



HAL
open science

On the key role of process parameters to control stability and properties of Pickering emulsions stabilized by montmorillonite

Sabine Vassaux, Michel Grisel, Géraldine Savary, Loïc Le Pluart

► To cite this version:

Sabine Vassaux, Michel Grisel, Géraldine Savary, Loïc Le Pluart. On the key role of process parameters to control stability and properties of Pickering emulsions stabilized by montmorillonite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2019, 583, 10.1016/j.colsurfa.2019.123952 . hal-04170964

HAL Id: hal-04170964

<https://imt-nord-europe.hal.science/hal-04170964v1>

Submitted on 8 Aug 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

On the key role of process parameters to control stability and properties of Pickering emulsions stabilized by natural clay montmorillonite particles

Sabine Vassaux^{*(a)}, Michel Grisel^{*(a)}, Géraldine Savary^(a), Loïc Le Pluart^(b)

- (a) Normandie Univ, UNIHAVRE, FR 3038 CNRS, URCOM laboratory, 76600 Le Havre, France, sabinevassaux@yahoo.fr ; michel.grisel@univ-lehavre.fr ; geraldine.savary@univ-lehavre.fr
- (b) Normandie Univ–UNICAEN, UMR CNRS 6507, FR 3038, ENSICAEN & Université de Caen, LCMT laboratory, 14050 Caen, France, loic.le_pluart@ensicaen.fr

PERSONNEL

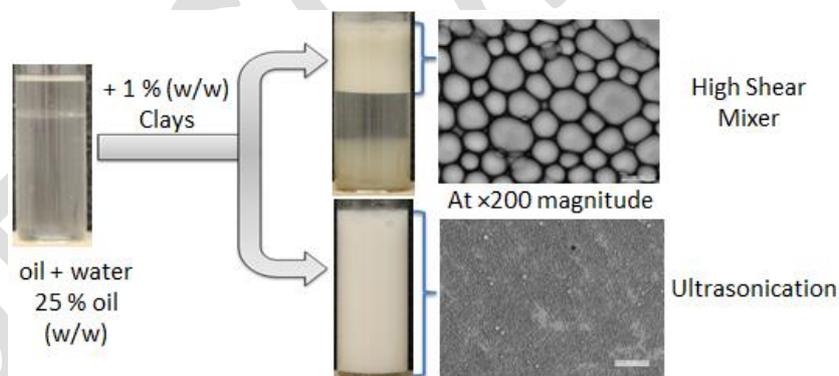
Abstract

In cosmetic applications, emulsions are largely developed thanks to organic surfactants which lower the interfacial oil/water tension thus enhancing dispersions stability. However, these organic surfactants may raise toxicity towards the skin and environmental contamination issues. The objective of the present work is to develop innovative emulsions stabilized by natural montmorillonite particles. The influence of the dispersion and emulsification times as well as the homogenization process (high shear mixer or ultrasonication) was investigated. Obtained mixtures were conditioned at 40°C and their properties were studied over 72 hours from macroscopic aspects, emulsified phase microstructure and droplet size assessments. The emulsion microstructure has been shown to be highly sensitive to the manufacturing parameters. When emulsification time increases, droplet size decreases leading to more stable emulsions. In addition, the macroscopic aspect of emulsions is mostly governed by the homogenization process as ultrasonication efficiently produces fully emulsified mixtures while high shear mixing does not. Therefore, the ultrasonication process is demonstrated as an efficient tool to produce homogeneous stable Pickering emulsions without surfactant and displaying microscopic droplet sizes. It also constitutes a promising method to control parameters in industrial processes when manufacturing emulsions.

Keywords

Pickering Emulsion, Clay particles, Montmorillonite, Stability, Process, Ultrasonication, Mechanical energy, Emulsification

Graphical abstract



1. Introduction

Nowadays, emulsions meet an important interest in several industries including food (Verkempinck et al., 2018), petroleum (Atta et al., 2014; Ronald and Luis, 2016), pharmaceutical (Bouyer et al., 2012) or cosmetic (Agredo et al., 2019; Terescenco et al., 2018) applications. As these emulsions are thermodynamically unstable, their development is guaranteed by organic surfactants which limit destabilization phenomena by lowering the oil/water interfacial tension. However, these conventional organic surfactants may raise toxicity issues to the skin (Lémery et al., 2015) and contaminate the environment (Könnecker et al., 2011; Lechuga et al., 2016). Therefore different

studies developed conventional surfactant-free dispersions such as so-called historical Pickering emulsions (Pickering, 1907; Ramsden, 1904) stabilized by solid colloidal particles.

Thus, stable Pickering emulsions were recently developed in food applications (Costa et al., 2018; Young et al., 2018; Zhang et al., 2018), in the oil recovery field (Li et al., 2018; Liu et al., 2018) or in the development of polymeric materials (Zeng et al., 2017). Compared to traditional emulsions, the Pickering emulsions resist destabilization phenomena thanks to particles adsorption mechanism at the oil/water interface. Due to high desorption energy per particle (Aveyard et al., 2003; Tzoumaki et al., 2011), such a system induces irreversible interfacial adsorption of particles thus assuring a high stability over time for the resulting mixture (Björkegren et al., 2017; Yan et al., 2015; Yusoff and Murray, 2011).

To develop stabilized oil/water/particle systems, previous studies used various particle types such as silica (Frelichowska et al., 2009; Katepalli et al., 2017; Vignati et al., 2003; Yan et al., 2015), clay (Ganley et al., 2017; Garcia and Whitby, 2012; Guillot et al., 2009; Jurgelane et al., 2017) or cellulose particles (Cherhal et al., 2016; Gestranus et al., 2017; Lu et al., 2018; Paximada et al., 2016). In other cases, hydroxyapatite (Zhang et al., 2017), whey protein (Destribats et al., 2014) or iron oxide particles (Udoetok et al., 2016) were also proven quite effective to stabilize oil/water emulsions. However, emulsion stability is not only affected by the nature of particles as for a given chemical composition the particle shape itself also plays a significant role on stability (Katepalli et al., 2017; Madivala et al., 2009).

In fact, the production of Pickering emulsions depends on factors related to both the formulation composition and the manufacturing process (Hall et al., 2011; Rosdi et al., 2018). As an example, several research studies have investigated the effect of the particle size (Ge et al., 2017; Tsabet and Fradette, 2015), particle wettability (Binks and Lumsdon, 2000; Björkegren et al., 2017; Li et al., 2012) or particle concentration (Frelichowska et al., 2010; Kargar et al., 2012; Yan et al., 2015). The influence of the dispersed phase nature (Fallah et al., 2018) and the oil/water ratio (Yan et al., 2015; Zhang et al., 2017) has also been investigated.

But Pickering emulsions properties also strongly depend on manufacturing process parameters (Chevalier and Bolzinger, 2013). Emulsions can be developed using various homogenizers such as high shear mixers, ultrasound, colloid mills or high-pressure valve homogenizers (Trujillo-cayado et al., 2018); further studies have investigated the influence of parameters such as the temperature (Li et al., 2018; Tzoumaki et al., 2011) or the stirring rate (Fallah et al., 2018) on emulsion properties.

However, some information is still missing in the development and the production of Pickering emulsions.

- On the one hand, few studies (Jurgelane et al., 2017) take an interest to the development of Pickering emulsions for specific cosmetic applications.
- On the other hand, the study of the emulsification process is poorly documented (Tsabet and Fradette, 2015) and a little knowledge is available about the effect of manufacturing parameters on both the microstructure and the stability of Pickering emulsions.

Yet, the industrial process development of emulsion-based products is an essential step which often results in loss of time, material waste and high development cost (Hall et al., 2011). At first view, it is therefore essential to study how process parameters may impact emulsion characteristics and stability. Furthermore, since emulsions are generally prepared in two steps including first a particle dispersion step by ultrasonication followed by an emulsification step with a high shear mixer (Ashby and Binks, 2000; Frelichowska et al., 2009; Pichot et al., 2009; Yan et al., 2015), a waste of time and

failings in the continuous control of properties for an industrial manufacture scale-up can be assumed.

Therefore, the main objective of this paper is to develop Pickering emulsions stabilized by clay particles for cosmetic applications with a unique homogenizer device. The second aim is to study the influence of manufacturing parameters on emulsions stability and properties in order to optimize the manufacturing process. For this purpose, the influence of different factors (dispersion time, emulsification time, energy...) has been investigated on emulsions properties. Emulsions were prepared in different dispersion and emulsification conditions using a high shear mixer on the one hand and an ultrasonic probe on the other hand. As the emulsion stability is greatly influenced by the storage temperature (Fallah et al., 2018), samples were stored at 40°C to accelerate aging phenomena. Emulsions stability and properties were then monitored and characterized during 72 hours. Results of this study will allow identifying the influence of process parameters and will determine how it is possible to obtain stable Pickering emulsions based on clay particles.

