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Rheology and Texture Analysis Used Together to Improve Raw Material Choices

Alicia Roso, SEPPIC
Castres, France
Riva Brinet, SEPPIC
Paris, France

Key words

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Abstract

SEPPIC has developed rheology and texture analysis protocols that, when used in combination, provide useful data regarding the impact of raw material choice on all the development steps: manufacturing procedure, formulation stability, skin feeling.

Texture and skin feeling of cosmetic formulations are becoming fundamental parameters that strongly influence the consumer's choice when selecting a suitable cosmetic product. In addition to the biological activity (such as anti-aging or soothing), the sensation experienced during use of cosmetics is becoming a key criterion for consumers and consequently for laboratory formulation teams. The sensation is drawn from parameters including consistency of the final product, ease of pick-up, good spreading properties, and the absence of any sticky or greasy sensations. All these factors need to be optimized.

Furthermore, these texture criteria should be stable over time during the entire life of the cosmetic formulation and also reproducible at the production stage.

Controlling the texture parameters is very challenging. SEPPIC has developed methodologies to help formulators optimize their product development to enhance texture and skin feeling. Rheology and texture analysis, used in combination, are very helpful for the formulator:

- They give quantified, reliable and objective results on texture parameters.
- They enable comparisons to be made between raw materials in terms of their texture, stability, resistance to shear and temperature, processing and other factors.
- They are able to predict the texture of cosmetic products at early stages of product development and thus minimize development time.
- They can predict the behavior of the cosmetic formulation under actual conditions of use and at all stages of its lifetime (manufacture, packaging, storage, transport, use).

Rheology and texture analysis study the reaction of the product under shear stress applied by different types of device and movement.

This article gives some examples of practical information obtained using these two techniques.

Materials and Methods

Definitions: Rheology is the science of the flow and the deformation of matter. Texture analysis is the investigation of the mechanical properties of a product, including its resistance, consistency and adhesion.

The application of these two techniques is of great interest for the consumer. For example, they provide information on how the product will pour out of a bottle, or on its behavior when picked-up from a jar, or on its elasticity, stringiness, adhesion, spreading on the skin, and other factors.

Both these techniques study the behavior of the product when subjected to shear stress; consequently, rheology and texture analysis can be used as models of real situations in which the cosmetic product is used. For example, if the goal is to predict the pick-up properties, the measurement is made directly in the container, the shear stress is applied by a high-speed translation movement with a low depth of penetration into the product, and the measurement is performed at room temperature. Conversely, to predict spreading behavior, it is preferable to work at about 32°C, which is closer to skin temperature, and a medium-speed rotating movement is selected to apply the stress to a very small amount of product.

Furthermore, both methods have the advantage of generating very reliable and reproducible results. With a trained operator and standardized protocols,

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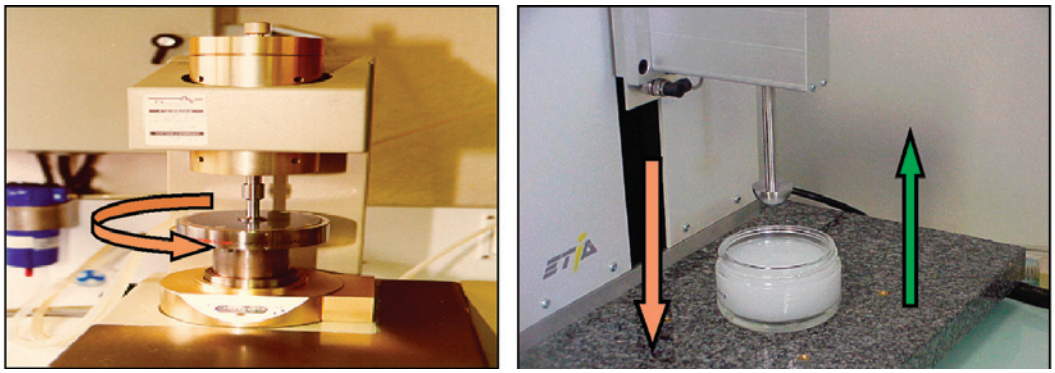


Figure 1. Instruments used to measure rheology and texture analysis Rheometer (left) Texture analyzer (right)

the standard deviation of the measured parameters is always below 10%.

Materials: Rheometric measurements are made using a controlled stress rheometer[a]. As shown in Figure 1, the rheometer applies the shear stress by a rotating movement on the product and measures the resulting stress as a function of the shear rate (unit = pascal Pa).

Texture analysis experiments are performed using a texture analyzer[b]. As shown in Figure 1, the texture analyzer controls a translation movement of the probe: down into the product and back up, recording the resulting force curve (unit = newton, N) during the displacement.

