

Rheology of Cosmetic Products: Surfactant Mesophases, Foams and Emulsions

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Synopsis

Cosmetic products such as shampoos, body washes, mascaras, and foundations can all be classified essentially as complex fluids. Depending on the product format, the specific complex fluid used in a formulation can range from self-assembled surfactant systems found in most cleansing products to oil-in-water and water-in-oil emulsions found in makeup, color cosmetics, and skin care. These complex fluids play a critical role in giving rise to rheological and tribological properties necessary for both sensory and functional performance. Critical functional properties such as product stability and wet hair conditioning are impacted significantly through any changes in the product rheology. Positive sensorial properties of products are always desired by consumers, and as such, it is critical to always consider how to optimize formulation rheology to adequately deliver desirable sensory performance and properties. This review will focus on the importance of understanding and characterizing the rheology of complex fluids used in cosmetic products. A review and analysis of the recent literature in this area is presented.

INTRODUCTION

Many formats of cosmetic products such as foundations, mascaras, cleansers, creams, and lotions need to be optimized for their rheological performance to yield stable and functional products. Understanding and engineering the rheology of the underlying complex fluids play a critical role in formulation and engineering high-performance products. Cosmetic products are usually formulated to be non-Newtonian complex fluids and exhibit shear-thinning properties (1). Rheology plays a significant role in dictating product stability, and as such, it is important to engineer certain rheological properties such as viscosity and yield stress into cosmetic products to enhance product stability. Engineering rheological performance can additionally impact the tribological or lubrication performance in these complex fluid-based cosmetic products. Certain cosmetic products such as hair conditioners require maintenance of high viscosity values to ensure that adequate lubrication is achieved. The Stribeck curve perfectly describes the relationship between viscosity and friction coefficient at three different regimes, that is, the boundary regime, mixed regime, and hydrodynamic regime. Hydrodynamic lubrication is important for initial

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sensory response, whereas mixed regime lubrication performance is important for in-use sensory performance (2). Viscosity plays an important role in both of these. Particulate lubricants, such as mineral oils containing dispersed solids are extensively used in industrial applications. It has also been shown that the tribological properties of cosmetic products affect its performance (3,4) and skin feel (5–7).

An understanding of the rheology is critical also for product processing where a knowledge of the product rheology dictates certain processing parameters such as pumping, pouring, and mixing. Product application and spreadability are also highly governed by product rheology (8). In addition to the importance of the rheology of surfactant mesophases and emulsions found in liquid and semisolid cosmetic products, the rheology of the foams generated during in-use conditions plays a critical role in sensory performance of products such as facial cleansers, body washes, and shampoos. Foams are a manifestation of the surface activity of the surfactants (9), which is itself related to the rheology of the foam itself.

It is also important to note that the demands of the present-day consumers have shifted dramatically from high-performing, aesthetically pleasing products to products that are eco-friendly, use ingredients from sustainable sources, and are tailored to individual needs. Another factor that is driving the cosmetic industry to a more sustainable path is laws and regulations placed by certain governments (10). This new trend requires an understanding of the rheology of sustainable ingredients.

The utilization of automated formulation platforms across the cosmetic industry enables one to perform complex formulation workflows in a fully automated manner. Its advantages over manual formulation include, but are not limited to, continuous real-time monitoring and control of all formulation parameters, including internal and jacket temperature, shear rate and viscosity, scraping speed, reflux and pH in an inert atmosphere, if desired, and automatic logging of all data. Its overall efficiency brings about a decrease in cost per sample up to 90% (8). Automated formulation platforms provide the flexible mode of operation and production necessary to meet the growing demands of individualization, personalization, and mass customization. These platforms can be used heavily in establishing an understanding of rheology and controlling formulation design rules in a much faster and effective manner.

APPLICATIONS OF RHEOLOGY IN COSMETIC PRODUCTS

SURFACTANT MESOPHASE: BODY WASHES, SHAMPOOS, AND HAIR CONDITIONERS

Surfactant mesophases have a huge impact on the rheology of products such as body washes, shampoos, and hair conditioners (8,11). Surfactants possess self-assembly properties in solution when the critical micelle concentration (CMC) is surpassed. Surfactants self-assemble to form various meso-structures that dictate the formulations' microstructure and various rheological properties (12). The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavorable contacts with water, and the desire for the hydrophilic parts to maintain contact with the aqueous environment. A thermodynamic description of the process of micelle formation includes both electrostatic and hydrophobic contributions to the overall Gibbs energy of the system (13). There are multiple mesophases that can be formed by surfactant systems, such as wormlike micelles and lamellar gel phases.

Wormlike micelles: shampoos, body, and face washes. Micelles are either discrete or continuous aggregates with overall circular cross section. Discrete micelles include spherical, prolate-shaped, and disk-shaped aggregates, whereas continuous micelles can include long unconnected rods with variable rigidity or branched rods. Although it is the amphiphilic character of surfactants that promotes self-assembly into the aforementioned aggregates, it is actually the surfactant packing parameter that mainly determines which kind of micelle will be formed (14). These aggregates may occur in water-rich or oil-rich solutions (15). Figure 1 highlights some of surfactant micellar microstructures that may be formed.