2. Materials & Methods

2.1. Materials

2.1.1. Raw materials

Three raw materials were selected to prepare emulsions:

- As the skin pH is comprised between 4.2 and 6.8 (Wagner et al., 2003), a phosphate buffer solution (pH= 5.0, $\sigma=1150 \mu\text{S}/\text{cm}$, 20°C) was prepared to allow controlling the emulsions pH. Sodium hydrogen phosphate NaH_2PO_4 was firstly dissolved in water to obtain a solution concentration of 0.02 M, then pH was adjusted with few drops of a NaOH solution.
- Isohexadecane ($\rho= 0.8 \text{ g}/\text{cm}^3$) was selected as the oil phase and supplied by Croda France.
- Natural clay montmorillonite particles, noted MMT, were chosen as the solid stabilizer due to its natural, environmental and cosmetic-friendly character. The product Nanofil EXM 588 was supplied by Süd Chemie (Germany).

During experiments, the clay powder was used as commercially provided, with storage at 40°C to prevent water absorption.

2.1.2. Emulsion manufacture

Manufacture procedure used as reference

The parameters of model emulsions stabilized by MMT were respectively fixed at 1.00 % (w/w) MMT concentration C_{MMT} (Equation 1) and at 25.0 % (w/w) isohexadecane fraction as defined by Equation 2.

$$C_{\text{MMT}} = \frac{m_{\text{MMT}}}{m_{\text{MMT}} + m_{\text{oil}} + m_{\text{water}}} \quad (\text{Equation 1})$$

$$f_{\text{oil}} = \frac{m_{\text{oil}}}{m_{\text{oil}} + m_{\text{water}}} \quad (\text{Equation 2})$$

In order to process emulsions, 0.20 grams MMT were firstly dispersed into a certain amount of the buffered aqueous phase (Figure 1, step ①) in a glass tube (Height 100 mm, \varnothing 24 mm). Then, the oil amount was added to the clay/buffered dispersion and emulsified (Figure 1, step ②).

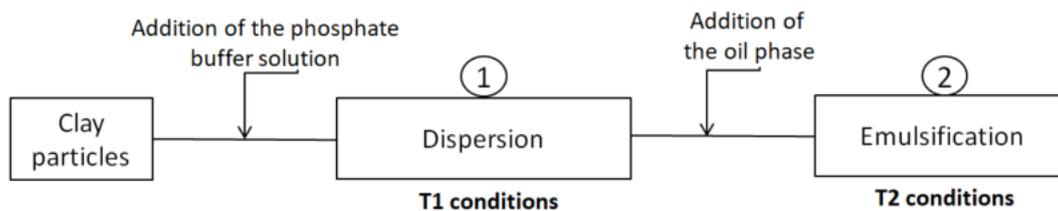


Figure 1: Fabrication route of emulsions stabilized by clays

Both the dispersion ① and emulsification ② steps were performed in an ice bath to control the manufacture temperature and prevent overheating due to emulsification energy. Thus, the final emulsion temperature was measured and did not exceed 30 °C. During the emulsification step, the homogenizer probe extremity was accurately positioned at the buffer solution/iso-hexadecane interface. At the end, emulsions were degassed and finally conditioned in sealed glass tubes at 40°C during 72 hours to accelerate the ageing and destabilization phenomena. In relation to Figure 1, dispersion and emulsification steps occurred in respective specific T1 and T2 conditions which are more detailed hereunder.

Influence of manufacturing parameters

In this study, two different homogenizers were selected to prepare emulsions:

- A high shear mixer (IKA Ultra-Turrax® T25 digital) equipped with a micro S25-18G dispersing tool (noted HSM) (max speed: 24,000 rpm)
- An ultrasonic processor (Fisher Scientific FB-705 Sonic Dismembrator, 20 kHz) equipped with a microtip probe (noted US) (maximum amplitude: 100 %)

The influence of both the dispersion and emulsification time was investigated on properties and stability of model Pickering emulsions for each homogenization process, as schematized on Figure 2.

More precisely, the dispersion time influence was firstly studied using the high shear mixer. Clay particles were dispersed in the buffer solution at a fixed 15,000 rpm speed. The dispersion time (T1) was successively tested for different periods of time (2, 4, 6 minutes) whereas the emulsification conditions were 4 minutes at 20,000 rpm (Figure 2A, triangles). In a second part, emulsions were prepared according to 2, 4, 6 emulsification times while keeping dispersion time constant (2 minutes) (Figure 2A, circles).

The other strategy consisted in producing emulsions using an ultrasonic homogenizer with identical emulsification times as above (2, 4, 6 minutes). The dispersion energy and time were respectively fixed at 20 % amplitude and 2 minutes whereas the emulsification energy equals to 20 % or 100 % (Figure 2B).

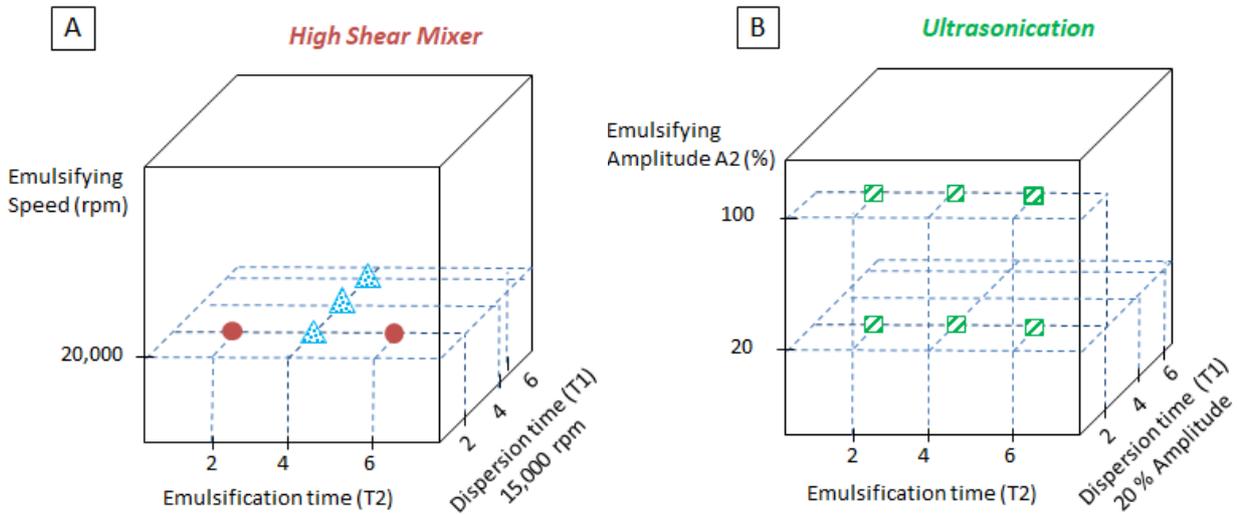


Figure 2: Schematic 3D representation of all tested manufacturing configurations

To summarize, the influence of the different factors exposed above was studied on emulsion initial microstructure and stability to optimize the process. Corresponding dispersions configurations were codified as follows for clarity:

Examples

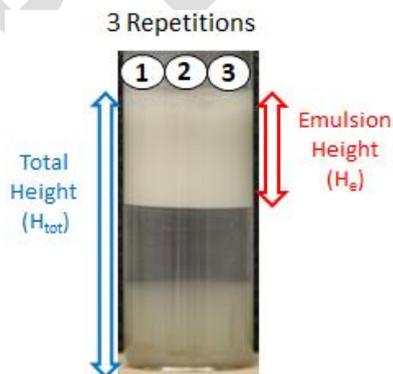
F- HSM-DT1/ET2
or
F- US-DT1-ET2-A2

With:

- F: Formulation
- HSM: High Shear Mixer
- US: UltraSonication
- T: Time
- D:Dispersion
- E: Emulsification
- A: Amplitude

2.2. Methods

Emulsions properties and stability were characterized over time at 24, 48 and 72 hours. Photographs allowed observing phase separation over time and assessing the emulsifying ability, as reported elsewhere (Ye et al., 2017). An emulsifying index (EI) was defined in accordance to Figure 3 and Equation 3 in order to describe macroscopic phase separation. More precisely, the emulsion height (H_e) and the total height (H_{tot}) were measured by digital image analysis (Image J software) at three positions (1, 2, 3) on the mixtures photographs.



$$EI = \frac{\text{Average } (H_e^1 + H_e^2 + H_e^3)}{\text{Average } (H_{tot}^1 + H_{tot}^2 + H_{tot}^3)} \times 100$$

(Equation 3)

Where:

- H_e : Emulsion Height
- H_{tot} : Total Height of mixture

Figure 3: Definition of the Emulsifying Index (EI)

The emulsion microstructure was also assessed using an optical microscope (Leica DMLP microscope) equipped with a camera under the bright field. A Leica IM 1000 software was used to acquire micrographs under magnifications x100 and x200. Emulsions droplets size distributions were determined by static light scattering (SLS) using a laser diffraction particle size analyzer (Shimadzu SALD-7500 Nano) equipped with a violet semiconductor laser (λ : 405 nm).

