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INFLUENCE OF PROCESSING ON COSMETIC, PHARMACEUTICAL AND FOOD EMULSIONS QUALITY, STABILITY AND RHEOLOGY

Abstract: Many pharmaceutical, cosmetic and food processes, such as new ingredient selections, formulation preparations, material packaging, and shelf storage are associated with a complex flow of materials. The application and acceptance of pharmaceuticals, cosmetic and food are also dependent on the flow properties of the final product. Therefore, rheological measurements, as an important route to revealing the flow and deformation behaviors of materials, cannot only improve efficiency in processing but can also help formulators and end users to find that these products are of optimal quality for their individual needs.
Keywords: Emulsion stability, Quality, Rheology, Droplet Size Distribution

1. INTRODUCTION

1.1. Rheological Properties of emulsions

Emulsions are the most common type of delivery system used in cosmetics and pharmacy. They enable a wide variety of ingredients to be quickly and conveniently delivered to hair, skin and internal use as well [1]. Further, they represent the basis for the many food products, such as ice cream, butter, margarine, mayonnaise, etc. Generally, emulsions can be defined as a thermodynamicaly unstable heterogeneous system formed by at least two liquids that are at best only slightly soluble [2]. The internal phase is dispersed in the other in the form of small droplets, with diameters higher than 0.1 μm [3]. Emulsions can be made in different forms. The most common forms are oil-in-water (o/w), emulsions, which are composed of small droplets of oil dispersed in a continuous phase. The other type is water-in-oil (w/o)

emulsion, which is composed of small droplets of water dispersed in a continuous oily phase. Emulsions can also be multiple emulsions, water-in-oil-in-water (w/o/w) emulsions. W/o/w, multiple emulsions are composed of oily globules dispersed in an aqueous phase, which themselves contain aqueous microglobules [4].

The rheology of emulsions is focusing a great interest mainly due to its relationship with emulsion stability, the most important factor to be considered in emulsion quality and technology. Thus, the huge numbers of structural parameters that influence emulsion stability also affect rheology, a fact that makes a systematic understanding of the complex rheological response of emulsions difficult. The flow properties of an emulsion are among its more important physical characteristics. From a technical point of view, the unit operations related to the manufacture of an emulsion (mixing, pumping, filling, etc.) require the knowledge of its flow behavior

to assess mixing efficiency, power consumption, etc. [5]. The consistency of the emulsion is controlled by controlling the phase volume of the dispersed droplets, their size distribution and by the addition of various rheology modifiers such as 'thickeners' (e.g. polysaccharides) or finely divided inert solids (such as silica and bentonite clays). Panels for acceptability usually assess the consistency of an emulsion.

Rheological measurements (steady state, controlled stress and oscillatory measurements) provide information on the physical stability of the emulsion. A challenging prospect is to relate the rheological measurements to consumer perception. Emulsions used in personal care application vary in their consistency from 'fluid-like' consistency (as is the case with many lotions) to 'semi-solid' consistency (as is the case with many hand creams). This requires measurements under various deformations (or stresses).

It is also essential to carry out rheological measurements as a function of temperature to obtain information on the physical stability and consistency of the product. Since the life span of most personal care products is relatively short (3–5 years), development of the product should be fast. Accelerated storage testing is needed for prediction of the long-term physical stability of the formulations as well as the change of consistency with time [6].

Several procedures can be applied to predict such stability: (i) subjecting the formulation to temperature changes as well as temperature cycling. (ii) Application of high centrifugal forces to detect separation of the emulsion. (iii) Subjecting the emulsion to vibration and investigation of the resulting system by microscopy.

The above-accelerated tests are of limited use and the formulator faces a challenge for prediction. The main objective is to relate the long-term physical stability (over 6–12 months) with the short-term rheological measurements that are carried out in the first few weeks of storage.
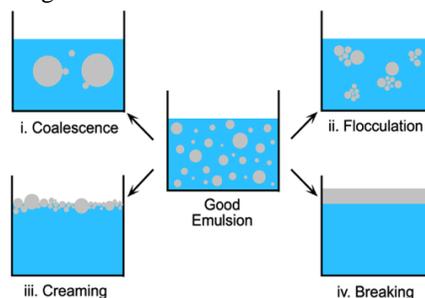

Figure 1. Schematic representation of stable emulsion and possible instabilities

Three different rheological measurements may be applied: (i) Steady state shear stress-shear rate measurements (using a controlled shear rate instrument). (ii) Constant stress (creep) measurements (carried out using a constant stress instrument). (iii) Dynamic (oscillatory) measurements (preferably carried out using a constant strain instrument).

