Rheological Study of a Pickering Emulsion Stabilized by Algerian Clay Particles

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ABSTRACT: *A Pickering Oil/Water (O/W) emulsion was formulated based on Algerian bentonite particles with small amounts of synthetic surfactant ranging between 0.01 and 0.05 %. A rheological study was carried out on the emulsions studied after 18 months of aging using a parallel plate geometry. The rheological study, under variable shear, has shown that the viscous behavior of these emulsions is of structural type, with the presence of two Newtonian regions at low and high shear. The oscillatory test revealed that emulsions have the character of a viscoelastic gel which is practically insensitive to frequency decreasing sweep and therefore potentially stable over time. Results showed that 7% of bentonite and 0.015% of cationic surfactant (cetyltrimethylammonium bromide) are necessary to obtain a Pickering emulsion with an adequate rheological behavior for a cutaneous application.*

KEYWORDS: *Bentonite; Pickering emulsion; Viscoelasticity; Stability.*

INTRODUCTION

Emulsions stabilized by solid particles or Pickering emulsions present a new field of research for pharmaceutical applications.

Bentonite, a natural clay widely available in nature, is widely used for the formulation of pharmaceutical Pickering emulsions. It has been included in the Foods excipients database and Drug Administration (FDA) and is used in many forms of drugs [1].

These clay particles can be advantageously treated in order to become sufficiently hydrophobic and compatible with the desired applications [2-4].

Bentonite is largely available in Algeria. There are

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1021-9986/2022/1/346-351 6/$/5.01

several deposits with a large exploitation capacity which can meet local needs and may even find export outlets.

The characteristics of this bentonite are proven by several research studies, namely its high adsorbing power as well as its swelling power allowing it to be an emulsion stabilizing agent by excellence [5].

Rheology is a key parameter for the stability study of semi-solid products and particularly emulsions.

It is well established that many cosmetic products such as emulsions show a non-Newtonian shear thinning behavior in which the viscosity decreases as a function of the increase in shear rate[6-8]. This behavior strongly depends on their composition as well as the conditions of the formulation. Viscoelasticity is the most important characteristic of semi-solid products such as emulsions, it is defined as a simultaneous existence of viscous and elastic properties [9].

A series of formulations of Pickering emulsions based on Algerian bentonite has been formulated. These emulsions are composed of bentonite as a stabilizing agent, a cationic surfactant CTAB to improve the hydrophobicity of bentonite, and salt as a flocculating agent.

The adsorption of a cationic surfactant on the negative surface of the clay particles forms an alkyl film on the surface, which partially covers the surface of the clay. This has the effect of modifying the wetting properties of the particles, thus promoting the adsorption of the particles at the oil/water interface to form an elastic film which promotes the stability of the emulsion. The presence of cationic surfactant on the surface of the clay also makes it is possible to neutralize the negative charges on the surface and reduce the electrostatic repulsions between the particles, which promotes the bringing together of the particles from one another and their flocculation [7, 10].

This physical modification was also used for other solid particles. The choice of surfactant depends essentially on the physicochemical properties of the solid particles used. Negatively charged particles such as hydrophilic silica particles or pectin for example require cationic surfactant such as surfactants of the ammonium class [11, 12] or benzalkonium chloride [13] which changes the particle surface through electrostatic interactions, whereas negatively charged particles (laponite, boehmite, and latex) only change with anionic surfactants such as sodium dodecylsulphate [14] with physical crosslinking interactions [13, 15].

The nonionic surfactant of the polyether family (polyethylene glycol) could adsorb to the surface of silica particles, giving rise to the change in wettability of the hydrophilic particles and making them surfactants [16].

In the case of clay particles, flocculation is ensured by the presence of electrolytes in small quantities. The addition of salt promotes, the adsorption of clay particles at the oil/water interface, and the neutralization of their charges on the surface. This will produce a reduction in the thickness of the electrical double layer and, at the same time, a reduction in the electrostatic repulsion interactions between the clay platelets. This mechanism generates partial flocculation of the particles and the formation of a mechanical barrier around the droplets preventing their coalescence and leading to the formation of a three-dimensional network, which slows down the creaming [3, 10]. The most widely used salt for the preparation of O/W emulsions stabilized by clay particles is NaCl.