Emulsions droplets sizes were characterized under dilution by dispersing the samples in a batch cell of deionized water. As D.Terescenco describes (Terescenco et al., 2018), diluted emulsion samples were stirred during the measurement and droplet size distributions were acquired using a Wing SALD II software.

In order to enhance reliability, measurements were performed twice within the whole emulsified phase produced with the high shear mixer. For these last emulsions, a 50 % diameter (D50) was used to highlight global evolutions of droplet size distributions. As D50 corresponds to the diameter which splits the distribution in two identical halves, this indicator constitutes one of the most meaningful values for particle size distributions. For ultrasonicated emulsions displaying higher emulsifying abilities, droplet size distributions were then thoroughly assessed at the top (T), middle (M) and bottom (B) locations of the emulsified phase.

Thus, the visual observation, droplet size distributions and optical microscopy made possible to assess the ability of prepared Pickering emulsions to resist to coalescence in different manufacturing conditions.

3. Results

3.1. Emulsions produced using a high shear mixer

3.1.1. Influence of the dispersion time on emulsions properties

Figure 4 displays the influence of the dispersion time on properties of three emulsions. The dispersion time varies between 2 and 6 minutes whereas other manufacturing parameters are arbitrarily fixed. The dispersion rate was 15,000 rpm and the emulsification time and rate were respectively 4 minutes and 20,000 rpm.

Visual aspects of mixtures are firstly observed at 24 hours on Figure 4A and show the coexistence of both an emulsified and an aqueous phase in all preparations. A phase separation initially appears after 24 hours. Most of the clay particles settled at the aqueous phase bottom. Nevertheless, the emulsified portion after 24 hours appears quite similar between tested emulsions (Figure 4A), as well as after 72 hours (Figure 4B). The emulsified phase amount is slightly reduced due to the ageing phenomena with remaining identical emulsified portions whatever the dispersion time. Therefore, macroscopic properties of emulsions are not significantly affected by the dispersion time.

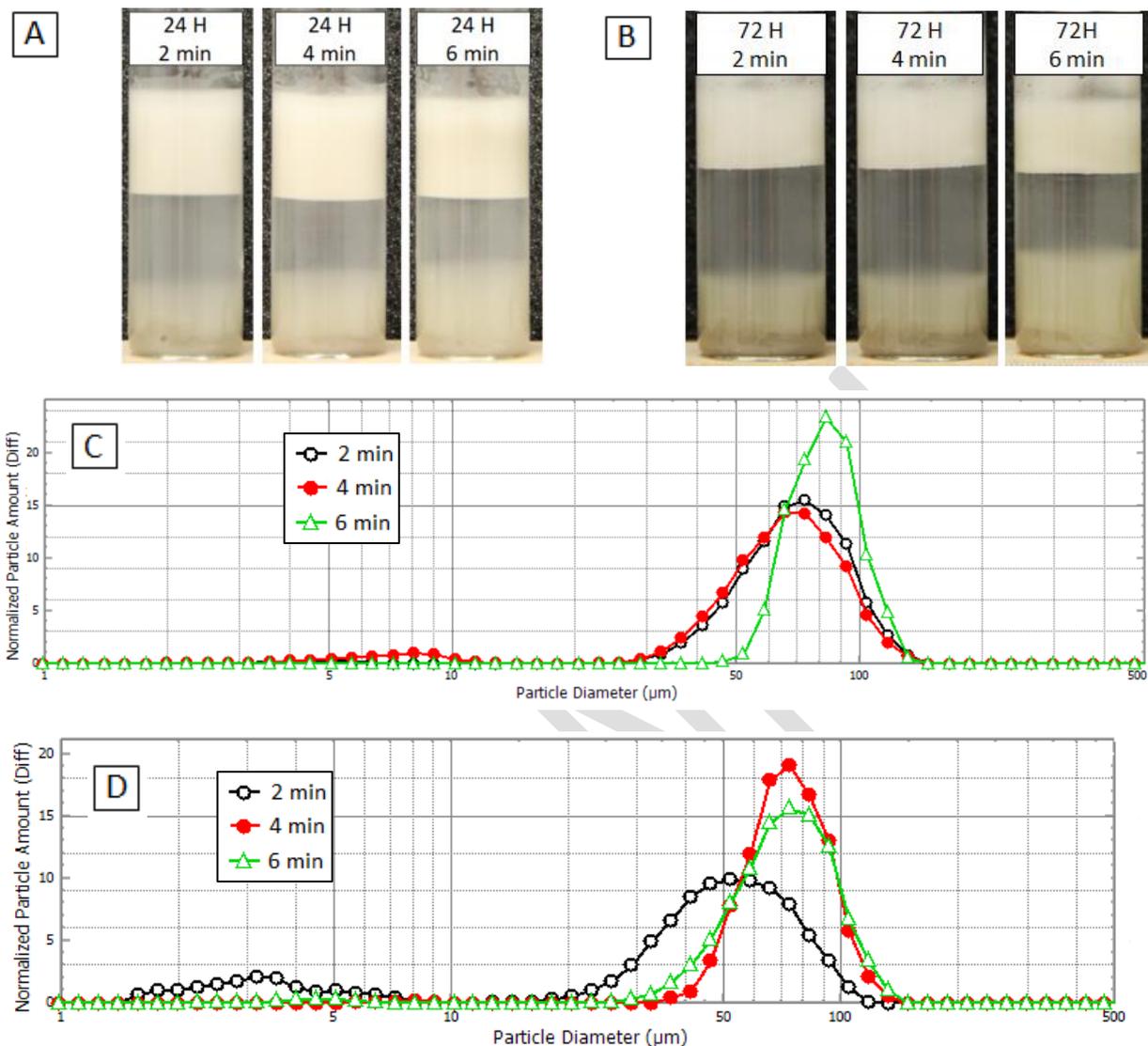


Figure 4: Comparison of emulsions produced at various dispersion times at 24 and 72 hours in terms of visual aspect (A, B) and droplet size distributions (C, D)

However, some differences are observed in the evolution of droplet size distributions with the dispersion time. At 24 hours (Figure 4C), the emulsions produced with 2 and 4 min dispersion times namely present droplet sizes ranging from 30 to 110 μm whereas the 6 min dispersion time produced emulsion exhibits, through a narrower distribution, larger droplet sizes beginning at 50 μm .

Differences in droplet sizes become more outlined at 72 hours, as shown on Figure 4D, in particular for the emulsion produced with a 2 min dispersion time (4D, black curve and unfilled circles). A secondary population of finer droplets appears ranging from 1 to 5 μm . This emulsion produced with the smaller dispersion time provides a distribution with smaller droplet sizes.

This observation is in good agreement with Figure 5 which refers to respective optical micrographs at 72 hours. In comparison to the F-HSM-D2-E4 emulsion (Fig 5 left), more coalescence and droplet fusion phenomena appear on micrographs of both emulsions produced with a 4 min (Fig 5 middle) and a 6 min (Fig 5 right) dispersion times (F-HSM-D4-E4, F-HSM-D6-E4). In correlation to droplet size distributions (Figure 4D), optical micrographs remain relatively similar for emulsions produced with

the 4 and 6 min dispersion times ; this clearly evidences a loss of stability when increasing dispersion step duration.

