

Handbook of Formulating Dermal Applications

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Handbook of Formulating Dermal Applications

A Definitive Practical Guide

Edited by
Nava Dayan



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SECTION II:

Formulation, Processing and Production Techniques

CHAPTER 6

Emulsions and their Characterization by Texture Profile Analysis

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Key Words

Emulsion, Sensorial Analysis, Textural Attributes, Texture Profile Analysis.

Introduction

Emulsions are the underlying basis of personal care formulations for skin. They are seemingly simple, yet complex systems, which allow the skin care chemist to combine otherwise immiscible ingredients into effective, commercially desirable skin care products.¹ Emulsions are very versatile vehicles that can incorporate a variety of ingredients and allow simultaneously delivery of hydrophilic and hydrophobic ingredients to the skin. This gives the advantage of developing custom-made formulations designed for various skin types or addressing many skin disorders or conditions. Over the last several decades significant advances in the understanding of emulsion behavior were accompanied by the availability of many new products, especially emulsification agents. Coupled with consumer demand for biologically functional actives, this trend persists. The success of a product often depends on its sensorial attributes, in which case the consumer is the best candidate to judge. Many of these sensorial perceptions stem from the textural properties of the formulation. Carrying out consumer tests is oftentimes expensive and time consuming. With this in mind, there is much interest to establish instrumental techniques to objectively quantify textural attributes of formulations, which may serve as rapid screening protocols allowing formulators to fine tune particular attributes into the final product. In this chapter, methodology is presented to perform such tests to characterize *firmness, compressibility, integrity of shape, tackiness, spreadability, cohesiveness, resilience, and elastic resistance to deformation.*

Basic Principles of Emulsion Technology

Emulsions

The majority of skin care formulations are complex multi-phase systems based on solid-liquid dispersions (suspensions) or liquid-liquid dispersions (emulsions).² Emulsion systems are used universally in skin care formulations to create creams and lotions for application to skin. An emulsion is a heterogeneous system in which two or more immiscible liquids or semi-solid materials are dispersed in another liquid in discrete droplets. The materials that are dispersed (or emulsified) form the dispersed or internal phase, while the rest of materials form the continuous phase or external phase. There are a variety of emulsion types that consist of oil-in-water (o/w), water-in-oil (w/o), multiple (oil-in-water-in-oil; water-in-oil-in-water), nano-, micro-, and Pickering emulsions (a type of oil-in-water emulsion). O/W emulsions are probably the most commonly employed vehicles in skin care formulations, which contain an oil phase dispersed in an aqueous continuous medium (**Figure 1**). These types of emulsions tend to feel less greasy because the water is the external phase (Epstein, 2006).¹ W/O emulsions, on the other hand, feel greasy due to the fact that the oil phase is the external phase. A schematic representation of a dispersed droplet in a w/o emulsion is shown in **Figure 2**. Generally, the type of emulsifier and the phase volume ratio dictate what type of emulsion will be formed.³ In terms of physical properties, the o/w and w/o emulsions, also known as macroemulsions, have particle sizes greater than 1,000 nm and appear opaque/white in color.

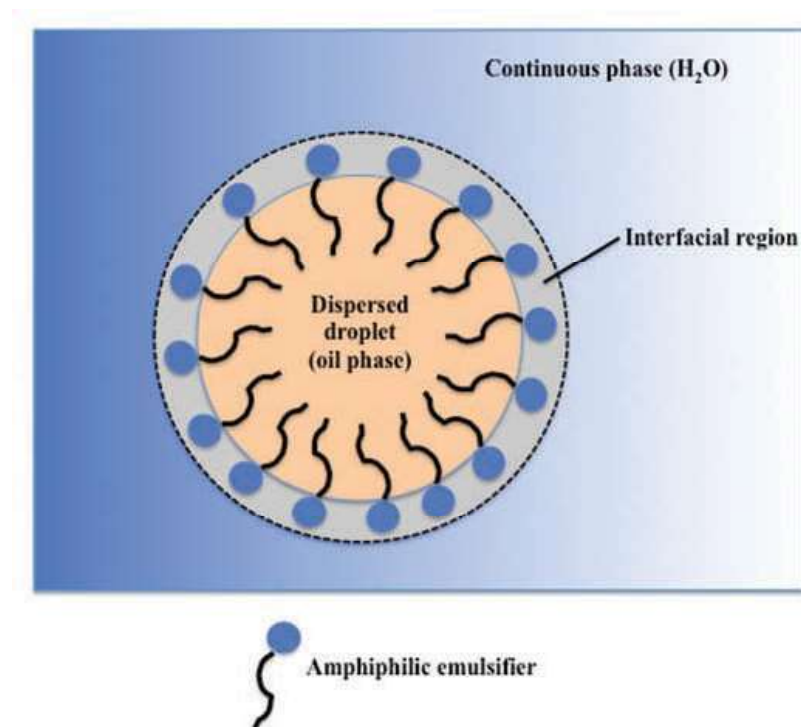


Figure 1. Illustration of a dispersed oil droplet in a typical o/w emulsion stabilized with an emulsifier.

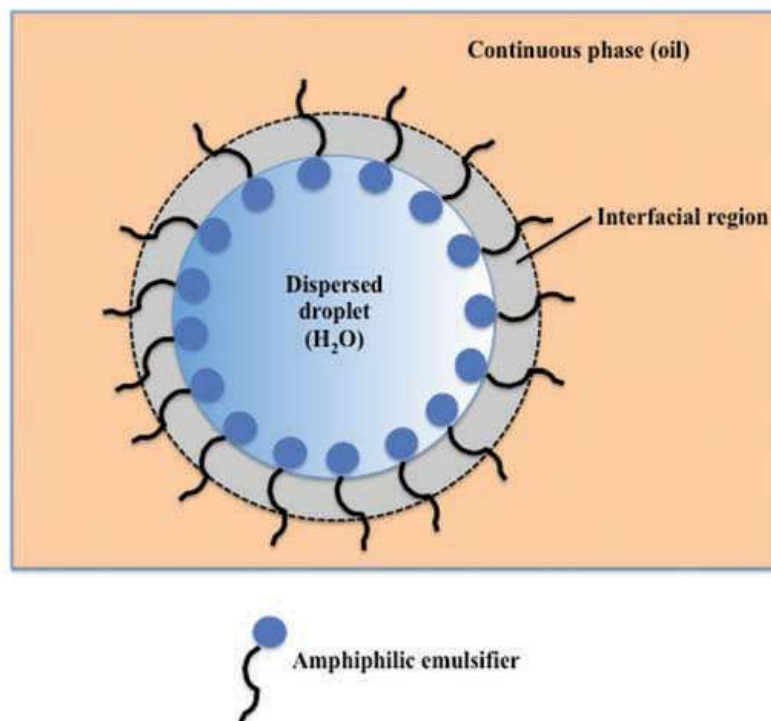


Figure 2. Illustration of a dispersed water droplet in a typical w/o emulsion stabilized with an emulsifier.

