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Daria Terescenco, Nicolas Hucher, Géraldine Savary, Celine Picard. From interface towards organised network: Questioning the role of the droplets arrangements in macroscopically stable O/W emulsions composed of a conventional non-ionic surfactant, TiO₂ particles, or their mixture. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2019, 578, pp.123630. 10.1016/j.colsurfa.2019.123630 . hal-02331451

HAL Id: hal-02331451

<https://hal.science/hal-02331451>

Submitted on 24 Oct 2019

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From interface towards organised network: questioning the role of the droplets arrangements in macroscopically stable O/W emulsions composed of a conventional non-ionic surfactant, TiO₂ particles, or their mixture.

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Keywords

Emulsion

Surfactant

Particle stabilization

Mixed emulsifier systems

Application properties

1. Introduction

An emulsion is a system in which one liquid is dispersed in a second liquid, the two liquids being partially or totally immiscible. The liquid droplets of the disperse phase are dispersed in a liquid medium, the continuous phase [1]. To disperse two immiscible liquids, a third component is needed to assure the stability of the interface. For this purpose surfactants and colloidal particles are often used.

The surfactant is an amphiphilic molecule able to reduce the oil/water interfacial tension and it forms an electrostatic and steric barrier at the interface between two liquids [2]. The mechanism of the particle stabilization is different: partial wetting of the surface of the solid particles by water and oil is the origin of the strong anchoring of solid particles at the oil-water interface [3,4] acting as a barrier against coalescence [5–8]. The hydrophilic-lipophilic balance number (HLB) of surfactant molecules is the parameter which determines both the type (oil in water or water in oil) and stability of emulsions using them [9], while it is the wettability of particles at the oil-water interface that is crucial in optimizing the stability of solid-stabilized emulsions [10,11]. Numbers of solid particles are good candidates for the interface stabilization: clay, chitosan, cyclodextrin [12], starch [13], iron oxides [14], titanium dioxide [15], silica [16–19], etc.

Moreover, particles can be employed in association with surfactants, as stabilizing additives of such disperse systems in different fields of practical interest [10]. Some studies show that surfactants can be added to colloid-stabilized emulsions and, as a consequence, to considerably increase the emulsion stability [7,20].

Midmore *et al.*, for example, discussed the stability of the silica/Brij and silica/Tween systems and compared them to the classical emulsions stabilized only by the surfactant [21]. Two most important observations were then made: at very low surfactant concentrations, where the surfactant cannot form a stable emulsion, the silica/surfactant system is

quite stable. The authors also explained that one should take into account the chemical structure of the emulsifier to govern its interactions with both particles and the oil phase.

The surfactant can adsorb on particle surfaces and modify their wettability in a manner to improve or reduce its efficacy. Or, if surfactant does not adsorb on particles, it is possible that both species will compete for the oil-water interface but one may dominate [11].

Emulsions stabilization by a mixture of particles and surfactant have been already investigated in the literature; the majority of the studies focus on the silica particle [22–26], but other types of particles are also discussed, like kaolinite [27], magnetite nanoparticles [28], carbon black particles [29] combined to anionic, cationic or non-ionic surfactants of different chain length (sodium dodecyl sulphate, dodecyltrimethylammonium bromide, cetrimonium bromide, polysorbates, etc.). However, in most cases, with the noticeable exception of the work authored by Pichot *et al.* [23], the particles were unable to stabilize the interface in absence of surfactant, and it was difficult to understand the role of each of them on the competition for the interface.

The research is moving forward towards the application interest for this type of systems. Particle-stabilized emulsions are of great interest in heavy oil processing, food science, controlled release systems, functional materials, microencapsulation [30], pharma-cosmetic applications.

For this reason, in our study, in addition to the interest for the interface stabilization, we also focused on the development of stable and totally emulsified systems, taking into account not only the droplet dispersion but also the droplet interaction mechanism. This is a new approach, never discussed in the literature before. Once the interface is stabilised, the droplets organisation should be understood. The created network will depend on the droplets size, their polydispersity, their interactions, and will govern the emulsions rheological, textural and, consequently, applicative properties.

The emulsifying systems were thoughtfully chosen. Classical emulsifier mixture of non-ionic surfactants Steareth-2/Steareth-21, often used for topical applications, is well known for its stabilizing properties [31] and was already used for the previous studies of the NP-based emulsions [32,33]. This emulsifier was used in combination with, or it was totally replaced by TiO₂ particles coated with silica and cetyl phosphate.

The aim of this study is to bring new explanations about the role of the particle alone and in combination with a conventional surfactant (a mixture of non-ionic polyethoxylated fatty ethers) not only at the oil/water interface but also on the macroscopic and applicative properties of the emulsions containing them. The novelty of this work lays in the investigation of the particle direct impact of the emulsion microscopic, macroscopic and thermal properties, and through the comparison with the reference system (surfactant/particles or surfactant exclusive stabilisation), to point out its unique contribution in emulsion structuration.

2. Materials and methods

2.1. Materials

The raw materials used in this study were kindly provided by the suppliers listed in Table 1. The selected raw materials were of cosmetic grade considering the further interest of emulsions topical application.

The surfactant chosen for this study is a combination of two ethoxylated ethers: Steareth-2 is a polyoxyethylene (2) stearyl ether and the Steareth-21 a polyoxyethylene (21) stearyl ether [34].

Each emulsion contained 10% of emulsifying system: 10% TiO₂; 10% Steareth-2/21 (6/4); 5% TiO₂ and 5% Steareth-2/21 (6/4). The oil/water for each system ratio was fixed at 40/60 and a preservative was introduced to avoid bacterial proliferation.

