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Abstract

Formulations incorporating different cosmetic grade TiO_2 nanoparticles were developed according to a self-produced protocol on the basis of typical sunscreen cream oil-in-water emulsions. Role of nanoparticles and, more specifically, the impact of two different lipophilic surface treatments on microstructure and stability of the formulations were assessed. Aging of formulations was performed under classical conditions at room temperature or under accelerated conditions at 50°C, with or without TiO_2, and was characterized by several tools such as rheology, microscopy, and particle size measurements. Changes in emulsion stability and aggregation state of nanoparticles were followed over time. Destabilization phenomena were identified: under accelerated aging, the formulation without nanoparticles underwent a coalescence occurrence whereas the formulation incorporating nanoparticles was subjected to aggregation of the colloidal particles. Besides, TiO_2 nanoparticles strongly affected the particle-droplets interactions and thus modified the emulsion microstructure with a coating-dependent effect: destabilization mechanisms occur more rapidly with *alumina (and) triethoxycaprylylsilane* (coating 1) TiO_2 nanoparticles as compared to *alumina (and) isopropyl titanium triisostearate (and) triethoxycaprylylsilane crosspolymer* (coating 2) nanoparticles.

Chemical compounds studied in this article:
Titanium Dioxide (PubChem CID 26042); Alumina (PubChem CID 14769); Triethoxycaprylylsilane (PubChem CID 76262); Isopropyl Titanium Triisostearate (PubChem CID 162941)

Introduction

A nanomaterial is defined by the European commission (Commission Recommendation of 18 October 2011 on the Definition of Nanomaterial," *Official Journal of the European Union*, 2011, sec. L 275/38) as "a natural material formed accidentally or manufactured, containing not bonded particles, in an aggregate or agglomerate form, and where at least 50% of the particles in number size distribution have one or several dimensions of between 1 nm and 100 nm". In March 2011, a nanotechnology consumer products inventory reported a list of more than one thousand goods, including 33 sunscreens ("Nanotechnology - Project on Emerging Nanotechnologies"). Nano-sized TiO_2 is the most used inorganic filter in the cosmetic industry, and is incorporated as UV mineral sunscreen because this mineral provides effective protection from solar radiation(Serpone, Dondi, and Albini 2007), together with a moderate skin covering effect related to their nanoscale size (Popov et al. 2005).

Raw TiO_2 nanoparticles have hydrophilic surfaces consisting in polar hydroxyl groups. Thus, surface treatment is used in cosmetic industry to improve both the compatibility and the performance of the particles. The most common treatments for nanoscale titanium dioxide cosmetic grade are:

- A grafting of aluminum oxide $Al(OH)_3$ or Al_2O_3 which reduces the photocatalytic activity and production of derived reactive oxygen species observed when TiO_2 is exposed to UV (Dunford, Salinaro, and Cai 1997);

- A lipophilic surface treatment in order to improve the dispersion of nanoparticles in the oily phase of the emulsion, such as dimethicone, stearic acid or silane components.

Assumptions on the locations of coatings have been issued (Lewicka et al. 2011): the lipophilic layer would overlap that of $Al(OH)_3$, which itself covers the nanoparticle.

TiO_2 based sunscreen emulsions have been until now poorly investigated (Botta et al. 2011; Labille et al. 2010; Lewicka et al. 2011). Recently, aging of commercial sunscreens has been studied in order to assess the alteration of the nanoparticles used in cosmetic formulations (Botta et al. 2011). However, as all previous investigations were based on commercial creams, authors could not state exactly on the role of the nanoparticle species by themselves. The originality of the present work lies in the production of a non commercial formulation, but similar to one, containing cosmetic grade nanoparticles. As a consequence, for the first time, characterization of the system was performed by using an emulsion where each ingredient was identified, obtained using a fully controlled process, and as a consequence, it was possible to understand the contribution of nanoparticles themselves.

From a general point of view, colloidal residues containing TiO_2 nanoparticles from personal care products may be released into aquatic environment (Botta et al. 2011). Indeed, destabilization mechanisms of such systems are important to understand, in order to optimize formulation processes, to adapt the duration of use of products or to correlate physicochemical properties with potential toxicity. Thus a detailed characterization and identification of nanomaterials is an essential requirement for risk assessment during its entire life cycle (Johnston et al. 2009).

Herein, we have developed three specific formulations consisting in an oil-in-water emulsion without nanoparticles and "derived" emulsions containing TiO_2 nanoparticles with two different coatings. A characterization was then performed at both initial state and during aging. Rheology, microscopy and particle size measurements were used to point out distinct features of the emulsions. Dynamic viscoelastic measurements provided information on the sample structure and more deeply on the intermolecular and interparticle forces in the material. Microscopy and particle size determination gave information on size distribution of the colloidal particles in the emulsion. Finally, combining the different results led to a better understanding of the role of the nanoparticles in the destabilization mechanisms.

1. ***Experimental section***

1.1. Chemicals and reference materials

Purified water, with a resistivity of 15 mΩ.cm, was used for all experiments, emulsions preparation and particle size analysis.