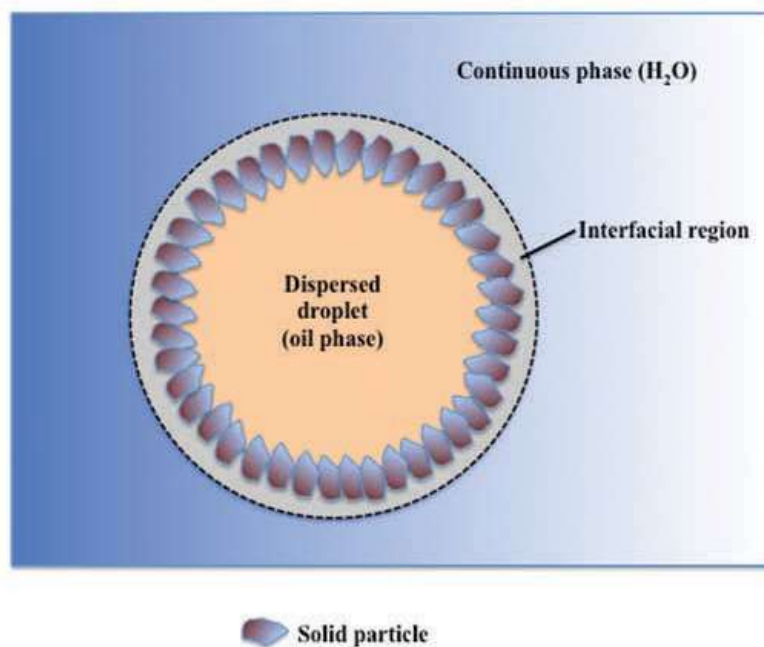


Figure 3. Example of a Pickering emulsion, a type of o/w emulsion, stabilized with solid particles at the interface of the oil and water phase.

The use of the terms “nanoemulsion” and “microemulsion” has created a lot of confusion in the literature. Nanoemulsions usually refer to a size range of 50–200 nm, while microemulsions are clear or transparent emulsions with a particle size between 5–50 nm.² O/W and w/o macroemulsions are thermodynamically unstable. In order to circumvent such instability, microemulsions evolved as alternative vehicles. In contrast, nanoemulsions are not thermodynamically stable.⁴ Pickering emulsions are another type of o/w emulsion system in which stability is conferred by solid particles present at the interface of the two phases, thereby reducing the surface energy (**Figure 3**). Multiphase o/w emulsions constitute a special type of emulsion in which lamellar gel phases form a complex network in the continuous water phase to hold the oil phase droplets in place preventing coalescence, as well as enhancing the viscosity and stability of the system.^{5,6}

Emulsion formation

Most emulsions are formed by dispersion or condensation methods. Dispersion techniques usually refer to mechanical agitation (e.g., with a homogenizer) resulting in the formation of a coarse dispersion, which is then further sheared producing a finer dispersion. During the course of such a process, emulsifiers are added to stabilize the increasingly unstable system (higher surface energy) due to the creation of a much larger interface. Condensation methods rely on the dissolution of the discontinuous phase molecules in the continuous phase. As an example, an o/w emulsion is formed by pouring the oil phase into the water phase with proper mixing or homogenization. There are also phase inversion (e.g., PIT emulsions) and electrical techniques to form emulsions. Phase inversion occurs when the concentration of the dispersed phase becomes so high that it inverts and the continuous phase becomes the dispersed phase and vice-versa. Electrical techniques refer to emulsions formed by the basis of electrostatic interactions.

Emulsifiers

An emulsifier (or emulsifying agent) is an amphipathic molecule, which arranges itself at the interfaces between the two immiscible phases (o/w), thus reducing the surface (interfacial) tension between the two phases, and is able to disperse oil droplets in water. When used with o/w emulsions, they arrange themselves with the hydrophobic tails in the oil (internal) phase and hydrophilic heads in the water (external) phase. The mechanism of action of emulsifiers and many other details will be discussed more in-depth later in this chapter.

Typical emulsion compositions

As an illustrative case, the oil phase of an o/w emulsion contains various chemical classes of organic ingredients such as: emollients and occlusive agents (e.g., esters, mineral oil, vegetable oils, waxes, and silicones); emulsifiers (anionic, nonionic, and cationic); and consistency agents/thickeners (e.g., fatty alcohols). The water phase of an o/w emulsion, on the other hand, typically contains: water as the solvent; humectants (e.g., glycerin, propylene glycol, and butylene glycol); chelating agents (Na₂EDTA); and thickeners (cellulose derivatives and gums, as well as carboxyvinyl polymers). Other ingredients normally found in an o/w emulsion are: preservatives,

pH adjusters, colorants, fragrances, botanicals, biofunctional ingredients, and antioxidants. **Table 1** contains a typical o/w emulsion composition.

Table 1. A typical o/w emulsion composition.

1.	Emulsifier systems ~ 3-5%
2.	Hydrophobic thickeners/consistency agents/stabilizers ~ 0.50-2%
3.	Oil phase ~ 10-35%
4.	Hydrophilic thickening agent ~ 0.1- 1%
5.	Humectants ~ 3-5%
6.	Preservatives, antioxidants, botanicals ~ as required
7.	Water (qs to 100%)

Phenomena Involved in Emulsion Instability

Emulsion stability is a major concern for the formulator. Without a properly designed system, some of the phenomena listed below may occur. Since macroemulsions are inherently unstable, such effects may be produced when an improper (or inadequate amount of) emulsifier or a rheology modifier/consistency agent is used. Such outcomes may also result due to excessive amounts of the dispersed phase employed in the formulation. In any event, brief definitions are provided for some of the most common phenomena that occur during emulsion instability. **Figure 4** contains an illustration to accompany this section.

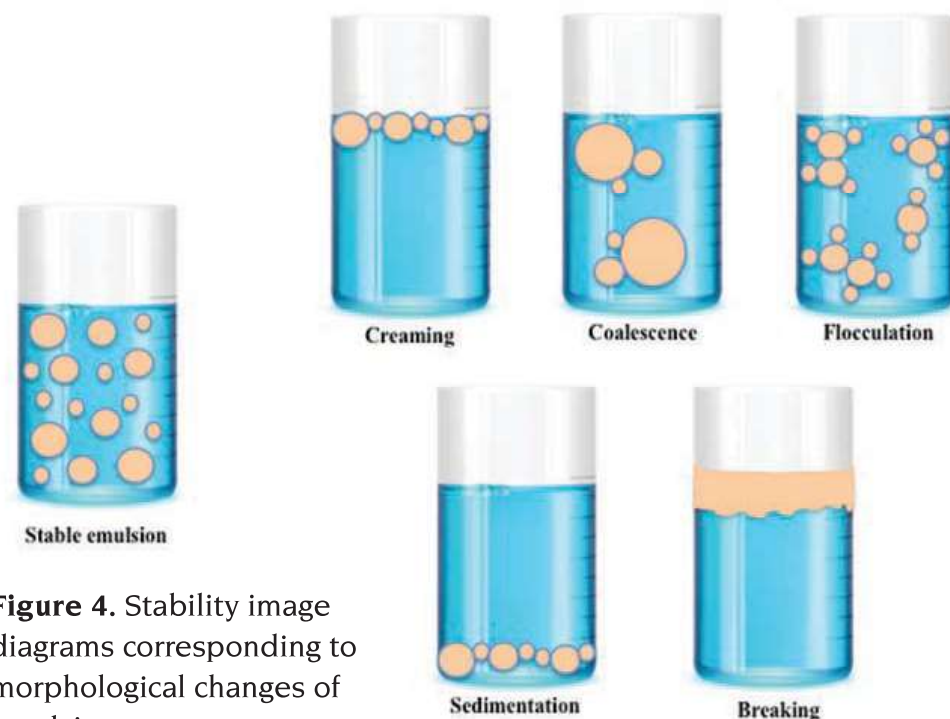


Figure 4. Stability image diagrams corresponding to morphological changes of emulsions.