Table 1. INCI, CAS, trade name and the supplier of each raw material, as well as the composition of the three formulated emulsions **TiO₂10**, **St10**, **TiO₂5 St5**

INCI	CAS	Trade name	Supplier	TiO ₂ 10	St10	TiO ₂ 5 St5
TiO₂, silica, cetyl phosphate	13463-67-7; 7631-86-9; 3539-43-3	Eusolex® T-Easy	Merck	10%	-	5%
Steareth-2	9005-00-9	Massocare® S2	Massó	-	6%	3%
Steareth-21	9005-00-9	Massocare® S21	Massó	-	4%	2%
Caprylic capric triglycerides (CCT)	73398-61-5	Triglycerides C8C10 55/45	Stéarinerie Dubois	35.6%	35.6%	35.6%
Deionized Water				53.4%	53.4%	53.4%
Phenoxyethanol and Methylparaben and Ethylparaben and Propylparaben and Butylparaben	122-99-6; 99-76-3; 120-47-8; 94-13-3; 94-26-8;	Sepicide HB	Seppic	1%	1%	1%

2.2. Methods

2.2.1. Emulsions formulation

TiO₂10 emulsion – the particles were first pre-dispersed in the water phase with an Ultrasonic Processor (Fisher Scientific FB-705) during 300 sec at 80% amplitude. Next, the oil phase is added to the water phase during 30 seconds under vigorous stirring (11000 rpm) using a rotor-stator T25 digital ultra-turrax (IKA, Freiburg, Germany) equipped with the dispersing head S25N-25F. Then, the homogenization is continued for 1.30 minutes to form an emulsion. Finally, after adding the preservative, the mixture was put under stirring (Turbotest, radial flow turbine of 55 mm diameter, VMI Raynerie) at 500 rpm for 15 minutes.

St10 emulsion– the oil phase and 10% of emulsifier were heated up to 80°C under mechanical stirring (400 rpm), as well as the water phase. Then, as for the previous system, the oil phase was added to the water for 30 seconds and the homogenisation was continued for 1.30 minutes at 11000 rpm. The formulation was left cooling down to 30°C under stirring (Turbotest, radial flow turbine of 55 mm diameter, VMI Raynerie) at 400 rpm. Next, the preservative was added and the emulsion was left under the same stirring for more 15 minutes.

TiO₂5St5 emulsion was prepared using both protocols – particles were pre-dispersed in the water phase and then heated up to 80°C, the surfactant is mixed with the oil phase and also heated up to 80°C. Next steps are identic to the previous emulsions.

Once prepared, the mixtures were split into three samples, stocked at 4°C, 40°C and ambient temperature, respectively, for stability monitoring.

2.2.2. Contact angle measurement

20 mg of TiO₂ particles coated with silica and cetyl phosphate were compressed under 5 tonnes to form compact pellets. Water and caprylic capric triglycerides contact angle measurements on the obtained pellets were performed using a portative goniometer PGX+ (ScanGaule, Gravigny, France) connected to the PGPlus software. It is equipped with a high-resolution camera to acquire images, with a specific lighting system associated with a mirror to visualize the liquid droplet deposited onto the surface. A syringe (Ø=0.77mm) is used to depose the first droplet on the surface and its volume is increased by the addition of five successive drops to approximately 7µL. Photography is taken after each liquid addition and the advanced contact angle is determined on the identified triple point (intersection of the liquid, solid and vapour phases using the software.). Advancing contact angle was measured at least in triplicate for both liquids.

2.2.3. Microscopy

The emulsions microstructure was observed by means of an optical microscope (Leica DMLP microscope) equipped with a digital camera at a magnification of x100 under the bright field. Leica IM 1000 software was used to analyse the micrographs.

2.2.4. Droplet size distribution

The emulsion droplets size were measured by static light scattering (SLS) using a laser diffraction particle size analyser SALD-7500 nano (Shimadzu Co., Ltd, Japan) equipped with a violet semiconductor laser (405 nm). The emulsions were diluted with deionized water to achieve the absorption parameter equal to 0.2. Considering the important chemical inhomogeneity of the medium (presence of the particles and their agglomerations besides to the oil phase droplets), and to get rid of the optical properties of all of them, the Fraunhofer theory was used. The droplets median values (D50) were acquired, representing the size in microns that splits the distribution with half above and half below this diameter.

2.2.5. Rheological measurements

Rheological tests were performed using a controlled stress rheometer (HR2, TA instruments). All the measurements were carried out in duplicate at 25°C. The solvent trap was used to prevent sample drying. Once loaded, the samples were left at rest for two minutes prior to any measurement. Samples were analysed once and then changed prior to further analysis.

Flow curves were obtained by recording shear stress and viscosity values at increasing shear rates ranging from 0,001 to final 5000 1/s (continuous ramp, logarithmic mode) for 300s. 60 mm aluminium parallel plate device was used for the test and the gap was fixed at 200µm.

The linear viscoelastic region was obtained through **oscillatory measurements** conducted at 1Hz with an increasing strain from 0.1% to 100% (logarithmic mode).

For each system were collected:

- G' (storage modulus) in the linear region of the deformation;
- $\tan \delta (=G''/G')$ in the linear region of the deformation;
- $\gamma_{90\%G'}$: the end point of the linear viscoelastic region was determined as a strain (%) when the storage modulus (G') value was dropped 10% from the linear level [35].
- $\gamma_{G'=G''}$: the strain value at $G'=G''$ ($\tan\delta=1$) which corresponds to a loss of viscoelastic properties and to the transition to the product flow process.

The **frequency sweep ramp** was performed from 0.01 to 10 Hz at a constant strain remaining within the previously marked linear viscoelastic region of each sample. Then, storage (G'), loss moduli (G'') were reported for the rheological characterization of investigated samples.

2.2.6. Differential scanning calorimetry

Emulsions thermal properties were described by the differential scanning calorimeter Pyris 1 DSC (PerkinElmer). A small amount of the sample (up to 20 mg) was weighted in 50 µL aluminium pan and hermetically closed. An empty aluminium pan was used as a reference. The cooling/heating program was applied in the temperature range from 10°C to -60°C with a 5°C/min rate. Two consecutive cooling/heating cycles were applied to each sample to confirm the repeatability of the observations.

Both, the temperature corresponding to the peaks maxima (T°C) and the enthalpy values (ΔH J/g) of each peak were collected.

2.2.7. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Setsys apparatus (Setaram, Caluire-et-Cuire, France) with the Setsoft software. Around 40 mg of emulsion were weighed and heated under the air atmosphere by the following procedure (Program 1):

- Isotherm: 10 min at 25°C;
- Ramp: 25°C to 350°C at 5°C/min;
- Isotherm: 2 min at 350°C.

The weight loss of the sample is registered as a function of temperature. The first derivative of the TGA curve (the DTG curve) was also plotted to visualise the dynamics of the weight loss (mg/min).