One of the most prevalent micellar structures used in shampoos and body washes is wormlike micelles. The nature, behavior, and performance of products having wormlike micelle structures depend heavily on the self-assembled nanostructure. Wormlike micelles can be formed by anionic, cationic, or nonionic surfactants (15). The structural characteristics of wormlike micelles are significantly impacted by specific primary surfactants' molecular structure and also by surfactant/cosurfactant choice and are additionally influenced significantly by various formulation conditions such as addition of electrolyte and changes in pH. In these systems, it is important to additionally control the dynamic equilibrium between the self-assembled state and dispersed surfactant molecules (16). Cosolvents/cosurfactants have also been long used to alter the dynamic balance of micellar systems (17). The following highlights some of the studies carried out on different wormlike micellar systems to understand the effect of surfactant type, charge, cosurfactant, cosolvents, electrolyte, etc.

Cosurfactant effect. In an attempt to understand the impact of cosolvents on micellar systems, Jiang et al. (18) investigated different combinations of non-ionic surfactant, ionic surfactant, and mixed surfactants. The two major aspects that were studied are the CMC and the size of micelles. The combination of sodium lauryl ether sulfate (SLES) and Cocamidopropyl betaine (CAPB) is one of the most frequently used surfactant base mixtures for cleansing cosmetic products, and the study and analysis of the structure and rheology of these binary mixtures are very common practice (19). In this report, a series of salt concentrations, sodium chloride (NaCl) at 3.01, 3.56, 4.01, 4.5, and 5.00 wt% (0.515, 0.609, 0.686, 0.770, and 0.856 M), with and without the cosolvent diol dipropylene glycol (DPG) was investigated at 25°C to understand the effect of DPG on the structure of wormlike micelles in the context of variable counterion concentration. Small-angle

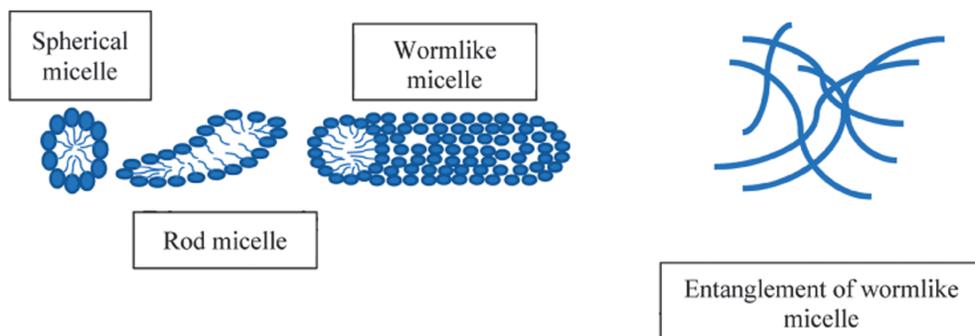


Figure 1. Diagrammatic presentation of spherical, rod, and wormlike micelles.

neutron scattering (SANS) was used to understand microstructural changes. The viscosity of wormlike micelle solutions is strongly dependent on the contour length, and the results show that the addition of DPG has a dramatic impact on the viscoelastic properties of wormlike micelles solutions because of a dramatic reduction in the contour length associated with the lower dielectric constant media. The decreased dielectric constant of the solvent with the addition of DPG may increase the electrostatic interaction between head groups and lead to the observed smaller micelle radii and dramatic reduction in contour length of the micelles.

Electrolyte effect. NaCl induces an electrostatic screening effect on surfactant mixtures, which imparts the rheology of the solution by elongating the micelles formed. Amin et al. (19) revealed structural properties of micelles using dynamic light scattering (DLS), microrheology, and Raman spectroscopy. In this study, Raman spectroscopy was combined with DLS–optical microrheology to investigate the impact of ionic strength on the molecular structure and associated changes in the microstructure and rheology of a mixture of anionic SLES and zwitterionic CAPB surfactants in solution. It is reported that DLS measurements and Raman spectroscopy were performed on surfactant mixtures in water containing 14% w/w sodium lauryl monoether sulfate (SLES), 2% w/w CAPB, and varying concentrations of NaCl, ranging from 73 to 500 mM. To perform the microrheological measurements, 900-nm polystyrene probe particles were added to obtain a final concentration of 0.15% w/w in the surfactant mixtures and 73 mM NaCl because of commercial preparation of CAPB. Sample aliquots (~20 μ L) for Raman work were placed into a titanium cuvette with 120- μ m-thick quartz windows and positioned in a temperature-stabilized sample holder. For the microrheological work, 1-mL aliquots were placed into a disposable polystyrene cuvette and placed in the same sample holder. It was also reported that all data were collected at 25°C. The effect of electrostatic screening on the rheological properties of anionic SLES and zwitterionic CAPB surfactant mixtures was studied by modulating the NaCl concentration. It was reported that the viscosity of the surfactant mixture increased with NaCl concentration to a maximum level and then decreased. This phenomenon can be attributed to either a conformational change to a branched micellar network or to a reversal to short cylindrical micelles. To further provide insights into this effect and the exact microstructure differences, Raman spectroscopy was carried out which highlighted that the Raman band at 170 cm^{-1} correlates well with the NaCl-induced viscosity changes; however, the values are different at low and high NaCl values. This indicated that although both low and high NaCl values exhibit low viscosity, the microstructures at these two extreme levels are different.

