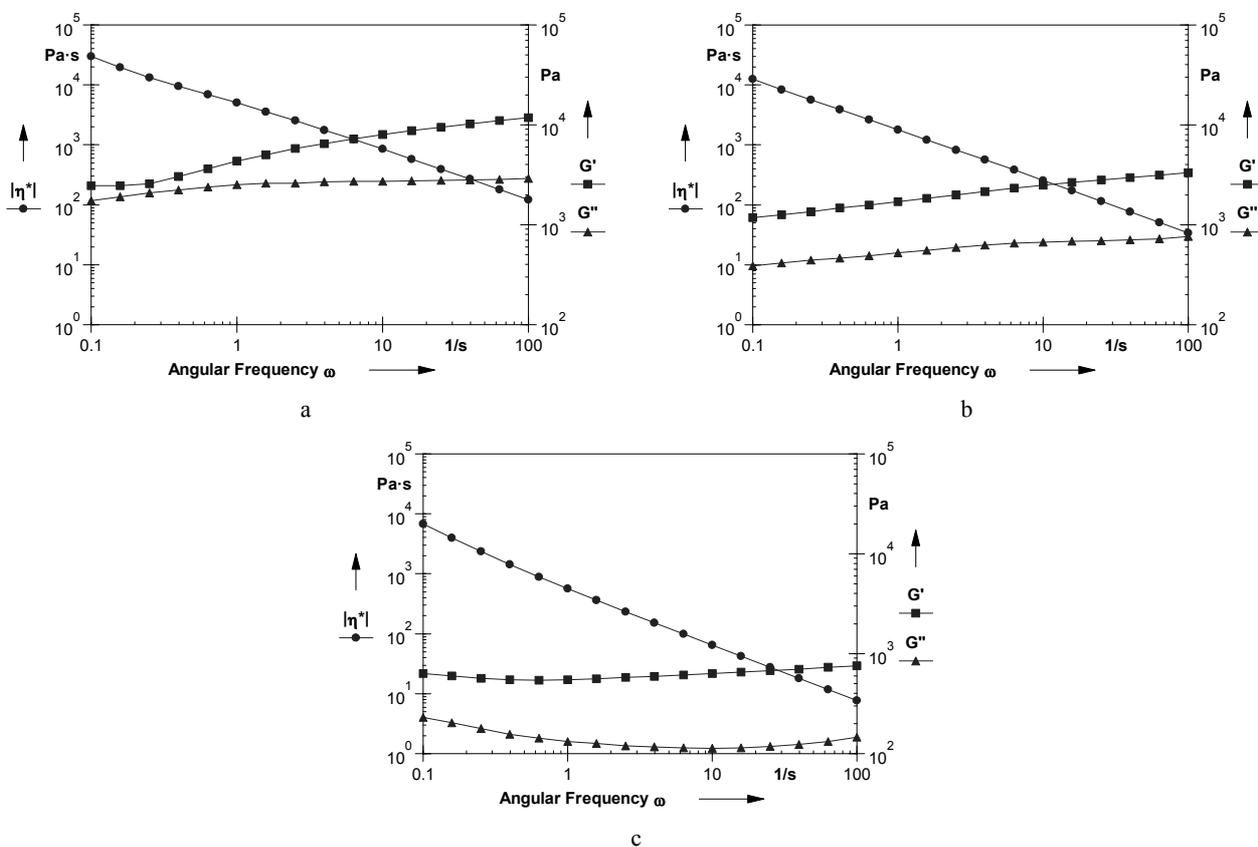


Fig. 2 – Frequency sweep for: (a) HC, (b) GC and (c) MC at  $37^\circ\text{C}$ .

To evaluate the consistency at rest, long-term behavior, and separation behavior of dispersions (sedimentation, settling, flotation or syneresis) the frequency sweep represents the test of choice. Within stable dispersions and gels, intermolecular interaction forces are forming a three-dimensional network of forces. These materials are showing a  $G' > G''$  relation within the whole frequency range. Therefore, the elastic behavior dominates the

viscous one. For all samples,  $G'$  and  $G''$  curves are occurring as almost parallel straight lines throughout the entire frequency range, with only a slight slope (a  $G'$  to  $G''$  ratio of 1.8, 5.2 and 33.3 for HC, GC and MC, respectively, for  $\omega = 0.1$  rad/s). The  $G'$  value at low angular frequency ( $\omega \leq 0.1$  rad/s) gives information about the behavior “at rest” ( $G'_0$ ). Here, the  $G'$  curve should show only a very small (negligible) slope. For many dispersions