TiO$_2$ nanoparticles with two different coatings (see Table 1) have been used in the present study: *alumina (and) triethoxycaprylylsilane*, named coating 1, *alumina (and) isopropyl titanium triisostearate (and) triethoxycaprylylsilane crosspolymer* named coating 2. Samples were kindly given by Kobo Products, France. According to the manufacturer, the caprylylsilyl group is chemically bonded to the pigment and the primary particle size of the particle is given to be 10 nm (Kobo 2012).

Ingredients were chosen to achieve an oil-in-water emulsion, close to a commercial sunscreen formulation. This formula was deliberately optimized in order to allow an easy nanoparticles incorporation procedure, and also with a view to study toxicity afterwards. The formulation without nanoparticles is called F-0, and those with nanoparticles are F-N1 for the coating 1 and F-N2 for the coating 2, respectively. All the ingredients used for the formulations and their content in both formulations are listed in Table 2.

1.2. Emulsion preparation

This protocol has been developed in order to obtain similar emulsions whether the nanoparticles are added or not.

Emulsion without nanoparticles

The emulsion was prepared according the following optimized procedure:

The gelling agent was first sprinkled in water and left without stirring for 20 min. This mixture and the phase A were then heated separately at 80°C under mechanical stirring to get homogenization. When both phases were at 80°C, phase A was added to the aqueous phase under stirring at 11,000 rpm for 1min30 with a rotor-stator type homogenizer (Ultra-Turrax, stator diameter 25mm, rotor diameter 18mm, *IKA*). Then the mixture was left cooling down under mechanical stirring at 500 rpm with mixer (Turbotest, radial flow turbine of 55mm diameter, *VMI Rayneri*), and triethanolamine was immediately added (before the temperature attained 50°C) to reach a final pH of 6.6 corresponding to polymer neutralization. The mixer speed was then increased to 1000 rpm, for 15 min thus making the cream becoming more consistent. Once at 40°C, the mixture was cooled down using a cold water bath, until 30°C was reached while continuously stirring. The preservative was added below 30°C, and the mixture was stirred for 5 additional minutes. The cream was then put under vacuum in order to remove the air bubbles incorporated during process.

Nanoparticle dispersion

To improve the dispersion of nanoparticles in the emulsion, a paste of TiO$_2$ nanoparticles was prepared by mixing with spatula 40% (w/w) titanium dioxide with 60% (w/w) cetearylethylhexanoate. This paste was then grounded on a 3-cylinder mill until a fine dispersion was obtained, controlled by optical microscopy for homogeneity. Typically, the dispersion with coating 1 needed to be grounded once, and the one with coating 2 required grounding for three times. The resulting paste was used to prepare the emulsion with nanoparticles.

Emulsion with nanoparticles

The previous protocol described above for emulsion preparation remains roughly the same except when phase A was added to the aqueous phase under stirring at 11,000 rpm for 1min; then the nanoparticle dispersion was immediately incorporated under stirring during one more minute under vigorous stirring. In order to get a final percentage of 5% of nanoparticles in the emulsion, the effective amount of cetearylethylhexanoate necessary to get a right dispersion had to be previously calculated.

1.3. *Monitoring stability and aging process*

In order to test the stability of the three emulsions over time, two batches of each emulsion were stored for three months at:
- Room temperature 20°C $\pm$ 2°C, in plastic opaque flasks,
- High temperature 50°C$\pm$ 1°C, in closed glass flasks in a heating ventilated oven (Heraues *Thermo Scientific*).

Storage at 50°C enabled to accelerate the aging process and speeded up the mechanism of destabilization of the emulsion. At each storage temperature, samplings for analysis were made at different time after emulsification: t_0 +24 hours, t_0+72 hours, t_0+7 days, t_0+14 days, t_0+21 days, t_0+28 days, t_0+43 days and t_0+65 days. The different analyses described below were performed on each sampling.

1.4. *Particle size measurement*

Particle size analysis was performed using a laser diffractometer Mastersizer 2000 (*Malvern Instruments*, UK). The complex refractive index of the material to be measured was required. The real part of the refractive index has been determined by refractometric measurements. Considering previous experiments which gave the more relevant results, optical properties of the sample were thus defined as follow:
- For F-0: refractive index 1.450 and absorption 0.1
- For F-N1 and F-N2: refractive index 1.458 and absorption 0.1;

The calculation model used was the general purpose model, with spherical particle shape.
Approximately 0.1 g of emulsion was diluted in 600 mL of distilled water. The mixture was dispersed using ultrasonic waves for 2 minutes, until an obscuration rate of 10–20% was obtained. Background and sample were measured for 10 s, each sample being measured in triplicate.