State of ionization or pH change. Understanding how pH and pH change impact wormlike micelle properties and ultimately affect and determine the final rheology of a cosmetic formulation is highly important. Silva et al. (20) did show how to tailor the structure and rheology of aqueous solutions of the cationic surfactant cetyltrimethylammonium tosylate (CTAT) by adding potassium phthalic acid (PPA) or by changing pH. It was reported that the addition of PPA to CTAT solutions greatly increases the viscosity of the solution. It is important to state that the addition of PPA to the mixture promotes a transition from spherical micelles to rod-like micelles and, eventually, to elongated and flexible wormlike micelles at much lower surfactant concentration. The interaction between both species is maximum at a determined PPA concentration, after which a gradual reduction in viscosity and shear thinning is produced; this is a phenomenon also observed in surfactant solutions where NaCl is added to build viscosity (21). The initial pH values for all

CTAT solutions evaluated ranged between 6.9 and 7.4, and any increase in the solution pH leads to a progressive decrease in the low-shear rate viscosities.

Move toward sustainability: Biosurfactant addition effect. Personal care and cosmetic companies are increasingly moving toward enhanced sustainability. This implies substituting synthetic surfactants with more biodegradable alternatives such as biosurfactants. This substitution will require gaining an understanding of how biosurfactants will self-assemble and impact on the traditional surfactants' self-assembly process. Xu and Amin (21) carried out a microrheological study of ternary surfactant–biosurfactant mixtures. This report explores the rheological impact of rhamnolipid biosurfactant [mono-/di-rhamnolipid mixture concentrated clarified broth (CCB)] on an SLES and CAPB mixed surfactant system. In this report, the evolution in the wormlike micellar structure in the SLES/CAPB system is explored when a rhamnolipid biosurfactant is introduced. Techniques used in this study include mechanical rheometry and microrheometry (diffusive wave spectroscopy). The biosurfactant mixture explored CCB has a rhamnolipid concentration of 49.7% in which the mono- to di-rhamnolipid ratio is 9:13. CCB is the target of investigation for all three experiments. It was found that the SLES/CAPB/CCB system had a Maxwellian-type response which indicates the formation of wormlike micelles. The viscosity of the SLES/CAPB system was significantly reduced on just substituting 2% of SLES with the biosurfactant CCB. Microrheometry measurements allowed for the extraction of microstructural parameters, and it was observed that the contour length of wormlike micelle formed by SLES/CAPB decreased from 445.8 to 88.37 nm with only 2 wt% addition of CCB. Change in electrostatic interactions obtained through changes in pH allowed for a rebuilding of the viscosity through re-formation of elongated wormlike micelles. This work identified understandings of microstructure–rheology linkages in complex biosurfactant/surfactant mixtures that can be used as a guideline for future applications of rhamnolipids in cosmetics and personal care products.

Cationic wormlike micelles. The most common type of wormlike micelle stems from anionic surfactants as discussed previously. Cationic surfactants also form wormlike micelles in solution. Raghavan and Kaler (22) investigated viscoelastic properties of unsaturated cationic surfactants, two C_{22} surfactants with a cis unsaturation at the 13-carbon position: erucyl bis(hydroxyethyl)methylammonium chloride (EHAC) and erucyl trimethylammonium chloride. These two surfactants were studied in the presence of sodium salicylate (NaSal) or NaCl. Previous reports and studies of similar surfactants with long, monounsaturated tails mostly focused on their drag-reducing ability where they effectively reduced drag at elevated (higher) temperatures when compared with their saturated counterparts (23,24). Solutions of these C_{22} surfactants also show complex phase tilted in the presence of salt (22). It is reported that EHAC/NaCl solutions phase separate at high salt content (ca. 2 M), whereas EHAC/NaSal solutions phase separate beyond a certain molar ratio of salt to surfactant. These differences are connected to the fact that the Cl^- counterion does not penetrate the surfactant aggregate, whereas the hydrophobic salicylate counterions can attach between the charged head groups, thus screening electrostatic repulsions and promoting micellar growth even at low salt concentrations (25). Giant wormlike micelles are reported to be formed by the surfactant EHAC on addition of NaCl. This makes it an ideal surfactant for rheology-control applications. The contour length at elevated temperatures of 60°C was estimated to be similar to that of other micellar systems at room temperature. Thus, the solution viscosity was extremely high, even at high temperatures of 90°C. Furthermore, a nonmonotonic dependence of viscosity on temperature was reported.

