Chapter 16

Cosmetics' Quality Control

Bruna Galdorfini Chiari,
Maria Gabriela José de Almeida,
Marcos Antonio Corrêa and Vera Lucia Borges Isaac

Additional information is available at the end of the chapter

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1. Introduction

The quality of a cosmetic product, in the same way as to other kind of products, is initially defined by the manufacturer that chooses the features that a product should present. On the other hand, the quality control of a product aims to verify if all of these defined features are in accordance with the standard definitions and if it will be maintained during the shelf life of the product (Shewhart, 1980).

The quality control of cosmetics is important to ensure the efficacy and safety of products and its raw-materials. Due to the rapid growth that cosmetic industries have exhibit all over the world, efficient, low cost and rapid methods to assay cosmetics' quality control are a priority. Some current techniques used by the cosmetic industry can be applied to the evaluation of cosmetics' quality control in an efficient manner, such as: rheology, sensory analysis and small angle X-ray scattering (SAXS).

Sensory analysis is a powerful tool, since there is no equipment able to measure the human feelings. It applies experimental design and statistical analysis to obtain information about a product in relation to what people feel when use or consume a product, in other words, it is used to indicate consumer acceptance of a particular product. It can be understood as the discipline that interprets, assess and measures characteristics of a product, after stimulating people in relation to their vital senses, as vision, touch, smell and taste (Stone et al., 1992). It is widely used in food industry and recently, it has also been applied in the cosmetic industry (Almeida et al., 2008; Aust et al., 1987; Backe et al., 1999; Lee et al., 2005; Parente et al., 2005; Wortel et al., 2000).

The sensory analysis can be applied in the research and development of a new cosmetic (Isaac et al., 2012a), in controlling the manufacturing process to evaluate raw-materials quality and, even, to make possible the substitution of a raw-material of a product that is traditional in the market without changes in the product's features (Meilgaard et al., 1991; Muñoz et al., 1993).

The application of sensory analysis could be related to the product control, referring to the storage, packaging and maintenance of sensory quality in relation to time and temperature (Muñoz et al., 1993), since these factors can change a sensory attribute that the product present originally (Zague, 2008) and people who participates of the sensorial panel could realize the changes in the sensorial attributes. Another function of this important tool is to performance comparative tests between competing products.

Another tool that could be applied to evaluate cosmetics' quality control is the rheology, which studies the flow and deformation of fluids. It has been used in research laboratories and industries as a tool for characterizing ingredients and products, and to predict the performance of products and consumer acceptance.

Rheology has been widely used because, by means of this tool, the researcher can determine physicochemical properties of a product. Constructing a rheogram, it is possible to check the flow curve, evaluate if there is a yield stress and a hysteresis area, which appears to be related to the release of drugs and actives. It is also possible to construct a creep and recovery curve obtaining information about viscoelasticity of each system.

Specifically, in relation to the quality control of cosmetics, specifically, rheology can be applied to help in determining the stability of products by means of the apparent viscosity measured periodically in a determined period exposing the samples to stress conditions (high and low temperatures, solar irradiation), and to monitor the flow characteristics during the shelf life or in the stability assay of a product.

The SAXS technique have being used for the analysis of cosmetics, in order to evaluate the presence of liquid crystalline structures, called liquid-crystals, which are known to increase the stability of formulations becoming, therefore, desirable in cosmetics (Makai et al., 2003).

Combining these three tools, it is possible to test the quality of cosmetics with a rich range of data, and obtain a deep characterization of the system. The results contribute to determining product use, or even, they provide indication of what need to be done to develop a product with predetermined characteristics.

2. Sensory analysis

Sensory analysis is defined by Piana et al. (2004) as the examination of a product through the evaluation of the attributes perceptible by the five sense organs (organoleptic attributes), such as color, odor, taste, touch, texture and noise, allowing the establishment of the organoleptic profile of diverse products, including cosmetics.

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The sensory analysis was first applied to the food industry, but the high advance in other areas, such as the cosmetic and pharmaceutical industries, and the important data obtained with the sensory analysis, demanded this useful technique to describe what the consumers fell.

An important advantage of the use of sensory analysis in the quality control of a cosmetic product is that it yields a complex analysis in relation to all sensorial attributes that a product could present, it means that, the volunteer who participates of the sensorial panel is able to give information about the fragrance, the sensation, the appearance, the consistence, and other features that this person experience when use such product. The description of these characteristics by means of equipment would be an arduous work and would provide not sufficient or not valuable data when compared to the data provided by the human senses. Beyond that, the acquisition of this equipment could be of high cost when compared to the sensory analyses' costs (Ross, 2009).

The association of data obtained from sensory analysis and instrumental analysis (especially physicochemical analysis) provides great information and a more complete profile of the product (Ross, 2009).

Nowadays, there are companies specialized in perform sensory analysis of cosmetic products, and thus, they could be contracted to perform this study for cosmetic industries that don't have a sector trained to do it.

The sensorial performance of cosmetics is essential to the acceptance of consumers (Almeida et al., 2008; Fouéré et al., 2005; Lee et al., 2005; Proksch, 2005), thus, especial attention should be given to this subject.

The sensorial features of a formulation are mainly related to the raw-materials and package (Dooley et al., 2009). The raw-materials influence directly in what the consumer feels when applies the cosmetic. The emollients, for example, are raw-materials of marked influence in the tactile sense (Parente et al., 2008; Gorcea and Laura, 2010). Other raw-materials are available at the market and are commercialized to be used in formulations as sensorial modifiers. The main representatives of this kind of product are the silicones and Polymethyl Methacrylate (Ozkan et al., 2012).

The package influences in the first impression of the consumer about a product, since the first sense used to choose a cosmetic in the market is the vision. After, the smell is used too. The tact is not involved in the first purchase attitude, but it will define if a consumer will become a loyal consumer.

In this context, it is possible to verify that the sensorial features of a cosmetic are of great importance in the success of it in the market.

Thus, the sensorial analysis could help a company to define the attributes that a product should or not present beyond the characteristics and intensity of these attributes.

Another point is that these desired sensorial characteristics should be maintained during the cosmetic shelf life. To obtain that, the raw-materials used should be of good quality, the

manufacture practices should be appropriate, the preservatives used need to be efficient and the formulation should be stable.

In conclusion, the sensorial analysis is an indispensable technique to help the formulator to evaluate the quality of its new product, in relation to its sensorial characteristics and to its stability, testing if the product will keep the nice sensorial feelings that transmit to the consumer during the time of use. This tool is helpful to the research and development area of a company which aims to obtain good quality products of high acceptance by the consumers. The suitable application of sensory evaluation could avoid the outlay of a company with the launching of a product in the market that was rejected by the volunteers of the preliminary study.

Currently, the sensorial analysis have gained more scientific rigor due to the need to offer to the consumers products that meet their expectations and due to the high competition between the major industries of this sector.

