Application of Oscillatory rheology in long-term stability studies of minimalist emulsion

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Resume

Introduction: Structured phase formulations combine the advantages of emulsifying and gelling systems such as the delivery of hydro- or liposoluble actives, pleasant sensorial and emollient. Oscillatory rheology provide relevant informations about formulation consistency and long-term physical stability. This study aimed to evaluate long-term stability of emulgels through their macroscopic and rheological properties.

Methods: Organolepetic (color, odor, homogeneity) analysis were performed. Oscillatory rheological characterization was carried out to evaluate critical analytical atributes: viscosity, viscoelastic behaviour (storage modulus -G' and loss modulus -G'') and thermosensitivity. Developed emulgel were analyzed after 24 hours it preparation (T0), after two years stored at room temperature (T2-Room) and stored in oven at 40ºC (T2-Oven).

Results: There was no organolepetic alteration in formulation after two years stored under room conditions compared to the initial sample (T0). Emulgel stored at 40ºC presented intensified color and odor. All formulations were characterized by a pseudoplastic behavior. Flow curve showed significantly lower viscosity values to emulgel submitted to thermal stress. Gel-like behavior was observed for the formulations kept under ambient conditions (G'>G''), while the difference in values for the storage and loss modulus was not significant for T2-oven sample. Systems studied showed, in general, a linear themosensitivity behavior.

Discussion and conclusion: In long-term, thermal stress conditions accelerated the changing processes of the organolepetic and rheological parameters. The flow properties and viscoelasticity showed that the binding forces of the polymeric chains

present in the emulgel are more easily deformed after being subjected to thermal stress conditions (T2-Oven).

Key words: Ocillatory rheology; emulgel; long-term stability; viscoelastic behavior

Introduction

Emulsion gels ou emulgels are soft-solid materials in which droplets are entrapped within a structured matrix. These systems maintain the thixotropy and spreadability properties of the gels and show several advantages for cosmetic application such as better stability, active delivery capability, good spreadability, pleasant sensory and easy removal [1,2].

The structured phase are usually formed by a three-dimensional polymeric network that limits the solvent movement. Among hydrophilic polymers, carbomers are thickeners widely used in cosmetic products made up of high molecular wight, cross-linked acrylic acid molecules [3]. Different factor such as the physicochemical propertise of the gel matrix, the distribuition of the droplets in emulsion, the strength and the interactions among the droplets and the gel may interfere with the mechanical properties of emulgels [4].

Rheological measurements provides important information about how the interaction among different ingredients of emulsions may affect their microstructure, sensory texture and long- term stability [5].

In oscillatory rheological assays, typical measured parameters are the storage modulus (G') and the loss modulus (G''). G' refers to the conservation of energy by the system and represents the elastic behavior of the material. G'' refers to the measure of the deformation energy used by the sample during the shear process and represents the viscous behavior of the material [6].

This study aimed to evaluate long-term stability of emulgels through their macroscopic and rheological properties.

Methods

Development of formulations

Formulations (Table 1) were prepared by dispersing the carbomer in DI water at room temperature. The pH was adjusted with aqueous NaOH solution. The emulsions were prepared by stirring aqueous and oily phases separately under heating

until it reached 75ºC. When the two phases were at the same temperature, the aqueous phase was added to the oily phase, with a stirring speed of 1000 rpm and cooled to room temperature. Preservative was added at temperature below 40ºC and homogeneized for 10 minutes.

Table 1 - Percentual composition of developed formulation

INCI name	Percentual composition (w/w)
Aqua	qs
Carbomer	0.90
Vegetable oil	9.50
Cetearyl Alcohol	0.50
Parabens (and)Phenoxyethanol	0.50

Formulations samples were submited to stability and rheological analysis in three conditions: after 24 hours it preparation (T0), after two years stored at room temperature (T2-Room) and stored in oven at 40ºC (T2-Oven).

Macroscopic characterization of developed formulation

Organolepetic analysis was carried out observing any possible alteration in sensorial parameters (color, odor and homogeneity) of the creams in relation to the initial sample (T0).