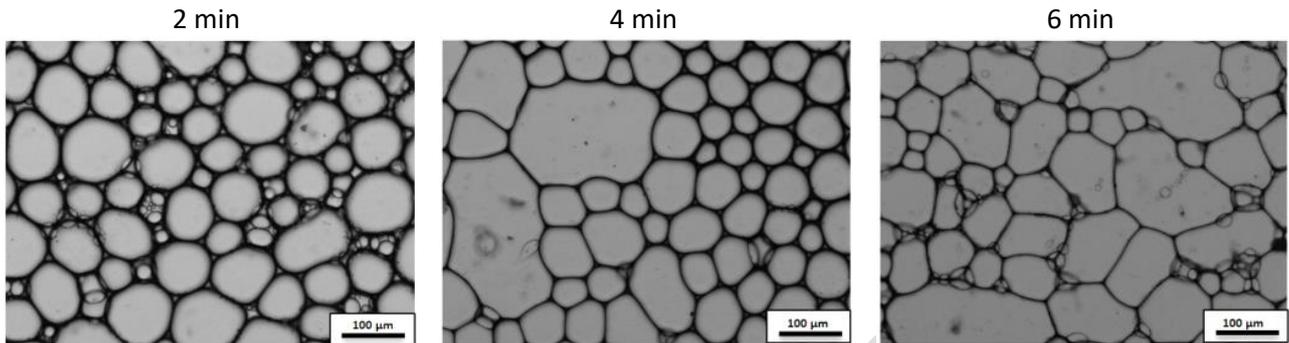


Figure 5: Influence of the dispersion time on the emulsion microstructure at 72 hours (Magnitude $\times 100$)

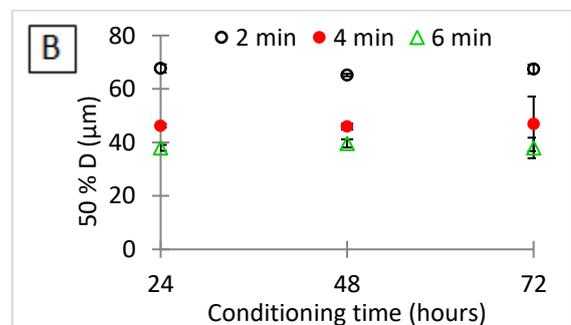
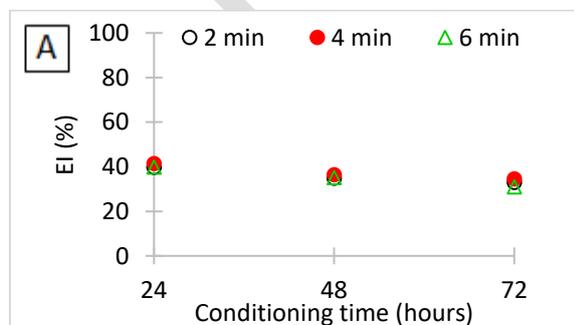
From these results, the combination of droplet size distribution curves (Figure 4C) and optical micrographs (Figure 5) leads to pursue the emulsion manufacturing process optimization and investigate the influence of the emulsification time on emulsions produced using a 2 min dispersion time.

3.1.2. Influence of the emulsification time on emulsion properties

The influence of emulsification time on emulsions properties was investigated using a 2 min dispersion time and keeping a 15,000 rpm rate. Then, emulsification was performed at 20,000 rpm during from 2 to 6 minutes. Figures 6A and 6B refer to the EI and statistical 50% diameter evolutions over time whereas Figure 6C displays respective micrographs observation at 24 hours.

In a similar way as above, only partial emulsification is observed as shown by the emulsification indexes around 40 % whatever the emulsification time (Figure 6A). This index slightly changes over time going from 40.3 ± 0.9 % at 24 hours to 32.8 ± 1.7 % at 72 hours, thus indicating an averaged stability for the corresponding emulsions over time.

Figure 6B reports then the average droplet size D50 (from static light scattering) for the emulsion phase of the corresponding mixtures. The 50 % diameter respectively equals to 67 μm , 46 μm and 37 μm for the 2 min, 4 min and 6 min emulsification times. Thus, the droplet size becomes smaller as the emulsification time increases. Another point is that D50 remains constant over the tested period of time (up to 72 hours) suggesting in a similar way a good stability of the emulsified phases and of the corresponding oil-water interfaces over time.



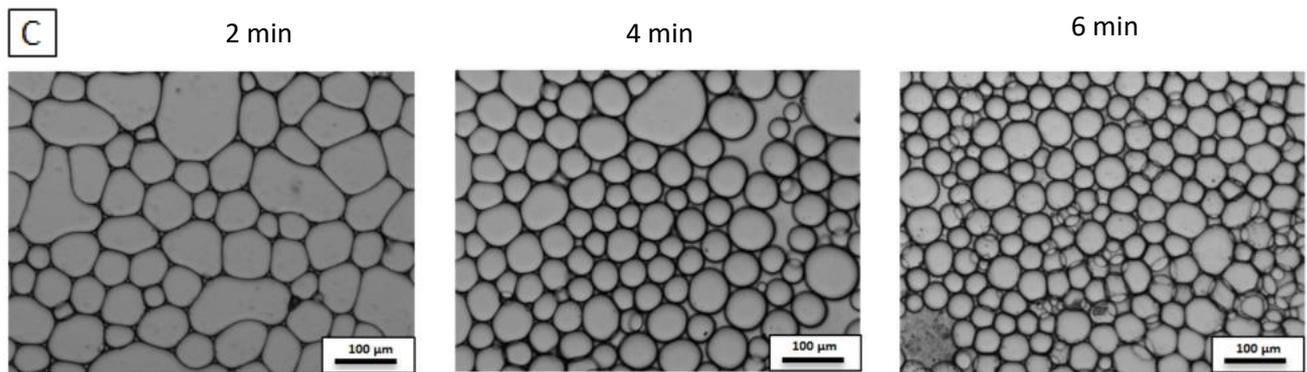


Figure 6: Influence of the emulsification time on the emulsifying index (A), on the 50 % diameter (B) and microstructures ($\times 100$) at 24 hours (C)

To sum up, initial emulsion phase characteristics are strongly affected by the manufacturing process. Results show that the longer 6 min emulsification time leads to smaller droplet sizes, as outlined by Figure 6B and 6C.

Results also highlight that emulsions remain partial (EI: 40 %) in the conditions tested in the present work. In addition, the longer the emulsification time, the smaller droplet sizes in the emulsion phase. Surprisingly, the resulting emulsion phase appears stable whatever the initial average droplet size thus indicating a stable oil-water interface. An attempt to increase the emulsifying index was performed by manufacturing the mixture with the maximal speed of the high shear mixer (24,000 rpm), but no EI improvement was observed on emulsion visual aspect (results not shown). Therefore, the next part describes the preparation of the same mixtures using another manufacturing process, namely ultrasonication, in order to investigate the effect of process energy on the resulting water-oil-clay mixtures properties.

3.2. Emulsions produced using ultrasonication

3.2.1. Optimization of the emulsification amplitude on the emulsifying index

In a first step, the influence of the ultrasonic probe amplitude was investigated on the visual aspect of mixtures displaying same mixture composition as the one investigated in the first part of this paper. The dispersion step was kept constant at 20 % amplitude whereas the emulsification energy was fixed at 20 or 100 % amplitudes. Emulsions were produced after a constant 2 min dispersion time by applying 2, 4, 6 min emulsification times.

Figure 7A firstly displays the visual aspect of emulsions produced using a 20 % emulsification energy after 24 hours. In an outstanding way, the emulsifying index of the oil phase is considerably increased with the ultrasonic process when compared to the results obtained with the high shear mixer. The emulsion phase appears predominant for all samples even if a weak phase separation occurs for the F-US-D2-E2-20% formulation (at 2 min emulsification time). Thus, both 4 and 6 min emulsification times (F-US-D2-E4-20% and F-US-D2-E6-20%) lead to macroscopically nearly fully emulsified mixtures as illustrated by a 96 % emulsifying index (plain blue curve and diamonds) on Figure 7B.

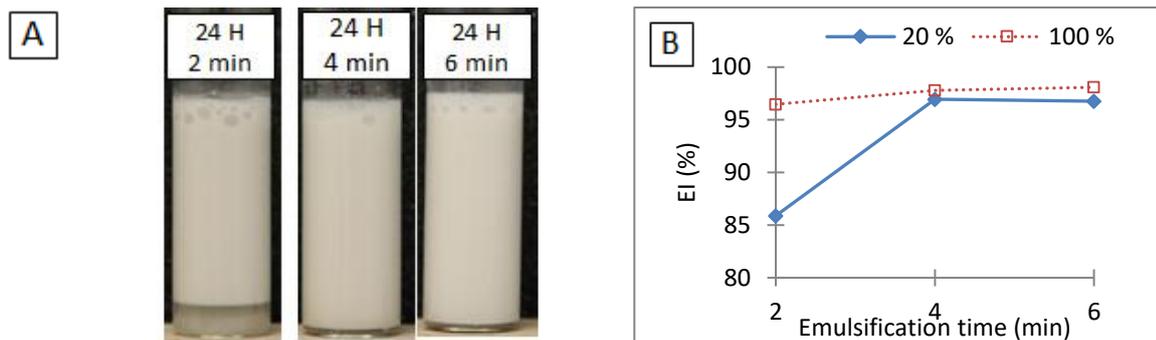


Figure 7: Observation at 24 hours of emulsions produced with a 20 % energy (A) and comparison of emulsifying indexes for two different ultrasonic amplitudes (B) (20 % and 100 %)

Furthermore, using a 100 % emulsification amplitude leads to an improvement of EI value as visible on Figure 7B. Indeed, the EI value is significantly increased for the emulsion produced with a 2 min emulsification time (F-US-D2-E2-100%) while only a slight EI improvement is observed for 4 and 6 min emulsification produced emulsions.