The concentrations of these different constituents were optimized by the experimental design methodology based on the study of the physical stability of the emulsions at the macroscopic scale [17].

In order to predict the stability of these emulsions in the long term, we proceeded to a rheological study of the emulsions that remained stable (zero creaming rate) after eighteen (18) months of aging.

EXPERIMENTAL SECTION

Materials

We used bentonite from Maghnia (Hammam Boughrara deposit, North-West Algeria), provided by the company BENTAL (Algeria). It is at 3% sodium treated and activated, composed of 93% montmorillonite and 7% illite with a specific surface area of 872 m^2/g, a swelling index of 35 cm^3/g, a plasticity index of 120%, a Cation Exchange Capacity (CEC) of 0.91 eq/g, and an average size particle of 74μm [18-20].

The cationic surfactant cetyltrimethylammonium bromide or CTAB (of formula $C_{19}H_{42}BrN$ with a molar mass of 364.45 g/mol) is a BIOCHEM Chemopharma brand, and sodium chloride NaCl is branded (Merck Eurolab, for analysis). The soybean oil is graciously supplied by the company Cevital (Algeria) and meets the specifications of the pharmacopeia, its viscosity is 80 mPa.s at 20 °C and its density is 916 to 922 g/cm^3. [1, 21].

Emulsions Preparation

The aqueous phase is prepared by mixing the bentonite, CTAB, and NaCl in water with stirring at a speed of 670 rpm for 90s. The oily phase is then added dropwise while maintaining stirring at the same speed using a Heidolph model RZR1 propeller stirrer. Once all of the oily phases are incorporated into the aqueous phase, the mixture is homogenized using an IKA brand Ultra-Turrax type homogenizer, model T10 at a speed of 14500 rpm. during 15 min. The prepared emulsions are stored at room temperature for the study of physical stability.

The composition of the studied formulations is shown in Table 1.

Rheological Study

The rheological study is carried out using a Paar Physica rheometer (Rheolab MCR 300) provided with the US 200 software to control the device and data processing. The geometry used is a parallel plate, with a diameter of 25mm and a gap of 1mm. All measurements were carried out at 20°C.

The main parameters were evaluated, in particular, the flow model and viscoelasticity.

RESULTS AND DISCUSSION

Rheological Behavior of Emulsion

The mechanical behavior of the emulsions studied is presented in Fig. 1. The shear rate varied from 10^{-4} to 10^3 s^{-1} at 20°C.

We note that the three emulsions studied have the same rheological behavior. It is a structural behavior that responds to the model of Cross which is written according to Eq. (1) [22].

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda \dot{\gamma})^n} \quad (1)$$

Where λ and n are constants; λ is a characteristic relaxation time, η_0 and η_∞ are the respective zero and infinite shear viscosities.

At rest, the emulsions have a high viscosity of the order of 5000 Pa.s, which indicates their stability. At a critical shear rate having a value $\dot{\gamma}_c = {}^{1}/_{\lambda}$ of the order of $10^{-3}s^{-1}$, the structure of the product begins destructuring and consequently, viscosity decreases to reach very low values of the order of 10^{-2} Pa.s.

Table 1: Composition of the studied formulations.

N°	Bentonite (%)	CTAB (%)	NaCl (mol/l)
01	7	0.015	0.015
02	7	0.015	0.05
03	7	0.05	0.05

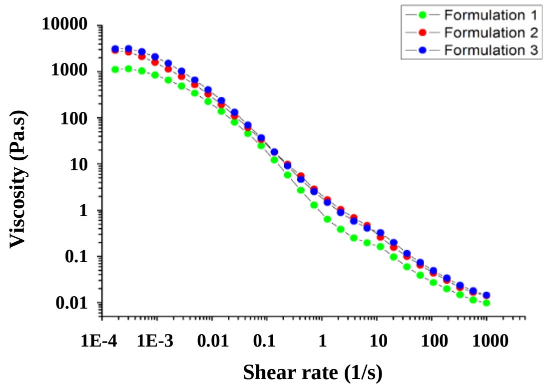

Fig. 1 Typical flow curves and their adjustment by Cross model, at T = 20°C.