Polymer effect. Neutral polymers and polyelectrolytes are used quite extensively in cosmetic formulations for rheology modifications and also to form complex coacervates that enable deposition in formulations where the deposition of certain active ingredients to the substrate (i.e., hair/skin) surface is necessary. Therefore, understanding the interactions of polymers and surfactant is a necessary and critical step for the formulation of efficient cosmetic products. Padasala et Al. (26) reported the effect of polymers on wormlike micelles of CTAT and discussed how the size of wormlike micelles can easily be controlled by different polymers. The ion tosylate belongs to the family of hydrotropes, and in the presence of hydrotropes, surfactants present pronounced changes in their viscosity as a result of the micellar growth induced by electrostatic screening which leads to the formation of longer, more flexible and entangled micelles, a change from linear to branched micelles or an increase in flexibility of wormlike micelles. CTAT is capable of forming wormlike micelles at very low concentrations (27–30) and was combined with a triblock copolymer made up of poly(ethylene oxide) 4000 (PEO 4K) and poly(propylene oxide) 1000 (PPO 1K). These homopolymers are nonamphiphilic in nature and do not self-assemble in aqueous solution, whereas their block copolymers, that is, PEO-PPO-PEO or PPO-PEO-PPO, form thermoresponsive micelles above their critical micelle temperature because they have distinct hydrophilic (PEO) and hydrophobic (PPO) parts which provide amphiphilic characteristics to them (31) and these polymers interact differently with wormlike micelles of CTAT. First, the formation of wormlike micelles at concentrations higher than its CMC (~ 0.26 mM at 25°C) was studied using SANS measurement, and the presence of wormlike micelles was studied using cryogenic transmission electron microscopy. The effect of temperature on solution viscosity of 20 mM CTAT solution was studied. It was reported that a slight increase in temperature results in significant loss in viscosity which becomes nominal at elevated temperatures. It was then concluded that an increase in temperature leads to an increase in the charge repulsion between charged head groups and favors demicellization, resulting in drop in viscosity at elevated temperatures. To gain information on the interaction of CTAT with polymers, surface tension and conductance of CTAT solutions over a wide range of concentrations well below and above the CMC in the presence of 0.1% polymers were carried out. It is reported that hydrophobicity of polymers plays a key role in altering the morphology of wormlike micelles. PEO-PPO-PEO-type triblock copolymers form core-shell micelles with PPO block as core and hydrated PEO blocks as corona. When such block copolymers are added to solutions containing wormlike CTAT micelles, depending on hydrophobicity, they can lead to demicellization. It was concluded in this report that the extent of demicellization largely depends on the hydrophobicity of block copolymers. This study extensively shows how nonionic polymers control the micelle forming and micelle size property of the cationic surfactant CTAT.

Effect of shear on wormlike micelles. Shear is used during formulation processing as well as during product application. It is important to have an understanding of how wormlike micelles respond to shear and the implications of high or low shear rates on its rheological properties. Developing this understanding is not simple and requires the utilization of advanced characterization techniques such as SANS. This information further helps in understanding certain processing issues that are observed in wormlike systems such as shear banding (32). Arenas-Gómez et Al. (33) used rheology combined with SANS (rheo-SANS) to determine the local structural order in the 3-[dimethyl (tetradecyl)azaniumyl] propane-1-sulfonate and sodium dodecylsulfate micelle solutions under flow and quiescent conditions. This information is critical in understanding the rheological performance

and link to the microstructure. As the shear rate increases and the solution is no longer at rest, there exists a shear banding region. At very high shear rates (shear rate $>100 \text{ s}^{-1}$), a rate where the micellar solution is supposed to be aligned, it presents two regions: a region where the orientation parameter decays and a second region where this orientation parameter linearly increases again. The origin of these regions is not clear, but the presented possible explanations of why they have been observed are stated. At high shear rate values of 100 s^{-1} and above, where no shear banding is observed and there are highly oriented micelles (paranematic region), the breaking rate increases because of friction, the contour length decreases, the fluid slightly thins, or viscosity is almost constant. In this region, micellar breaking is important, and there is an immediate micelle shortening due to the entropic forces that instantaneously forces a coil structure that impacts the ordered flow prevalent before the rupture of the wormlike micelles. As a result of this, the orientation parameter decreases, the shortened micelles equilibrate to the local conditions of the surrounding media, elongate again, and realign properly when the shear rate is above approximately 500 s^{-1} , and the system presents shear thinning of the unclear origin.

Lamellar gel network: Hair conditioners. Hair conditioners primarily use a mixture of cationic surfactants and fatty alcohols in an aqueous medium to form a structured mesophase that gives rise to good lubrication properties and performance. These conditioner emulsions usually have high viscosity, and understanding the viscosity buildup and meso-structure and how it breaks down on dilution is essential for controlling the conditioning performance. The gel network theory of emulsion stability gives a coherent explanation for the manner in which fatty amphiphiles and surfactants combined as mixed emulsifiers not only stabilize multiphase oil-in-water (o/w) lotions and creams but also control their viscosities. Although most of the early work was performed using long-chain (C_{16} – C_{18}) fatty alcohols, the theory is general, and the same broad principles apply to whichever amphiphile or surfactant (ionic or nonionic) is used. The theory relates the stabilities and physicochemical properties of multiphase o/w emulsions to the fact that the lamellar gel network is mainly an extended, highly interconnected lamellar structure of surfactant bilayers and interlamellar water layers, which is called the lamellar gel phase (L_{β}) (34–37).