To perform the sensorial analysis with rigor and organization, the laboratory destined to it must have the following areas:

A room destined to the analyst who leads the team (Figure 1a)

A conference room (Figure 1b)

A room for the samples preparation (Figure 1c)

An area to the analyses with the volunteers (Figure 1d)

The laboratory should be located in an easy access place.

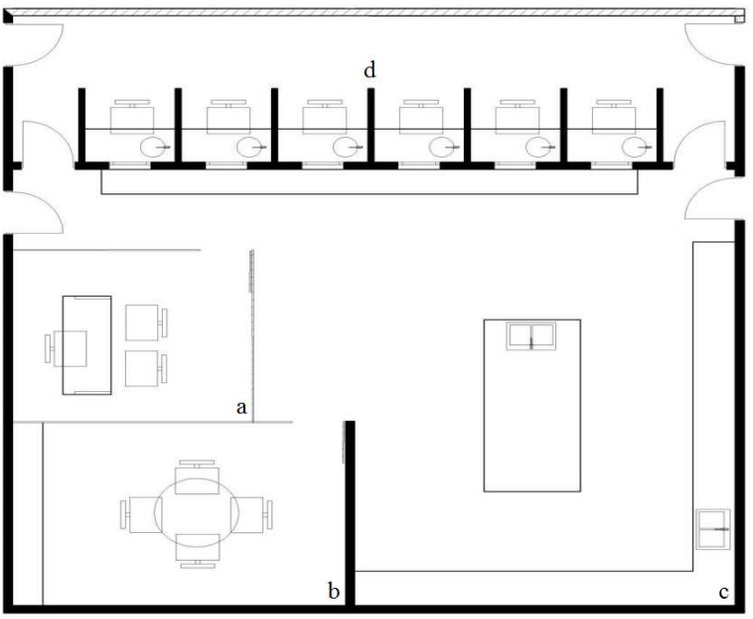

Figure 1. An example of layout of a sensorial analysis laboratory (Isaac et al., 2012a).

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The area where will be performed the analyses should be divided in individual cabins (Figure 2) with a window, where the analyst must offer the samples to the volunteer, sink and faucet, to the volunteer use when necessary (Isaac et al., 2012).

Figure 2. An example of layout of sensorial analysis cabine (Isaac et al., 2012a).

The cabins must be ventilated and odor free, to avoid interferences in the analyses. The temperature and humidity should be controled around 22 ºC and at 45% of humidity (Isaac et al., 2012).

It is recommended that the walls and furniture of the rooms are colored with neutral and light colors to not disturb the attention of the volunteers and to not interfere in the attributes analyzed by the vision, such as color and appearance of the product.

The volunteers should not smoke, should be healthy, with ease of memorization and communication.

In the study, the volunteers judges could be an experienced judge or not, depending on the kind of evaluation and the answers that the professional team needs to obtain. In the case of utilization of sensorial analysis in the quality control of a cosmetic, usually the volunteers are regular users of the product in analysis, since they need to be familiarized with the characteristics of the product and have sensibility to perceive slight modification on it. When the aim of the sensorial analysis is to evaluate the acceptance of a product that should be launched in the market, it is recommended that the volunteers are potencial users of this new product, orienting the formulator to make changes in the formulation and guiding the company to evaluate if the costs of the product launch are recommended or not.

There are four different methods to perform the sensorial analysis that are most used, they are: affective, discriminative, descriptive (Aust et al., 1987) and methods to evaluate the effective of the product.

Independent of the method of sensory analysis suitable for each evaluation, the professional team should use printed questionnaires to obtain the answers from each volunteer. The use of printed questionnaires avoids the contact between the professional and the volunteers preventing that the professional is biased in his responses, beyond that, it facilitates the data collection.

In the elaboration of these questionnaires the professional team should use suitable lexicons for each class of product, for example, the lexicons used to the evaluation of lip products are different from that used for corporal lotions (Dooley et al., 2009). Some researches had developed suitable lexicons for different classes of cosmetic products (Civille and Dus, 1991; Wortel and Wiechers, 2000; Dooley et al., 2009). The manner as the volunteer is questioned is fundamental to obtain the information required from them. An inadequate formulary could invalidate a sensory evaluation. It is interesting also, that a description of all descriptors attributed to the formulation being provided to the volunteer, for example: "Thickness: Viscosity of the cream when picking up from the container", "Ease of spreading: Ease of rubbing the sample over the skin", "Absorption: Ease of absorption of the product through the skin", "Residue: Amount of product left on the skin after application" (Parente et al., 2010).

The affective methods represent the consumer opinion and evaluate how much consumers like or dislike a product. It is a quantitative method that is performed in order to know the consumers preferences (Aust et al., 1987). This technique could be applied in the development of new products and when it is necessary to replace a constituent of a formulation without loss of the product quality. It could be performed in two different ways: offering two different samples to the volunteer asking him about what sample he prefers between them or using a hedonic scale for the volunteer attributes grades of intensity of its acceptation in relation to the sample.

The hedonic scale either can be presented to the panel of evaluators in different manners, as shown in Figure 3.

The affective methods provide quantitative data and allow more than one attribute in each sample being evaluated at the same time.

The discriminative test is better represented by the Triangular test. It allows differentiating one between three different samples and is very useful in shelf life studies and in the quality control of cosmetics. The ideal is to perform this evaluation with twelve to forty volunteers, who will receive the three samples and should indicate the different one between them (Zenebon et al., 2008).

The descriptive tests provide a broad sensory description about the product that is being evaluated (Almeida et al., 2008), helping to predict the consumer acceptance and what consumers think about such product (Almeida et al., 2006; Aust et al., 1987).

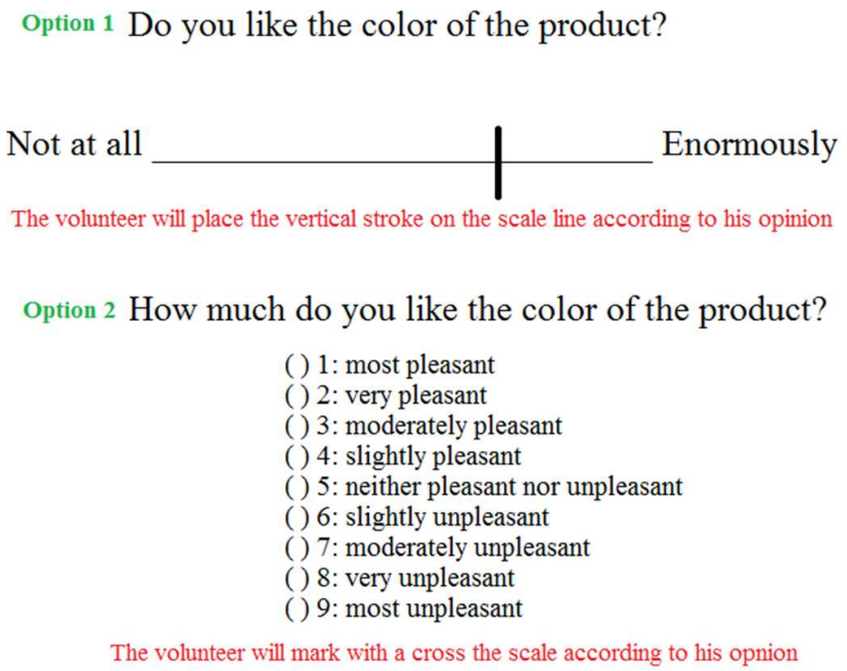

Figure 3. Examples of presentation of hedonic scale (Olshan et al., 2000; Barkat et al., 2003).