1.5. *Rheology*

Rheological properties were carried out on a controlled-stress rheometer (AR 2000, *TA Instruments*) using a cone-plate acrylic geometry (diameter: 40 mm, nominal cone angle: 0.59°, truncation: 27 μm). Because of the presence of solid nanoparticles aggregates in emulsions F-N1 and F-N2, preliminary tests were performed on both emulsions with different measuring systems (plate-plate and cone-plate) in order to determine the right experimental conditions. Strain sweeps were carried out at 25°C, as controlled by Peltier effect, with imposed strain ranging from 0.01 to 100% at a fixed frequency of 1 Hz. This measurement permitted to evidencing the linear viscoelastic plateau corresponding to constant viscoelastic parameters whatever the applied strain. Measurements were performed in triplicate for each batch.

The rheological parameters measured are listed below:
- $\tan(\delta)$ where δ is the phase angle of the stress with respect to the strain;
- G'', the loss (or viscous) modulus, $G''=G^* \sin \delta$;
- G', the storage (or elastic) modulus, $G'=G^* \cos \delta$;
- γ_c, the critical strain, corresponds to the value of the strain percentage when G' reaches 90% of its initial value, as determined within the linear viscoelastic region.

1.6. *Microscopic measurements*

Microstructure visualization, droplet sizes of the emulsions and nanoparticle sizes of the dispersion and their distribution in the emulsions were qualitatively and, when possible, quantitatively determined at a magnification of ×200, using an optical microscope (*DMLP/DC300, Leica Microsystems*) equipped with a camera and the software IM1000.

2. Results and discussion

2.1. Formulation process

In the present work, we developed lab scale formulations without or with nanoparticles, as detailed in material and methods section. The corresponding specific step-by-step process aiming at producing such formulations similar to commercial products is described in Figure 1.

Three emulsions with identical formulation were obtained, including or not nanoparticles: a raw emulsion (F-0) and emulsions with alumina and triethoxycaprylylsilane-coated nanoparticles (F-N1) and with alumina, isopropyl titanium triisostearate and triethoxycaprylylsilane crosspolymer-coated nanoparticles (F-N2). Primary nanoparticle size given by the supplier was 10nm [10]. This value corresponds to the size of the crystals obtained after the manufacturing process. In powder form, the crystals are known to aggregate, inducing global sizes larger than one micron (Aldous and Kent). Therefore, the milling step (step n°2, Figure 1) of nanoparticles dispersion enabled an optimal dispersion of nanoparticles in the final formulation (Delrieu and Shao). As an example, results of particle size analysis for coating 2 dispersion, showed that 36% of the resulting particles are smaller than 1µm while 10% are larger than 10µm (details not shown). The way of adding the nanoparticles paste was also an important parameter; the dispersion quality was better when the paste was incorporated after the emulsifying step.
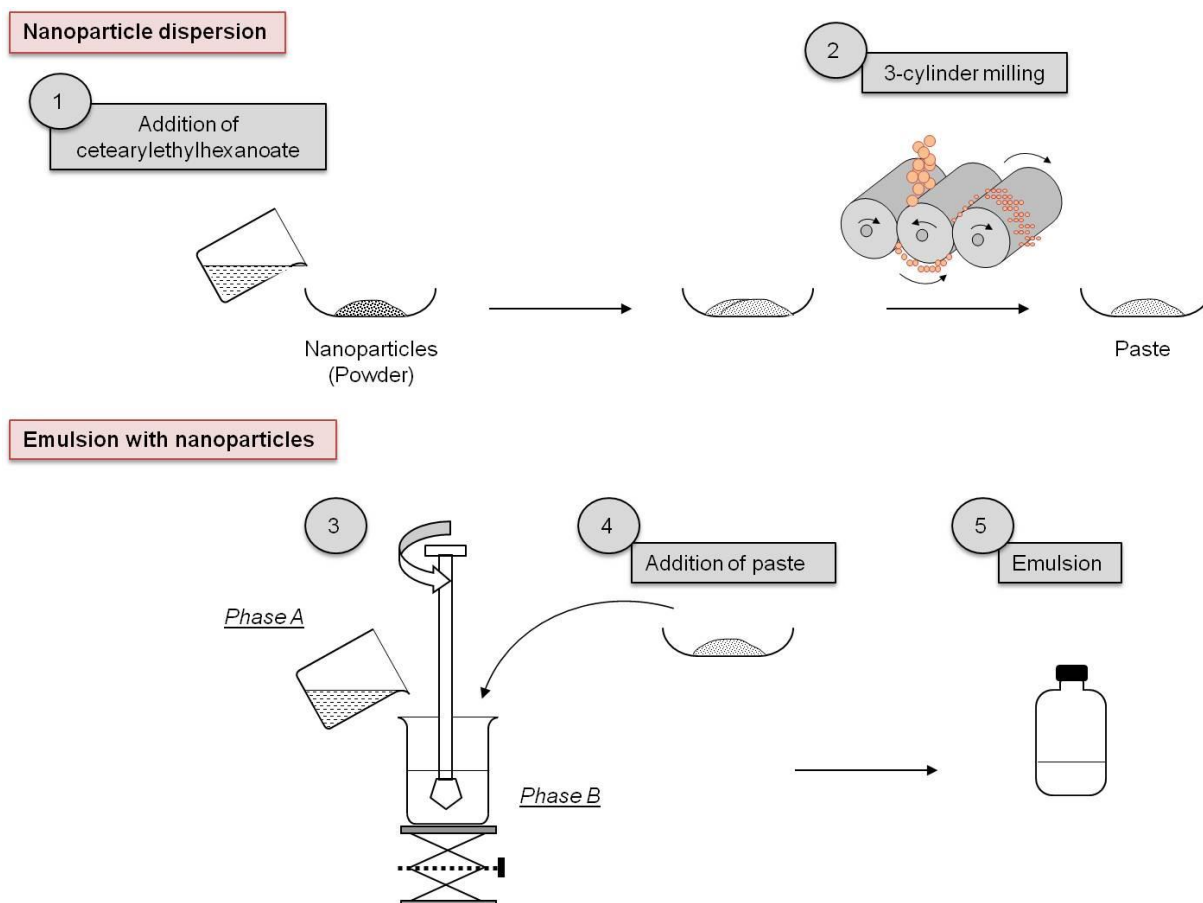