Davies and Amin (8) reported that high yield stress values were engineered through formulation variation and observed in the surfactant–fatty alcohol systems with higher ratios of fatty alcohol, that is, at an increased fatty alcohol concentration of 10% w/w and an abundance of surfactant in the system, an increased swelling rate was observed and reported in the aqueous phase. This ultimately dictates the viscosity of the formulation, causing a significant increase in viscosity which also impacts the overall yield stress of the system. This is in accordance with the literature that states that an excess or increase in fatty alcohol in an aqueous phase with surfactants in solution controls and predicts the overall consistency or viscosity of the formulation as the gel phase is formed (38), at a temperature high enough to melt the fatty amphiphile by the swelling of the fatty amphiphile and its ability to incorporate significant quantities of water in the interlamellar space. This high yield stress values impacted wet lubrication as a result of higher structural integrity of the microstructure during the dilution process, resulting in both higher viscosity and deposition of larger more interconnected meso-structures on the hair surface, giving rise to a more continuous film. An overall reduced combing force is observed in hair treated with the systems with highest yield stress values, further validating this effect.

FOAM RHEOLOGY

Foams are generated during in-use conditions for shampoos, body washes, and face cleansers. Ordinary foam is polydisperse and isotropic, and its elastic properties are characterized by its bulk modulus and its shear modulus. There is a range of strain over which the foam is elastic. Beyond the elastic range of strain, the foam is plastic. Under continuous shear, polydisperse foams show a tendency to separate into regions of smaller and larger bubbles (39). The structure and dynamics of foams and emulsions strongly depend on the particle size and on the dispersed phase volume fraction. The structure of foams and emulsions is metastable. It evolves with time because of drainage, coarsening (also referred to as Ostwald ripening in dilute emulsions), or coalescence (40–42).

Foam instability mechanisms. Two major foam instability mechanisms are foam drainage and foam coarsening. Coarsening in foams and emulsions arises from diffusion of the chemical species of the dispersed phase between neighboring particles, driven by Laplace pressure differences (43). Foam drainage is a complex physicochemical hydrodynamic process governed by many simultaneous factors, which are not fully understood. The rate of foam drainage depends not only on the hydrodynamic parameters of the foam system but also on the rate of internal foam destruction by the bubble coalescence. The foam drainage plays a critical role in the foam stability. Foam drainage causes both a decrease in the liquid volume fraction and an increase in the capillary pressure, which are related through the size of the foam bubbles and the height of the foam column. The mechanism of the foam decay depends not only on the liquid volume fraction but also on the types of the surfactant and the foam films separating the foam cells (44). In foams, drainage can be eliminated in microgravity (45) or by using a continuous phase which has a yield stress.

Coarsening in foams and emulsions arises from diffusion of the chemical species of the dispersed phase between neighboring particles, driven by Laplace pressure differences. When foam dries out, its structure becomes very fragile as the liquid film becomes thinner and more susceptible to breakage, which means the foam collapses. Coarsening leads to a growth of the average particle diameter with time, accompanied by intermittent structural rearrangements (42). For similar droplet and bubble sizes, coarsening in emulsions is generally much slower than that in foams because of differences of internal phase density and solubility in the continuous phase. Foam drainage and foam coarsening are interconnected and tend to impact on the rheological response of the system as highlighted in the figure.

Materials for impacting foam performance. Foam quality is largely controlled by the properties of the surfactant monolayers that protect the air–water and oil–water interfaces. It is therefore critical that they are both optimized in cosmetic formulations to deliver optimal foaming during cleansing and positive sensorial attributes to consumers. The knowledge of surface tension alone is not sufficient to understand the foam and emulsion properties. The surface viscoelasticity and compression viscoelasticity, in particular, play an important role in a variety of dynamic processes (46).

Marinova et al. (47) studied surfactant mixtures for fine foams with slowed drainage. In this study, systematic investigation of foams stabilized by a triple surfactant mixture containing a nonionic alkyl polyglucoside, an ionic sodium lauryl dioxethylene sulfate, and zwitterionic CAPB was performed. The foaming of the triple surfactant mixture was found to be comparable with that of the single components and with the binary mixture without alkyl polyglucoside at alkaline pH. It was reported that fatty alcohol and/or

hydrophobically modified starch added to the different mixtures successfully reduced the drainage and the Ostwald ripening of the foams. Also, systematic model experiments showed that the surface tension and dilatational rheology were also strongly dependent on the presence of the additives. These effects were also strongly temperature dependent because drainage slowed down with the decrease in the temperature from 25 to 15°C. Most significant drainage retardation was observed at 15°C in the presence of additives, where the surface tension was lowest and the surface viscoelasticity was highest. Drainage of thin horizontal films was also dependent on the presence of additives and the temperature. This was observed to be significantly slower when the surface viscoelasticity increased. The obtained results demonstrated that additives leading to increased surface viscoelasticity of surfactant solutions could be used successfully for tuning the foam properties of complex surfactant mixtures, of three and more surfactants even at alkaline pH, thus increasing the application range of the foams and ingredients to harsh conditions and requirements.