The tests to evaluate the effective of the products should be performed in true conditions of use and the volunteer may use only the product that is being assessed. These tests could be conduct by the evaluation of dermatologists, by the evaluation of volunteers, and even, by the measurement of one parameter by un equipment, such as the equipment that measures hydration, sebum and transepidermal water loss, to define if a product is really effective. Based on these clinical evaluations, a company could create an efficacy claim to the product (Wortel and Wiechers, 2000).

The sensory analysis could be also applied when a cosmetic industry needs to replace a raw-material of a commercialized product without changes in the performance of it. This replacement could be originated by many factors, such as the reduction of costs, problems with the firm who provides this raw-material problems with same raw material which causes irritation, comedogenicity or other problems that affect the consumer. In this field, the sensorial analysis helps the formulator, who proposes different raw materials as substitute, to evaluate if the consumer will notice the adaptation in the cosmetic product.

The statistical analysis is indispensable in the sensory studies. The sensory analysis data should be evaluated transforming them in scores which allows the application of statistical analysis to calculate the mean and standard deviation of the results, and the determination if the difference between the scores obtained is statistically significant. Graphics, tables and preference maps could be elaborated with the results obtained to facilitate the analysis of the data by the professional team.

The sensory analysis is especially indispensable in the industries of fragrances and perfumes, and because of that, high-resolution instrumental methods for evaluation of flavor

and aroma have been developed and between them are the breath analysis via mass spectrometry (Dijksterhuis and Piggott, 2001; Ross, 2009). Instrumental measurements are thought to be objective, representing an independent fact or truth, however, the human smell sense is irreplaceable, being considered by Ross (2009) not necessarily valid because instrumental methods cannot account for the complexity of human perception.

Nevertheless, rheological studies have been applied to objectify the sensations when cosmetic emulsions are applied to the skin (Brummer and Godersky, 1999).

3. Rheology

Rheology is a tool widely applied in the food, petrochemical and pharmaceutical industries, but to the cosmetic industry it is incipient yet. Until now, the majority of cosmetic industries use viscometers to guarantee that the viscosity of different batches of a product is maintained.

This chapter was elaborated in order to show that many other rheological characteristics could be used to evaluate and to predict the stability of cosmetic products and could be applied to compare competing products in the market and to assay if a change in the composition will cause alterations that could be perceived by the consumer.

First, it is necessary to define the three parameters of most importance in rheology: shear stress, shear rate and viscosity. Shear stress can be defined as a force applied in an area. Shear rate is the ratio of the velocity of material to its distance from a stationary object (Naé, 1993). The shear rate can be calculated by the ratio between the velocity and the layer or film thickness. In a lipstick application, for example, with a velocity estimated in 5 cm/s and a layer thickness of 0.1 mm, the ratio (shear rate) is 5.10^2 s^{-1}. Finally, the viscosity can be defined as the resistance to flow. Thus, a viscous product presents smaller flow than others.

Concluding, rheology is the study of deformation and flow of materials under external forces. Some equations and the units of these parameters are (Naé, 1993):

$$\sigma = F / A \quad (1)$$

Where:

σ = shear stress (Pa = $kg.m^{-1}.s^{-2}$)

F = force (N or $kg.m.s^{-2}$)

A = area (m^2)

The viscosity can be defined as the ratio between shear stress and shear rate:

$$\eta = \sigma / \dot{\gamma} \quad (2)$$

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Where:

= viscosity

= shear stress (Pa)

$\dot{\gamma}$= shear rate (s^{-1})

Since the unit of shear stress is Pa and the unit of deformation is s^{-1}, the unit of viscosity is Pa.s. These parameters are involved in scientific measurements of rotational assays.

Using controlled shear rate and measuring shear stress is possible to carry out rotational assays, and determine flow curves and describe the models: Newtonian or non-Newtonian and, among the last one, plastic, pseudoplastic, dilatant, tixotropic and reopetic fluids. Newtonian fluids are materials that present constant viscosity, independent of time and temperature. These materials present flow curves with proportionality between shear stress and shear rate. The Figure 4 represents the flow curve of a Newtonian material.

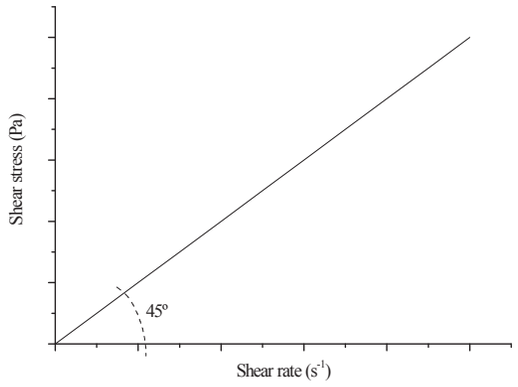

Figure 4. Flow curve of a Newtonian material.

In the case of non-Newtonians materials, this proportionality between shear stress and shear rate does not happen.

If in the beginning of the flow curve there is an increasing in the shear stress but the shear rate is equal to zero, and after to it is verified a Newtonian flow, this material is called plastic. This initial shear stress with shear rate equal to zero is called yield value and it represents the shear stress necessary for the material flow. The Figure 5 represents a plastic material. The yield value is related to the energy required to deform the material sufficiently so that they can flow. The value of the yield stress can be determined by measuring the deformation of the material as a function of the applied stress (Abdel-Rahem et al., 2005).

For non-Newtonian materials time-dependents, if the viscosity decreases with the shear rate, the material is called pseudoplastic and if the viscosity increases, the material is called dilatant. On the other hand, if the material is time-independent, it will be called tixotropic if the viscosity decreases with the shear rate or reopetic if the viscosity increases with the shear

rate (Naé, 1993). When the ascending and the descending curves of the flow curve do not overlap it shows thixotropy which is a desirable feature for cosmetics and semisolid drug carriers for topical application (Lippacher et al., 2004). The Figures 6, 7, 8 and 9 represent the flow curves of non-Newtonian materials (Naé, 1993).