Figure 1 – Step-by-step process of formulations containing nanoparticles. A paste of TiO$_2$ nanoparticles is prepared with cetearylethylhexanoate (step 1). This paste is then ground on a 3-cylinder mill until a fine dispersion is obtained (step 2), and controlled by optical microscopy. When both phases of the emulsion are at 80°C, phase B is added to the aqueous phase under stirring (step 3) and the nanoparticle dispersion is immediately incorporated under stirring during (step 4). The emulsion with nanoparticles is obtained (step5).

2.2. Initial state and microstructure of the emulsions

Emulsion without nanoparticles
Our first criterion for characterization of the emulsion quality was the droplet size distribution. Figure 2a presents this distribution for emulsion F-0 as measured 72h after preparation. It appears as a polydisperse, bimodal distribution centered on two main sizes, 0.2 and 2.5 µm. Approximately 58 % of the droplets were smaller than 2.5 µm. Only 0.4% of the droplets were larger than 10 µm. The mean diameter by surface area to volume, commonly used to represent the finesse of an emulsion (Abismail et al. 1999), is 1.33 µm, providing additional evidence that this emulsion is mainly made up of small droplets. The corresponding optical micrograph presented on Figure 2b clearly confirms the major presence of fine droplets. However, care is required for such an interpretation of particle size results, as analysis demands large dilution of emulsion sample in water followed by ultrasonic treatment. Such a preparation procedure might be unrepresentative of the initial droplets size distribution in the bulk emulsion. Therefore, the above results would rather reflect the dispersion ability of the emulsion in a diluted medium.
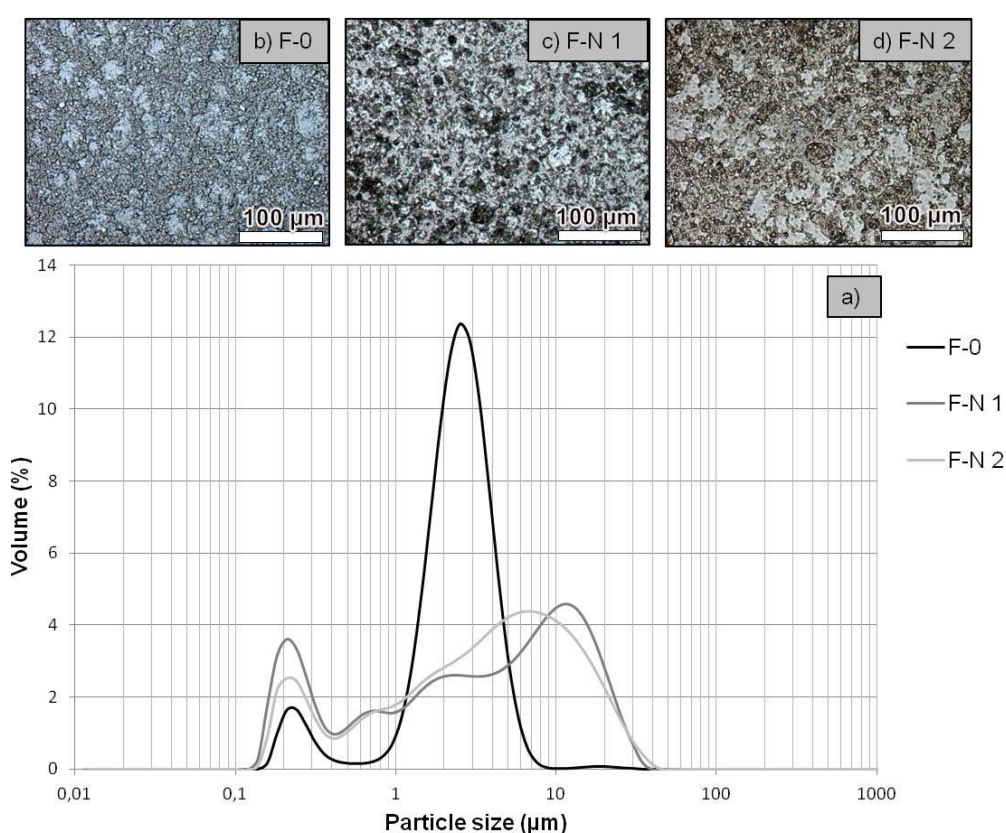