Some materials are of interest for additional performance control of foams, and these include proteins. Proteins are excellent foaming agents because they strongly adsorb to the gas–water interface, and they tend to give good steric stabilization and some electrostatic

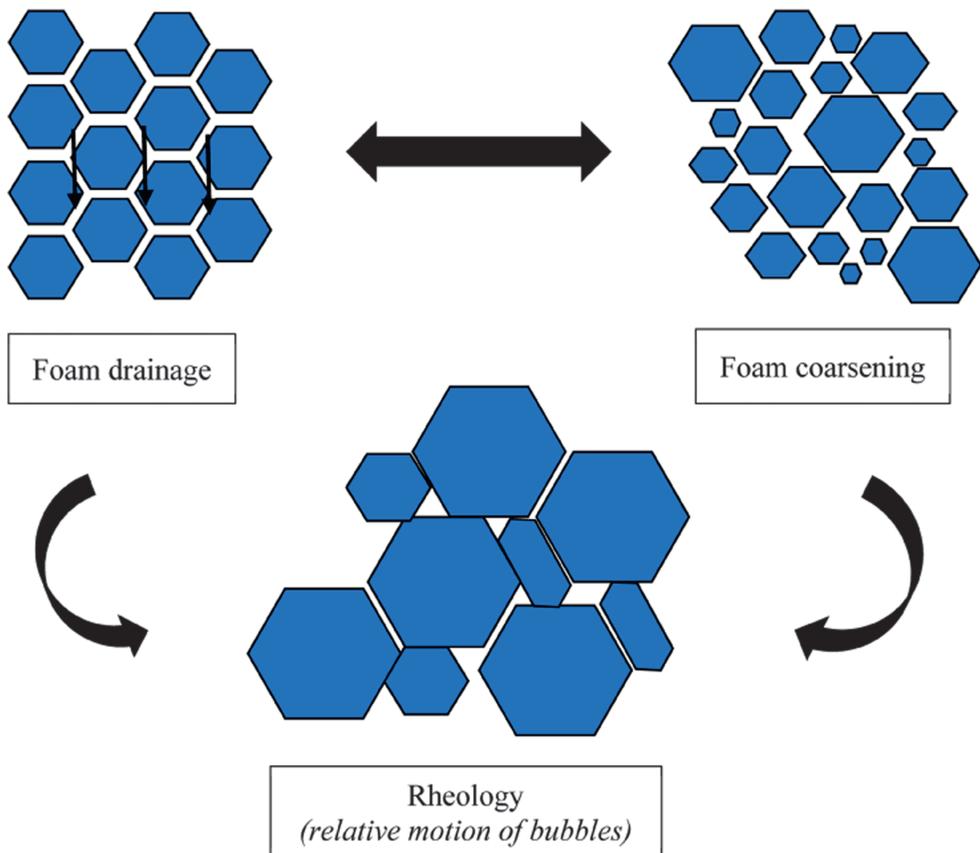


Figure 2. Schematic diagram showing interconnection between foam drainage, foam coarsening, and subsequent rheology of foam.

stabilization, and also the adsorbed film tends to have a reasonably high surface rheological modulus which is because of interactions between the adsorbed molecules. Proteins adsorb well at the water–air interphase as a result of the hydrophobic patches they possess as a result of the hydrophobic amino acid deposits. Any factor that increases the exposure of the hydrophobic patches to the solvent will increase protein surface activity. Sánchez and Patino (48) show that there is a good correlation between the foaming of caseinate solutions and the rate of diffusion to the interface, which depends on the protein concentration and the state of aggregation of the caseinate.

Foam as delivery systems. Foams as delivery systems for actives have gained popularity in both cosmetics and pharmaceutical products because they possess advantages over traditional methods of active or drug delivery such as gels, creams, and ointments. Foams, to a relatively high extent, eliminate negative sensorial attributes such as greasiness or tackiness. Although there is no direct connection between good foaming properties and good cleansing, it is important to note that consumers desire good foam generation and unconsciously link good cleansing to adequate foaming and any cleansing agent that does not generate adequate foam is termed an ineffective cleanser (49). There exist multiple applications of the foam technology to cosmetic products which include hard fine-pore shaving foam which helps uphold the hair during the shaving process. Hair mousse is able to give hair desirable shape and volume (50). For shampoos, good foamability of a shampoo formulation even under a strong fat contamination is of tremendous importance (51). There are also foam compositions for application to the skin as a barrier to skin irritants in the prevention of contact dermatitis caused, for example, by sodium lauryl sulfate. Fowler (52) reported that a protective foam containing dimethicone and glycerine was shown to improve chronic hand dermatitis in individuals with previously uncontrolled dermatitis, despite continuing their regular occupation. Cosmetic foaming compositions can also contain keratolytics, lubricating agents, and germicide agents such as triclosan or sunscreens (53).