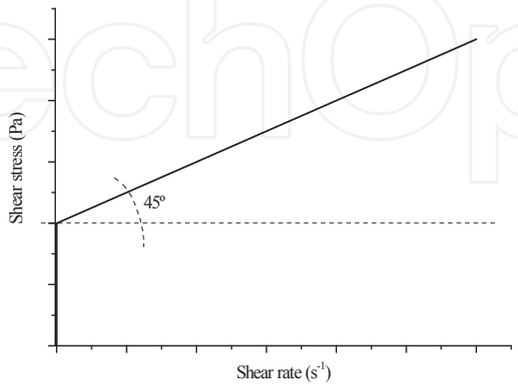

Figure 5. Flow curve of a plastic material.

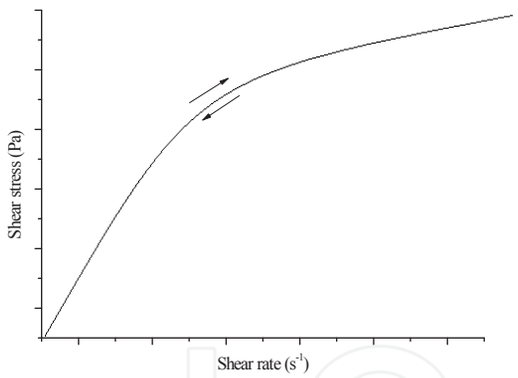

Figure 6. Flow curve of a pseudoplastic material.

For screening purposes and in the initial phases of the formulation development, the rheological tests proved to be very useful for the study of stability.

In a stability assay to determine the shelf life of a recently developed product, the formulation should be exposed to stress conditions, such as storage at -5 ºC, 45 ºC, and cycles of -5 ºC during 24 hours followed by exposure to 45 ºC during more 24 hours. This procedure is done in order to induce the appearance of instability signals in the formulations, where can be cited the darkening of the formulation, the precipitation of a constituent, the phase separation in the case of emulsions, and other signals. These stressing conditions are kept for a period around 2 or 3 months.

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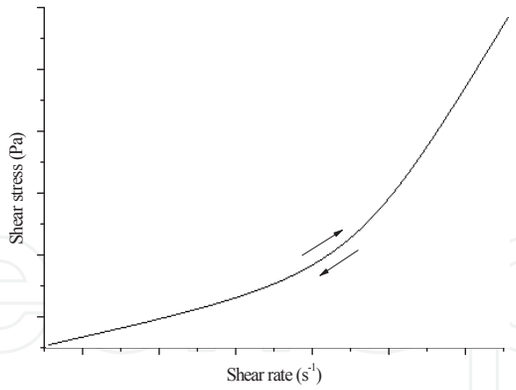

Figure 7. Flow curve of a dilatant material.

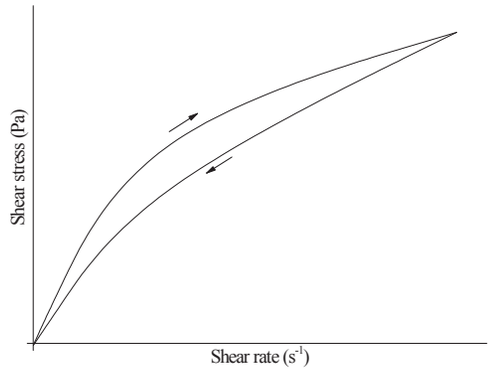

Figure 8. Flow curve of a thixotropic material.

Figure 9. Flow curve of a reopetic material.

It is usually measured the viscosity of the stressed formulations periodically during the stability assay. It could be done by means of a viscometer or by using a rheometer.

With a viscometer, it is possible to carry out rotational assays or measurements by steady-state flow. On the other hand, the rheometer allows the development of oscillatory assays or dynamic measurements (Biradar, 2009).

When using an oscillatory rheometer it is necessary to carry out a flow curve assay and determine the apparent viscosity of the formulation in a defined shear rate. It is recommended to use the higher shear rate in the ascendant curve of the flow curve, since in this point the sample is in a suitable condition, it means that the formulation is not starting to flow and is not excessively sheared (Figure 10).

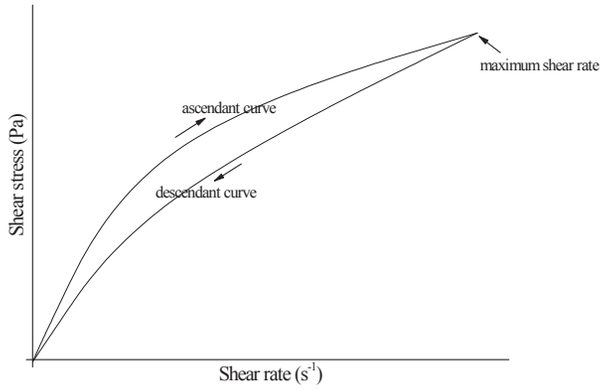

Figure 10. Example of a flow curve indicating the condition to the measurement of apparent viscosity.

In some papers, the flow curves have been plotted as viscosity as a function of shear stress instead of the traditional approach of plotting it versus shear rate because has been previously found that such curves are more discriminating and give better results for evaluation (Roberts, 2001; Samavati, 2011).

After obtaining, periodically, the minimum apparent viscosity of the samples exposed to stress conditions during a period, they should be compared with the initial value, and also compared the viscosity values of the control with the samples exposed to stress conditions, which allows the verification of the increase, decrease or maintenance of this attribute of the formulations.

Further exploiting the same assay, it is possible to calculate the hysteresis area of the formulation in each flow curve performed during the stability assay. The hysteresis loop areas can be obtained through a three-step experiment: upward curve, plateau, downward (Benchabane and Bekkour, 2008) and represents a way to measure, indirectly, the spreadability of the formulation, so it is possible to define if the formulation losses or gains easiness on spreadability during the shelf life. How much bigger is the hysteresis area, higher is the spreadability.

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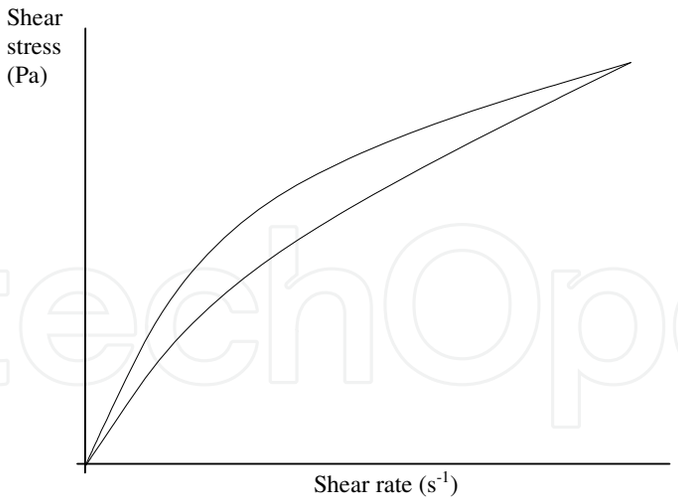

Figure 11. Flow curve with hysteresis area.