Rheological analysis

Rheological analysis was carried out using Anton Paar MCR-102 Modular Compact rheometer with a cone-plate geometry (50 mm diameter; 0.9815 cone angle and 0.97 um gap) at 32.6ºC. Viscoelastic measurements of formulations were carried out in formulations in three conditions: T0, T2-Room and T2-Oven.

The linear-viscoelastic range (LVE = 1%) of each test formulation was determined with the amplitude of strain varying from 0.1 to 100% at a fixed frequency of 10Hz. Frequency sweep tests were performed in the range of 1 to 1000 rad/s. The G' value represents elastic (stored energy) behavior, whereas G'' is associated with viscous modulus (dissipated energy). Rheological behaviour was evaluated in terms of elastic modulus (G') and viscous modulus (G'') as a function of frequency for each sample (T0, T2-Room and T2-Oven) analyzed in triplicate.

Temperature sweep tests were performed in the temperature varying from 20ºC to 50ºC.

Results and dicussion

Organolepetics and physical-chemical characterization

Different criterias must be taken into consideration during the development of cosmetic formulations such as long-term physical stability under various conditions, rheological aspects and safety of ingridients.

Macroscopic stability analysis did not show any alteration in color, odor or phase separation in formulation after two years stored at room temperature (T2-Room) compared to the initial sample (T0). Although the formulation stored in oven (40ºC) did not appear to exhibit phase separation, it presented a darker appearance and intensified odor as shown in Figure 1.

Figure 1. Macroscopic aspects of formulations after 24 hours (T0) and two years (T2 -room and T2 -Oven) their preparation

Thus, it was observed that long-term thermal stress conditions accelerated the changing processes of the organolepetic parameters studied.

Rheological analysis

Rheological characterizarion may provide informations about the consistency, the design of flow processes and predict storage and physical stability of the formulation.

In Figure 2, it has been observed that the apparent viscosity decreases wih increasing shear rate of 10 s^{-1} to 1000 $s^{-1.}$

The structural integrity of carbomer gels is related to crosslinked polymer chain that results in packed individual microgel particles. At a critical stress, these binding forces are deformed and the polymer chain segments in the microgel network align in the flow direction [7]. At shear rate of 10 s^{-1}, polymer chains are entangled and the viscosity of formulation is higher. As the shear rate increases, chains structures are affected , decreasing the apparent viscosity.

It has been also observed that the formulation T2-Oven showed lower initial viscosity value when compared to formulations T0 and T2-Room, which may indicate a deformation of the bonding forces resulting from thermal stress.

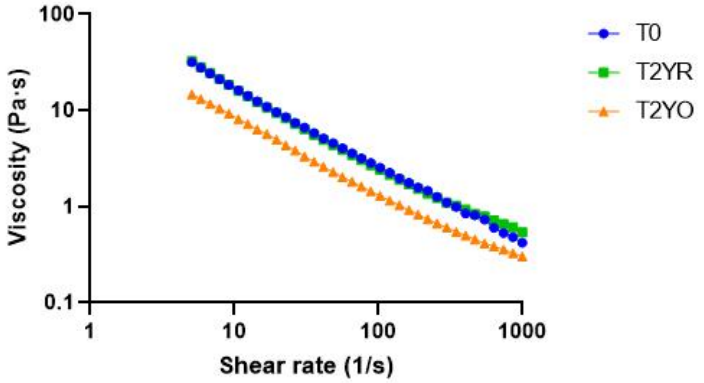

Figure 2. Steady shear deformation test.

Viscoelastic behaviour may be determined by frequency sweep tests as shown in Figure 3. As observed, the storage modulus (G') was higher than the loss modulus (G'') over the frequency range analyzed for formulation in the three conditions (T0, T2-Room and T2-Oven), indicating that the samples behave like gels (elastic behaviour). The elastic characteristic of the material implies its higher ability to return to the original structure after being subjected to deformation forces. Thus, the behavior G'>G" determines a more stable and stronger microstructure of the gel since its reversibility properties are prevalent to irreversible deformations (G").