The emulsion obtained using a 6 min process (F-US-D2-E6-100%) is undoubtedly the most complete emulsion according to Figure 7B (EI = 98 %). On this basis, the microstructure of the corresponding formulation was thoroughly investigated over time in the next part to test its stability over time.

3.2.2. Droplet size distributions of the emulsion produced with a 6 min emulsification time

Figure 8 displays local droplet size distributions of the ultrasonicated emulsion produced at 100 % amplitude with a 6 min emulsification time. As described in the experimental part, granulometry measurements were performed by sampling distinct parts of the emulsion vial. Corresponding droplet size distributions analyzed at the emulsion top, middle and bottom are superimposed at 24 hours (8A), 48 hours (8B) and 72 hours (8C).

Figures 8A and 8B interestingly show identical distributions curves referring to the top, middle and bottom analyzed locations, thus suggesting that the produced emulsion is completely homogeneous. Furthermore, droplet size distributions appear highly similar at 24 and 48 hours but show significant differences at 72 hours (Figure 8C). Size distribution curves clearly indicate the occurrence of a destabilization process with a shift of smaller droplets population to larger droplets for both bottom and middle part of the emulsion. Figure 8C also evidences a relative increase of larger droplet population, thus illustrating the possible start of flocculation or coalescence phenomena.

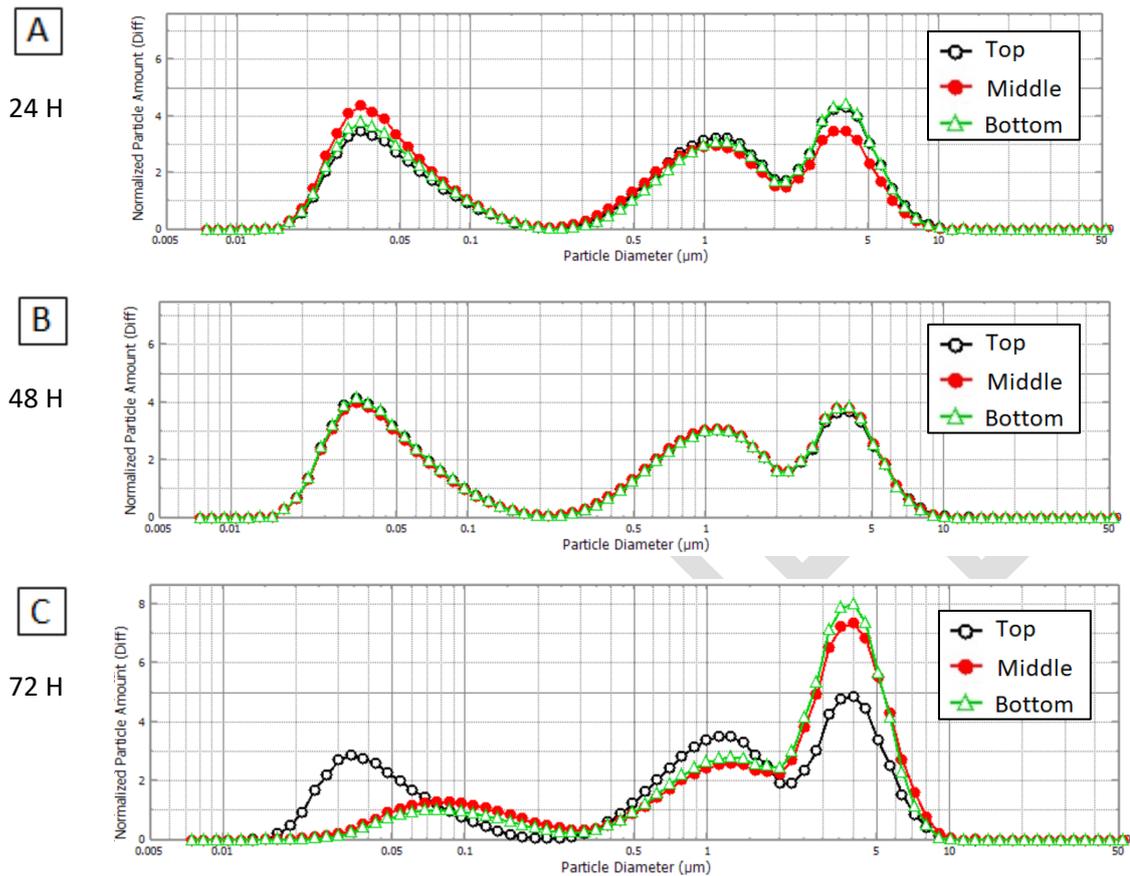


Figure 8: Evolution at 24 hours (A), 48 hours (B) and 72 hours (C) of droplet size distributions in the emulsion produced with a 6 min emulsification time at 100 % amplitude

Nevertheless, it can be concluded that ultrasonication produces fine, homogeneous and relatively stable emulsions, which is not achieved by the mechanical high shear mixer in spite of process optimization. In order to outline the important results of the present development, macroscopic and microscopic properties of emulsions produced using both the high shear mixer and ultrasonic processes were finally extensively compared in the following section.

3.3. Comparison of emulsion properties using both high shear mixer and ultrasonic homogenization processes

Previous preparations obtained either by high shear mixer and ultrasonic processes and having the best initial structure and stability over the ageing time (Figures 6 and 8) were selected and compared at 24 hours. Thus, Figure 9 presents the emulsion visual aspect (9A), the emulsifying index (9B), the 50 % diameter obtained by static light scattering (9C) and the optical microstructures (9D) as a function of the emulsification time. On Figure 9A, the emulsification process appears as the most significant factor impacting the ability to get oil phase emulsification. Indeed, ultrasonication leads to complete and visually homogeneous emulsions ($EI \approx 100\%$) while the high shear mixed emulsions display a multi-phase character ($EI \approx 40\%$) and clay sedimentation. The multi-phase character does not evolve with the emulsification time for emulsions produced with the high shear mixer as the EI equals to 40 % and the regression slope is almost null (Figure 9B). On the contrary, ultrasonicated

formulations display an EI close to 100 % and show a slight increase with emulsification step duration, as illustrated by the trend curve positive slope (Figure 9B).