Using the flow curve is possible to compare two samples in relation to its hysteresis area and viscosity. A simple way to verify what formulation have a higher viscosity is by simple observation of the rheogram, since the curve that forms a bigger inclination in relation to the *x* axis of the graphic is the one with higher viscosity. On Figure 12 is showed an example of it, where sample 2 is more viscous than sample 1. It happens because the tangent of the angle formed is correspondent to the viscosity of the formulation in each shear rate.

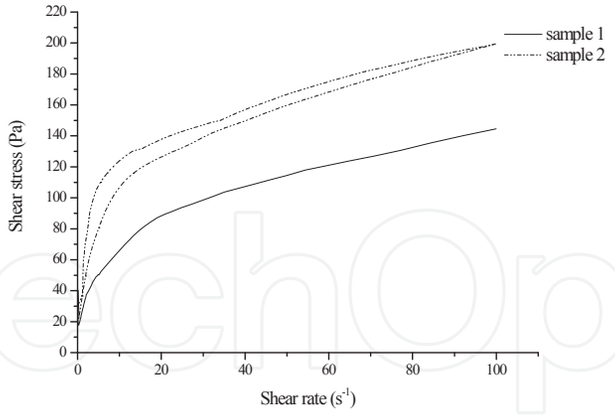

Figure 12. Comparison between flow curves of different samples (a thixotropic and a plastic fluid).

Beyond the different sensorial features caused by the differences in viscosity is known that the viscosity of emulsioned systems is one of the factors that retards or avoids the phase separation processes. The coalescence of dispersed phase can be due to the emulsifier agent and can be related to an instability because of low viscosity of dispersed phase (Corrêa & Isaac, 2012). This low viscosity can occur because of high shear stress (Samavati et al., 2011).

In general, for emulsioned systems, the continuos phase is shear thinning, which means that its viscosity decreases with the increasing on shear rate and viscoelastic, which means that it has viscous and elastic components (Tadros, 2004).

An example of the verification of differences in viscosity and thixotropy between two samples is shown on Figure 13.

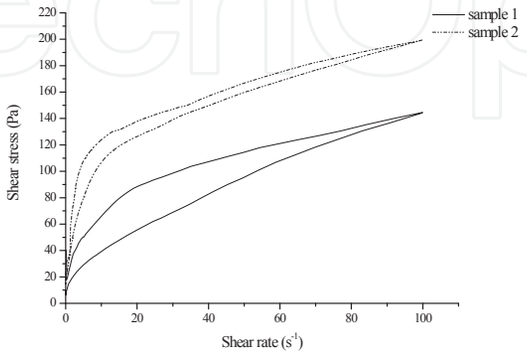

Figure 13. Comparison between flow curves of different samples.

Sample 1 is less viscous but more thixotropic than formulation 2. This simple verification gives to the analyst wide information, depending on what he needs.

Lescanne et al. (2004) studied organogels and aging properties of them. Organogels can be obtained by precipitation processes. These authors verified that, when aggregates are formed by the cooling rate, can be observed a elastic behavior, however, these aggregates can be aligned in the direction of the flow without lost the structure and when the flow is stopped, the aggregates are quickly rearranged and it inducing an thixotropic behavior. When the hot solution is introduced between the flat and the conical plates of the rheometer cell it is cooled to 5 ºC with a cooling rate of 20ºC/min, during the first hour of the gel life, it was measured the elastic properties of a gel as a function of time just after the cooling. Five minutes after its formation, the gel was submitted to a periodic stress (0.5 Pa) at a constant frequency (f = 1Hz). The authors showed that the shear moduli are constants and the aging phenomenon did not modify the elastic properties at least in a period of 1 h. However, when more than a week of aging is waited the samples lost most of its elastic properties.

The flow curve is a rotational assay, but using a rheometer it is possible to perform oscillatory assays too. Among the oscillatory assays are stress sweep and the frequency sweep assays.

The elastic (storage) modulus G' and the viscous (loss) modulus G'' are determined as a function of frequency or stress. The elastic modulus is a measure of energy stored and recovered per cycle of deformation and represents the solid-like component of a viscoelastic material. If a sample is elastic or highly structured then the elastic modulus will be high. The

viscous modulus is a measure of the energy lost per cycle and represents the liquid-like component. If a sample is viscous the viscous modulus will be high.

In the stress sweep analyses, the structure of the sample is progressively destroyed by applying oscillations with an increasing stress amplitude at a fixed frequency (Callens et al., 2003). The linear viscoelasticity region occurs over that region of strain where the complex modulus is independent of the strain (Hemar, 2000). The linear viscoelastic region is determined by the maximum stress which can be applied without affecting G' and G''. Furthermore, the relative magnitude of the moduli is a qualitative indication for the structure in the sample. Two different situations can occur: G' > G'' for a network consisting of secondary bonds and G'≤ G'' for a physically entangled polymer solution (Callens et al., 2003).

Frequency sweep tests are performed in the linear viscoelastic region of each sample, keeping the structure of the system intact during the measurement. By performing such small stress amplitude oscillations at a whole range of frequencies, the type of network structure can be revealed. The main difference between a network of secondary bonds and one of physical entanglements is located in the low frequency range: in an entangled network the polymers can disentangle if the available time is long enough (low frequency). In a network with secondary bonds the bonds are fixed irrespective of the time scale. This results for an entangled solution in a limiting slope of 2 for G' and 1 for G'' at low frequency in a log-log plot of moduli versus frequency, while at intermediate frequency a plateau develops. For a network of secondary bonds an almost constant value of G' and G'' is observed over the whole frequency range, with the value of G' exceeding that of G''(Callens et al., 2003; Madsen et al., 1998).

The stress sweep is important to evaluate the linear viscoelastic region of a sample that is a range of shear stress in which the formulation does not suffer profound alterations on it structure, being not disrupted. When a shear stress of the linear viscoelastic region is applied in an oscillatory assay, only the intermolecular and interparticle forces are being evaluated (Martin, 1993). To determine the linear viscoelastic region, the oscillating stress sweeps are carried out for the most extreme values. These measurements are used to determine where the reological properties are independent of the applied stress and the identify the critical rheological properties (Tuarez, 2011).