To refine the obtained results, a second procedure was developed and focused on the slow water evaporation (Program 2):

- Isotherm: 120 min at 70°C;
- Ramp: 70°C to 500°C at 2°C/min;
- Isotherm: 10 min at 500°C.

2.2.8. Texture analysis

Analysis of emulsions texture properties was performed using a texture analyzer TAXT Plus (Stable Micro Systems, Cardiff, UK).

A **compression test** was carried out with the cylindrical probe P/35. 1 mL of the product was compressed by the probe at a constant speed of 1 mm/s up to a 0.5 mm gap between the probe and the base.

An **extrusion test** was carried out with a compression disc of 45 mm diameter in a 180 mL container (50 mm diameter) filled with cream on 45 mm height. The probe compressed and extruded the product up and around the edge of the disc at a constant speed test of 1 mm/s to a distance of 30 mm, and then returned to its start position.

Spreading properties were recorded in compression traction mode, equipped with friction module A/FR (ASTM-D 1894-90). A polypropylene plastic sheet was fixed to the base and the Helioplate™ HD 6 (Helioscreen, Marseille, France) plate, consisting of 50×50 mm² PMMA substrate and with homogeneous roughness on the entire surface, equal to 6 µm, was fixed to the sled (63.5×63.5 mm²). 200 µL of the cream was applied onto a 20×20 mm² surface of the PMMA plate in four lines, parallel to the movement of the sled. The sled was then pulled across the polypropylene support at a constant speed (3 mm/sec) on 120 mm and the force of the emulsion spreading was measured. The test conditions were adapted from similar studies of the spreading properties developed in our laboratory [36,37].

For each test, the positive area under the curve was calculated (A_+ g.sec) to express the work to spread, to compress or to extrude the product. Each test was performed at least three times.

During the **stretching test**, 100 µL of the product is compressed and then stretched between the cylindrical probe P/0.5R and the base at 40 mm/s, respecting a 0.8 mm gap. The filament stretching was monitored with a camera to identify the breakpoint of the filament in order to measure its breaking length, as developed by Gilbert *et al.* [38].

2.2.9. Data analysis

Results were presented as the mean value $\pm$ standard deviation (SD).

XLSTAT software (Addinsoft, Paris, France) was used to perform the statistical analyses of the collected data. The ANOVA test (two-way analysis of variance) was applied to the results to spot the significant differences between the emulsions ($P < 0.05$). Mean intensities were compared using the Tukey multiple comparison tests to distinguish different groups of products.

3. Results

3.1. Building up an emulsion – formulating stable, totally emulsified systems using an emulsifier, TiO_2 particles or surfactant/particles mixture

All the emulsions were formulated at 10% of emulsifier and with oil phase (CCT)/water phase ratio equal to 40/60. The Steareth-2 possesses the HLB value (hydrophilic/lipophilic balance) equal to 4.9 and the Steareth-21 value equals to 15.5, thus the 60/40 mixture oriented the emulsion towards O/W type with a final HLB=9 [39].

Meanwhile, the particles behave differently. Their ability to form an emulsion is guided by their physical and chemical properties: size, specific area, and the most important, the coating. According to Bernauer *et al.* [40], the silica (16%) and cetyl phosphate (6%) coated TiO_2 particles are of 70 nm size (number weighted median). They have a rutile crystalline form (>98%) and a volume specific surface area of $150 \text{ m}^2/\text{cm}^3$. All these parameters will favour the adsorption of the particle on the liquid/liquid interface, and, consequently, its capacity to emulsify the water and the oil phase. The discussed TiO_2 particle is considered amphiphilic, as shown by contact angle measurements (Figure 1) that indicated good compatibility with both phases; it can be dispersed in either the oil or the water phase, even if it has more affinity with the oil phase.

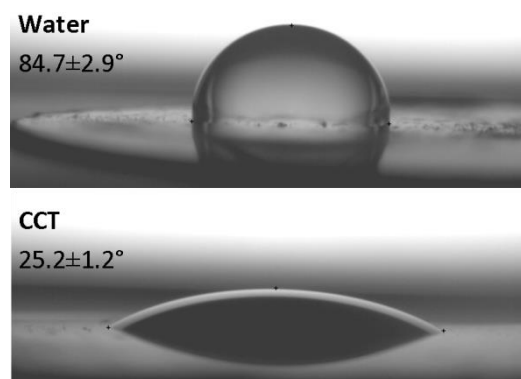


Figure 1. Images of the droplets and calculated values of the contact angle formed between water and caprylic triglycerides liquids on a TiO_2 /silica/cetyl phosphate pellet.

It is important to note that in our study, the incorporation method had a major impact on emulsion formation. The incorporation of the particles to the more suitable oil phase will not permit the emulsion formation (during the emulsification step, the two phases remain non-homogeneous). On the other hand, the initial dispersion of the particles in the water phase makes possible the formation of the emulsion and the total incorporation of the oil phase.

The obtained systems were first analysed in terms of the microstructure. As can be seen from Figure 2, the gradual changing of the emulsions microscopic properties is totally dependent on the emulsifying system.

The TiO_2 10 emulsion is heterogeneous; with a polydisperse droplet population and the agglomerations of particles present in the continuous phase (Figure2b). The $\text{St}10$ surfactant forms fine droplets as presented in Figure2d. The addition of the particles to the surfactant (Figure2c) has a consequence on the droplet size and the size distribution. There is an appearance of a small population of large drops due probably to coalescence. The same phenomenon was also observed by Binks *et al.* for the systems stabilized by C_{12}E_7 emulsifier coupled with hydrophilic fumed silica particles [11].