EMULSION RHEOLOGY

Emulsions are heavily used in the cosmetic industry in formulating several kinds of cosmetic products. The composition of an emulsion plays a critical role in its rheological behavior, not only by influencing the long-term stability of droplets but also by affecting the kinds of interfacial interactions that exist between droplets through the emulsions' overall interfacial structure (54).

An interesting aspect of emulsions is that although being composed entirely of viscous liquids or solutions, they can be made into soft solids that have tunable rheological properties which depend upon their compositions and flow histories. These solid-like properties emerge through crowding of deformable droplets as the droplet volume fraction ϕ is raised, which can lead to glassy behavior and, ultimately, jamming and deformation of droplets. The positional and interfacial structures of droplets in a concentrated emulsion, which are inherently linked to droplet size distribution through prior emulsification and to be applied flow history, are crucial aspects that govern an emulsion rheological properties. Kim and Mason's (55) review focuses on the important fundamental aspects governing the rheological properties of concentrated emulsions near and above the jamming transition.

Developing and establishing a link between emulsion rheology and texture analysis could be really helpful to improve raw material choice for cosmetic formulations (56).

Jones et al. (57) examined both the flow behavior and the textural properties of pharmaceutical polymer gels and interpreted textural data using rheology in terms of shear stress shear rate. Also, Lukic et al. (58,59) studied the influence of emollients on rheological and textural properties of water in oil cosmetic creams to predict their sensory properties.

Effect of polymers on emulsion rheological behavior. Polymers are one of the main routes of modifying the rheological properties in cosmetic products. This also holds for emulsion-based systems where the rheological properties of the system can be impacted by the concentration of the emulsion and lead to glassy behavior as discussed earlier. However, for more dilute systems, the addition of polymers to impact the rheological response is the preferred route used by formulators. A complete analysis of the various types of polymers used for rheological modification is beyond the scope of this review. However, some of the more recent studies on polymer effects on emulsions are discussed in the following texts.

The objective of the research work by Gilbert et al. (60) was to evaluate the effect of various polymers on both the rheological and mechanical/textural properties of cosmetic o/w emulsions. To achieve this, eight hydrophilic polymers, natural [*Ceratonia siliqua* gum (carob) and xanthan gum], or natural modified [hydroxypropyl (HP) guar gum, hydroxypropylmethyl (HPM) cellulose, or hydroxyethyl (HE) cellulose], or synthetic [carbomer, polyacrylamide (PA) (and) C₁₃–C₁₄ isoparaffin (and) laureth-7, or ammonium acryloyldimethyltaurate/VP copolymer] were selected. Each one was incorporated in an o/w emulsion at a concentration of 1% w/w, and a formulation without any polymer was also prepared to be used as a control. The rheological and mechanical/textural properties of the equivalent dispersions were then investigated, and this assessment was carried out by analyzing continuous shear flow, creep recovery, and dynamic oscillatory tests. Penetration and compression tests were also performed using a texture analyzer. The effects of experimental parameters (probe type, speed of displacement, and diameter of the container) on the textural properties of the emulsions were examined. Rheological and textural data were then statistically analyzed, thus uncovering correlations between both approaches and highlighting the effects of incorporating the different polymers. The effect of the polymer was significant on most of the parameters collected from various tests. Emulsions containing synthetic polymers used as gelling agents [ammonium acryloyldimethyltaurate/VP copolymer–co-VP (AADMT), Laureth-7, C13–C14 isoparaffin, and PA, carbomer (PAA)] exhibited yield stress, high viscosity, high G' and G'' values corresponding

Table I

Values of Viscosity (Means \pm SD) Obtained at Different Shear Rates (in s^{-1}) from the Shear Flow Test for the Nine O/W Emulsions. Values of Viscosity (Pa.s) are Given in Descending Order for Each Shear Rate

Cream	η (0.1)	η (1)	η (10)	η (100)	η (1000)
PAA	748.2 \pm 35.2	162.7 \pm 9.2	43.8 \pm 1.3	7.7 \pm 0.1	1.6 \pm 0.0
AADMT–co-VP	380.4 \pm 13.1	105.7 \pm 1.5	25.3 \pm 0.1	4.7 \pm 0.1	1.0 \pm 0.0
PA	136.5 \pm 5.7	40.8 \pm 0.2	9.3 \pm 0.1	1.8 \pm 0.0	0.5 \pm 0.00
HP guar	108.2 \pm 0.4	19.2 \pm 0.3	3.6 \pm 0.0	0.76 \pm 0.00	0.18 \pm 0.00
Xanthan	128.4 \pm 9.3	20.1 \pm 0.4	3.2 \pm 0.0	0.44 \pm 0.00	0.10 \pm 0.00
HE cellulose	101.1 \pm 2.5	22.2 \pm 0.3	4.8 \pm 0.0	1.0 \pm 0.0	0.26 \pm 0.00
Carob	85.9 \pm 4.0	19.2 \pm 0.7	4.4 \pm 0.1	0.99 \pm 0.01	0.25 \pm 0.00
HPM cellulose	53.6 \pm 2.3	10.5 \pm 0.0	2.6 \pm 0.0	0.75 \pm 0.01	0.24 \pm 0.00
Control	42.4 \pm 2.3	8.6 \pm 0.4	1.5 \pm 0.0	0.27 \pm 0.00	0.07 \pm 0.00