and gels, as a rule of thumb based on experiments, one can state for the  $G'$  value determined at  $\omega = 0.1$  rad/s (if the pre-condition  $G' > G''$  is met, i.e. the presence of a “gel character”, and if the test is performed in the LVE range) that if  $G' \geq 10$  Pa, a certain dispersion stability or gel stability can be assumed, that if  $G' \leq 1$  Pa the stability related to practical use is however hardly present, and for a  $G'$  value in-between, further tests should be carried out (e.g. yield stress and flow point)<sup>2</sup>. For the three types of cosmetic systems  $G'_0$  is 2,455 Pa for HC, 1,185 Pa for GC and 637 Pa for MC, an indication of the satisfactory stability for common use of all the formulations ( $G' > 10$  Pa in all the cases). By applying the Carreau-Yasuda model, the zero-shear viscosity ( $\eta_0$ ) can be determined and correlated with the sensory perception. As expected, the highest  $\eta_0$  value corresponds to HC ( $3.0134 \cdot 10^4$  Pas), and the lowest one to MC ( $5.977 \cdot 10^3$  Pas), in good correlation with the tough perception of the HC and smooth sensation offered by MC.

(c) Creep and creep recovery tests are used to analyze the viscoelastic behavior by performing two shear stress steps. This method is mostly used to examine chemically unlinked and unfilled polymers (melts and solutions), but is also suitable to evaluate the behavior of chemically crosslinked polymers, gels or dispersions showing a physical network of forces. Using creep and creep recovery tests zero-shear viscosity can also be estimated and thus valuable information on emulsions and suspensions stability are obtained. In such a method the first step involves the recording of the creep curve at constant shear stress  $\tau_0$  within the

LVE range. After a period of time, denoted as  $t_2$ , the shear stress is set to 0 and the recovery curve is recorded. General creep (from  $t_0$  to  $t_2$ ) and creep recovery (from  $t_2$  to  $t_4$ ) curves with all the important rheological characteristics are depicted in Figure 3. Unsteady flow behavior with a non-constant rate of deformation (shear rate)  $\dot{\gamma}$  occurs between  $t_0$  and  $t_1$ , and thus  $\gamma = f(\tau_k, t)$ . Here, the  $\gamma = f(t)$  curve depends on both preset shear stress  $\tau_k$  and time. Steady-state behavior with  $\dot{\gamma} = \text{constant}$  is reached between  $t_1$  and  $t_2$ , when  $\gamma = f(\tau_k)$ . The  $\gamma$  curve shows a constant slope depending only on  $\tau_k$ . Steady-state creep is finally reached, when the curve is displaying a constant slope (angle  $\beta$ ). The zero-shear viscosity  $\eta_0$  is determined at the end of

the creep phase as  $\eta_0 = \frac{\tau_k}{\dot{\gamma}_3} = \frac{\tau_k}{\tan \beta}$  (Pa $\times$ s) (the

constant shear rate is  $\dot{\gamma}_3 = \frac{\dot{\gamma}_3}{t_2 - t_1} = \tan \beta$ ).

Another significant quantitative information important for the rheological behaviour of the studied systems estimated using creep and creep recovery curves is  $\gamma_0$ . It is determined as the intersection of the  $\gamma$  axis and the straight line showing the curve slope  $\tan \beta$  which fits to the steady-state sector of the creep curve. Considering  $\gamma_0$ , the instantaneous (shear) modulus  $G_0$  and shear compliance ( $J_0$ ) can be evaluated. Maximum deformation, elastic ( $\gamma_e$ ) and viscous ( $\gamma_v$ ) deformation can be determined as parts of total deformation<sup>1,2</sup>.