Creaming: Oftentimes emulsion droplets cluster together in a process known as flocculation. This phenomenon refers to the case when particles cluster together without actually merging.⁷ This is very common in o/w emulsions as the dispersed oil phase flocculates, and then rises to the surface, a process known as creaming.

Sedimentation: Emulsion droplets may also settle to the bottom of the vessel in a process known as sedimentation. Such instability, in some cases, may be reversible by mechanical agitation or shaking.

Flocculation/aggregation: As already stated, flocculation occurs when particles (droplets) aggregate together without merging together; they clump together. In this case, flocculated particles retain their individual characteristics and may be re-dispersed by agitation (or shaking).

Coalescence: In contrast to flocculation, coalescence is the actual merging together of droplets forming a new entity. Droplets lose their distinctness and may not be easily re-dispersed in the continuous phase.

Breaking: An emulsion is said to break when the dispersed phase settles out of the continuous phase. Normally, this occurs first by flocculation (clumping of droplets together) followed by coalescence (actual merging of droplets).

Inversion: Inversion occurs in an emulsion when the dispersed phase becomes the continuous phase and vice versa.

Improving stability of emulsions

To prevent creaming, sedimentation, and aggregation in emulsions, several strategies may be employed. A first measure would be to reduce the particle size of the internal phase by homogenization. In this way, one obtains a more uniform particle size distribution, ultimately leading to an increase in viscosity. Further, the addition of thickeners (natural gums or synthetic acrylic acid polymers) to the external phase will increase the viscosity of the continuous phase and enhance the high temperature stability.⁸ Emulsion stability is also conferred by the addition of emulsifiers. Typically, nonionic emulsifiers provide steric stabilization, while ionic emulsifiers provide electrostatic or charge stabilization. In any event, emulsifiers prevent dispersed phase droplets from coalescing.

Mechanisms of Emulsion Stabilization by Emulsifiers

Normally, creaming, sedimentation, and aggregation are prevented by employing emulsifiers with specific stabilizing properties. For example, nonionic and polymeric emulsifiers are used to provide steric stabilization, while ionic emulsifiers are employed to provide repulsive electrostatic interactions, which keep emulsion droplets apart. In addition, coalescence may be prevented by adding amphiphilic surfactants that form lamellar gel phases (multiphase systems) or other agents that improve emulsion stability or increase consistency of the dispersed and continuous phase.

Electrostatic/charge stabilization (repulsive electrostatic forces)

Ionic emulsifiers, both anionic and cationic, stabilize emulsions by formation of an electrical double layer on the surface of the droplet, creating a repulsive electrostatic

barrier to keep droplets apart. Fatty acid salts (soaps) are typical examples of anionic emulsifiers that provide electrostatic charge stabilization.

Steric stabilization

An emulsion may also be stabilized by the presence of molecular entities on the surface of the dispersed phase droplet; in many cases, a nonionic or polymeric emulsifier is employed. Portions of the molecular structure of the emulsifier branch out into the continuous phase and impede droplets from coalescing together. Block copolymers and polyethylene glycols are especially useful for such applications, as one segment of the molecule will be in contact with the dispersed phase droplet and the other will extend into the continuous phase. In particular, one example of a block copolymer is a polymeric surfactant that contains a hydrophobically modified segment.⁹ To reiterate, the portion of the molecule in the continuous phase provides steric hindrance to interaction of other oil droplets in the case of an o/w emulsion.

Stabilization by lamellar gel phases

The formation of lamellar gel phases can stabilize an emulsion by forming a third phase or third layer (a rigid film about 1 μm thick) between the oil and water phases. These lamellar gel systems form a network of bilayers, which surround the oil interface, and extend into the continuous phase, forming a third phase between oil and water, thus preventing coalescence (oil droplets are less likely to rise and collide with each other) and stabilizing the emulsion (the lamellar network increases the viscosity of the water phase). While such vehicles can be classified as three-phase systems (e.g., oil-in-lamellar gel-in-water), they contain two interfaces, one shared by the oil-lamellar gel and the other, lamellar gel-water.^{6,10} An example of such a system consists of a commercial product based on a customized blend of glyceryl stearate, behenyl alcohol, palmitic acid, stearic acid, lecithin, lauryl alcohol, myristyl alcohol, and cetyl alcohol.¹¹

Measurement of Emulsion Stability

A number of general techniques are available to monitor emulsion stability. In this section we cover some of the most fundamental methods that can be carried out in most laboratories. More advanced techniques to study phenomena associated with emulsion technology are available; however, for the sake of brevity these methods are not discussed herein.

Formulation pH measurements

General pH measurements should be carried out utilizing a probe designed for more viscous systems, such as creams and lotions. The pH of the system is of utmost importance, as this will determine the electrostatic conditions of the head group of any of the added emulsifiers, as well as polymeric thickeners in the continuous phase of an o/w emulsion. Increasing or decreasing the charge will affect the interactions between the dispersed phased droplets. Oftentimes, the emulsion is stabilized by opposing electrostatic forces that keep droplets from coalescing together. If the head group of an emulsifier is pH sensitive, it could convert from a negatively to a

positively charged species when the pH is lowered below its pKa. This could result in agglomeration of the dispersed phased droplets, eventually leading to instability in the emulsion.

Rheological techniques

Rheological measurements provide extremely important physical and aesthetic information about emulsions. Formulation and processing parameters of emulsions influence a number of its characteristics, including dispersed phase volume, size distribution, particle-particle interactions, and particle deformability.¹² Traditionally, standard viscometers capable of measuring the linear viscoelastic shear properties were used routinely to characterize the viscoelastic properties of emulsions. In recent years, this has changed (to some extent) due to the availability of more sophisticated dynamic instruments, which allow for measurement of important rheological parameters such as the storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$).

Optical microscopy

The visualization of emulsions is a straightforward process that can provide extremely useful information to characterize the nature of the dispersed phase droplets, including their shape, size, and interaction with each other. If bright field microscopy is employed, colorful lipid-soluble dyes can be added to the emulsion in order to provide a striking image with clear contrast between the dispersed and stationary phase. Fluorescence microscopy may also be employed in conjunction with a fluorescent probe; however, this requires a more technically specialized fluorescence microscope.

Liquid conductivity measurements

Emulsions are commonly characterized by electrical conductivity measurements. Emulsion electrical resistivity can provide important information with regard to emulsion stability with temperature, ion concentration, and emulsifiers or other surfactants employed in the formulation. Its most practical use is to determine the amount of oil present in an emulsion. The measurement determines the electrical conductivity of water, which decreases as the oil phase increases.