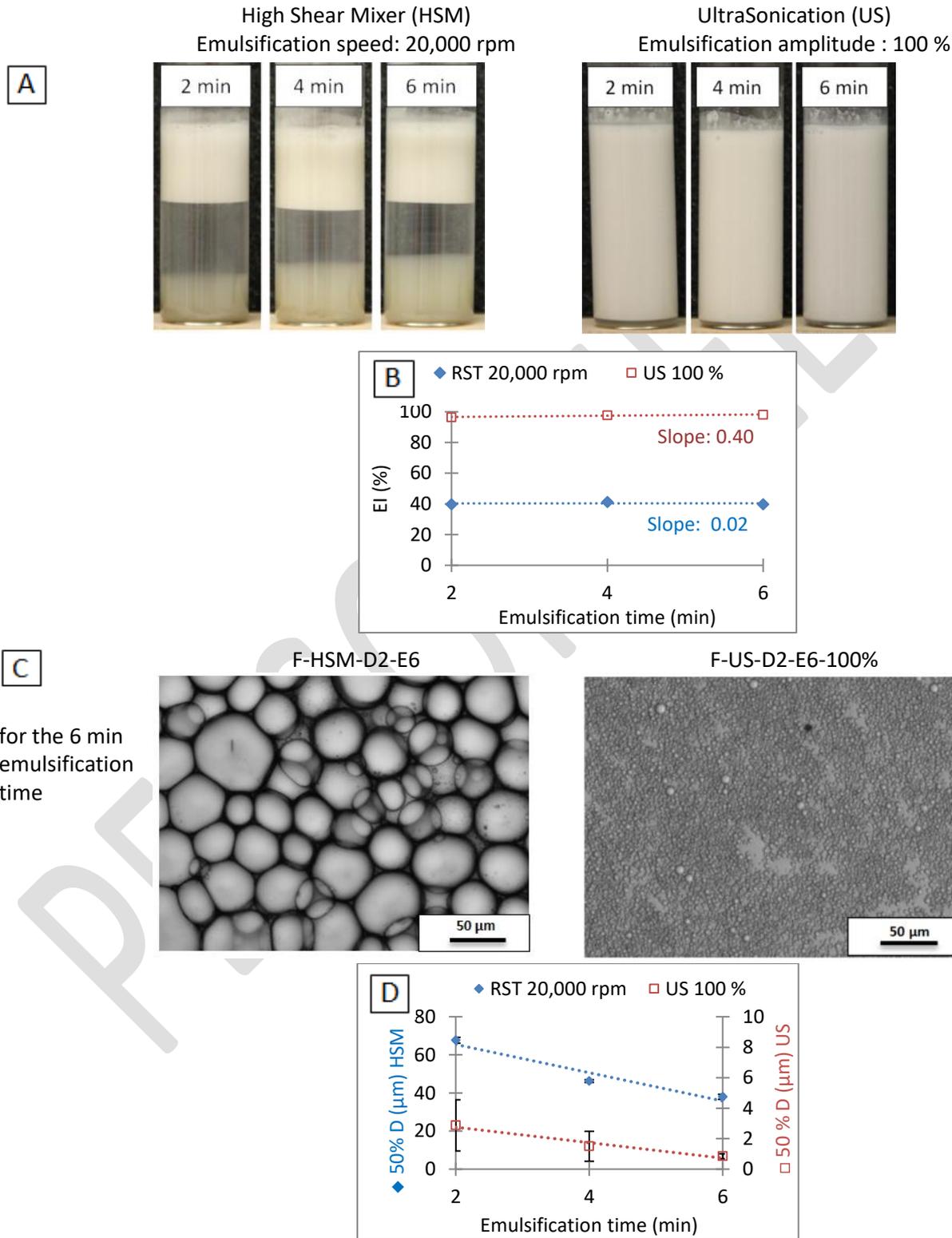


Figure 9: Effect at 24 hours of High Shear Mixer (HSM) and UltraSonication (US) homogenization processes on emulsion visual aspect (A), Emulsifying Index (EI) (B), optical microstructure (× 200) (C) and 50% diameter extracted from particle size distributions (D)

Therefore, the ultrasonic process is much more efficient for producing complete emulsions than high shear mixing (Figures 9A and 9B). The ultrasonic process is also efficient to produce emulsions displaying fine droplets of the order of 1 micron. As illustrated by Figure 9C, the mechanical high shear mixer only provides large droplets of the order of tens microns with clay particles observed at the oil droplet surface.

Furthermore, the influence of the emulsification time on both kinds of emulsions is revealed when considering the droplet size evolution (Figure 9D). In both cases, the 50% diameter markedly decreases by 50 % when the emulsification time increases. However, the order of magnitude of droplet sizes remains different between two processes and the droplet size reduction with the increasing emulsification time leads to distinct 50% diameters, what remains in good correlation with distinct microstructures (figure 9C).

Thus, besides the emulsification time influence on macroscopic and microscopic properties of emulsions produced by both process, results of this study have undoubtedly highlighted the major impact of the homogenizing process on emulsion formation, microstructure and stability. Optimization of experimental conditions made possible to obtain stable and totally emulsified systems with montmorillonite clay particles. In the next part, results will be discussed with an attempt to highlight some links and potential correlations with other studies.

4. Discussion

The first objective of this paper was to prepare emulsions stabilized by clay particles for cosmetic applications by studying the effect of homogenizing process. Results show that montmorillonite clay particles have a high potential for the stabilization of O/W emulsions, as it was suggested by previous Guillot's observations (Guillot et al., 2009). Both high shear mixer and ultrasonic processes successfully provided a certain amount of emulsified fraction, the ultrasonication technology being much more efficient. Furthermore, the one-step process used allows a better control of incorporated ingredients amounts whatever the homogenizer. It also induced less time (Costa et al., 2018) and a better reliability during the manufacture of emulsions.

Then the second aim was to study the influence of manufacturing parameters on the emulsion stability and properties in order to better understand and control the manufacturing process. Thereby, several manufacturing parameters were tested on emulsion properties. Results firstly show that the emulsions produced with high shear mixer are very likely to undergo clay sedimentation, as Zhang already observed with emulsions produced with another mechanical vortex mixing (Zhang et al., 2015).

Nevertheless, the droplet size distributions of these emulsions slightly evolve once the phase separation has occurred. A barely significant difference in droplet sizes (Figure 4D) and microstructures (Figure 5) appears after 72 hours and shows that the emulsion produced with a 2 min dispersion time leads to smaller droplets and thereby less coalescence phenomena than others. In other words, the smallest dispersion time leads to the more stable emulsion over the time. Such a result is enough surprising and it could be explained by some hypothesis. On the one hand, clay particles would tend to settle less at smaller times leading to the presence of a greater amount of particles to stabilize the oil/water interface during emulsification. On the other hand, this result could be also explained by the particle size generated by the dispersion and powder disaggregation step. At shorter times of 2 minutes, clay particles would be less individualized and their sizes would

be also larger, leading to thicker interfacial films stabilizing the water/oil interface. Conversely, for longer dispersion times of 4 and 6 minutes, the particles disaggregation would be more efficient than for the 2 minutes dispersion time. The particle sizes would be also smaller, leading to thinner and more sensitive interfacial films to destabilization phenomena. This hypothesis seems to be in good agreement with Figure 5 but it would need to confirm. Through this observation, the dispersion step would represent a crucial step to indirectly adjust emulsion properties and stability from particle sizes and the powder disaggregation quality.

Nevertheless, the dispersion time doesn't influence the visual aspect of emulsions in this study (Figure 4A). In similar way, the emulsification time neither plays a significant role on the emulsifying index (Figure 6A) which is relatively low (40 %). The produced emulsions remain partial and the phase separation appears in the early hours. As outlined by the results by Lee and Zhang (Lee et al., 2019; Zhang et al., 2017), the ultraturrax shear force energy may be insufficient to overcome the energy barrier of particle adsorption and to totally stabilize oil droplets in the mixture, leading to macroscopic phase separation.

Inversely, the ultrasonic homogenizer leads to fine, stable and homogeneous emulsions. The droplet size distributions are polydisperse but the average droplet size is very low (around 2 μm) (Figure 8 and 9) and the emulsifying index equals to 100 % (Figure 7A and 9B). The droplet network appears dense (figure 9C). In an outstanding way, the US process is efficient in the production of Pickering emulsions. The ultrasonicated emulsions display better stability and lower droplet sizes than those produced by high shear mixer. That result is in good agreement with other studies (Paximada et al., 2016; Zhang et al., 2015). Nevertheless, it is worth noticing that the emulsification time variation has a similar effect on the droplet size whatever the process used. When the emulsification time increases, the 50% diameter namely decreases (Figure 9C). That observation may be explained by different migration kinetics and by a greater ease for the clay particles to be located at the interface for longer mixing times.

Thus, ultrasonication constitutes an effective tool for the production of Pickering emulsions stabilized by solid particles, as confirmed by Cichoski (Cichoski et al., 2019). In correlation to Zhang conclusions (Zhang et al., 2015), the emulsification process can be used as a trigger to modify and adjust oil droplets microstructures and emulsions properties. As ultrasonication leads to a heat increase, specific conditions should be used to regulate the temperature of an industrial process in order to prevent raw materials degradation. As noted in the experimental part (2.1.1), produced emulsions temperatures did not overcome 30 °C. Furthermore, emulsions were prepared using only 1 % (w/w) montmorillonite clay particles, which is low compared to other studies using a 6 mass % illitic clay (Jurgelane et al., 2017). Therefore, this study allows demonstrating that both the US cold homogenization process and the low clay amount lead to the development of stable ecologically-optimized emulsions. This is a highly promising result for answering to requirements of more environmentally-responsible cosmetic and personal-care applications.

5. Conclusion

The objective of this study was to develop innovative surfactant-free emulsions only stabilized by solid particles for cosmetic applications. As clay represents a natural and cosmetic-friendly raw material, montmorillonite particles were selected to stabilize model oil/water emulsions. To better optimize the emulsion production, the influence of manufacturing parameters on macro/microstructure properties and stability of a model emulsion was investigated. Among the

different parameters, the influence of both the emulsification time and the homogenizer tool (ultrasonic probe and high shear mixer) was studied. Emulsions were monitored over time at 40 °C and characterized to test their stability. Results of this study show that:

1. Emulsions stabilized by clay particles were successfully produced and are very stable over the time: despite possible observed phase separation in some cases, the associated microstructure and droplet size remain constant over time.
2. Whatever the homogenization process, increasing the emulsification time leads to reducing the emulsion droplet size, and consequently improving emulsion stability.
3. A low mechanical dispersion time improves emulsion stability and may be due to the presence of larger particles stabilizing the oil/water interface thanks to a thicker clay interfacial film.