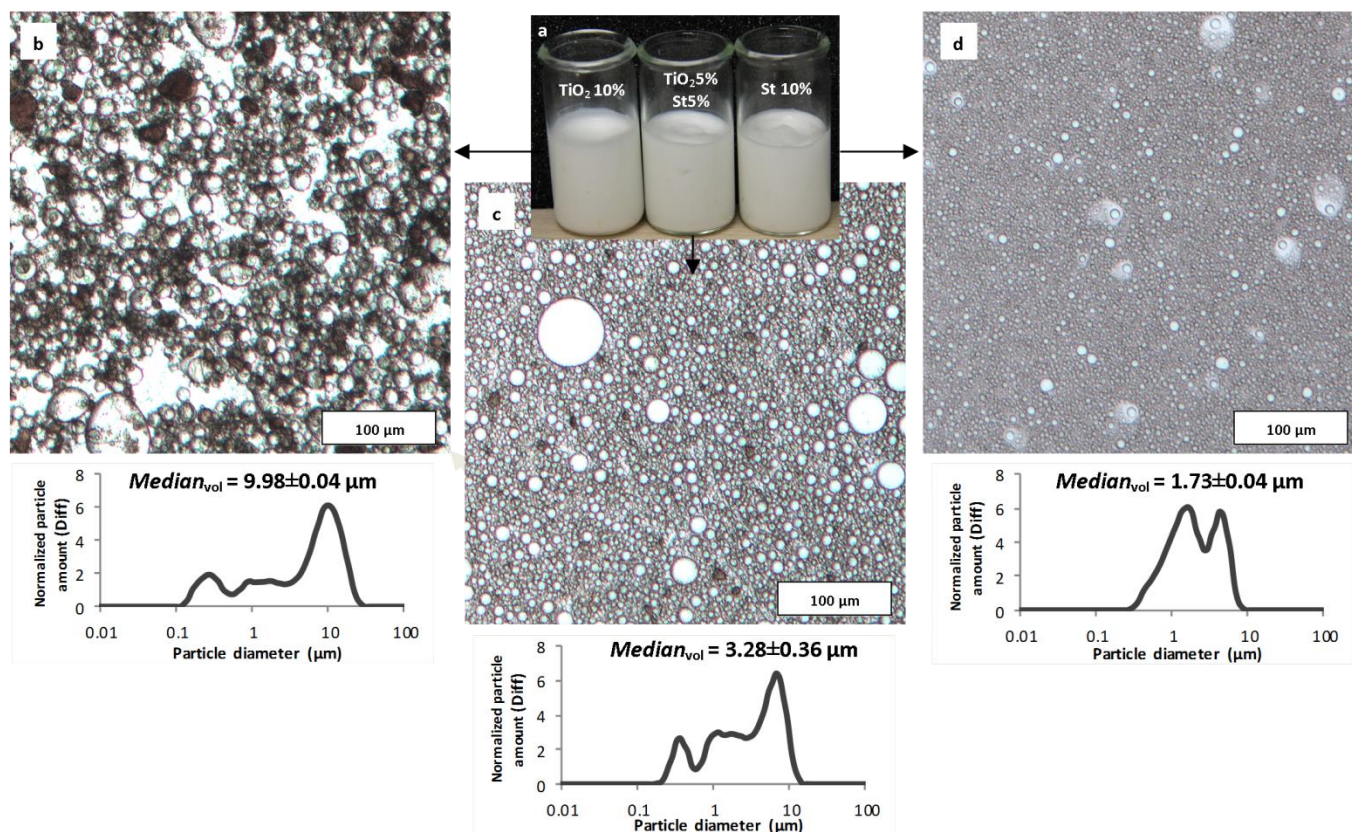


Figure 2. (a) Photography of three homogenous and totally emulsified emulsions as well as their bright field micrographs ($\times 100$), median_{vol} (D50) values and particle size representation in volume for (b) **TiO₂ 10**, (c) **TiO₂ 5 St 5** and (d) **St 10** emulsion respectively.

Several studies observed the destabilization of the emulsion stabilized by the surfactant coupled to the particles due to the loss of the surfactant from water interfaces and its adsorption on particle surfaces [11]. In this study, the structure of the emulsion was also modified by the particles (increasing twice the D50 in volume from **St10** to **TiO₂5St5**), but the systems remain macroscopically stable at 4°C, 40°C and room temperature for more than 3 months. The full emulsification, without any water or oil phase separation during the time, made possible the further macroscopic analysis of the systems.

3.2. How the matrix is affected by the emulsifying system? Rheological and thermal investigation

The first step in the macroscopic approach combined three rheological tests.

3.2.1. Viscoelastic and flow behaviour

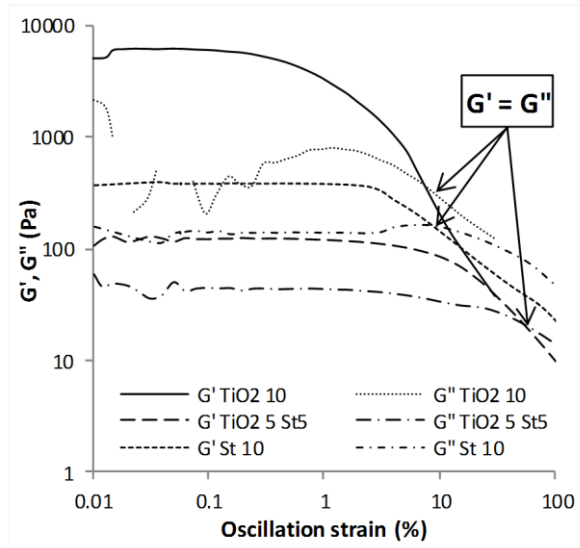


Figure 3. Evolution of the elastic (G') and viscous (G'') moduli as a function of the oscillation strain of three studied emulsions stabilised exclusively by TiO_2 particles at 10%, by a surfactant/particle mixture TiO_2 5% and Steareth2/21 at 5%, or by the Steareth2/21 10% alone. The destruction of the system is represented by the G' and G'' intersection.

Figure 3 presents the evolution of the elastic (G') and viscous (G'') moduli as a function of the oscillation strain and the calculated parameters are reported in Table 2.

Table 2. Calculated G' (Pa) and $\tan\delta$ values at the plateau; the plateau length expressed by oscillation strain point at 10% of G' plateau decrease; and the network destruction point represented by the oscillation strain value at G' and G'' intersection for **TiO₂10** emulsion, **TiO₂5St5** and **St10** one.