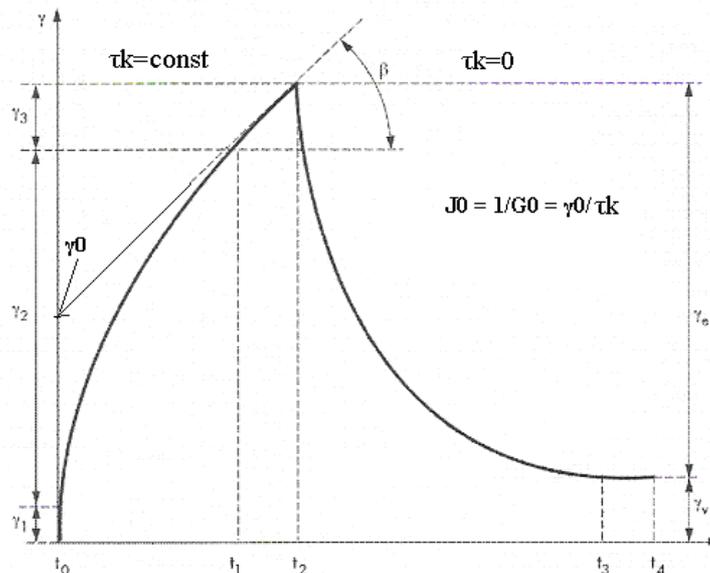


Fig. 3 – Creep and creep recovery curve  $\gamma = f(t)$ , illustration of the parameters used for the analysis.

Figure 4 presents the creep and creep recovery curves for the three cosmetic systems. The preset shear stress for the first step ( $\tau_k$ ) was established for each sample within the LVE range.

According to the methodology presented above, some important rheological characteristics were evaluated using the specific soft of the instrument (Rheoplus). The results are listed in Table 2.

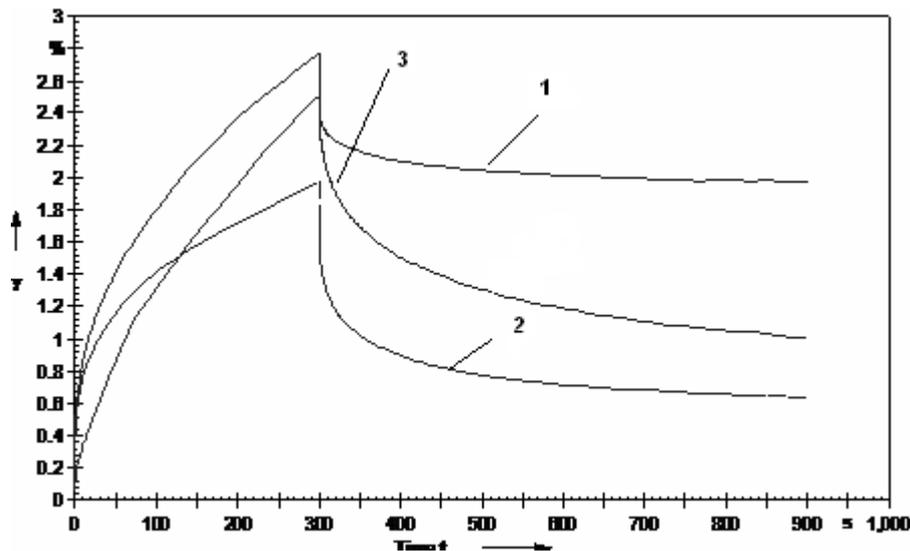


Fig. 4 – Creep and creep recovery curve for: 1 – HC; 2 – GC, and 3 – MC at 37°C.

Table 2

Viscoelastic characteristics evaluated from creep and recovery curves

| Sample Characteristic                  | HC                               | GC                               | MC                               |
|--|----------------------------------|----------------------------------|----------------------------------|
| $\tau_k$ (Pa)                          | 6                                | 10                               | 5                                |
| $\gamma_{max}$ (%)                     | 2.52                             | 1.97                             | 2.77                             |
| $\gamma_1$ (%)                         | 0.20                             | 0.50                             | 0.50                             |
| $\gamma_2$ (%)                         | 0.92                             | 1.10                             | 1.90                             |
| $\gamma_3$ (%)                         | 0.40                             | 0.37                             | 0.37                             |
| $\gamma_e$ (%)                         | 0.51 (20.23% of $\gamma_{max}$ ) | 1.31 (66.50% of $\gamma_{max}$ ) | 1.77 (63.90% of $\gamma_{max}$ ) |
| $\gamma_v$ (%)                         | 2.01 (79.77% of $\gamma_{max}$ ) | 0.66 (33.50% of $\gamma_{max}$ ) | 1.60 (36.10% of $\gamma_{max}$ ) |
| $\gamma_0$ (%)                         | 0.96                             | 1.20                             | 1.60                             |
| $\tan \delta$                          | 0.00421                          | 0.00224                          | 0.00336                          |
| $G_0 = \tau_k / \gamma_0$ (Pa)         | 625                              | 833                              | 312                              |
| $(t_2 - t_1)$ (s)                      | 95                               | 165                              | 110                              |
| $t_3$ (s)                              | 760                              | 900                              | 1000                             |
| $\eta_0 = \tau_k / \tan \delta$ (Pa.s) | 1425                             | 4460                             | 1488                             |

It is easy to see, from Table 2 that the highest maximum deformation ( $\gamma_{max}$ ) appeared for MC sample, even if the lowest preset shear stress ( $\tau_k$ ) was used in this case. The less deformable sample proved to be GC, in spite of the highest preset shear stress. The elastic deformation ( $\gamma_e$ ) higher than 60% from the total deformation was obtained for both MC and GC, while HC has an elastic deformation of only 20%. These observations are in agreement with the results given by the previous rheological tests and offer important information on higher structured samples MC and GC as compared to HC.