Figure 2 - Initial particle size volume distribution of F-0, F-N1 and F-N2.
Optical micrograph of F-0 (a), F-N1 (b) and F-N2 (c) taken at x200, represents droplets and nanoparticles distribution of the emulsion at 72 hours after emulsion preparation at room temperature. Particle size volume distribution (d) is performed on a particle size analyzer, at 72 hours after emulsion preparation

An emulsion is generally regarded as a viscoelastic material that has both solid and viscous liquid properties; both behaviors were measured through dynamic oscillatory tests within the linear viscoelastic plateau. Figure 3 shows the results of the strain sweep test for F-0. G', G'' and tan(δ), remain constant, as far as the maximum strain amplitude remains below a critical value γ_c corresponding to the limit of the linear viscoelastic region (strain below 3% for this example). In this region, the only measurement of G', G'' and γ_c were sufficiently discriminating to provide valid identification of the sample. For F-0, the elastic modulus G' is much greater than the viscous modulus G'' and tan(δ) remains below 1, thus illustrating a predominant elastic behavior (Tabilo-Munizaga and Barbosa-Cánovas 2005). Beyond this domain, moduli sharply change as the emulsion structure

6

progressively disrupts. When submitted to an increasing strain, the emulsion structure resists against deformation up to the critical strain γ_c, where G' starts decreasing, and G'' increases, simultaneously. This behavior is interpreted as a weak strain overshoot (Hyun et al. 2002) and clearly illustrates the emulsion's structure breaking down under strain. The gel structure is related to the aqueous phase gelling agent used in the present emulsion, namely C10-30 Alkyl Acrylate Crosspolymer. Above the crossing point (G'=G''), the material behaves more and more markedly as a liquid.
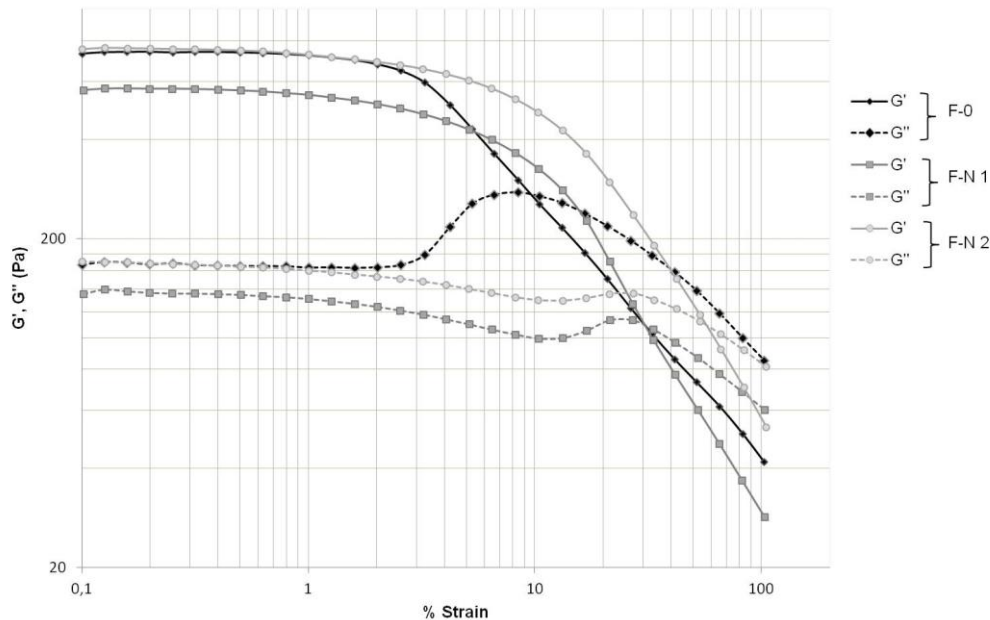

Figure 3 - Dynamic strain sweep test of F-0, F-N1, and F-N2 at a frequency of 1 Hz, at 25°C: G' and G'' as a function of applied strain from 0.1 to 100 %