Size distribution

One of the most popular instruments for measuring emulsion size is a Coulter Counter. It is an extremely common method that is used universally in the pharmaceutical and medical industries to measure the particle size of ingested or injected emulsions used for treatment protocols or diagnostic exams. The Coulter Principle (electrical sensing zone method) uses the proportionality between the volume of a particle and the height of the electric pulse generated from passage of the particle through a small aperture to directly count it and measure its size. The measurement is not affected by color, shape, and optical characteristics of particles.¹³

Zeta potential

Zeta potential is a measure of the repulsive/attractive electrostatic forces between particles, and is a very good indicator of emulsion stability.^{14,15} Its measurement

can shed light on the causes of instability whether it be flocculation/aggregation, coalescence, breaking, or inversion. In most cases, emulsion droplets normally bear an electrical charge at their surface. In addition, the outer surface of the emulsion is surrounded by a cloud of ions (from the continuous phase liquid) consisting of both negative and positive charges (**Figure 5**). The zeta potential is the voltage difference between the surface charge of the droplet and the collective charge of the ion cloud from the surrounding continuous phase. Zeta potential measurements are especially useful for charge stabilized emulsions and can provide us with a measure of the electrical repulsive force between dispersed droplets. Even in sterically stabilized emulsions, knowledge of zeta potential can provide us with information related to the state of the droplet surface. Overall, increased emulsion stability is normally associated with larger (either more negative or positive) zeta potential values, which indicates that the repulsive forces are great enough to keep particles apart.

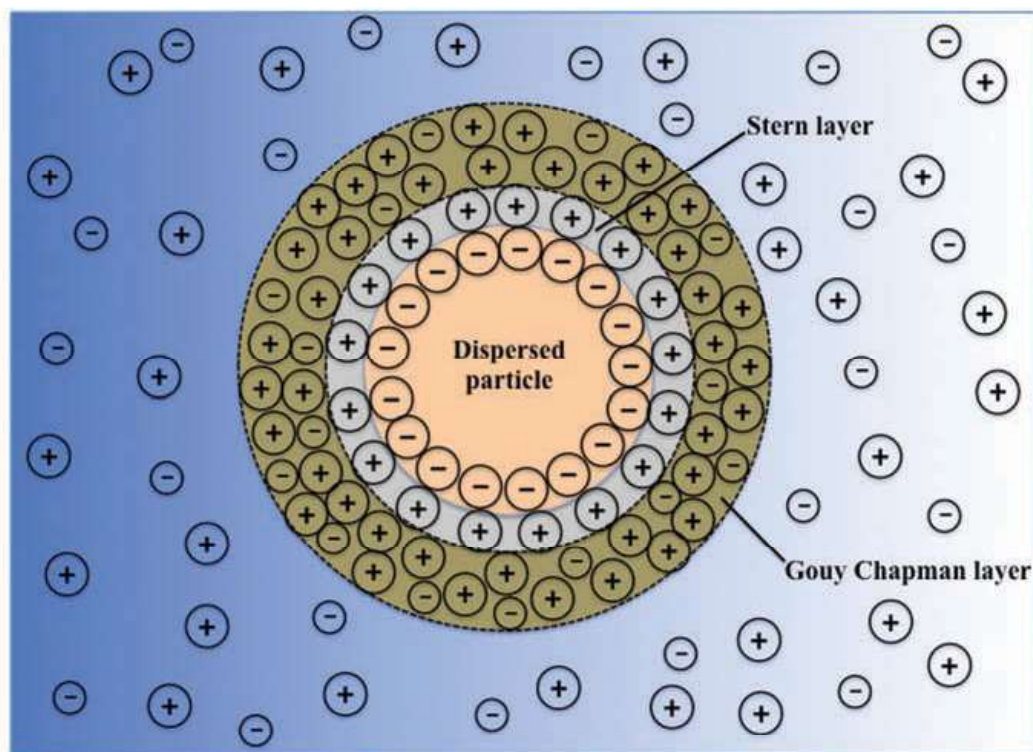


Figure 5. Zeta potential diagram of a negatively charged emulsion droplet.

Definitions of Key Phenomena in Emulsion Technology

Bancroft's rule: The phase in which an emulsifier is more soluble is considered the continuous phase.

Cloud point: The temperature at which two phases are not soluble with one another. In the case of emulsions, increasing cloud point indicates increased stability of the system.

Gibbs-Marangoni effect: A situation that occurs when there is insufficient

coverage by surfactant on the droplet surface. As two droplets come together this causes coalescence due to the resulting interfacial tension gradient between the surface of adjacent droplets.

Hydrophile-lipophile balance: A guideline, which allows the formulator to predict the hydrophilicity or lipophilicity of a molecule. It is based on a scale of 0 to 20 with 0 corresponding to the most lipophilic/hydrophobic compounds and 20 to the most hydrophilic/lipophobic materials. The values are calculated based on a weighted grading system that takes into account hydrophilic and lipophilic components of a molecule.^{16,17}

Janus particles: These are nanoparticles that have dual functionality in terms of their surface properties (e.g., it can have hydrophilic and lipophilic sections). Amphiphilic Janus particles are used to stabilize Pickering emulsions.

Ostwald ripening: This phenomenon is common in w/o emulsions, in which case oil molecules tend to migrate through the water phase to agglomerate with large lipid particles.

Phase inversion temperature (PIT): An existing emulsion, e.g. an o/w emulsion can undergo phase inversion to a w/o emulsion as the temperature of the system is raised. These PIT emulsions, when prepared properly, have very good long-term stability.

Sensorial and Textural Properties of Emulsions

The sensorial and textural properties of an emulsion play an integral role in a formulation's acceptance as a final product by the consumer. Typical sensorial properties consist of odor, color, consistency, spreadability (initial and rubout), and stickiness or tackiness.¹⁸ Many sensorial attributes correspond to the textural properties of the skin care preparation. In addition, several other important parameters are governed by the textural properties of the emulsion and include pick-up, stringiness, cushion, and slipperiness.¹⁹

Early on, a skin feel index was developed to characterize the skin feel after application of a skin care treatment, examining the initial slip of a product in relation to its end feel. In a systematic comparison of the structure-property relationships of various molecules, it was found that molecular weight, oiliness, polarity, unsaturation, and chain branching were found to be key contributing factors to observed skin feel.²⁰

In the early 1990s, an ASTM standard was developed as a guideline for sensorial analysis of skin creams and lotions.²¹ This dossier provides guidelines and procedures for qualitative description and quantitative assessment of the sensorial properties of skin care products, and continues to be an updated model for panel studies. Using this methodology, products are graded on appearance, pick-up, rub out, immediate afterfeel, and afterfeel at additional time points. Appearance refers to the visual attributes of the product and may deal with its optical or rheological properties. Integrity of shape and gloss are two key components of appearance and, respectively, deal with the ability of a product to retain its shape and the amount of reflected light

from a product. Pick-up describes the rheological properties of a product when it is manipulated between the fingers (usually the index finger and thumb) and consists of several components: firmness, stickiness, and cohesiveness. Rub out describes the physical and rheological attributes of a product during application; i.e. from initial application until the product has been absorbed by skin. Several characteristics are normally evaluated with respect to rub out and consist of: wetness, spreadability, thickness, waxiness, greasiness, and absorbency. As its name implies, afterfeel is an attribute corresponding to the skin feel after application of the product. Usually, gloss, stickiness, slipperiness, amount of residue, and type of residue (waxy, greasy, silicone, powdery, or chalky) are evaluated immediately after application and at prescribed time points following the treatment.