Depending on the movement applied to generate the stress, these two devices are complementary, and representative of the major movements applied to the cosmetic product during manufacturing, transfer, packaging, and use (for example, translation movement for pick-up, rotating movement for spreading).

Rheology methods: Two main types of measurement are made using the rheometer: flow experiments and oscillatory experiments. The two experiments give complementary data on the flow properties of the product and on the internal structure of the product at rest.

- During flow experiments, an increasing shear stress is applied to the product for two minutes and then a decreasing shear stress is applied. The resulting shear stress is monitored as a function of the shear rate. One of the most useful ways to express the measurements is to monitor the viscosity as a function of the shear rate, which provides information on product flow characteristics. For instance, a product which shows decreasing viscosity with increasing shear rate (i.e., shear thinning behavior) facilitates bottle filling and also improves the pouring step. For the consumer, such behavior is also commonly associated with good spreading properties.
- The purpose of oscillatory experiments is to apply very low periodic shear stress for a long time to investigate the internal structure of the product at rest. The resulting parameters are the storage modulus G′ (expressed in Pa), which represents the elastic character of the product, and the loss modulus G″ (expressed in Pa), which represents the viscous character of the product. The ratio G′/G″ represents the tendency of the product to be more elastic (able to recover from deformation). A predominant elastic character is typically related to a network structure and consequently helps to stabilize the product.

Texture analysis methods: The texture profile follows the behavior of the product on compression and/or on stretching.

- Monitoring the force during compression gives information about the consistency (or firmness) of the product: the higher the force required to achieve the defined movement, the more consistent the product.
- Monitoring the force during stretching gives information about the adhesion properties of the product: how the product stretches (stringy effect or elastic return) and the quantity of product that remains on the probe. All these parameters give indications on the ease of pick-up.

These two methods are fully representative of the stresses of manufacture, packaging, transfer, storage and use.

[a] *Carrimed CSL500, Waters-TA Instruments, New Castle, Delaware, USA. Carrimed CSL500 is a registered trademark of Waters-TA Instruments.*
[b] *TEC texture analyzer, Jean Lamy, Caluire, France. TEC is a registered trademark of Jean Lamy.*

Results and Discussion

How the choice of ingredients governs the texture: The first study shows how polymer selection influences the ease of pick-up of gels and cream gels in relation to their adhesion properties. We prepared aqueous gels (Formula 1) and cream gels (Formula 2) at two viscosities: 20,000 mPa.s and 50,000 mPa.s (Brookfield LVT, speed 6, spindle 4 at 25°C). Five different versions of each gel were prepared by choosing one of five polymers commonly used in cosmetic products.

- Polymer 1. Polymer in inverse emulsion 1. This polymer[c] was sodium acrylate / acryloyldimethyl taurate copolymer / isohexadecane / polysorbate 60.
- Polymer 2. Polymer in inverse emulsion 2. This polymer[d] was hydroxyethyl acrylate / sodium acryloyldimethyl taurate copolymer / squalane / polysorbate 60.
- Polymer 3. Acrylates / C10-30 acrylate crosspolymer
- Polymer 4. Carbomer 1 (INCI = Carbomer)
- Polymer 5. Carbomer 2 (INCI = Carbomer). Compared to Carbomer 1, Carbomer 2 is known to be easier to disperse, and to have superior thickening efficiency in emulsion formulations.

The polymer in each formula was used in sufficient quantity to achieve the required viscosity.

The texture profile of each formulation was determined by a cyclic measurement protocol: compression followed by

Formula 1. Aqueous gel and cream gel used to study how choice of ingredients governs the texture. Five polymers were used.

1 = Sodium acrylate / Acryloyldimethyl taurate copolymer / Isohexadecane / Polysorbate 60 (Simulgel EG, SEPPIC)
2 = Hydroxyethyl acrylate / Sodium acryloyldimethyl taurate copolymer / Squalane / Polysorbate 60 (Simulgel NS, SEPPIC)
3 = Acrylates / C10-30 acrylate crosspolymer
4 = Carbomer 1
5 = Carbomer 2

Ingredient	Aqueous gel	Cream gel
Polymer	as needed*	as needed*
Cetearyl ethyl hexanoate	-	15% w/w
~~*Aqua* (water)~~	~~qs 100% w/w~~	~~qs 100%~~

* dose required for viscosity of 20,000 mPa.s or 50,000 mPa.s

[c] *Simulgel EG, SEPPIC, Paris, France*
[d] *Simulgel NS, SEPPIC, Paris, France*