	G' (Pa)	$\tan\delta$	$\gamma_{90\%G'}$ (%)	$\gamma_{G'=G''}$ (%)
TiO₂10	6534.9±449.9	0.175±0.008	0.28±0.02	8.8±1.2
TiO₂5St5	125.8±2.8	0.353±0.004	3.00±0.23	49.9±4.0
St10	369.9±15.4	0.362±0.003	3.11±0.32	9.9±1.2

Three studied emulsions clearly showed a different response to the applied oscillation strain. The storage modulus, G' , of **TiO₂10** was at least one order of magnitude higher than the emulsions containing Steareth-2/21 emulsifier. Meanwhile, it shows a quick response to the deformation, as revealed by a short linear plateau length $\gamma_{90\%G'}=0.28\%$. Since the **TiO₂10** emulsion does not contain texturing agents, the only network that is formed within the matrix is the arrangement of the droplets. As a consequence, this nonhomogeneous system is more elastic at rest but is quickly deteriorated once solicited.

It is noteworthy that the differences between these two systems intervene at higher deformations: the loss of the viscoelastic properties is strongly delayed for the mixture **TiO₂5St5** ($\gamma_{G'=G''} = 49.87\%$).

It is interesting to notice that the viscoelastic properties of the studied emulsions are not directly governed by the droplet sizes. While the droplet sizes increase with the particle quantity in the emulsion, for the oscillatory strain measurements, it is more likely that the mixture of both surfactant and particle stabilizers favours the formation of a more flexible and resistant system.

The flow behaviour of the studied systems can be split into three domains, as presented in Figure 4. Region I corresponds to low shear rates (from 0.01 to 1 s^{-1}): the **TiO₂10** is the most viscous at low shear rates, followed by

St10 and, finally, the mixture. According to Barnes [41], the first zone corresponds to the draining of the emulsion under gravity. At low shear rates, the products behave similarly to the oscillation test according to the elastic modulus G' : the combination of two emulsifying systems decreases the viscosity of the product.

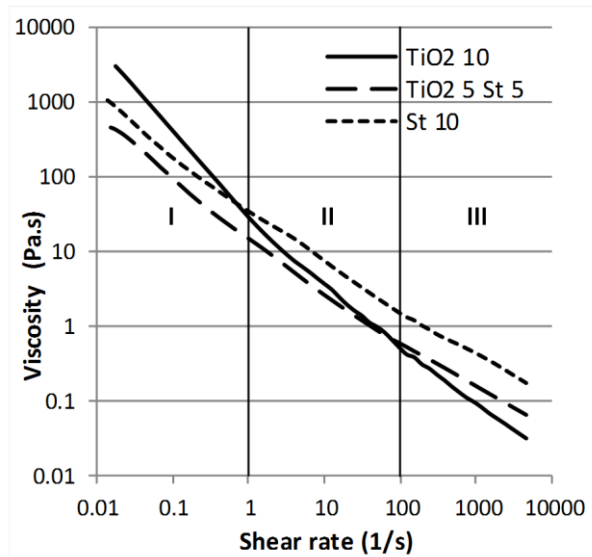


Figure 4. Viscosity evolution of three emulsions as a function of the shear rate. The shear-thinning behaviour of the samples is divided into three regions: **I** 0.01-1 1/s (low shear rates); **II** 1-100 1/s (medium shear rates); **III** 10-10000 1/s (high shear rates).

When the shear rate increases (region II), the **TiO₂10** and **St10** reverse their order and, finally, in the region III, the emulsion stabilized by **TiO₂** particles shows the lowest viscosity and the most important shear thinning behaviour. According to the literature, high shear values can create new interfaces in the system, leading to imperfect coverage and when two imperfectly-covered droplets interact, bridges can be formed in the places where particles are shared between both interfaces [42]. Consequently, the further coalescence of the bridge-connected droplets will favour the important shear thinning behaviour.

On the contrary, two surfactant containing emulsions present a similar mechanic resistance of the network build by Steareth-2/21, resulting in a comparable appearance of the viscosity evolution function of the shear rate. Consequently, decreasing the quantity of the surfactant from 10% to 5% decreases the viscosity of the emulsion but does not affect the general shear thinning behaviour.

The results point out the fact that all the studied systems (particles, non-ionic emulsifier or their mixture) are able to form droplets and stabilise their interface over time. Meanwhile, they also influenced the droplets interactions within the matrix, which results in individual response to the oscillatory and continuous solicitations.

3.2.2. Frequency response

The frequency test results can give complementary information about the investigated systems. According to Tadros *et al.* [43], one usually obtains part of the frequency dependence of G' and G'' when analysing viscoelastic emulsions. This frequency dependence can be observed for **St10** and **TiO₂5St5** (Figure 5), two emulsions containing the conventional emulsifier. This suggests the idea that for the **TiO₂5St5** mixture emulsifier, it is more likely that the Steareth emulsifier controls the network properties and prevails over the **TiO₂** particles. Probably, this Steareth network is developed in 3 dimensions and, at higher frequencies, there is less time for droplet “sliding” one on each other and the droplet arrangements are responding more like a solid. For this reason, the moduli values are increasing with higher frequencies.

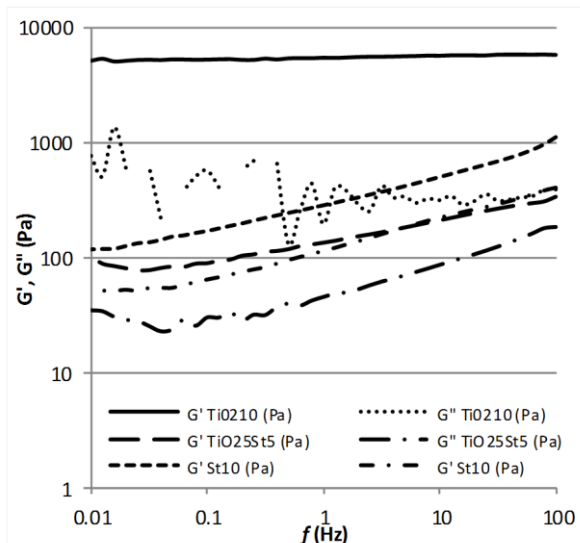


Figure 5. Double logarithmic plots of G' and G'' as a function of frequency. Frequency independent $\text{TiO}_2\text{10}$ emulsion, with no moduli evolution and frequency dependant $\text{TiO}_2\text{5St5}$ and St10 with moduli, increasing at higher frequencies.

Frequently, when the storage modulus is independent of the frequency this is due to the “strong gel-like” behaviour of the analysed product [44]. But, this explanation cannot be applied in case of the $\text{TiO}_2\text{10}$ emulsion. However, one can observe that the G' value is almost independent of the frequency and that of G'' gradually decreases. This specific behaviour can be mainly attributed to the formation of a 3D network of the flocculated TiO_2 particles on the oil droplets [45].