In recent years, significant efforts have focused on better understanding the sensorial properties of skin care emulsions by sensorial profiling.²² Traditionally, there were two analytical procedures for the sensorial evaluation of products: Spectrum Descriptive Analysis and Quantitative Descriptive Analysis. The Spectrum Descriptive Analysis method is a very detailed characterization of the sensorial attributes of a product.²³ It provides detailed information on how to carry out such sensorial tests and provides guidelines for statistical analysis of the data. More recently, this technique was applied specifically to the sensory evaluation of skin care products in which panelists were trained and surveyed a pool of samples for 26 attributes.²⁴ Principal component analysis was performed and revealed that oiliness, viscosity, adhesiveness, thickness, transparency, wetness, coolness, and spreadability were in the first principal component, while gloss and stickiness were the basis of the second principle component.

The Quantitative Descriptive Analysis method, developed by Tragon Corporation in collaboration with the Department of Food Science at the University of California Davis, was designed for the food industry to provide enhanced statistical treatment of sensorial data.²⁵ In this test, greater weight is given to panelists' ability to make relative sensory judgments rather than to distinguish absolute differences among products.

The two descriptive techniques discussed above provide a nice alternative to the traditional tests that utilize a trained panel. However, despite the utility of Spectrum Descriptive Analysis and Quantitative Descriptive Analysis, they have their drawbacks. For example, these tests can be laborious, requiring panelists to undergo a significant amount of training and to develop vocabulary specific to the test product. An alternative approach to gather consumer preferences is to use check-all-that-apply (CATA) questions. This methodology has had considerable success in the evaluation of foods, and was also successfully implemented for the evaluation of skin care products.²²

Despite the benefits of panel testing, oftentimes a more rapid approach to evaluate and screen numerous products with quantitative, objective data is desirable. Great efforts have been put forth to correlate sensorial properties with

instrumental approaches. A number of research groups have concentrated much effort on correlating rheological measurements to sensorial properties of skin care emulsions.^{19,26-30} Brummer and Godersky correlated rheological parameters to the skin feel of the formulation, at the onset of application (primary skin feel) and after the product has been applied and rubbed into the skin (secondary skin feel).³¹ According to their studies, the primary skin feeling correlates with the shear stress at the onset of flow (τ_F) and the dynamic viscosity (η_{dyn}). The secondary skin feeling correlates with the value of the stationary viscosity (η) for the rate of shear prevailing at the end of application to the skin.

Gilbert and coworkers investigated various sensorial properties of skin care emulsions, including integrity of shape, firmness, compression force, stringiness, and difficulty of spreading, comparing panel sensory tests with rheological measurements (flow, creep, and oscillation tests) and texture analysis (with a Texture Analyzer).³² They found very good correlation between subjective evaluation and instrumental analysis for most of the parameters, although this required developing empirical models of analysis.

Likewise, other physicochemical parameters (spreadability, surface tensiometry, and viscosity) measured by instrumental techniques also correlated with sensorial analysis of emollients.³³ These data suggest that gloss, residue, and oiliness correlate well with surface tension and spreadability measurements. Viscosity measurements, on the other hand, were found to correlate with spreading, thickness, softness, and slipperiness. In a separate study, another research group correlated *in vitro* physicochemical properties of several emollient esters with *in vivo* sensorial characteristics perceived by panelists. The results showed that spreading, contact angle, surface tension, dielectric contact, viscosity, refractive index, and molecular weight of the emollient esters correlated well with perceived sensorial attributes such as initial spreading, skin feel after application and absorption, shine, residue after spreading, and tackiness. This approach in correlating *in vivo* perceived sensory attributes with physicochemical parameters can provide insightful information for the skin care formulator in selecting specific emollient esters for topical products and ultimately predicting a product's sensorial profile.³⁴

Texture Profile Analysis (TPA)

The principles of texture profile analysis have been well established in the food industry to provide sensorial and textural descriptions of food as it feels in the mouth including its anatomical components: lips, tongue, palate, gums, and teeth.³⁵ Some of the most common words used to describe food texture in the United States are: crisp, dry, juicy, soft, creamy, crunchy, chewy, smooth, stringy, and hard.³⁶ As should be expected, each culture has distinct ways of describing food texture, and some have many more descriptive indicators of texture than others. Such accurate descriptions lead to the development of instrumental techniques to characterize the textural properties of foods. Utilizing Texture Profile Analysis, characteristics such

as resilience, chewiness, gumminess, springiness, and cohesiveness may be easily measured for a variety of foodstuffs.³⁷ The most commonly employed instrument for carrying out such measurements is a Texture Analyzer. It should be pointed out that while similar instruments with load cell capacity may also be employed for these purposes, the Texture Analyzer is particularly suited for Texture Profile Analysis due to its software development and variety of available probes. Not surprisingly, adaptations of techniques for measuring food texture with Texture Profile Analysis have been employed to perform similar measurements of skin care formulations.³² In the section that follows, we provide a comprehensive examination of the adaptation of the Texture Profile Analysis technique to measurement of important sensorial attributes of typical skin care emulsions used in skin care preparations.

Determination of Textural Attributes from Texture Profile Analysis

The aforementioned description of Texture Profile Analysis provides alternative nomenclature to that employed for the analysis of food texture; furthermore, we have also offered insight into other calculable parameters that are especially useful for the descriptive analysis of skin preparations. As stated, the most common instrument used for carrying out Texture Profile Analysis is a Texture Analyzer (see **Figure 6**).



Figure 6. Image of a Texture Analyzer (TA.XT Plus, Texture Technologies, Scarsdale, NY).

It is essentially a mechanical device with a load arm that contains a load cell with either 2 Kg or 5 Kg capacities. The formulation is placed in a sample cell underneath the probe, which is attached to the load arm, and then the emulsion is subjected to deformation by the probe. There are a number of probes available to use with the Texture Analyzer and custom designed pieces may also be employed. **Figure 7** contains photographs of several probes, fabricated from both acrylate and stainless steel, which have been utilized to conduct Texture Profile Analysis of skin care emulsions.

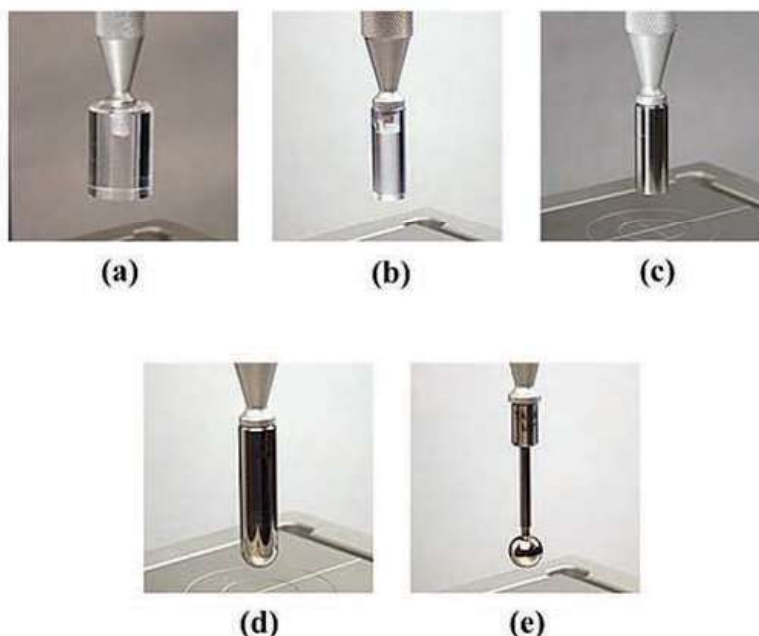


Figure 7. Probes utilized to conduct Texture Profile Analysis:
(a) TA-11; (b) TA-10; (c) TA-10ss; (d) TA-23; and (e) TA-18.