Knowing the values of shear stress that do not cause the disrupt in the formulation by means of the stress sweep, the analyst could perform a frequency sweep of the formulation. The frequency sweep is carried out in a constant shear stress found in the linear viscoelastic region. With this assay it is possible to evaluate the elastic or storage modulus (G') and the viscous or loss modulus (G''). The cosmetic excipients most used, emulsions and gels, are often viscoelastic samples. The viscoelastic samples when evaluated by means of the frequency sweep present G' and G'' values. When the G' value is higher than G'' it is an indicative that the formulation is more elastic than viscous. It is a characteristic of gels.

Emulsions which exhibits G' values higher than G'' (Figure 14) are described as more stable than formulations with G'' values higher than G' (Figure 15), since they tends to recovery its initial structure faster and more efficiently than the others, and are less susceptible to the

gravitational forces which retards or avoids the coalescence process and the phase separation of emulsions (Alam and Aramaki, 2009). So, the G' values higher than G'' in emulsions is a desirable feature, being an indicative of stability of the cosmetic system.

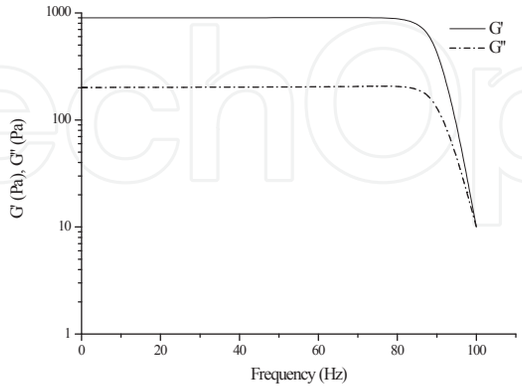

Figure 14. A frequency sweep example (G'>G'').

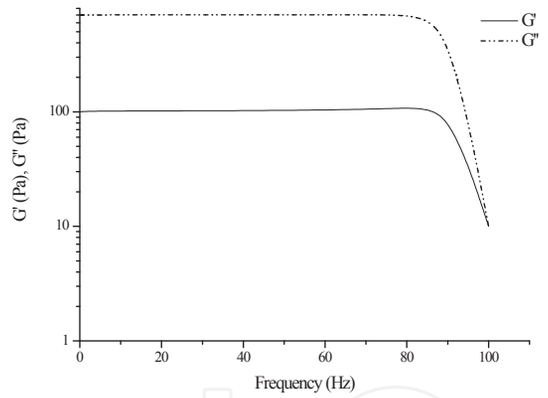

Figure 15. A frequency sweep example (G''>G').

Another assay that could be conducted using an oscillatory rheometer is the creep and recovery assay. It is done by submitting the samples to a constant shear stress during a period, and after, removing this shear stress and monitoring the formulation in relation to the deformation (measured by the compliance - J) during the same period. The compliance parameter is the resulting strain divided by the applied stress (Koop, 2009; Toro-Vazquez et al., 2010). If the compliance parameter is the relationship between strain and the applied stress, the strain is dimensionless and stress is measured in Pa, then, the compliance can be measured in 1/Pa.

In the example showed on the Figure 16 the samples were submitted to a shear stress during 300 seconds, and after removing this shear stress it was monitored during more 300 seconds.

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Analyzing the result obtained in the first 300 seconds is verified that sample 1 exhibited lower compliance values than sample 2, which represents a higher difficult on being deformed than sample 1. The difficult on being deformed is always linked to higher viscosity values.

In the second part of the assay, where the shear stress imposed to the sample is removed, represented in the graphic by the time 301 to 600 seconds, is verified the viscoelastic properties of the samples. Formulations that are able to recovery its initial structure or part of it exhibit a gradually decrease in the compliance values. On Figure 17 there is an example of a formulation that is not a viscoelastic sample, it means that it do not exhibits storage modulus, and is not able to recovery its structure when the shear stress is ceased.

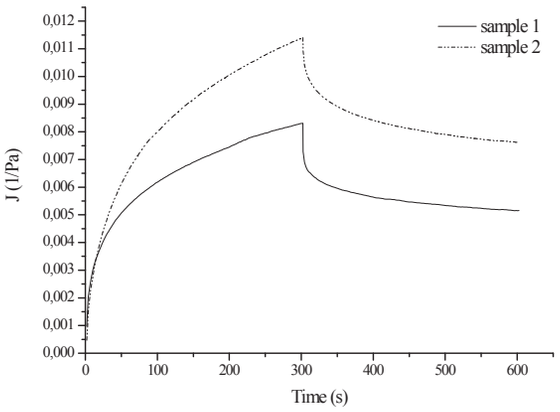

Figure 16. A creep and recovery example of viscoelastic samples.

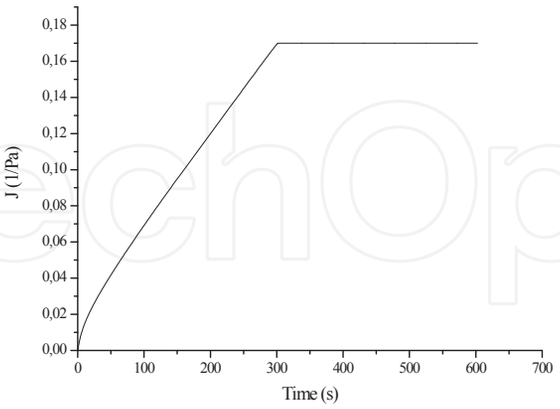

Figure 17. A creep and recovery example of a non-viscoelastic sample.

In addition, the rheology can be used to evaluate the stability over the time by dynamic and oscillatory rheological measurements (Pénzes et al., 2004; Vasiljevic et al., 2006) and the release of active principles. According to Martinez et al. (2007), the transdermal absorption of

topically administered drugs depends on the rate of release and the permeability of them into the skin and also of the viscosity of the formulation (Martinez et al., 2007).

Thus, it is possible to say that different categories of products should present peculiar rheological properties inherent to its application (Gregolin et al., 2010).

In this way, the rheology can influence the diffusion coefficient, altering the release and permeation of cosmetics active substances (Welin-Berger et al., 2001; A-sadutjarit et al., 2005; Vasiljevic et al., 2006). Some authors have related the influence of rheological characteristics on the release profiles and consequently in the permeation of active substances in the skin; thus, the addition of thickening agents or attainment of a weak-gel because of physical entanglement of polymer chains must be considered in the choice of cosmetics bases (Spiclin, et al., 2003). Thus, rheology can help in the assay of release and permeation in the skin. Some studies have been published about it.

So, in a short way, the rheology is a valuable tool that helps in the quality control of cosmetics, being used in the stability tests, in the comparison between competing samples, in the comparison between an original product and a product with an alteration in a constituent, and in the development of new products, aiming to develop cosmetic with rheological characteristics which indicate stability.

4. Small Angle X-ray Scattering (SAXS)

The use of this technique in determining the quality control of a cosmetic is closely related to the stability of the product, which could be improved with the presence of liquid crystals.