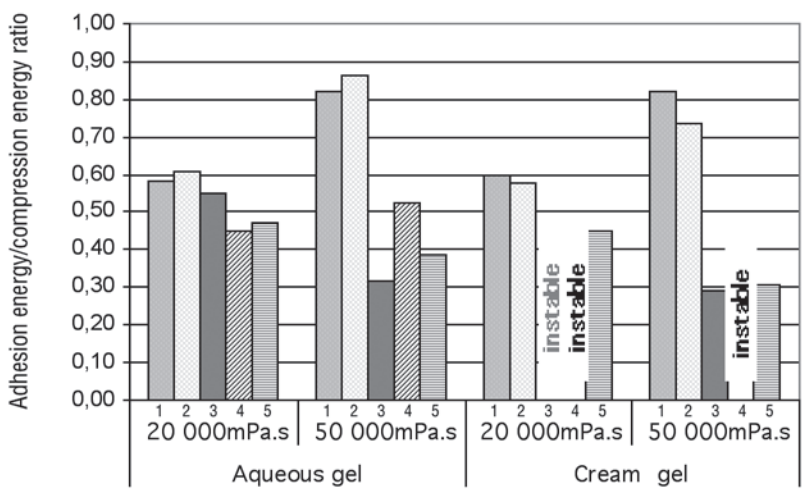


Figure 2. Comparison of the adhesion properties of gels on pick-up, as a function of their viscosity. Five polymers were used.
1 = Polymer in inverse emulsion. Sodium acrylate / Acryloyldimethyl taurate copolymer / Isohexadecane / Polysorbate 60 (Simulgel EG, SEPPIC)
2 = Polymer in inverse emulsion. Hydroxyethyl acrylate / Sodium acryloyldimethyl taurate copolymer / Squalane / Polysorbate 60 (Simulgel NS, SEPPIC)
3 = Acrylates / C10-30 acrylate crosspolymer
4 = Carbomer 1
5 = Carbomer 2

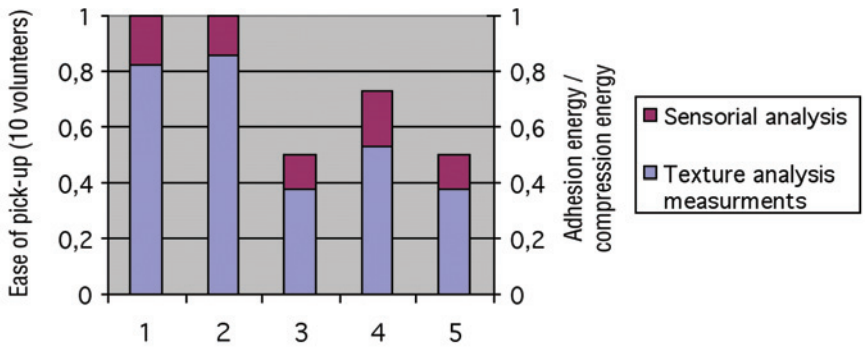


Figure 3. Comparison of the results between sensorial evaluation and texture analysis measurements regarding ease of pick-up. Five polymers were used.
1 = Polymer in inverse emulsion. Sodium acrylate / Acryloyldimethyl taurate copolymer / Isobexadecane / Polysorbate 60 (Simulgel EG, SEPPIC)
2 = Polymer in inverse emulsion. Hydroxyethyl acrylate / Sodium acryloyldimethyl taurate copolymer / Squalane / Polysorbate 60 (Simulgel NS, SEPPIC)
3 = Acrylates / C10-30 acrylate crosspolymer
4 = Carbomer 1
5 = Carbomer 2

stretching with a hemispherical probe. Two parameters were determined:

- Compression energy (units of mJ) is the energy necessary to push the probe into the sample.
- Adhesion energy (units of mJ) is the energy necessary to pull the probe out of the sample.

To avoid the effect of firmness differences between the gels, despite viscosity adjustment, the adhesion of the product to the probe was expressed as the adhesion energy/compression energy ratio. The higher this ratio, the more the product stays on the probe.

The results are shown in Figure 2. The texture profiles of cream gels are similar to texture profiles of aqueous gels, which means that the polymer clearly governs the texture behavior of cream gels. An additional study (results not shown here) has demonstrated that the quantity of oil incorporated and the nature of the oils have very little influence on the adhesion properties of the cream gel.

The adhesion of gels and cream gels on the probe is viscosity-dependent, and different behaviors can be observed depending on polymer tested.