Probe TA-11 is a standard multi-purpose acrylic probe with a 1-in diameter. Probe TA-10 (0.5-in diameter) differs from Probe TA-11 only in its dimensions. Probe TA-10ss has the same dimensions as Probe TA-10, but is constructed with stainless steel. Probe TA-23 has the same diameter as Probe TA-10, and is constructed with stainless steel, but has a rounded bottom (0.25-in radius end), analogous to the anatomical structure of a human finger. Probe TA-18, also constructed of stainless steel, contains a spherical structure (0.5-in diameter) that comes into contact with the sample, which was originally designed for food texture analysis applications. It should be noted that the surface energy of the probe, due to the material of which it is constructed, affects the magnitude of forces encountered by the probe. Overall, regardless of the probe type employed, similar trends are observed when comparing skin care creams and lotions.

In a typical test, two deformations are carried out during the course of Texture

Profile Analysis. Data, similar to that shown in **Figure 8**, is obtained in which case each peak corresponds to a deformation of the sample. Typical settings are: probe speed, 1.0 mm/s; deformation, 2.0 mm; deformation time, 1 s; initial trigger force (point where the 1.0 mm deformation begins), 2 g. From the plot in Figure 8, we can calculate several parameters that can be related to textural properties of the cream or lotion. Area 1 and Area 2 are the calculated areas under the first and second peaks, corresponding to the first and second deformation. These values are used to calculate the *cohesiveness* ($\text{Area 2}/\text{Area 1}$) and *compressibility* ($1 - \text{Area 2}/\text{Area 1}$) of the emulsion. Peak 1 is the maximum value of the first peak and corresponds to the *firmness* or penetration force required to deform the sample. The first peak can further be analyzed by taking the ratio of Area 5 to Area 4, which provides a measure of *resilience*. *Adhesiveness of the emulsion to itself* can be taken to be Area 3, while *adhesiveness of the emulsion to the probe* corresponds to Area 6. *Integrity of shape* corresponds to the springiness of the sample and may be calculated by taking the ratio of Length 2 to Length 1. *Elastic resistance to deformation* corresponds to: $(\text{Area 2} \cdot \text{Peak 2} \cdot \text{Length 2}) / (\text{Area 1} \cdot \text{Peak 1} \cdot \text{Length 1})$. Finally, *stringiness* corresponds to Length 3, which begins in the negative force region of Area 6 and ends when the force becomes asymptotic to zero force.

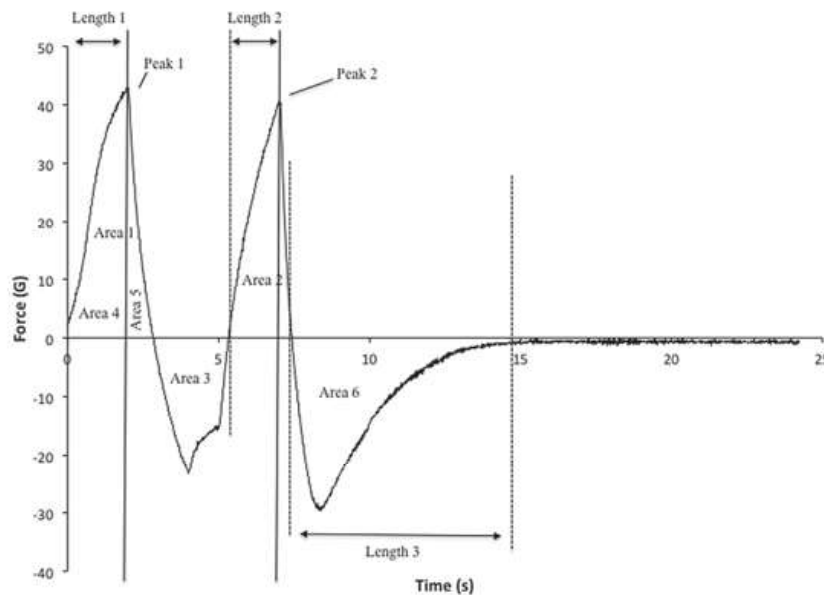


Figure 8. Example of a typical Texture Profile Analysis curve denoting specific length, peak height, and area measurements used to calculate textural attributes.

To measure *spreadability* and *tackiness* requires two separate tests with the Texture Analyzer. First, a simple measure of spreadability is attained by placing a small amount of emulsion in a weighing boat and applying a given force that partially deforms the sample, causing it to spread. Using a digital camera mount with fixed

dimensions and a scale included in the photograph, image analysis provides the area dimension of the spread emulsion. Tackiness, on the other hand, is measured by placing a small amount of the emulsion on a flat surface and bringing the probe in contact with sample. The adhesive forces corresponding to tackiness are measured as the negative peak forces and averaged from five deformations.

Analysis of Commercial Lotions and Creams by Texture Profile Analysis

Creams and lotions available in the skin care market can vary considerably in their textural properties. For example, a typical anti-aging cream would be distinctly different from a body milk formulation. The anti-aging cream normally would have much more consistency or structure as well as a distinct rub out profile, cohesiveness, etc. The body milk, on the other hand, would spread very easily, even without additional external forces, such as spreading by fingers. These characteristics are captured in Texture Profile Analysis experiments. In the current study, a total of fourteen commercial products were evaluated by Texture Profile Analysis. All of these samples were skin care emulsions in the form of either a cream or lotion. **Table 2** identifies four of the commercial products and their key structure-modifying ingredients, which provide viscosity and stability to the product. The ingredients listed include emulsifiers/co-emulsifiers as well as rheology modifiers/thickeners for both the oil and water phases of the emulsion.

Table 2. Selected commercial products subjected to Texture Profile Analysis. Viscosity data, courtesy of Timothy Gillece, were obtained with an Ares G2 strain controlled rheometer utilizing parallel plates geometry.