The rheology approach demonstrates that there are at least two types of networks formed in the analysed samples. The one formed by Steareth surfactant is more flexible during the longer times of solicitation, being able to rearrange and less flexible with increasing frequency and the system has less time to “relax”. In the meantime, the frequency test confirms that $\text{TiO}_2\text{10}$ emulsion also forms a network from flocculated solid particles as shown by the high consistency of the product at rest. But, this network, developed in the continuous phase, is quickly destroyed as showed by the oscillatory strain and flow tests.

3.2.3. Emulsions thermal response

Till today, the emulsions thermal properties were studied in some specific cases, like in crude oil case (water in oil emulsion) [46] or in the food industry (oil in water emulsion) [47].

Considering the O/W emulsions with potential applicative interest, the thermal properties of such systems were never or very little discussed to our knowledge. That’s why thermal studies were performed on the investigated samples. Each emulsion gave a specific response to the thermal solicitation depending on the emulsifier system. Two techniques were adapted: DSC for low temperatures investigation and the TGA for high ones.

For both techniques, it was clearly observed that the use of the surfactant of Steareth-2/21 type changes the behaviour of raw materials. In Figure 6, it can be seen that the use of the Steareth delays the solidification of the water and oil phases.

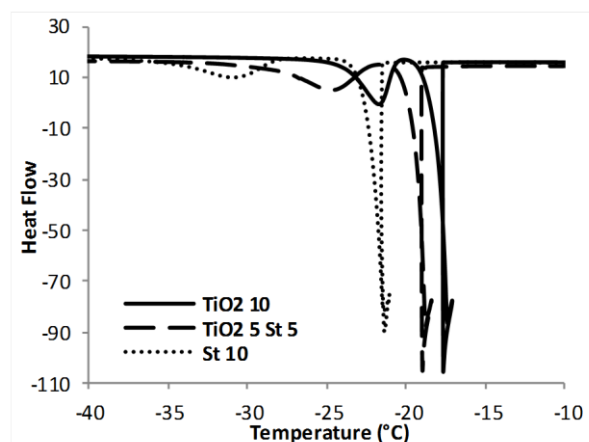


Figure 6. DSC freezing profiles of **TiO₂10**, **TiO₂5St5** and **St10** emulsions. The sharp peak corresponds to the water freezing, while the second represents the oil phase solidification. The addition of the Steareth-2/21 emulsifier delays the solidification of both: continuous and internal phases.

The continuous phase (water) freezing was very intense for the studied systems as it represents the continuous phase of the emulsions. In order to explore more precisely the droplet organisation, the interest was focused on the oil phase solidification.

Table 3 gives information about the temperatures of the oil phase solidification of pure raw materials: pure CCT, the mixture St/CCT (1/7.12) and TiO₂/CCT near to the studied emulsions.

Table 3. Temperatures of solidification of oil phases: of three studied emulsions EM_ **TiO₂10**, EM_ **TiO₂5St5**, EM_ **St10** and of the raw materials pure CCT and the TiO₂/CCT, St/CCT mixtures. a-c Values with a different letter in one column indicate that corresponding products are significantly different from the considered measurements.

Sample	Oil phase solidification T°C
TiO ₂ /CCT	-19.18±0.07 ^a
EM_ TiO₂ 10	-21.26±0.29^a
St/CCT	-21.59±0.27 ^a
EM_ TiO₂5 St5	-24.72±0.24^b
CCT	-26.89±2.69 ^b
EM_ St 10	-30.94±0.05^c

Firstly, it can be observed that the addition of solid raw materials (Steareth and TiO₂) to the CCT switched the solidification point of the oil to higher temperatures due to the physical state of these substances at such temperatures. Then, when subjected to the dispersion state and the presence of an aqueous continuous phase (emulsions), the solidification of these emulsifying mixtures was also influenced and tends to decrease. Finally, the addition of the Steareth in the emulsion brought closer the solidification of the oil phase to the pure CCT freezing point.

It is obvious that the presence of the Steareth-2/21 molecules or of TiO₂ particles mixed to the pure CCT changes its solidification mechanism. It is susceptible to be present not only at the water/oil interface but also in both internal and external phases [48]. Indeed, the TiO₂ particles, present in the water phase and at the interface are susceptible to migrate towards the oil phase, because of their affinity with CCT. However, the freezing behaviour of the emulsions is not exclusively linked to the behaviour of pure raw materials, as shown by statistically different temperatures between the raw materials and the emulsions (Table 3), the emulsions droplet dispersion should be also considered. In the case of **St10** emulsion, for example, the droplet sizes are small, resulting in their important number and strong

organisation, making the internal phase less accessible to the solidification. When increasing the TiO_2 quantity in the emulsion, the formation of bigger and less numerous droplets favours a quicker solidification of the internal phase.

These results show that the solidification point of the oil phase depends on the size and number of oil droplets, their dispersion and the positioning of the raw materials inside or on the interface of the droplets of the emulsion.

To complete the observations, the TGA analyses were executed. Firstly, classical heating from 25°C to 350°C was performed on each sample to evaluate the weight loss (Table 4). Evidently, the total weight loss was statistically different between the three studied emulsions because of the TiO_2 solid particles residue at a 5% level in **TiO₂5St5** emulsion and at a 10% level for **TiO₂10** emulsion. Meanwhile, the weight loss corresponding to the water evaporation (Step 1) and oil phase evaporation (Step 2) is difficult to interpret. The evaporation dynamics are different, but not well represented only by the weight loss value.

Table 4. Percentage of the total weight loss, water loss during Step 1 (25°C-170°C) and oil phase loss during Step 2 (170°C-350°C). ^{a-c} Values with a different letter in one column indicate that corresponding products are significantly different from the considered measurements.