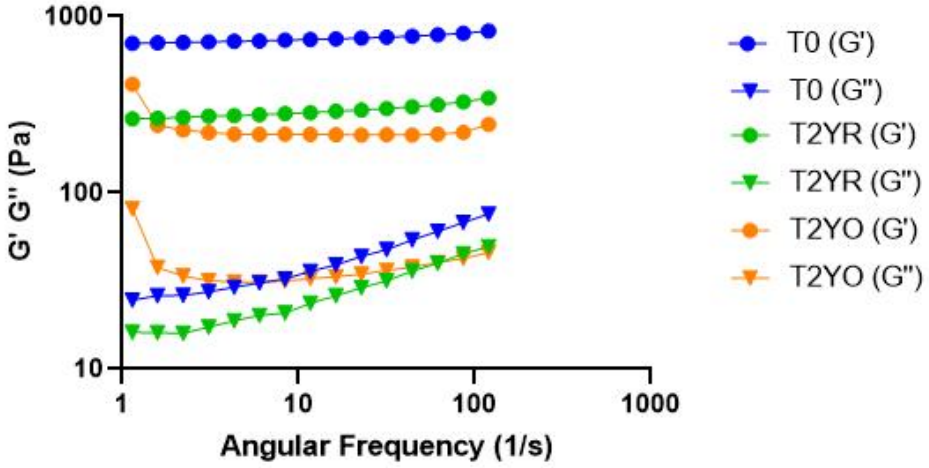

Figure 3 . Viscoelastic behaviour determined by frequency sweep tests of developed fomulations after 24 hours (TO) and after 2 years (T2- Room and T2- Oven)

The temperature sweep tests did not show significant differences in the viscosity values of the samples during the heating step (figure 4). Thus, it has been observed that these systems linear themosensitivity behavior when exposed to slightly increased temperature.

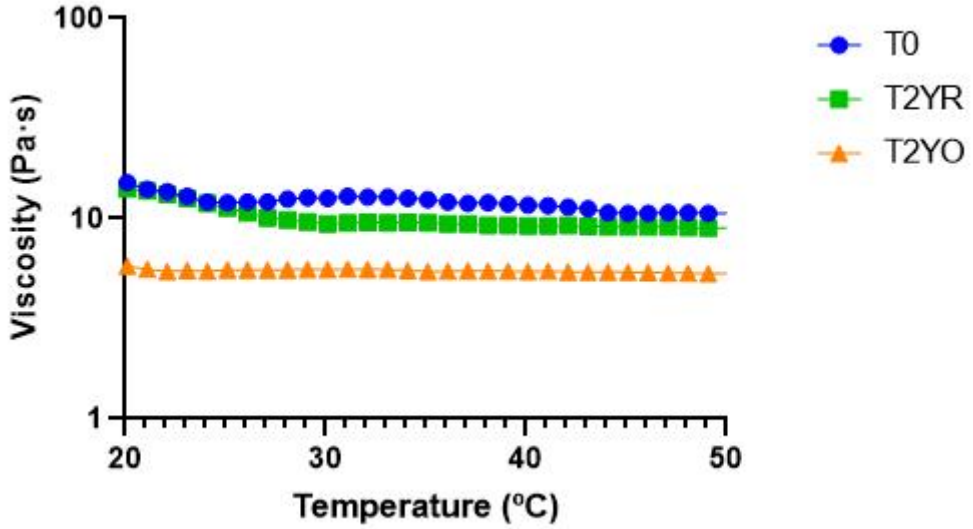

Figure 4. Temperature sweep test of fomulations TO, T2- Room, T2- Oven

Conclusion

In long-term, thermal stress conditions accelerated the changing processes of the organolepetic and rheological parameters. Elastic behavior of formulations T0 and T2-room implies a more stable and stronger microstructure of the gel. The flow properties and viscoelasticity showed that the binding forces of the polymeric chains

present in the emulgel are more easily deformed after being subjected to thermal stress conditions (T2-Oven).

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Conflict of Interest Statement

None.

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