	Product type	Viscosity (Cp)	Key structure-modifying ingredients
Product A	Thick cream	29,000	Stearyl alcohol, Cetyl alcohol, Glyceryl stearate, Carbomer, Sodium polyacrylate
Product B	Low viscosity lotion	1,840	Glyceryl stearate, Cetearyl alcohol, Carbomer, Hydroxymethylcellulose
Product C	Medium viscosity lotion	10,450	Glyceryl stearate, Cetearyl alcohol, Steareth-21, Distearyl dimonium chloride, Behentrimonium methosulfate
Product D	Very low viscosity lotion	1,960	Glycol stearate, Carbomer, Glyceryl stearate, Cetyl alcohol, Magnesium aluminum silicate

Table 3 contains the results of selected textural attributes for several of the analyzed commercial creams and lotions. Upon inspection of the data, it is immediately apparent that *firmness* is the greatest for the cream sample (Product A), which is, by far, the most structured/viscous of the tested products. Products B and D, which are much lower viscosity lotions require less force to penetrate the sample at a fixed distance. The *compressibility* is more difficult to discern upon initial inspection. The very low viscosity lotion (Product D), which contains very little body, is the most compressible system. The cream (Product A), on the hand, is the least compressible. Likewise, the *integrity of shape* does not adhere to basic rheological parameters and depends on the complex interactions of the product with itself and with the probe. The analysis is pretty straightforward when we observe the properties of the product with the most structure and viscosity (Product A). As we would expect, the cream changes shape the most without returning to its original state. In addition, it is not surprising that Product B (low viscosity lotion) loses a significant amount of its body. However, Product C (medium viscosity lotion), which appears to have properties similar to Product A upon physical inspection, loses its shape upon deformation. In the case of Product B, this very low viscosity lotion is almost like water and does not change shape upon deformation.

The results of *elastic resistance to deformation* follow a trend corresponding to the consistency of the sample. The products with the highest consistency (Products A and C) have the greatest *elastic resistance to deformation*. Finally, we also report the *adhesiveness to the probe*, which more than likely also contains a strong cohesive component for the emulsion. Again, the two products with the greatest structure (Products A and C) have the strongest adhesion. The data for *adhesiveness of the emulsion to the probe* correlate well with the *adhesiveness of the emulsion to itself* (data not shown), again demonstrating the important role of the cohesiveness of the sample.

Table 3. Selected textural attributes of several commercial creams and lotions.

	Firmness (g)	Compress- ibility	Integrity of shape	Elastic resistance to deformation (g)	Adhesive- ness to probe (g•s)
Product A	87.85 ± 9.10	0.31 ± 0.0059	0.88 ± 0.0068	54.02 ± 1.48	255.80 ± 4.64
Product B	10.93 ± 2.68	0.32 ± 0.0064	0.94 ± 0.038	6.61 ± 0.22	38.16 ± 0.43
Product C	51.28 ± 4.39	0.35 ± 0.011	0.95 ± 0.0096	28.12 ± 1.32	135.00 ± 2.20
Product D	9.10 ± 0.13	0.37 ± 0.011	0.90 ± 0.0074	4.78 ± 0.15	22.63 ± 0.24

Overall, Products A and C follow the same trends in terms of *firmness*, *elastic resistance to deformation*, and *adhesiveness to the probe*. As already mentioned, these two products contain more structure than Products B and D, and it is probably safe to conclude that the structure/viscosity in the product correlates well with these parameters. On the other hand, we do not find such a clear correlation when examining the calculated values for *compressibility* and *integrity of shape*. These parameters may be less dependent on the formulation's physical properties and may rely more on the chemical properties of particular ingredients.

Table 4. Composition of four selected cream base emulsions subjected to Texture Profile Analysis.

Phase	Ingredient Trade Name	A % wt/wt	B % wt/wt	C % wt/wt	D % wt/wt
A	Deionized water	76.40	76.40	73.30	76.70
	Carbomer (Ashland 940 Carbomer, ASI)	0.5			
	Acrylic acid/VP crosspolymer (Ultrathix P-100, ASI)		0.5		
	PVM/MA decadiene crosspolymer (Stabileze QM, ASI)			0.5	
	Sodium polyacrylate (Rapithix A-100, ASI)				0.5
	Glycerin (99.7%) (Ruger)	2.00	2.00	2.00	2.00
	Disodium EDTA (Versene NA, Dow Chemical)	0.1	0.1	0.1	0.1
B	Isodecyl neopentanoate (Ceraphyl SLK, ASI)	7.00	7.00	7.00	7.00
	Ethylhexyl palmitate (Ceraphyl 368, ASI)	10.00	10.00	10.00	10.00
	Glyceryl stearate and PEG-100 Stearate (Arlacel 165, Croda)	2.75	2.75	2.75	2.75
	Cetyl Alcohol (Lanette 16, Cognis)	0.25	0.25	0.25	0.25
C	Triethanolamine (99%) (Dow Chemical)	0.30	0.30	0.40	
D	Propylene glycol (and) Diazolidinyl urea (and) Iodopropynyl butylcarbamate (Liquid Germall Plus, ASI)	0.70	0.70	0.70	0.70

Analysis of O/W Emulsions by Texture Profile Analysis

In order to discern the influence of thickening polymers on the properties of emulsion systems, we studied four o/w emulsion systems composed of the same vehicle and that only differed in composition by their thickening polymer. For simplicity, **Table 4** provides the example of the polymer used at 0.5% (w/w). The behavior of neat polymer solutions containing the same polymer were also examined, although the rheological profile was considerably different and did not present a suitable system for Texture Profile Analysis.

As already stated, a number of textural attributes were determined for the emulsion systems described in Table 4. All of the emulsion systems were evaluated at two concentrations of the selected polymers, 0.25% and 0.50% (w/w). Before delving into the Texture Profile Analysis data, there are several factors we should consider about the structural properties of the tested polymers.

Normally, when we think about rheology modification and structuring in relation to polymers, the concept of chain entanglements tends to come to mind. In this case, a polymer chain may be in a random coil conformation forming a small compact structure. By increasing the pH of the polymer solution, for example, the acid groups on the polymer chains become deprotonated, thereby bearing a negative charge and repulsing one another. As a result, chains of the polymer extend and entangle with neighboring chains. Overall, this transition causes an increase in the viscosity of the polymer solution. This is the typical situation for sodium polyacrylate, which is a linear polymer. The other three polymers included in the emulsion system, carbomer, acrylic acid/VP copolymer, and PVM/MA decadiene crosspolymer, are highly cross-linked and form microgels in solution. In this case, neutralization results in profuse swelling of the microgels and ensuing increases in the viscosity and measurable rheological structuring attributes such as the yield stress and G' . Further, factors such as the concentration, neutralization level, electrolyte type and level, cross-link density, and mole fraction of carboxylate in the repeating unit affect the way the microgels associate and respond to shearing forces. For example, at the same concentration and neutralization, a lower cross-linked microgel may produce a softer, or less elastic bulk gel than its more highly cross-linked analogue. In any event, we must keep in mind that the current study involves emulsions with many other components, which present a much more complex system than simple polymer in water gel solutions.

Figure 9 contains a graph of *firmness* at two concentrations for the four tested emulsion systems. The system containing carbomer provides high resistance to penetration at the low concentration, relative to the other systems; however, at 0.5% solids the systems based on acrylic acid/VP crosspolymer and sodium polyacrylate perform similarly, while PVM/MA decadiene crosspolymer requires much greater force to penetrate its structure. The requirement for such strong forces in PVM/MA decadiene crosspolymer may stem from the polymer's inherent networked structure due to chemical cross-linking as manifested by swelling of its microgels.