Liquid crystals are described as a state of matter between solids and liquids, it means that, they are fluid like liquids but are organized like solids, being called mesophases (Marsh, 1973; Kelker and Hatz, 1980; Müller-Goymann, 2004). These organization contributes to the highly stability of systems.

The formation of liquid crystals in emulsions could be induced by some components present in this system, such as surfactants (Müller-Goymann, 2004). So, what happens is that it is possible to find a peculiar system that is not a simple emulsion and not a genuine liquid crystal, but an emulsioned system that contains liquid crystals, commonly lamellar structures, that are formed around of the inner phase of the emulsion (Oka et al., 2008), making difficult the coalescence, flocculation and the separation of the oily and water phases, what makes the system formed more stable than a simple emulsion (Figures 18 and 19). Flocculation is defined as the formation of aggregates of droplets of an emulsion under the influence of interparticle colloidal forces which are net attractive (Dickinson, 1992) and the formation of lamellar structures avoid or prevent the occurrence of this phenomenon. The formation of lamellar structures is essential to obtain emulsified oil/water systems finely dispersed, with balanced hydrophilic-lipophilic properties, resulting in minimal interfacial tension between aqueous and oily phases, thus contributing to the stability of the system (Engels et al., 1995). Previous studies have also shown that it is possible to make correlation between SAXS and

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rheological analysis, since were verified that the thicker the interlamellar water layers, the higher the viscosity of the cream (Eccleston et al., 2000). Thus, liquid crystals could be responsible by the emulsion stabilization and by the increasing in the viscosity (Klein, 2002), being the presence of this structures desirable in cosmetic emulsions which could be an indicative of quality of them.

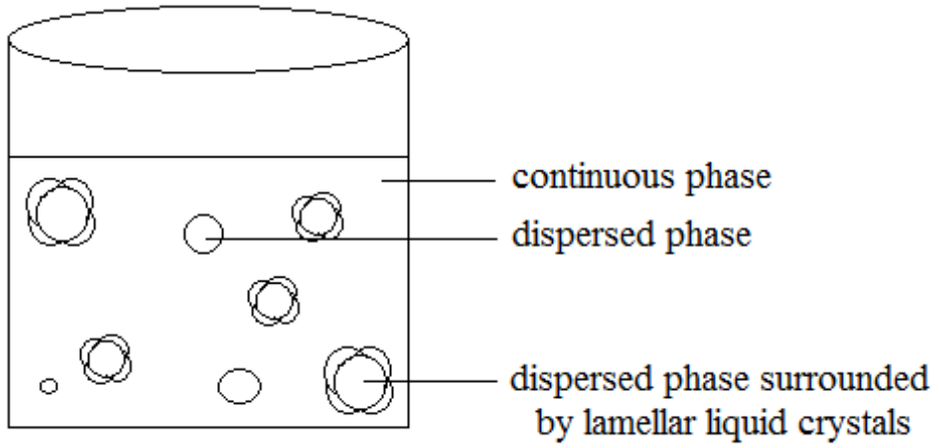

Figure 18. Scheme of a cosmetic emulsion containing liquid crystals.

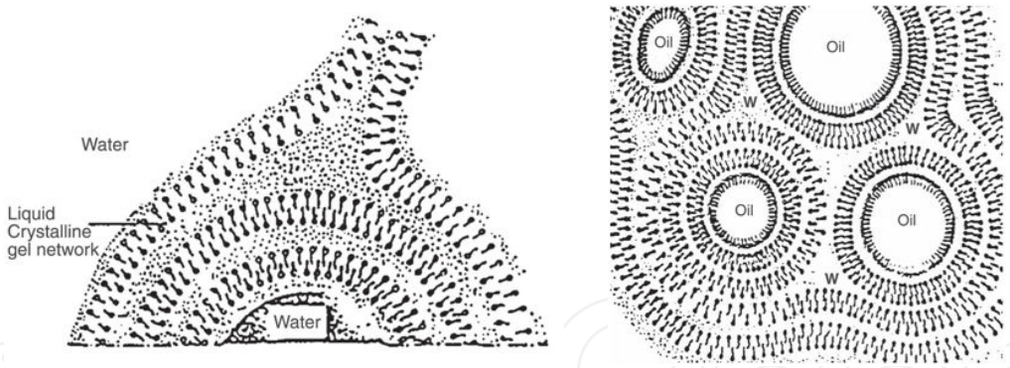

Figure 19. Schemes of the microscopic visualization of lamellar gel networks surrounding emulsion droplets proposed by Klein (2002).

This kind of structure is more commonly found in cosmetics due to the high diversity of components used in it in order to obtain a moisturizer, emollient, humectant, good sensory and, above all, stable cosmetic. In other pharmaceutical forms, usually are used a less diversified composition, which gives a system easier to understand, described as emulsion or liquid crystal, or even, a gel, a suspension, etc. The quantity of these lamellar structures, found in cosmetic emulsions, probably is dependent of three main factors: the raw-materials, the amount of it used and the process of preparation, where should be cited, the temperature and the speed of agitation.

In cosmetics, other kinds of systems could be used, such as genuine liquid crystals aiming to explore its characteristics of controlled delivery systems.

There are different kinds of liquid crystals and different classifications, but this chapter has not the function of describe them, since it have been done by many authors (Bechtold, 2005; Formariz et al., 2005; Atkins and Jones, 2006), the aim was to demonstrate the importance of these structures in the maintenance of the cosmetics' quality. Nevertheless, according to the literature data (Klein, 2002) and to our experience in this subject, it is possible to say that the lamellar arrangement is the most commonly found in cosmetic emulsions.

An initial analysis of the presence of liquid crystals in a cosmetic emulsion could be done using a polarized light microscope, but it should be confirmed and better analyzed by means of Small Angle X-Ray Scattering. When a microscope slide containing a sample of the system is studied and it presents structures that reflect the incident light, it is an evidence of the presence of liquid crystals (Figure 20). So, they should be submitted to SAXS analysis to confirm this expectation (Savic et al., 2011).