Emulsion with nanoparticles : coating 1
Figure 2a indicates that F-N1 displays broader polydisperse distribution as compared to F-0. In addition, a new population of particles with larger sizes is observed. 43% of the colloidal particles are smaller than 2.5 µm while 24% are larger than 10µm. The curve reflects the distribution of both the droplets of the emulsion and the nanoparticles *per se*. As mentioned in section 2.1., our results indicate that the larger sizes in the emulsion F-N1 are mainly due to nanoparticles aggregates. The optical micrographs Figure 2c and d clearly confirm the presence of dark objects corresponding to aggregates larger than 10 µm and homogeneously dispersed in the presence of many smaller droplets and particles. During emulsification, presence of particles and surfactants might lead to a competitive adsorption onto the oil droplet surfaces. In addition, surfactant molecules may partially adsorbed onto particle surface, thus modifying their wettability, and consequently affecting the emulsifiers efficiency (Binks, Desforges, and Duff 2007). The work of (Pichot, Spyropoulos, and Norton 2010) shows that at high surfactant concentration, the particles are completely displaced from the interface to the hydrophilic continuous medium and that the stability is only achieved by the presence of a minimum amount of surfactants. In the present work, the surfactant-particles system together with the concentration ranges used are different from those utilized by Pichot *et al*. Although a high surfactant concentration was used, the introduction of particles was performed after the emulsification process. Moreover, TiO_2 particles used in this study were hydrophobic and dispersed in the non-continuous oil phase. As a consequence, the whole process enabled surfactants species to reach the water-oil interface before particles did. At the initial state, droplets of the emulsions with or without nanoparticles were probably of similar size. As greater droplets sizes (>2.5 µm) were observed for F-N1, an important competition between surfactants molecules and hydrophobic particles may be considered, inducing a partial coalescence phenomenon.

Figure 3 illustrates that F-N1 presents a predominant elastic behavior similar to F-0. However, the presence of nanoparticles significantly affected the viscoelastic properties of this emulsion with a decrease of G' and G''. This is attributed to the increase in the oil droplets size resulting from coalescence, as classically described (Tadros 2010). Another observation is that G'' of F-N1 shows weaker strains overshoot than F-0, thus indicating that the presence of nanoparticles weakened the network structure of the emulsion and prevented the droplets network structuring.

Emulsion with nanoparticles : coating 2
Emulsion incorporating nanoparticles with coating 2 shows the same initial colloidal particles size distribution than for the coating 1 (Figure 2a,c,d). This demonstrates that the protocol enabled to produce comparable emulsions, whatever was the coating used.

Again, as for F-N1, nanoparticles with coating 2 affected in the same way the final structure of the emulsion by weakening the strain overshoot

Interestingly, the decrease of rheological parameters described for F-N1 is no more observed for F-N2, as the moduli remain equal to F-0 within the linear region (Table 3). This suggests a major role of particle coating on the viscoelastic properties of emulsions. As the coating 1 was made of short alkyl chains (C8) grafted on an alumina surface, electrostatic interactions with the oil phase components were probably superior to steric effects. On the opposite, with an hybrid coating as coating 2 (See Table 1), steric effects occurred predominantly. The reduction in G' may result from a change in particle-particle interaction, that can be estimated by the computation of cohesive energy ($E_c = \frac{1}{2}$ G' γ_c^2) according to (Tadros 2004). High E_c reflects stronger particle-particle interaction giving rise to a more flocculated state. Both emulsions showed very similar droplet size distribution so that quantitative comparison between both systems could be assessed. E_c values are 2292 Pa and 4955 Pa for F-N1 and F-N2, respectively.

At the initial state, those differences are coating-dependent rather than due to the presence of nanoparticles by themselves. However, such systems are known as thermodynamically unstable, evolving to the physical separation of the aqueous and oil phases. Such instability may occur more or less rapidly through different mechanisms of destabilization, which could be influenced by initial interactions between components.

2.3. *Stability at room temperature*

Aging experiments were conducted on the three emulsions (F-0, F-N1 and F-N2) at room temperature over 65 days.

Formulation without nanoparticles

Results reported in Table 4 indicate no variation for the main rheological parameters (G', G'' and tan(δ)) measured on the plateau. This may be explained by the small droplet size and the highly packed structure evidenced for this emulsion at initial state (Figure 2b). However, the slight increases of both γ_c (Table 4) and droplet sizes (Table 5) over time are characteristic of an evolution towards coalescence. This could be explained by greater interdroplet interaction forces occurring in such highly packed emulsion system (Tan Hsiao 2009).

Formulation with nanoparticles

F-N1 and F-N2 show greater variations of rheological parameters with a decrease of G' by -29% and -39% respectively. A slight increase of tan(δ) together with a drop of γ_c are also observed, thus indicating that the emulsions become less elastic (Table 4). As for F-0, formulations with nanoparticles display a time-dependent increase of the average particle size.

To summarize, on the basis of rheological properties evolution, one can consider that the formulation developed without nanoparticles is relatively stable during three months, while the emulsions containing nanoparticles markedly destabilize.

2.4. Stability under accelerated aging

For accelerated aging conditions, as far as the temperature remains reasonable, the temperature stress applied speeds up, without altering, the mechanisms of deterioration operating at room temperature (Masmoudi et al. 2005). Aging experiments were conducted on F-0, F-N1 and F-N2 at 50°C over 65 days.

Thus, observations performed on emulsions stored at 50°C evidenced destabilization processes, as significant changes for all rheological parameters were observed up to the creaming phenomena of the emulsion; for this reason F-N1 is followed over time for 21 days corresponding to the macroscopic creaming of the product.