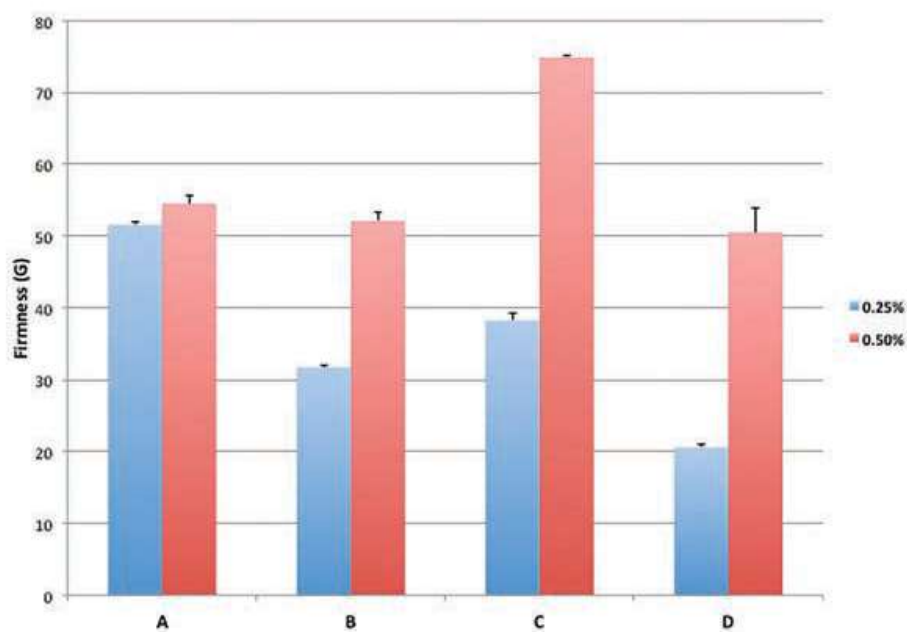


Figure 9. Chart of firmness for emulsion systems based on (A) carbomer, (B) acrylic acid/VP crosspolymer, (C) PVM/MA decadiene crosspolymer, and (D) sodium polyacrylate.

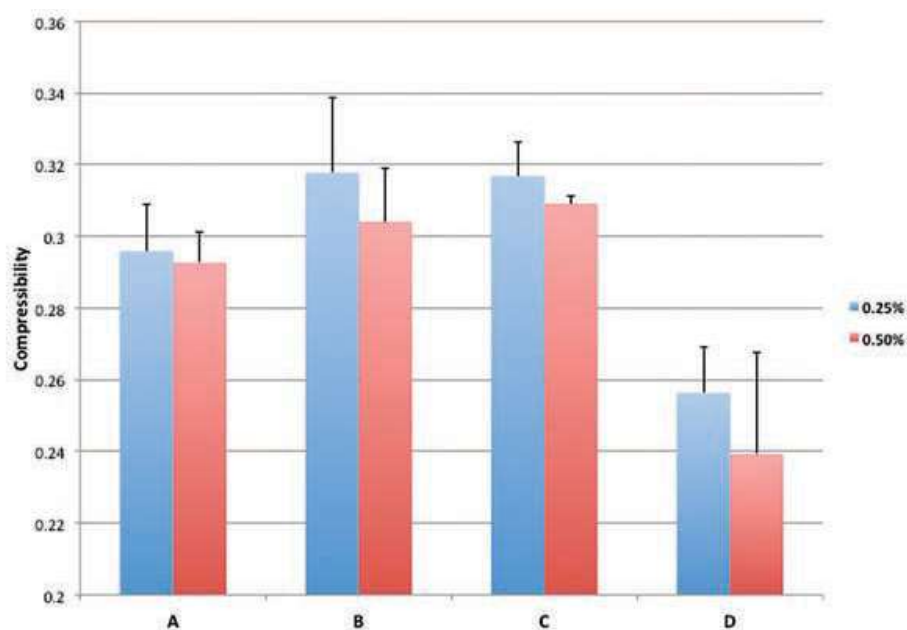


Figure 10. Chart of compressibility for emulsion systems based on (A) carbomer, (B) acrylic acid/VP crosspolymer, (C) PVM/MA decadiene crosspolymer, and (D) sodium polyacrylate.

From a slightly different perspective, the *compressibility* of each cream is reported in **Figure 10**. One should bear in mind that compressibility is proportional to the ratio of Area 2 to Area 1 in the Texture Profile Analysis plot. The three cross-linked systems—acrylic acid/VP crosspolymer, carbomer, and PVM/MA decadiene crosspolymer—are more compressible than sodium polyacrylate. Such a result is in contrast with what one might expect for highly cross-linked systems, which should be more elastic in nature. In this case, the shearing forces between the microgels may play a more prominent role.

Figure 11 contains *resilience* data, demonstrating the ability of the cream to break down as a result of shear forces. Such a result may be rationalized by the chemical structure of the polymer. A highly cross-linked system would be more likely to bounce back to its original structural, rather than to become molded by the deformation, as is the case with the linear, non-branched sodium polyacrylate system.

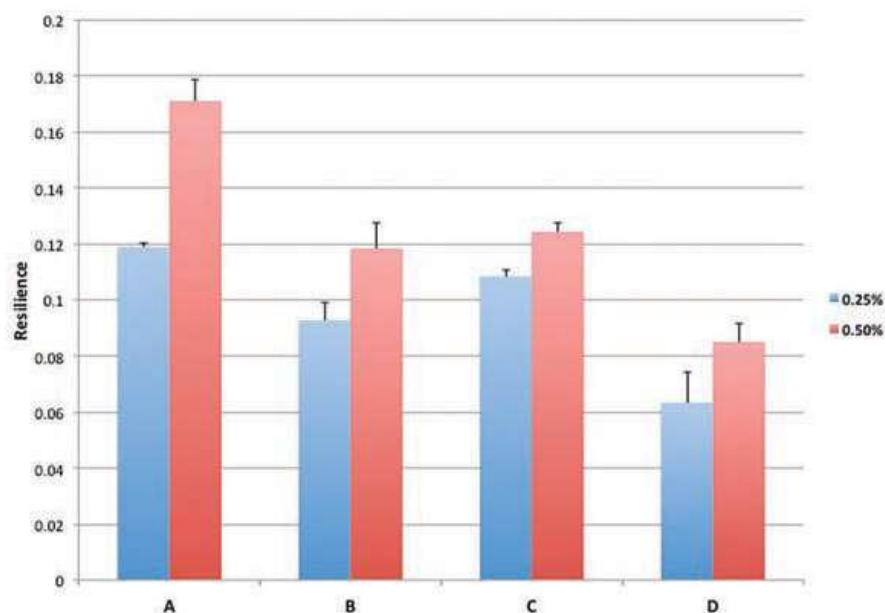


Figure 11. Chart of resilience for emulsion systems based on (A) carbomer, (B) acrylic acid/VP crosspolymer, (C) PVM/MA decadiene crosspolymer, and (D) sodium polyacrylate.

Concluding Remarks

In this chapter, we provide a broad overview of emulsion technology and its fundamental concepts. We also take a preliminary look at the textural attributes of skin care formulations as determined by Texture Profile Analysis. It is a promising and novel technique that can help us better engineer finished formulations with desired sensorial characteristics. It is our hope that future studies will include a full comparison of this technique to the sensorial attributes as determined by a pool of panelists.

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