Therefore, the dispersion conditions have an interesting effect on emulsion properties and stability. The mechanical high shear mixer use would allow improving the emulsion stability from a rougher disaggregation of particles. This hypothesis would be to deepen for a better manufacturing emulsion process adjustment.

Nevertheless, it is shown that the emulsification process is the most significant factor impacting the emulsion stability. Ultrasonicated emulsions are visually complete in contrast to the mechanical high shear mixer produced ones which are multi-phased. Therefore, results highlight that the ultrasonic process constitutes an efficient tool to produce complete and stable Pickering emulsions displaying fine droplet sizes. It appears as an interesting and promising technology to better control and regulate emulsion properties during a continuous industrial manufacture.

6. Acknowledgments

The work was funded by the Innovation Chemistry Carnot (I2C) Tremplin research structure. Authors also would like to thank Croda France for generously providing the isohexadecane oil.

7. References

- Agredo, P., Rave, M.C., Echeverri, J.D., Daniela, R., Salamanca, C.H., 2019. An evaluation of the physicochemical properties of stabilized oil-in-water emulsions using different cationic surfactant blends for potential use in the cosmetic industry. *Cosmetics* 6, 1–12. <https://doi.org/10.3390/cosmetics6010012>
- Ashby, N.P., Binks, B.P., 2000. Pickering emulsions stabilised by Laponite clay particles. *Phys. Chem. Chem. Phys.* 5640–5646. <https://doi.org/10.1039/b007098j>
- Atta, A.M., Allohedan, H.A., El-Mahdy, G.A., 2014. Dewatering of petroleum crude oil emulsions using modified Schiff base polymeric surfactants. *J. Pet. Sci. Eng.* 122, 719–728. <https://doi.org/10.1016/j.petrol.2014.09.017>
- Aveyard, R., Binks, B.P., Clint, J.H., 2003. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* 102, 503–546.
- Binks, B.P., Lumsdon, S.O., 2000. Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions. *Langmuir* 16, 8622–8631. <https://doi.org/10.1021/la000189s>
- Björkegren, S., Nordstierna, L., Törnecrona, A., Palmqvist, A., 2017. Hydrophilic and hydrophobic

- modifications of colloidal silica particles for Pickering emulsions. *J. Colloid Interface Sci.* 487, 250–257. <https://doi.org/10.1016/j.jcis.2016.10.031>
- Bouyer, E., Mekhloufi, G., Rosilio, V., Grossiord, J., Agnely, F., 2012. Proteins, polysaccharides, and their complexes used as stabilizers for emulsions: Alternatives to synthetic surfactants in the pharmaceutical field? *Int. J. Pharm.* 436, 359–378. <https://doi.org/10.1016/j.ijpharm.2012.06.052>
- Cherhal, F., Cousin, F., Capron, I., 2016. Structural Description of the Interface of Pickering Emulsions Stabilized by Cellulose Nanocrystals. *Biomacromolecules* 17, 496–502. <https://doi.org/10.1021/acs.biomac.5b01413>
- Chevalier, Y., Bolzinger, M., 2013. Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids Surfaces A Physicochem. Eng. Asp.* 439, 23–34. <https://doi.org/10.1016/j.colsurfa.2013.02.054>
- Cichoski, A.J., Silva, M.S., Sena, Y., Leães, V., Cristina, C., Brasil, B., Menezes, C.R. De, Barin, J.S., Wagner, R., Cezar, P., Campagnol, B., 2019. Ultrasound: A promising technology to improve the technological quality of meat emulsions. *Meat Sci.* 148, 150–155. <https://doi.org/10.1016/j.meatsci.2018.10.009>
- Costa, A.L.R., Gomes, A., Cunha, R.L., 2018. One-step ultrasound producing O/W emulsions stabilized by chitosan particles. *Food Res. Int.* 107, 717–725. <https://doi.org/10.1016/j.foodres.2018.02.057>
- Destribats, M., Rouvet, M., Gehin-Delval, C., Schmitt, C., Binks, B.P., 2014. Emulsions stabilised by whey protein microgel particles: toward food-grade pickering emulsions. *Soft Matter*.
- Fallah, F., Khorasani, M., Ebrahimi, M., 2018. Factors affecting the properties of nitrocellulose emulsions: A comparative study. *Carbohydr. Polym.* 189, 267–272. <https://doi.org/10.1016/j.carbpol.2017.11.002>
- Frelichowska, J., Bolzinger, M., Chevalier, Y., 2010. Effects of solid particle content on properties of o/w Pickering emulsions. *J. Colloid Interface Sci.* 351, 348–356. <https://doi.org/10.1016/j.jcis.2010.08.019>
- Frelichowska, J., Bolzinger, M., Chevalier, Y., 2009. Pickering emulsions with bare silica. *Colloids Surfaces A Physicochem. Eng. Asp.* 343, 70–74. <https://doi.org/10.1016/j.colsurfa.2009.01.031>
- Ganley, W.J., Ryan, P.T., Van Duijneveldt, J.S., 2017. Stabilisation of water-in-water emulsions by montmorillonite platelets. *J. Colloid Interface Sci.* 139–147.
- Garcia, P.C., Whitby, C.P., 2012. Laponite-stabilised oil-in-water emulsions: viscoelasticity and thixotropy. *Soft Matter* 8, 1609–1615. <https://doi.org/10.1039/c1sm06660a>
- Ge, S., Xiong, L., Li, M., Liu, J., Yang, J., Chang, R., Liang, C., Sun, Q., 2017. Characterizations of Pickering emulsions stabilized by starch nanoparticles: Influence of starch variety and particle size. *Food Chem.* 234, 339–347. <https://doi.org/10.1016/j.foodchem.2017.04.150>
- Gestranius, M., Stenius, P., Kontturi, E., Sjöblom, J., Tammelinn, T., 2017. Phase behaviour and droplet size of oil-in-water Pickering emulsions stabilised with plant-derived nanocellulosic materials. *Colloids Surfaces A Physicochem. Eng. Asp.* 519, 60–70. <https://doi.org/10.1016/j.colsurfa.2016.04.025>
- Guillot, S., Bergaya, F., Azevedo, C. De, Warmont, F., Tranchant, J., 2009. Internally structured pickering emulsions stabilized by clay mineral particles. *J. Colloid Interface Sci.* 333, 563–569.