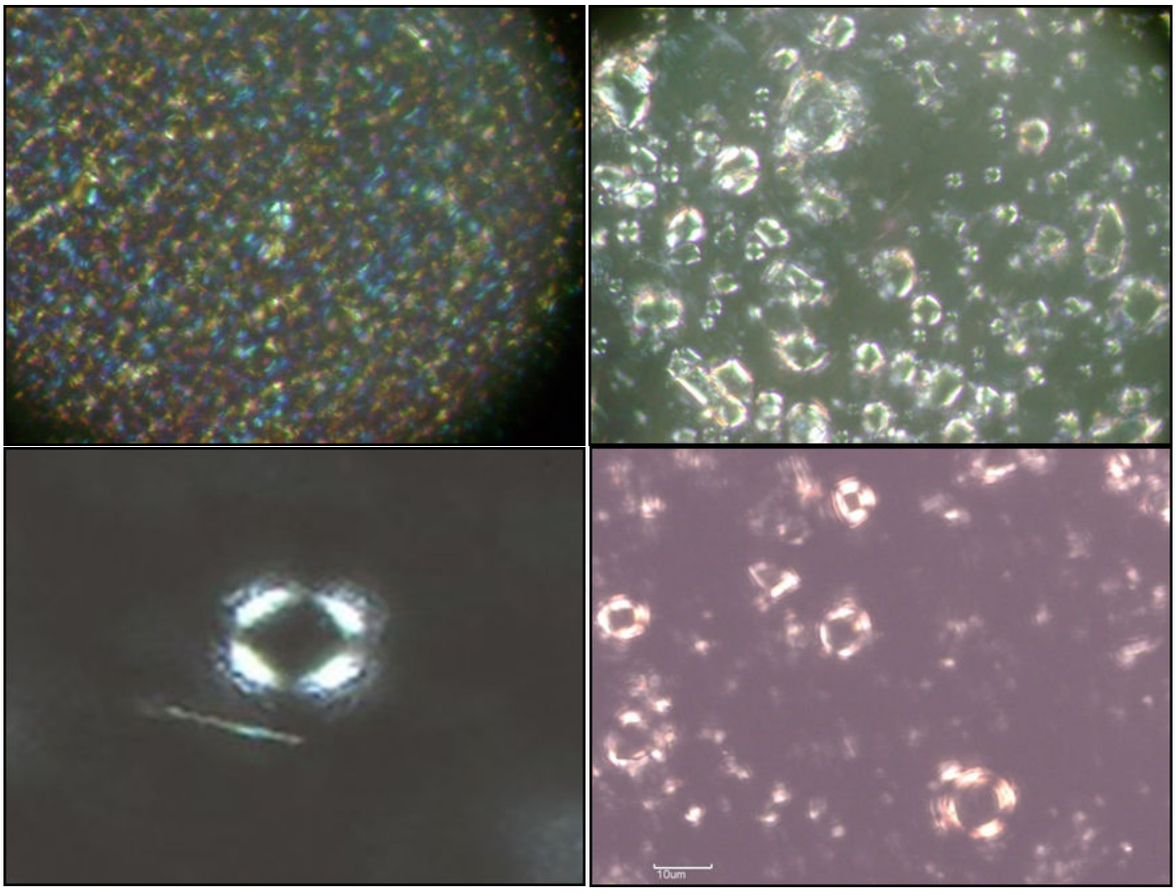

Figure 20. Photomicrographs of liquid-crystal present in emulsions evaluated by polarized light microscope.

The SAXS method requires a synchrotron light source that is formed by means of a particle accelerator, and using a monochromatic beam, that is used to irradiate the sample. After

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that, the scattering of the rays in small angle should be analyzed (Glatter and Kratky, 1982; Urban, 2004; Koch, 2010). Liquid crystals can be analyzed by SAXS since they are able to disperse the X-rays focused on it. In the SAXS line is used an X-rays detector and an multichannel analyzer to capture the intense of the SAXS measures ($I(q)$) in function of the modulus of the scattering vector (q) (Glatter and Kratky, 1982; Molina et al., 2006; Koch, 2010).

Analyzing the data obtained (Figure 19), the d value obtained represents the distance between the particles able to scatter the X-rays. It is calculated by the equation: $d = 2\pi / q\ max$, where $q\ max$, is the maximum intensity of scattering (Craievich, 2002). The relation between the d values obtained indicates the type of arrangement found in the system (Glatter and Kratky, 1982; Craievich, 2002; Alexandridis et al., 1998).

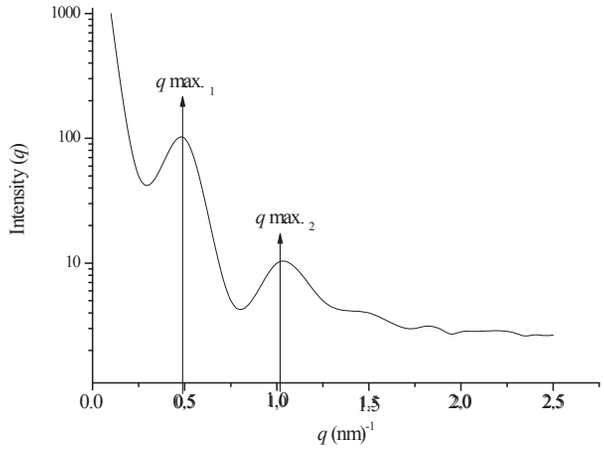

Figure 21. Hypothetical SAXS curve.

In the case of the hypothetical curve showed in Figure 19, d_1 / d_2 would result in 2, which describe lamellar structures (Alexandridis et al., 1998).

Beyond the advantages already mentioned, in a research conducted by Moaddel and Friberg (1995), the authors showed that the presence of lamellar liquid crystals in an emulsion avoids the water evaporation rate in this system, thus contributing in another way to the stability and maintenance of the cosmetic quality.

According to the advantages obtained with the presence of liquid crystals, these mesophases can be of great importance to the Cosmetic Industry in the development of very stable cosmetics and, the SAXS technique, an efficient tool to confirm the presence of these desirable structures that helps in the maintenance of cosmetics' quality control.

Camerel et al. (2003) pointed the importance in correlate the microstructure of a colloidal suspension with its rheological behavior to define its better use in industry and in life, beyond that, according to these authors there are few reports correlating these analyses.

Our research group has invested in researches to assess the stability of cosmetics (Isaac et al., 2008); evaluating of the influence of the addition of thickening agents in creams using rheological measurements (Isaac et al., 2012a); evaluating the thickeners' influence on the rheological properties of a cosmetic (Isaac et al., 2012b,c); proposing alternative methods to assay the efficacy and safety of them (Chiari et al., 2012a; Chiari et al., 2012b) and using of the sensory analysis in the cosmetics development (Isaac et al., 2012a) which, in different points of view of what was demonstrated in this chapter, also influence in the product quality.

5. Conclusion

This chapter aimed to show the facility that some simple or advanced techniques already used, sometimes to other finalities, could offer to the quality control of cosmetic products. The sensory analysis, rheology and SAXS technique have earned attention due to the important contribution that they can offer to the cosmetic area.

Author details

Bruna Galdorfini Chiari, Maria Gabriela José de Almeida, Marcos Antonio Corrêa and Vera Lucia Borges Isaac*

*Address all correspondence to: veraisaac@fcfar.unesp.br

Faculdade de Ciências Farmacêuticas, UNESP - Univ Estadual Paulista, Departamento de Fármacos e Medicamentos, Laboratório de Cosmetologia – LaCos, Araraquara, Laboratório de Cosmetologia, São Paulo, Brazil

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