	Total weight loss(%)	Step 1(%)	Step 2(%)
TiO₂10	85.61±0.7 ^c	46.9±3.4 ^b	38.7±2.8 ^b
TiO₂5St5	91.7±0.2 ^b	53.3±0.2 ^a	38.4±0.1 ^b
St 10	97.1±0.4 ^a	51.9±0.7 ^{ab}	45.2±0.3 ^a

To better observe the described phenomena, the complementary test was performed. The heating of each sample was realized in two steps: an isotherm at 70°C for 2 hours, followed by the heating step, from 70°C to 500°C. During the first step (Figure 7a), the temperature was maintained at 70°C to favour slow water evaporation. At that temperature, the surfactant Steareth-2/21 is already in a liquid state but still assuring the emulsion stability. Pure water evaporation dynamics is given as a reference and it shows a similar DTG curve with **TiO₂10** emulsion continuous phase evaporation. For **TiO₂10** emulsion the process is quicker, finished in one step with almost no retention of the bulk water. Only the end of the evaporation reveals the presence of the droplet network, with 10%-15% water retention over 15 more minutes. In contrast, both emulsions containing Steareth-2/21 molecules exhibit slower water evaporation, pointing out the retention of water over a larger time scale, due to water/surfactant interaction. The following suggestion can be proposed: at these high concentrations (5% and 10%) the surfactant is placed not only on the interface but also in oil and aqueous phases. Unlike solid particles, the amphiphilic molecules are able to build different structures (micellar organisation, liquid crystalline phases, etc.) and to retain an amount of the bulk water inside these structures.

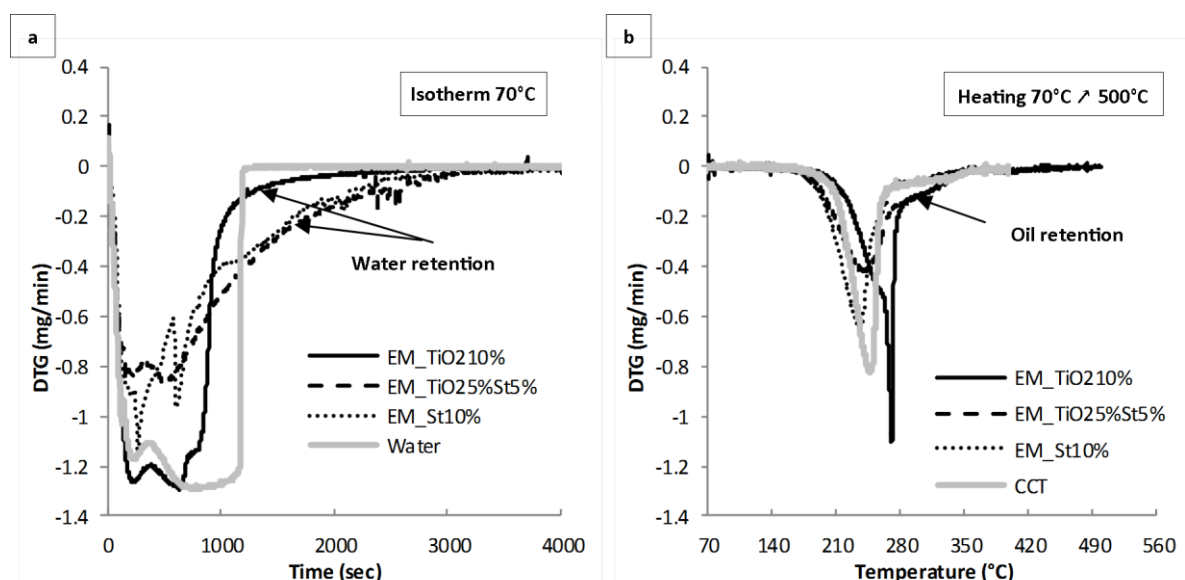


Figure 7. TG derivative (mg/min) is plotted as a function of (a) time for isothermal step at 70°C and (b) temperature during the heating step from 70°C to 500°C. Emulsions are represented by black lines, while the pure water (a) and CCT (b) reference are plotted in grey.

During the second step, the weight loss corresponds to the loss of the caprylic/capric triglycerides for **TiO₂10** and of CCT/Stearth for the emulsions **TiO₂5St5** and **St10** (Figure 7b). During a slow heating process, one can observe that the oil phase evaporation peaks are not identical for the three emulsions.

St10 emulsion, which holds the water during the first step, is gradually losing its CCT/Stearth mixture, showing that the surfactant and the oil phase are degraded in the same range of temperatures. On the contrary, for the internal phase evaporation of **TiO₂10** emulsion, TiO₂ particles create a physical barrier at the oil droplet surface and are retaining the CCT evaporation, which occurs abruptly at higher temperatures with the boiling of the oil. For the **TiO₂5St5** mixture, the behaviour is more similar to the **St10** emulsion in terms of degradation temperatures, as if the Steareth-2/21 molecules were the principal stabilizing mechanism. Interestingly, the mixture and **TiO₂10** share the same shoulder at the end of the degradation process, pointing out the possible adsorption of the small amount of oil phase on the particle surface.

The combination of the microstructure observation with the rheology response and the thermal properties of the studied systems is an innovative way to understand the distribution of the raw materials inside the matrix and to interpret the organisation of the dispersed phase. Once the arrangement of the model systems was described, the interest was focused on the textural properties, in connection with a potential applicative interest (food industry, pharmaceutical application, etc.).

3.3. How the emulsifying system impacts the applicative properties? Textural approach

Textural analyses were performed to describe the emulsions applicative properties. This approach is often used for the characterisation of formulated systems and gives information about the network organisation and its response to different types of solicitation. It is an interesting tool to complete the results of the rotational rheology [49] and to evaluate the firmness, consistency or other textural parameters [50], dermal and pharmaceutical efficiency [51]. To our knowledge, very few studies in the literature deal with the texture properties of such emulsions and the compared effect of different type of interfacial agents.

Moreover, some of the textural tests were developed to predict the sensory properties of the texture of emulsions. For example, parameters from the extrusion test are a part of the “integrity of shape” attribute model that is related to the properties at rest of a product. Parameters from the compression test are correlated to the “compression force”

evaluated by a sensory panel that is directly related to the consistency of an emulsion. And the stringiness of the emulsion can be quantified through a compression/stretching test [36] that is related to the extensional properties of products. Connecting data from texture analysis to microstructure and droplets arrangements of emulsions is a key to understand the differentiated impact of raw materials on emulsions formulation but also interaction with skin and surfaces.