Based on these characteristics, our product remains stable at rest (on storage); at the same time it is easy to spread on the skin with a low shear rate, and destruction allows the release of the active ingredient.

CTAB does not require the addition of other additives to give such rheological behavior to the formulation. Marto et al. used benzalkonium chloride to stabilize an emulsion based on corn starch particles. This emulsion required the addition of disteryldimonium chloride (DMDC) as a rheological modifier [23].

Viscoelasticity

An emulsion is considered stable if the modulus of elasticity (G') is greater than the loss modulus (G") and both G' and G" are independent of frequency, particularly in the domain of very low frequencies, associated with longer times of stability ($f_r \sim 1/t$). Under these circumstances, the emulsion displays gel-like properties. An emulsion is classified as physically unstable if G" > G' and G' and G" are dependent upon frequency since by these criteria, the emulsion exhibits the properties of a dilute solution [7, 8, 24, 25].

The representative curve of viscoelasticity for emulsion No. 1 (FIG. 2) shows that G' is greater than G",

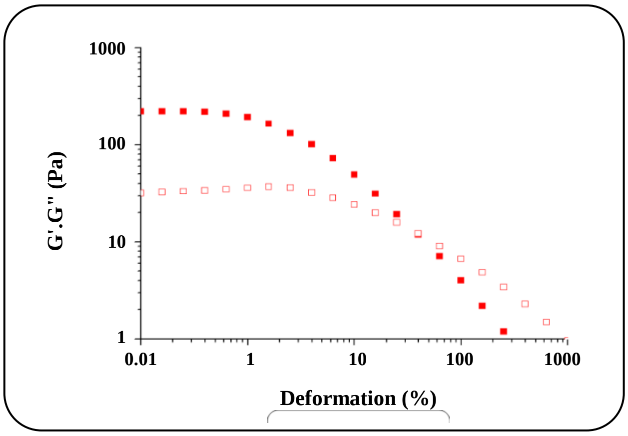

Fig. 2: Variation of G'(■) and G''(□) as a function of the deformation for formulation N°1.

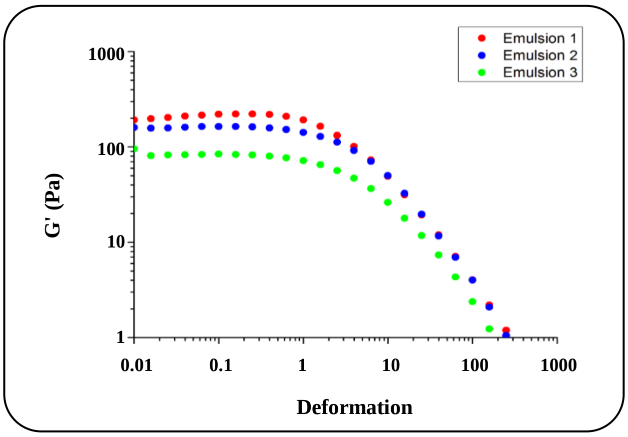

Fig. 3: Variation of G' for formulations as a function of strain.

which makes it possible to deduce that the behavior of the emulsion is that of a viscoelastic solid whose structure has certain rigidity and therefore potentially stable [26,27]. The same observation stands for the other two formulations.

This behavior results essentially from the state of flocculation of the drops, induced by the attraction of the solid particles adsorbed at the interfaces. It is the flocculated dispersions that give the best results in terms of stabilization [28].

Fig. 3 shows the variation of the elastic modulus G' as a function of strain, γ, for the 3 emulsions. Emulsions No.1 and No2 appear to have similar behaviors. The value of G' in the viscoelastic linear region is substantially the same, despite the difference in salt concentration, 0.015 M for formulation No1 and 0.05 M for formulation No. 2. This suggests that the amount of salt needed to flocculate the structure is relatively low. Indeed, it is known in the literature that the use of low salt concentration in Pickering clay emulsions allows the formation of a three-dimensional network of flocculated clay particles having a thixotropic rheological behavior [7, 26]. This network promotes the stability of the emulsion. It can therefore be concluded that the variation of the salt concentration does not affect the rheological behavior of the emulsion.