Formulation without nanoparticles

F-0 becomes less elastic with time (Table 4); the elastic modulus G' decreases by 56% after 28 days, thus illustrating a marked destabilization of the emulsion. This is mainly the consequence of droplets coalescence (Tadros 2004). This result is consistent with the microscopic observation that clearly evidences the occurrence of larger droplets aggregates. The formation of larger droplets enhanced the creaming rate of the droplets, thus increasing the phase separation occurrence. At 28 days, the linear viscoelastic plateau is no more reached, even at the lowest strain amplitude. Thus, after this time, physico-chemical investigations were stopped.

Particle size measurements and optical micrographs (Table 6 and Figure 4) unambiguously confirm the hypothesis of coalescence occurrence for F-0 stored at 50°C since an increase of larger sizes of the droplets was observed.
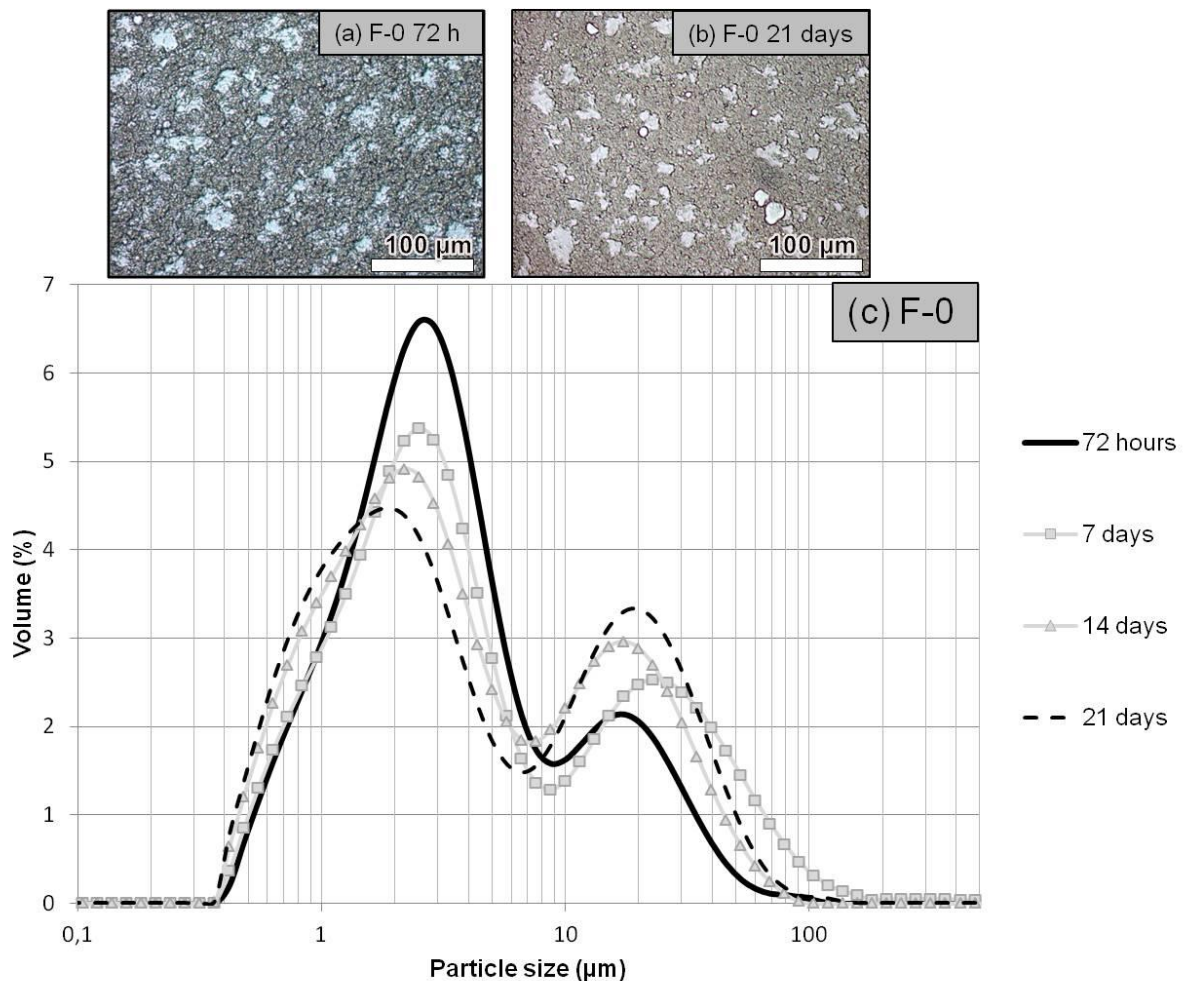
Figure 4 - Optical micrograph taken at x200 of F-0 aged at 50°C, 72 hours after emulsion preparation (a) and after 21 days (b). Particle size volume distribution (c) over time from 72 hours until 21 days of F-0 aged at 50°C

Formulation with nanoparticles

For F-N1, the storage at 50°C first induced a significant decrease of G' and γ_c, interpreted as the consequence of droplets coalescence. Afterwards, a sharp increase of G' is observed and interpreted as a result of nanoparticles aggregation (Tadros 2004). Particle size measurements confirm an increase of the mean size and a shift to larger sizes (Table 6). In addition, an inhomogeneous distribution with different sizes of particles was observed on micrographs after 72h (Figure 5a). At 22 days, three different phases of the system were observed: solid particles and highly aggregated particles well separated from the emulsion consisting of polydisperse oil droplets in the aqueous continuous phase (Figure 5b).