With Polymers 1 and 2, the adhesion increases similarly with the viscosity of the aqueous gel or the cream gel. In contrast, Polymer 5 showed decreasing adhesion as the viscosity increased. And in the aqueous gels, Polymer 3 showed decreasing adhesion as the viscosity increased, while Polymer 4 showed a slight increase. For these polymers, the sensorial evaluation demonstrated good pick-up for the 20,000 mPa.s gels but poor adhesion for the 50,000 mPa.s gels (data not shown).

These results demonstrate how texture analysis can help to select the optimum polymer for formulating firm and viscous aqueous gels or cream gels that still have good pick-up characteristics.

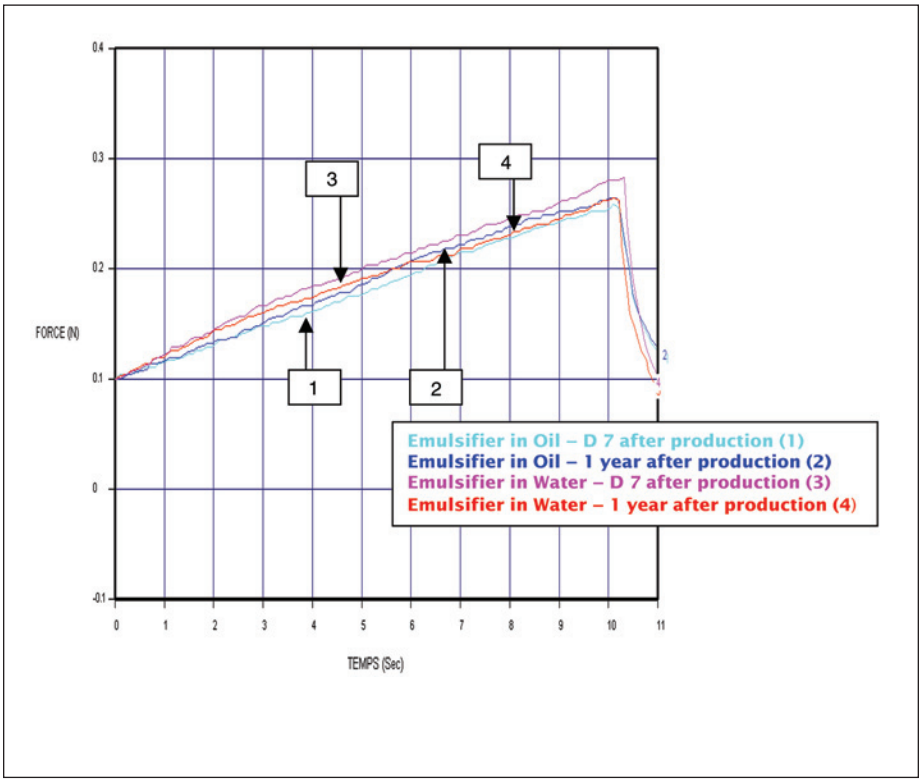
The ease of pick-up of these polymers was confirmed by a trained sensorial panel (10 volunteers) with the products in jar packaging. The "ease of pick-up" descriptor from sensorial analysis is perfectly well correlated with the "ease of pick-up" parameter from the texture analysis instrument (i.e., adhesion measurements) as shown in the Figure 3. This good correlation allows SEPPIC to validate the usefulness of the texture analysis equipment as an analytical tool to predict the behavior of the cosmetic product when used by consumers.

How the manufacturing process influences texture: In this second example, we studied the texture profile of a basic emulsion (Formula 2) made with different procedures using a pre-defined mixer.

The emulsion is made by emulsification for four minutes with a rotor/stator turbine[e] and then cooling while stirring with an anchor blade.

The emulsifier can be added either to the hot water phase or to the hot oil phase. The texture of the emulsion is then monitored over time with the texture analyzer using a compression protocol. The maximum compression force (unit=N) – this is the

[e] *Silverson Turbine, Chesham, Buck, England*



Formula 2. Basic emulsion used to study the texture profile resulting from different manufacturing processes

Ingredient	% w/w
Cetearyl alcohol / Cetearyl glucoside (Montanov 68, SEPPIC)	5
Paraffin oil	20
Aqua (water)	qs 100

Table 1. Maximum compression force (N) (±standard error)

Procedure	Emulsifier in oil	Emulsifier in water
7 days after production	0.25 N (± 0.01)	0.28 N (± 0.015)
1 year after production	0.26 N (± 0.01)	0.26 N (± 0.01)

Formula 3. Aqueous gel and cream gel used to test the optimizing of the stability of the texture

Aqueous gel	Cream gel	
Hydroxyethyl acrylate/Sodium acryloyldimethyl taurate copolymer / Squalane / Polysorbate 60 (Simulgel NS, SEPPIC)	3% w/w	3% w/w
Caprylic/capric triglyceride	-	10
Aqua (water)	qs 100	qs 100

force necessary to push the probe into the sample to a given depth at a fixed speed – is well correlated with the consistency of the emulsion as evaluated by consumers picking up the product from a jar. The higher the maximum compression force, the more consistent the emulsion.