Formulations No. 2 and No. 3 differ only in their content of cationic surfactant, CTAB, 0.015%, and 0.05%, respectively. Obviously, the increase of the CTAB has caused a reduction of the storage modulus G 'of the emulsion No. 3 and therefore its elasticity.

Torres et al.[29] studied the influence of CTAB on the rheological behavior of emulsions stabilized by bentonite particles. They noticed that emulsions without CTAB are very unstable viscous liquids that break quickly. The most stable emulsions are those produced in the presence of small amounts of CTAB.

Torres et al.[7] explain the decrease of the modulus of elasticity as a function of the CTAB percentage by the formation of large aggregates of clay particles. The value of using the CTAB is based on its adsorption ability on the negatively charged clay particles, forming a surface alkyl film that partially overlies the surface of the clay. This has the effect of modifying the wetting properties of the particles thus promoting the trapping of the particles at the oil/water interface to form an elastic film which promotes the emulsion stability.

In the present study, and from an elasticity point of view, 0.015% of CTAB is sufficient to stabilize a Pickering emulsion containing bentonite particles. The antibacterial activity of CTAB also influences the improvement of the emulsion stability. According to *Fasihi et al.* the action of polyvinyl alcohol is not limited to its emulsifying character but is mainly due to its very important antibacterial properties [30].

Viscoelasticity Frequency Sweep

This technique allows for assessing the stability of an emulsion. The smaller the frequency, the longer the appreciation time is. When the frequency tends towards zero, the time of appreciation tends towards infinity, which

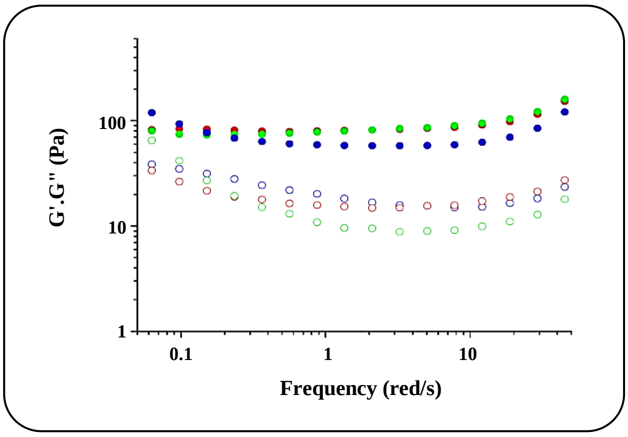

Fig. 4: Variation of G '(full symbols) and G' '(empty symbols) as a function of frequency.

makes it possible to make projections for long lengths of time and to see if the parameters increase or decrease.

An emulsion is considered stable if the modulus of elasticity G' is greater than the storage modulus G" and the two G' and G" are independent of the frequency since under these circumstances the emulsion has the properties of a gel. It is classified as a physically unstable emulsion if G" > G' and G' and G" depend on the frequency since these criteria reflect the properties of a dilute solution[7].

According to Figure 4, G' is larger than G" for all the studied formulations, therefore they behave like a viscoelastic gel. The first condition of stability is verified.

According to the same figure, the two elasticity and storage modules are independent of the frequency. This indicates the physical stability of the studied emulsions (Formulations 1, 2, and 3).

CONCLUSIONS

Algerian bentonite is an excellent stabilizing agent when used in O / W emulsions containing small amounts of cationic surfactant.

The rheological study of the formulations after 18 months of aging showed that the three emulsions are characterized by a viscoelastic behavior which ensures stability over time. The modulus of elasticity is indeed much higher than the loss module and these modules are independent of the frequency.

It is found that from a theological point of view, the most suitable formulation for the intended application is composed of 7% of bentonite, 0.015% of CTAB, and 0.05M of NaCl.

Received :May 14, 2020 ; Accepted : Sept. 7, 2020

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