2. EMULSION INSTABILITY

As has been previously mentioned, stability is the most important factor to be considered in emulsion technology and it is one of the most important factor for describing the emulsion quality. An emulsion is stable when there is no change in the size distribution or the spatial arrangement of droplets over the experimental time-scale. The three main mechanisms of destabilization are the flocculation, creaming and especially coalescence of oil droplets (figure 1). Creaming results from the action of gravity on oil droplets, of lower density than the continuous medium, yielding a vertical concentration gradient of droplets but no change in the overall size distribution. The rupture of the emulsion may be detected by the appearance of a separated aqueous phase at the bottom. The aggregation of

the droplets without breakdown of the emulsifier layer is called flocculation. Flocculation may frequently be an intermediate step to the rupture of the emulsion by coalescence, which implies the irreversible process of the droplets becoming larger yielding a flee oil phase at the top of the sample.

The dominant mechanism of instability will be determined by the interparticle and hydrodynamic interactions. Whether or not aggregation or coalescence occurs, depends on the composition and surface viscoelasticity of the adsorbed surface layer [7] and may be predicted by the classical DLVO theory [8] or, more usually, combined with the steric stabilization theory [9].

All of these mechanisms are interrelated among them. Thus, flocculation generally favors creaming since the aggregates of oil droplets have a settling velocity higher than that of the individual droplets or, on the contrary, even when creaming takes place without flocculation the final state is a flocculated emulsion that may favor coalescence.

3. INFLUENCE OF PROCESSING ON EMULSIONS STABILITY

Emulsification is a complex unit operation in which many variables influence the processing and the final rheological characteristics of the product. The manufacture of emulsions is an energy-intensive and highly dynamic process, which usually requires the application of mechanical energy. The two critical steps are the consecutive disruption of droplets and their coalescence, both of which are favored by an intense agitation. Consequently, the improvement of the emulsification process requires the measurement of the droplet size of the dispersed phase and its polydispersity, as well as knowledge of its rheological properties [10]. The emulsification process may be greatly affected by the viscous and viscoelastic properties of the continuous phase at which the disperse phase is added. Thus, Gallegos et al. [11] have studied the influences of temperature, agitation speed and emulsification time on droplet size distribution and viscoelasticity of vegetable oil-in-water emulsions. These emulsions were manufactured using an anchor impeller and are stabilized by a well-known polyoxyethylene nonionic surfactant, which produces a low-viscosity micellar continuous phase.

Figure 4 shows the droplet size distribution (DSD) curves as a function of the agitation speed of the anchor impeller (N). A well-pronounced maximum at droplet diameters larger than 5 μm and a very smooth maximum at lower sizes are noticed, although the curves move to lower sizes as N increases. The broad droplet size distribution at these lower agitation speeds is evidencing that the disruption of the droplets has occurred, and a coalescence process follows it. On the other hand, only one maximum was found when the emulsion was prepared with a rotor-stator turbine (4000 rpm), evidencing that the most of the droplets are of the same size and that there was not the coalescence process. These DSD curves determine the linear viscoelastic response of the emulsions. The agitation speed also influences the storage (G') and the loss (G'') modulus values. As can be observed in Figure 5, the systems prepared with the anchor impeller show higher values of the loss modulus at lower frequencies, although G' and G'' curves crossover at a frequency ω_c (critical frequency). Above this characteristic frequency, a plateau region in G' develops as agitation speed increases [11]. On the contrary, the emulsion prepared with the rotor-stator turbine only shows a plateau region, similar behavior to that found for highly concentrated o/w emulsions stabilized by a macromolecular emulsifier [12]. From this observation it can be concluded that

emulsion processed by a rotor-stator turbine posses linear viscoelastic region over a wide range of frequencies.
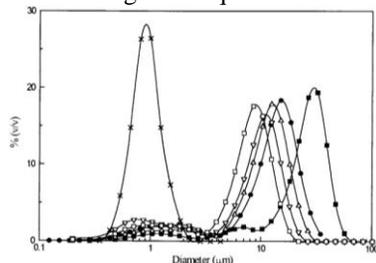