- <https://doi.org/10.1016/j.jcis.2009.01.026>
- Hall, S., Cooke, M., El-hamouz, A., Kowalski, A.J., 2011. Droplet break-up by in-line Silverson rotor – stator mixer. *Chem. Eng. Sci.* 66, 2068–2079. <https://doi.org/10.1016/j.ces.2011.01.054>
- Jurgelane, I., Sevjakova, V., Dzene, L., 2017. Influence on illitic clay addition on the stability of sun flower oil in water emulsion. *Colloids Surfaces A* 529, 178–184. <https://doi.org/10.1016/j.colsurfa.2017.05.086>
- Kargar, M., Fayazmanesh, K., Alavi, M., Spyropoulos, F., Norton, I.T., 2012. Investigation into the potential ability of Pickering emulsions (food-grade particles) to enhance the oxidative stability of oil-in-water emulsions. *J. Colloid Interface Sci.* 366, 209–215. <https://doi.org/10.1016/j.jcis.2011.09.073>
- Katepalli, H., John, V.T., Tripathi, A., Bose, A., 2017. Microstructure and rheology of particle stabilized emulsions : Effects of particle shape and inter-particle interactions. *J. Colloid Interface Sci.* 485, 11–17. <https://doi.org/10.1016/j.jcis.2016.09.015>
- Könnecker, G., Regelman, J., Belanger, S., Gamon, K., Sedlak, R., 2011. Environmental properties and aquatic hazard assessment of anionic surfactants : Physico-chemical , environmental fate and ecotoxicity properties. *Ecotoxicol. Environ. Saf.* 74, 1445–1460. <https://doi.org/10.1016/j.ecoenv.2011.04.015>
- Lechuga, M., Fernández-serrano, M., Jurado, E., Ríos, F., 2016. Acute toxicity of anionic and non-ionic surfactants to aquatic organisms. *Ecotoxicol. Environ. Saf.* 125, 1–8. <https://doi.org/10.1016/j.ecoenv.2015.11.027>
- Lee, Y., Li, D.S., Ilavsky, J., Kuzmenko, I., Jeng, G., Donnell, M.O., Pozzo, L.D., 2019. Ultrasound-based formation of nano-Pickering emulsions investigated. *J. Colloid Interface Sci.* 536, 281–290. <https://doi.org/10.1016/j.jcis.2018.10.047>
- Lémery, E., Briançon, S., Chevalier, Y., Bordes, C., Oddos, T., Gohier, A., Bolzinger, M.-A., 2015. Skin toxicity of surfactants : Structure/toxicity relationships. *Colloids Surfaces A Physicochem. Eng. Asp.* 469, 166–179. <https://doi.org/10.1016/j.colsurfa.2015.01.019>
- Li, W., Yu, L., Liu, G., Tan, J., Liu, S., Sun, D., 2012. Oil-in-water emulsions stabilized by Laponite particles modified with short-chain aliphatic amines. *Colloids Surfaces A Physicochem. Eng. Asp.* 400, 44–51. <https://doi.org/10.1016/j.colsurfa.2012.02.044>
- Li, Z., Wu, H., Yang, M., Xu, D., Chen, J., Feng, H., Lu, Y., 2018. Stability mechanism of O / W Pickering emulsions stabilized with regenerated cellulose. *Carbohydr. Polym.* 181, 224–233. <https://doi.org/10.1016/j.carbpol.2017.10.080>
- Liu, D., Yan, Y., Bai, G., Yuan, Y., Zhu, T., Zhang, F., Shao, M., Tian, X., 2018. Mechanisms for stabilizing and supporting shale fractures with nanoparticles in Pickering emulsion. *J. Pet. Sci. Eng.* 164, 103–109. <https://doi.org/10.1016/j.petrol.2018.01.048>
- Lu, X., Zhang, H., Li, Y., Huang, Q., 2018. Fabrication of milled cellulose particles-stabilized Pickering emulsions. *Food Hydrocoll.* 77, 427–435. <https://doi.org/10.1016/j.foodhyd.2017.10.019>
- Madivala, S.B., Vandebriel, S., Franssaer, J., Vermant, J., 2009. Exploiting particle shape in solid stabilized emulsions. *Soft Matter* 5, 1717–1727. <https://doi.org/10.1039/b816680c>
- Paximada, P., Tsouko, E., Kopsahelis, N., Koutinas, A.A., Mandala, I., 2016. Bacterial cellulose as stabilizer of o / w emulsions. *Food Hydrocoll.* 53, 225–232. <https://doi.org/10.1016/j.foodhyd.2014.12.003>

- Pichot, R., Spyropoulos, F., Norton, I.T., 2009. Mixed-emulsifier stabilised emulsions : Investigation of the effect of monoolein and hydrophilic silica particle mixtures on the stability against coalescence. *J. Colloid Interface Sci.* 329, 284–291. <https://doi.org/10.1016/j.jcis.2008.09.083>
- Pickering, S.U., 1907. Emulsions. *J. Chem. Soc.* 91, 2001–2021.
- Ramsden, W., 1904. Separation of solids in the surface-layers of solutions and suspensions (observations on surface-membranes, bubbles, emulsions, and mechanical coagulation). *Proc. R. Soc. Lond.* 72, 156–164.
- Ronald, M., Luis, F.P., 2016. Asphalt emulsions formulation : State-of-the-art and dependency of formulation on emulsions properties. *Constr. Build. Mater.* 123, 162–173. <https://doi.org/10.1016/j.conbuildmat.2016.06.129>
- Rosdi, M.R.H., Ariffin, A., Ishak, Z.A.M., 2018. Optimizing homogenization parameters for improving ethylene vinyl acetate emulsion stability in pour point depressant application. *J. King Saud Univ. - Eng. Sci.* 30, 105–115. <https://doi.org/10.1016/j.jksues.2016.01.006>
- Terescenco, D., Picard, C., Clemenceau, F., Grisel, M., Savary, G., 2018. Influence of the emollient structure on the properties of cosmetic emulsion containing lamellar liquid crystals. *Colloids Surfaces A* 536, 10–19. <https://doi.org/10.1016/j.colsurfa.2017.08.017>
- Trujillo-cayado, L.A., Alfaro, M.C., Santos, J., Calero, N., Muñoz, J., 2018. Influence of primary homogenization step on micro fluidized emulsions formulated with thyme oil and Appyclean 6548. *J. Ind. Eng. Chem.* 66, 203–208. <https://doi.org/10.1016/j.jiec.2018.05.031>
- Tsabet, È., Fradette, L., 2015. Effect of the properties of oil , particles , and water on the production of Pickering emulsions. *Chem. Eng. Res. Des.* 97, 9–17. <https://doi.org/10.1016/j.cherd.2015.02.016>
- Tzoumaki, M. V, Moschakis, T., Kiosseoglou, V., Biliaderis, C.G., 2011. Oil-in-water emulsions stabilized by chitin nanocrystal particles. *Food Hydrocoll.* 25, 1521–1529. <https://doi.org/10.1016/j.foodhyd.2011.02.008>
- Udoetok, I.A., Wilson, L.D., Headley, J. V, 2016. Stabilization of pickering emulsions by iron oxide nano- particles. *Adv. Mater. Sci.* <https://doi.org/10.15761/AMS.1000107>
- Verkempinck, S.H.E., Kyomugasho, C., Salvia-trujillo, L., Denis, S., Bourgeois, M., Loey, A.M. Van, Hendrickx, M.E., Grauwet, T., 2018. Emulsion stabilizing properties of citrus pectin and its interactions with conventional emulsifiers in oil-in-water emulsions. *Food Hydrocoll.* 85, 144–157. <https://doi.org/10.1016/j.foodhyd.2018.07.014>
- Vignati, E., Piazza, R., Lockhart, T.P., 2003. Pickering Emulsions : Interfacial Tension , Colloidal Layer Morphology , and Trapped-Particle Motion. *Langmuir* 19, 6650–6656. <https://doi.org/10.1021/la034264l>
- Wagner, H., Kostka, K., Lehr, C., Schaefer, U.F., 2003. pH profiles in human skin : influence of two in vitro test systems for drug delivery testing. *Eur. J. Pharm. Biopharm.* 55, 57–65. <https://doi.org/10.1016/S0>
- Yan, H., Zhao, B., Long, Y., Zheng, L., Tung, C., Song, K., 2015. New pickering emulsions stabilized by silica nanowires. *Colloids Surfaces A Physicochem. Eng. Asp.* 482, 639–646. <https://doi.org/10.1016/j.colsurfa.2015.07.004>
- Ye, F., Miao, M., Jiang, B., Campanella, O.H., Jin, Z., Zhang, T., 2017. Elucidation of stabilizing oil-in-water Pickering emulsion with different modified maize starch-based nanoparticles. *Food*

Chem. 229, 152–158. <https://doi.org/10.1016/j.foodchem.2017.02.062>

Young, S., Basiana, E., Nitin, N., 2018. Effects of interfacial composition on the stability of emulsion and encapsulated bioactives after thermal and high pressure processing. *J. Food Eng.* 231, 22–29. <https://doi.org/10.1016/j.jfoodeng.2018.02.022>

Yusoff, A., Murray, B.S., 2011. Modified starch granules as particle-stabilizers of oil-in-water emulsions. *Food Hydrocoll.* 25, 42–55. <https://doi.org/10.1016/j.foodhyd.2010.05.004>

Zeng, T., Wu, Z., Zhu, J., Yin, S.-W., Tang, C.-H., Wu, L.-Y., 2017. Development of antioxidant Pickering high internal phase emulsions (HIPEs) stabilized by protein / polysaccharide hybrid particles as potential alternative for PHOs. *Food Chem.* 231, 122–130. <https://doi.org/10.1016/j.foodchem.2017.03.116>

Zhang, M., Wang, A., Li, J.-M., Song, N., Song, Y., He, R., 2017. Factors in fluencing the stability and type of hydroxyapatite stabilized Pickering emulsion. *Mater. Sci. Eng. C* 70, 396–404. <https://doi.org/10.1016/j.msec.2016.09.007>

Zhang, N., Zhang, L., Sun, D., 2015. Influence of Emulsification Process on the Properties of Pickering Emulsions Stabilized by Layered Double Hydroxide Particles. *Langmuir* 31, 4619–4626. <https://doi.org/10.1021/la505003w>

Zhang, Y., Zhou, F., Zhao, M., Lin, L., Ning, Z., Sun, B., 2018. Soy peptide nanoparticles by ultrasound-induced self-assembly of large peptide aggregates and their role on emulsion stability. *Food Hydrocoll.* 74, 62–71. <https://doi.org/10.1016/j.foodhyd.2017.07.021>