## EXPERIMENTAL

The studied cosmetics are oil/water base creams (without fragrances, color or preservatives). The aqueous phase (Part A) and the oil phase (Part B) ingredients are listed in Table 3. As rheology modifier, xanthan gum (Keltrol RD, CP Kelco, USA) was used for HC and GC. For GC, sodium benzoate (Microcare SB, Thor GmbH Germany) and corn starch (National Starch, UK) were also added. Carbomer 940 (Carbopol ULTREZ 21, Lubrizol Corporation, USA) and triethanolamine (TEA) (Lubrizol Corporation, USA) were used as rheology modifiers for mousse cream. All the other oil phase and aqueous phase ingredients were cosmetic grades and purchased from Lipotech, Italy. The Part A and the Part B ingredients were mixed separately and heated at 70°C. The oil

phase was then added to the aqueous phase and mixed in a lab mixer firstly at 500 rpm for 2 minutes and then at 1,000 rpm for 10 minutes. The heated creams were poured in suitable forms and cooled for solidification. The rheological measurements were performed after one day from the preparation.

The rheological measurements were performed on a Physica MCR 501 rheometer (Anton Paar, Austria) equipped

with electronically commutated synchronous motor, allowing rheological measurements in controlled-stress and controlled-strain modes.<sup>14</sup> The polymer samples were heated using a Peltier system, with direct detection of sample temperature. All measurements were carried out in parallel-plate geometry with a diameter of 50 mm, and a gap of 1 mm. To avoid sample slippage, serrated plates were used.

Table 3

## Cream formulations

| Formulation (w/w %) |                             | HC     | GC     | MC     |
|---------------------|-----------------------------|--------|--------|--------|
| Part A              | Deionized water             | to 100 | to 100 | to 100 |
|                     | Glycerin                    | 10.0   | 10.0   | 10.0   |
|                     | Magnesium aluminum silicate | 0.6    | 0.6    | 0.6    |
|                     | Xanthan gum                 | 0.3    | 0.3    | -      |
|                     | Sodium benzoate             | -      | 0.8    | -      |
|                     | Corn starch                 | -      | 2.0    | -      |
|                     | Carbomer 940                | -      | -      | 0.3    |
|                     | Triethanolamine (TEA)       | -      | -      | 1.5    |
| Part B              | Stearic acid                | 5.0    | 5.0    | 5.0    |
|                     | Mineral oil                 | 8.0    | 8.0    | 8.0    |
|                     | Cetearyl alcohol            | 3.0    | 3.0    | 3.0    |
|                     | Glyceryl monostearate       | 1.0    | 1.0    | 1.0    |
|                     | Cetyl alcohol               | 2.0    | 2.0    | 2.0    |
|                     | Laureth-23                  | 0.8    | 0.8    | 0.8    |

## CONCLUSIONS

Simple and oscillatory rheological tests can offer valuable information about creams structure and stability<sup>15</sup>. Sensory perception proved to be in good correlation with the rheological measurements and rheology offers a versatile tool to appreciate the behavior of a cream when applied on skin. The lower strain necessary to break down the structure is a desirable feature since it simulates the onset of spreading of cream on the skin and allows a better absorption. The higher the percent strain, the stronger the cream structure and mechanical stability, but the greater strain is needed to cause effective spreading. Mousse cream (MC) proves the best structure stability but needs greater strain to completely spread on the skin. The lower  $G'$  and  $G''$  values are indication of smooth feeling. The hard cream HC needs lower strain and easily spreads on the skin, but higher  $G'$  and  $G''$  values indicate a tough feeling. The investigated gel cream (GC) exhibits a balance between HC and MC and seems to combine a pleasant feeling with a good structure stability and spreadability on skin. Therefore, knowledge of viscoelastic parameters of cosmetics can be used to predict the performances of different creams and the possibility to use them for specific applications.

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