Obviously, the destabilization mechanisms were mainly controlled by the particles behavior in the emulsion. The aggregation might result from the strong attractive interactions between TiO_2 particles as repulsion forces did not dominate anymore. Moreover, when the solids were much larger than the oil droplets, the emulsion acted as a continuous phase towards the solids, and the interaction between the solids and the oil droplets became negligible (Masmoudi et al. 2005).

As for initial state and during room temperature aging, G' values for F-N2 are higher than for F-N1. Evolution of rheological parameters and particle sizes are similar but delayed for F-N2 (Table 4). The fact that F-N2 was less fluid when compared to F-N1 might explain that the diffusion of nanoparticles in the emulsion was slower and therefore the aggregation phenomenon arose later. These observations point out general coating-dependent effects.
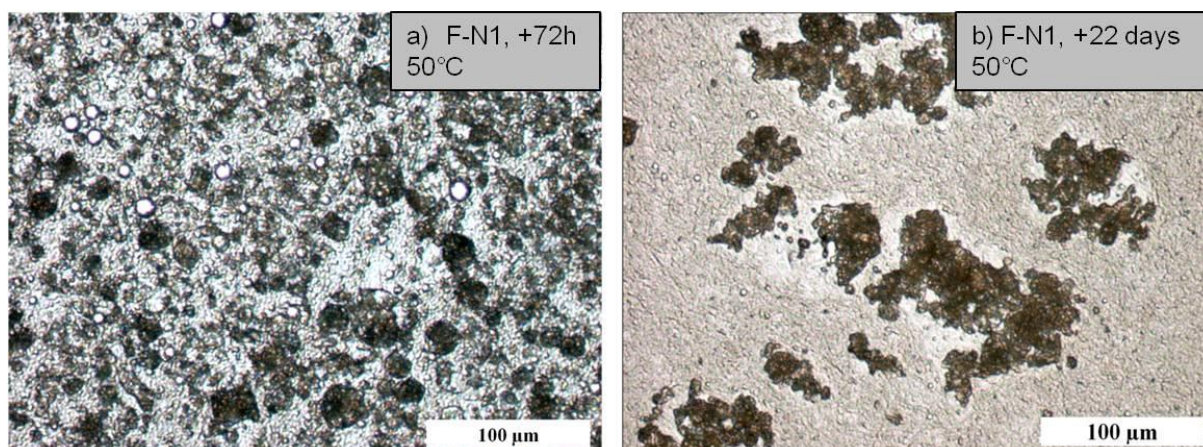
Figure 5 - Optical micrograph taken at x200 of F-N1 aged at 50°C, 72 hours after emulsion preparation (a) and aged at 50°C after 22 days (b)

Conclusion

The impact of two TiO$_2$ nanoparticles, differing from their surface coating, in a cosmetic oil-in-water emulsion has been investigated. To this end, O/W emulsions have been developed at lab-scale, and the physicochemical behavior of the emulsions, with and without nanoparticles, has been examined at initial state and during aging. The whole results demonstrate that the presence of nanoparticle in O/W systems does not only affect the characteristics of emulsions at initial state, but also markedly governs its evolution over time. Particle size measurements, rheological properties and microscopic observations allowed evidencing that the presence of nanoparticles affected the initial microstructure of the emulsion by modifying the oil droplet size distribution. Indeed, the nature of the particle's coating *alumina (and) triethoxycaprylylsilane* (coating 1), and *alumina (and) isopropyl titanium triisostearate (and) triethoxycaprylylsilane crosspolymer* (coating 2) respectively, strongly affected the particle-droplets interactions and thus modified the emulsion microstructure in terms of particle aggregation and rheological properties. During accelerated aging, it is obvious that the destabilization phenomena of the emulsions were mainly related to the nanoparticles. Oil droplets coalescence was observed without nanoparticles whereas nanoparticles aggregation was evidenced in the presence of TiO$_2$. In the presence of nanoparticles, the kinetic of destabilization appeared coating-dependant but the mechanism remained unchanged. As we did not work with commercial sunscreens, unlike studies that focused on similar destabilization mechanisms but in an environmental context (Botta et al. 2011), our knowledge of the emulsion process and our control of the ingredients enabled us to clarify the role of nanoparticles in such a formulation. In all cases, nanoparticles coating appears of primary importance as it governs the emulsion properties at both initial and aged times. Further investigations are in progress to characterize coated nano-sized TiO$_2$/emulsion interactions and nanoparticle surface modifications during aging.

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