Table II
Viscoelasticity Data (Means \pm SD) Obtained from the Strain and Time Sweep
Tests for the Nine O/W Emulsions

Product	G' (Pa)	G'' (Pa)
PAA	1,841.0 \pm 15.0	335.8 \pm 3.4
AADMT-co-VP	1,268.7 \pm 43.3	263.1 \pm 10.1
PA	668.0 \pm 13.2	161.1 \pm 3.3
Control	84.3 \pm 1.6	31.0 \pm 0.5
Xanthan	62.6 \pm 0.3	17.6 \pm 0.1
Carob	58.9 \pm 0.0	51.3 \pm 0.1
HP guar	56.5 \pm 0.9	35.0 \pm 0.4
HPM cellulose	48.6 \pm 0.3	27.2 \pm 0.4
HE cellulose	46.6 \pm 0.3	36.2 \pm 0.4

to a strong gel network, and a great resistance to penetration and compression. On the other hand, emulsions containing natural or modified polysaccharides (carob, HE cellulose, HPM cellulose, HP guar, and xanthan) displayed different shear thinning characteristics, low viscosity, and G' and G'' values and were less structured as behaving as viscous or weak gel systems. Among these polysaccharides, xanthan showed a singular behavior, in particular in terms of shear thinning and deformability it confers to emulsion.

Kettler et al. (61), characterized rheological properties of emulsions containing C₁₀–C₃₀ acrylate polymeric thickener (close to polyacrylic acid). They found that the physical network built up by acrylate polymers in the range of 0.1–1 wt% was the dominant factor for rheological properties and increases both the moduli and the viscosity of emulsions. They also showed that oil droplets size and distribution do not affect emulsion elasticity when the polyacrylate concentration is higher than 0.1 wt%. Concerning emulsions containing polysaccharides, very few studies deal with the impact of droplet size or chemical composition on textural or rheological properties of the emulsions; most results are related to much simplified emulsions, with very limited number of ingredients (62,63), and not necessarily cosmetic ones. The rheological behavior of various polymers in emulsions is highlighted in Tables I and II.

Nano-emulsions and processing challenges. Future directions for emulsions include the potential use of nano-emulsions which would potentially yield benefits in terms of optical clarity and potential enhancement of skin stratum corneum penetration of various actives. Nano-emulsions are a form of emulsion whose formation, properties, and stability are well discussed and reviewed in two publications (64,65). Although several articles on nano-emulsions indicate that nano-emulsions can be stable even by years, the small droplet size makes nano-emulsions break by the Ostwald ripening mechanism (66–68) in time periods too short so that to constitute a limitation for developing applications.

Emulsification processing can pose significant challenges. Kim and Mason (55) conclusively state that it is still challenging to formulate and to tailor emulsification processes for large-scale production of emulsions having desired compositions, droplet sizes distributions, and rheological properties. Formulators still regularly design emulsions and emulsification processes for particular applications based on modifying a set of compositional parameters and processing conditions empirically, often by trial-and-error or iterative approaches, until the resulting emulsion composition, structure, and rheological properties are within desired ranges. Although a lack of control over droplet polydispersity is typically one reason for the

persistence of empirical formulation approaches, other factors, such as the possibility of attractive interactions between droplets, can also be important in some cases. Although much progress has been made, there is still considerable room for improvement in the development of predictive tools for the design and formulation of emulsions, and no single theory or simulation yet describes emulsion rheology over the very broad range of possibilities of compositions and flow histories of these interesting systems.

CONCLUSION

The colloidal and complex fluid properties are critical in optimizing the performance of cosmetic products. In this review, it was described how the microstructural properties of various materials used in the formulation of cosmetic products affect and influence the rheological performance of the formulations. A deep understanding of rheology and factors that influence and govern it as well as its properties and the vast applications of rheology in the cosmetic industry is key in establishing structure–property–performance linkages. This is critical to the engineering and formulation of novel cosmetic products. As the new trends in cosmetics are moving toward increased personalization of cosmetic products and sustainability (69), a profound knowledge of rheology is an important skill that should be harnessed in ensuring that consumer needs are satisfied at all times.

The future direction of complex fluids used in cosmetic products is the utilization of bio-ingredients such as bio-surfactants (19,70), and biopolymers (71) as well as the utilization of an automated formulation platform which makes it possible to vary the formulation composition of each sample simultaneously thereby saving time and cost (72). The mass introduction of automated formulation into the cosmetic industry (production line) will be beneficial to formulation and postformulation processes in the industry because it enables its operator to perform complex formulations simultaneously as customized operations for consumers.

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