Figure 2. Droplet size distributions for emulsions containing NPE-PEG-10, prepared with different process conditions, (■100 rpm, ● 150 rpm, Δ200 rpm, ▽ 250 rpm, □ 300 rpm, x 4000rpm), reprinted from [11]

Furthermore, long plateau of G' corresponds to an emulsion having much smaller sizes and narrower droplet distribution than those prepared with the anchor impeller (as confirmed at the figure 2). When processing emulsions, the temperature is also an important parameter. An increase in temperature favors the coalescence process, leading to larger droplet sizes and broader distributions. In the same way, the plateau region in G' tends to vanish and the crossover frequency increases. On the contrary, an increase in the emulsification time enhances the development of the plateau region.
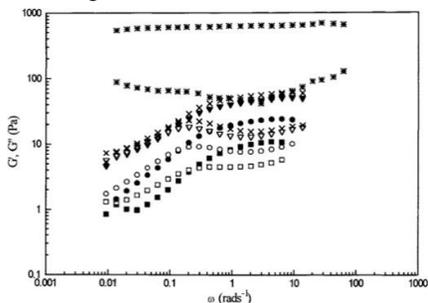

Figure 3. Evolution of the storage and loss moduli with frequency, for an emulsion containing NPE-PEG-10 as emulsifier, prepared with different process conditions, (□ 100 rpm, O 150

rpm, V 250 rpm, X 300 rpm, + 4000 rpm). Reprinted from [11]

4. INFLUENCE OF STORAGE TIME FOR EMULSION AT DIFFERENT PH VALUES

Romero et al. (2009) [13] studied the influence of pH values on linear viscoelasticity and droplet size distribution for protein stabilized O/W emulsions. Droplet size distribution measurements and linear viscoelastic properties were carried out along storage time, in order to study long- term stability for emulsions containing 5wt% CF at different pH values.

Figure 4 shows the evolution of DSD profiles along storage time for emulsions prepared at two different pH values. The first value selected is close to the lowest protein solubility (pH 3.4), whereas the second corresponds to the control emulsion prepared at the highest protein solubility experimentally studied (pH 11.5), Romero et al. (2009) [13]. An evolution towards larger sizes and wider DSD polydispersity takes generally place along time. However, the presence of a high level of electrostatic interactions among protein segments (i.e. at pH 11.5) causes inhibition of such evolution.
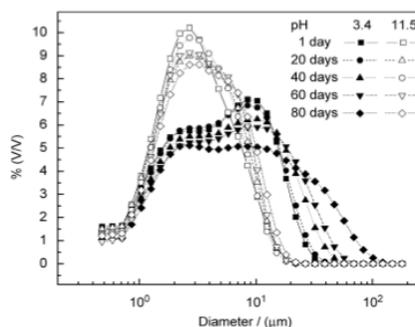

Figure 4. Evolution of droplet size distribution for emulsions containing 75 wt% oil and 5 wt% crayfish flour processed at 6000 rpm at different pH values, as a function of storage time. Reprinted from [13]

At the isoelectric point (pI), at which the net charge at protein surfaces is zero, the above-mentioned evolution is apparent, being typical of emulsions undergoing destabilization by creaming and/or coalescence. Occurrence of phase separation by creaming process has been previously reported for CF stabilized emulsions prepared at high pH and CF concentration lower than 1.25 wt% (Romero et al., 2009).

5. CONCLUSION

In presented paper, the influence of processing parameters on emulsion stability and quality has been briefly discussed. It is shown that parameters such as agitation speed, temperature and pH value of the continuous phase can have great influence on the emulsion stability. One of the most important parameters regarding emulsion stability is in fact the droplet size distribution. It can be concluded that the narrower DSD leads to stable emulsion, while the broader distribution is evidencing that emulsion is unstable. Broadening of DSD leads to conclusion that instability processes, such as coalescence and/or floaculation has already occurred. Further, the importance of short-term rheological measurements for estimating emulsions long-term properties has been briefly discussed in chapter one. It is also shown how processing parameters are influencing the rheological properties of emulsion in terms of storage and loss moduli of an emulsion. It is shown that processing emulsion on higher agitation speeds improves the linear viscoelastic region of the emulsion.

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