



Effects of aging on structure and stability of TiO₂ nanoparticle-containing oil-in-water emulsions



Manon Rossano^{a,b}, Nicolas Hucher^{a,*}, Céline Picard^a, Daniel Colletta^a, Frank Le Foll^b, Michel Grisel^a

^aURCOM, EA 3221, FR CNRS 3038, University of Le Havre, 25 rue Philippe Lebon B.P. 540, 76058 Le Havre Cedex, France

^bLEMA, EA 3222, University of Le Havre, 25 rue Philippe Lebon B.P. 540, 76058 Le Havre Cedex, France

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ABSTRACT

Formulations incorporating different cosmetic grade TiO₂ 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 TiO₂, 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, TiO₂ 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) TiO₂ nanoparticles as compared to alumina (and) isopropyl titanium triisostearate (and) triethoxycaprylylsilane crosspolymer (coating 2) nanoparticles.

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1. 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 1000 goods, including 33 sunscreens (“Nanotechnology – Project on Emerging Nanotechnologies”). Nano-sized TiO₂ 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 et al., 2007), together with a moderate skin covering effect related to their nanoscale size (Popov et al., 2005).

Raw TiO₂ 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 Al₂O₃ which reduces the photocatalytic activity and production of derived reactive oxygen species observed when TiO₂ is exposed to UV (Dunford et al., 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.

* Corresponding author. Tel.: +33 232744399; fax: +33 232744391.

E-mail address: nicolas.hucher@univ-lehavre.fr (N. Hucher).

Table 1
Nanoparticles INCI name and composition depending on the coating used.

Name	INCI name	Composition (% w/w)
Coating 1	Titanium dioxide	73.5–82
	(And) Alumina	12.5–17.5
	(And) Triethoxycaprylylsilane	6–8
Coating 2	Titanium dioxide	73.5–82
	(And) Alumina	12.5–17.5
	(And) Isopropyl titanium triisostearate	3–4
	(And) Triethoxycaprylylsilane crosspolymer	3–4

TiO₂ 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 TiO₂ 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 a nanomaterial 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 TiO₂ 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.

2. Experimental section

2.1. Chemicals and reference materials

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

TiO₂ 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.

2.2. Emulsion preparation

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

2.2.1. Emulsion without nanoparticles

The emulsion was prepared according to 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 1 min 30 with a rotor-stator type homogenizer (Ultra-Turrax, stator diameter 25 mm, rotor diameter 18 mm, IKA). Then the mixture was left cooling down under mechanical stirring at 500 rpm with mixer (Turbotest, radial flow turbine of 55 mm 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.

2.2.2. Nanoparticle dispersion

To improve the dispersion of nanoparticles in the emulsion, a paste of TiO₂ nanoparticles was prepared by mixing with spatula 40% (w/w) titanium dioxide with 60% (w/w) cetearylethylhexanoate. This paste was then grounded on a three-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.

2.2.3. 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 1 min; 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.

2.3. 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 3 months at:

- Room temperature 20 ± 2 °C, in plastic opaque flasks,
- High temperature 50 ± 1 °C, in closed glass flasks in a heating ventilated oven (Heraeus Thermo Scientific).

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