Based on the literature, four tests were selected: compression, extrusion, spreading and stringiness, to collect the characteristics of the emulsion with an applicative interest. The obtained results are presented in Table 5.

Table 5. Positive areas A+(g.sec) under the force curves, corresponding to the work of compression, extrusion and spreading of the TiO₂ 10%, TiO₂5% Steareth 2/21 5%, and Steareth 2/21 10% containing emulsions. The stringiness of the same emulsions is represented in mm. ^{a-c} Values with a different letter in one column indicate that corresponding products are significantly different from the considered measurements.

	Compression A+(g.sec)	Extrusion A+(g.sec)	Spreading A+ (g.sec)	Stringiness (mm)
TiO₂10	118.1±3.5 ^b	4608±95 ^b	628.9±14.5 ^c	5.9±0.4 ^b
TiO₂5St5	87.5±3.3 ^c	4122±72 ^c	1065.3±12.2 ^a	10.1±0.2 ^a
St10	207.9±1.1 ^a	5833±192 ^a	1007.6±22.8 ^b	10.8±0.4 ^a

For the compression test, **St10** exhibit the highest value compared to **TiO₂10** and finally the **TiO₂5St5**. It is mainly due to shearing during compression [49]: the squeezing of the small quantity of the sample provokes the beginning of network breakdown, identic with the **II** zone of the flow test (1-100 1/s). Similarly, the force necessary to extrude the products is most important for **St10**, followed by the **TiO₂10** and finally, by **TiO₂5St5** emulsion, which was proved (by oscillatory strain test) to possess the most flexible, but less consistent organisation.

The compression and extrusion tests are dealing with partial 3D network destruction, but still keeping the individual droplet interactions. These interactions can be accessed by the spreading and stringiness tests.

The product is spread between two nonpolar surfaces: PMMA and polypropylene. The examples of the spreading traces are given in Figure 8. The traces show the fragility and quick breakdown of the **TiO₂10** emulsion with a non-homogenous trace and less affinity with nonpolar surfaces. The Steareth-2/21 containing emulsions present homogenous spreading, pointing at the flexibility of the system, but also the strong droplet interactions as shown by higher A+ values. This behaviour was already evoked during the frequency test: the slow spreading of the sled is similar to low frequencies effect when the network of the viscoelastic system has time to rearrange and to adapt its structure. **TiO₂10**, behaving more like an elastic system, is immediately broken down. Interestingly, **TiO₂5St5** exhibit the highest value of spreading, in a relationship with their ability to deformation resistance ($\gamma_{G^*=G''}$).

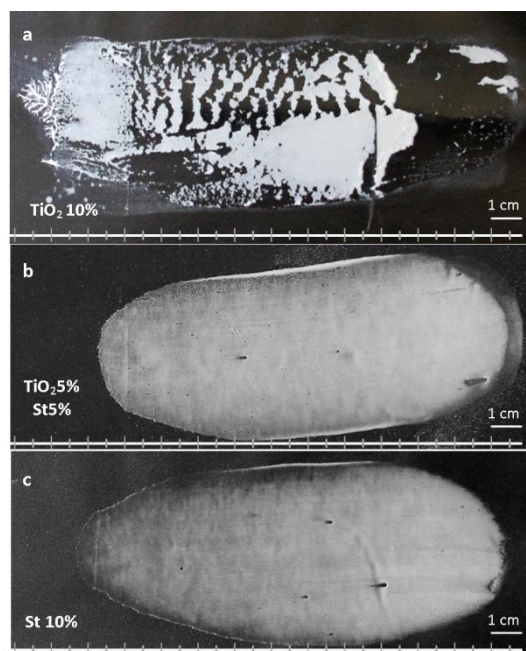


Figure 8. Example of spreading traces (spreading over 120 mm distance at 3 mm/sec between a polypropylene and PMMA surface) for (a) TiO_2 10, (b) TiO_2 5St5 and (c) St10 emulsions.

The attempt of the Steareth-2/21 containing systems to keep its organisation and stretching properties is more pronounced than in case of TiO_2 stabilised system. This test gives a complementary proof of the Steareth-2/21 surfactant main role in the emulsion stabilisation and network formation, even if it is introduced in the system containing the TiO_2 particles, which are also able to stabilise the interface. However, the stringiness values show poor stretching properties of all the studied emulsions. Consequently, the type of system stabiliser does not significantly impact the emulsions capacity to stretch. Considering the emulsions applicative interest, the poor stretching properties is a good characteristic for our products.

4. Conclusion

This study focused on development (composition, formulation process) and the analysis of three emulsions stabilised by TiO_2 particles, by a conventional polyethoxylated fatty alcohol surfactant/co-surfactant namely Steareth-2/21 surfactant and by the mixture of both. The aim was to raise the scale from the interface stabilisation towards building up a macroscopically stable and totally emulsified system and to access the mechanism of droplets interactions and organisation which is less investigated today.

Depending on the interfacial agent used, the size, droplet size distribution and droplets network organisation are different. Probably due to a different decrease of the interfacial tension, emulsions containing TiO_2 particles exhibit bigger droplet size and higher polydispersity compared to conventional ones. Moreover, we showed that conventional surfactant has a major impact on the microstructure of the emulsions as one of the emulsions containing the mixture of TiO_2 particles and surfactants is very close to the conventional ones. Meanwhile, the stability over time is not affected by the type of the emulsifying system.

Combined to the microstructure analyses, the study of the rheological and thermal analyses revealed the impact of the different interfacial agent on the droplets network organisation and its heterogeneity but also how the TiO_2 particles, surfactants and the mixture of both organized between both phases and interphase. Once again, it puts in evidence the major impact of the conventional surfactants compared to the TiO_2 particles on the viscoelastic

properties and the thermal properties. Thanks to the mixture of TiO_2 particles and surfactants, it is possible to obtain a system with higher deformability.

The thermal analysis was successfully used here, on oil-in-water emulsions, and brought complementary and original data to explain the role of the ingredients on the organisation of the microstructure.

This study brings new interesting results, valuable from a theoretical and practical point of view: by modulating the composition of the emulsifying system, one can develop unique texture properties of the emulsions. This approach is very promising as these textural data are related to topical applications of products and should be considered when developing products of practical interest. Contrary to the systems developed in the literature, the emulsions developed during this study present great applicative potential.

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