With such firm creams, texture analysis is very helpful for monitoring the real "consistency" of the emulsion, because the compression movement is not sensitive to the sliding effect. With rotational devices such as the Brookfield viscosimeter, there is a strong sliding effect. There is absolutely no correlation between the measured viscosity and the apparent consistency of the emulsion (underestimated).

The compression profiles shown in Figure 4 and the maximum compression forces given in the summary Table 1 show that the consistency of the emulsion is similar whatever phase the emulsifier is introduced in; moreover, both emulsions have very good stability over time. Therefore, such glucolipid emulsifiers provide extensive freedom of formulation.

This type of study could also be performed to examine the influence of scale-up on the texture of the emulsion, and provides very useful data for adjusting the procedure when stirring devices are non-homothetic.

Optimizing the stability of the texture: Cream gels lead to new textures and have an increasing share of the cosmetics market. However, many questions are often left unanswered. What is the mechanism of stabilization of a cream gel? How can the very good stability of this outstanding texture over time be explained?

The viscoelasticity profile of polymers illustrates their ability to stabilize oil phases without any additional surfactant.

The behavior of an aqueous gel (Formula 3) and a cream gel (Formula 3) was studied by oscillatory experiments: shear stress sweep (frequency 1 Hz), frequency sweep (from 0.1 to 10 Hz), temperature sweep (from +5°C to 80°C) to monitor the G'/G'' ratio.

As shown in Figure 5, the cream gel had a strong elastic character, stable over the whole frequency range. Further investigation by temperature sweep also confirmed this strong elastic character over the range from 5°C to 80°C, which indicates a strong and stable polymeric network in the aqueous phase.

The comparison between the aqueous gel and the cream gel in the same shear stress sweep (Table 2) shows that the elastic character was enhanced in the presence of the oil, which is in perfect correlation with the stability of the cream gel over time, even after prolonged storage at 50°C (no exudation of the oil phase). The presence of the oil phase reinforces the elasticity of the polymer, which illustrates the stabilization of the oil droplets in the polymeric network.

Further experiments indicated that this phenomenon is not dependent on the nature of the oil: polar or nonpolar

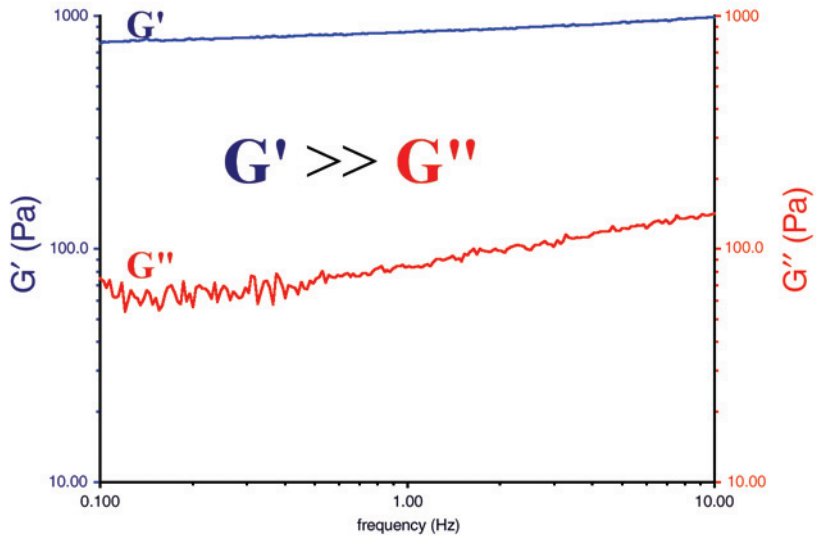


Figure 5. Frequency sweep of the cream gel from 0.1 to 10 Hz

oils could be easily stabilized in the polymeric network.

Conclusions

These three examples illustrate some applications of rheology and texture analysis. The combined use of these two techniques could be very helpful in formulation studies thanks to the complementary movements and types of data obtained.

These two technical tools help to obtain a better understanding of which ingredient has the leading role in the formulation and provide technical data for selecting suitable ingredients for optimizing the manufacturing procedure, the stability of the formulation, and the skin feeling.

Table 2. Comparison of elastic character of aqueous gel and cream gel

Gel type	G′/G″ Mean ratio Linear region
Aqueous gel	6.4
Gel cream	9

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