Formulation of Pickering Emulsions for topical applications: The feasibility of cosmetic formulations and the forecasting of environmental impacts

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Abstract

This study deals with the development of complex Pickering emulsions close to industrial ones for dermo-cosmetic and topical applications. In the literature, generally simple Pickering emulsions are studied (composed of one oil phase, one aqueous phase, and the particles at the interface). There is no information about a complex system composed of several ingredients which could interact with the particle. Furthermore, the ecological impact of such systems is weakly explored. Thus, our aim is to bring data concerning the model particle of cosmetic grade TiO_2 studied by the URCOM laboratory and extend this to other selected particles.

The influence of the added components is studied by the analysis of the microstructure, the droplet size, and the viscoelastic properties of the emulsions. Moreover, the surface properties of the particles are investigated to highlight modifications that could be an indicator of toxicological or environmental toxicity.

In the case of the selected TiO_2 particles, the surface modification reduces the influence of the oil proprieties (viscosity, polarity) and wettability. In the case of the non-modified bentonite, the microstructure depends on the polarity of the oil used. The addition of glycerin has no impact on the emulsion, contrary to the addition of a texturing agent which affects the viscosity and the anchoring of the particles at the interfaces. The non-destructive extraction method permits obtaining particles in the same state as before the extraction and demonstrates that the addition of glycerin and xanthan gum also has no impact on the surface properties of the TiO_2 particles.

Keywords: Complex Pickering emulsions, topical application, environmental impact

Introduction

An emulsion is a thermodynamically unstable medium composed of a dispersed fluid phase in a continuous fluid phase. To stabilize such systems, emulsifiers are used, the most common are surfactants[1]. Emulsions are widely used in the field of cosmetics, however, studies show that surfactants have a measurable activity on the skin's barrier functions[2] and the cutaneous microbiota[3]. In addition, these molecules are responsible for environmental contamination (non-degradable) and have an ecotoxicological activity[4–6].

An alternative to surfactants is possible: solid particles; this type of emulsions is called Pickering emulsions. The particles are insoluble in the two phases but partially wettable in both of them. The stabilization of Pickering emulsions has several advantages: increased resistance to coalescence[7]; very high fixation energy at the interface (very stable systems)[8]; some are derived from natural sources which makes them less toxic than usual surfactants; and finally internal factors (size, shape, surface activity, concentration, etc.)[9] modify their stabilizing properties.

Many studies have been carried out on Pickering emulsions, but very few of them concern complex, stable, and homogeneous cosmetic formulations [10,11]. The majority of emulsions are simply composed of an aqueous phase (water), an oily phase, and particles. The interactions between the particles and the constituents of a complex emulsion have not been explored. Furthermore, the ecological impact of such systems is not explored yet.

Particles that we qualify as models, TiO_2 and silica, previously studied in the URCOM laboratory permit us to obtain fully emulsified and cosmetic grade simple emulsions [10]. Then, this approach was extended to other particles, chosen for their occurrence in the current market of cosmetic ingredients, their physicochemical characteristics, and a consequent bibliography. The following particles were selected: modified and pristine starches, chitosan, montmorillonite, and bentonite.

The second objective is to complexify the formulations to get closer to the reality of commercial cosmetic products. The ingredients selected for the complexification are widely used in cosmetic formulations and of having, according to their chances to interact with the particles.

To study their environmental impact, the particles have to be extracted from the media, which will allow the characterization of their surface. A modification of the surface structure or physicochemical properties should be an indicator of the non-stability of the particles in the formulation and could be an indicator of potential ecological or skin toxicity. The developed extraction methods must be non-destructive and the particles must remain unchanged during the process. The structure and the surface of the particles are studied in the pristine state, after a shear similar to the emulsification shear, and after the extraction from the media.

Materials and Methods.

1. Materials

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

Table 1: INCI, Trade name, and Suppliers of raw material

Function	Trade name	INCI	Suppliers
Particles	Eusolex Teasy	Titanium Dioxide (and) Silica (and) Cetyl Phosphate	Merck - Germany
	Gel White H-XR	Bentonite	BYK - USA
Emollients	Refined olive oil	Olea europaea (Olive) Fruit Oil (OO)	Bertin - France
	DUB MCT 55/45	Caprylic/Capric Triglyceride (CCT)	Stearinerie Dubois - France
	Massocare	Squalane (PS)	Comercial Química Massó - Spain
Humectant	Vegetable glycerin	Glycerin	Aromazone – France
Texturing agent	Rhodicare T	Xanthan gum	Solvay - Belgium
Preservative	Geogard ECT	Benzyl Alcohol (and) Salicylic Acid (and) Glycerin (and) Sorbic Acid	Arxada - Switzerland

Surface properties of the particles

The TiO_2 used, trade name Eusolex Teasy, of cosmetic grade, is a titanium dioxide particle coated with 16% silica (passivation layer for the deactivation of the photocatalytic properties of TiO_2) and 6% cetyl (C_{16}) phosphate providing amphiphilic and amphoteric properties.

According to the supplier, the bentonite used GEL WHITE-H XR is a “highly purified white bentonite manufactured from carefully selected, extremely pure ore deposits. […] used as a thixotropic agent in water-based systems for excellent anti-settling and stabilizing properties. GELWHITE-H XR has been sterilized by gamma irradiation.”. The bentonite is a natural, non-modified, and inorganic particle.

2. Methods

The formulation and characterization protocols were adapted from previous work of the URCOM team on the study of Pickering Emulsions[10,11].

2.1. Formulation of the simple system (water, particles, oil, and preservative)

The formula of the simple emulsions can be found in Table 2:

Table 2: Formula of the simple emulsion

Phase of introduction	Components	Wt%
Phase A	Water	qsp
	Particles	10 TiO_2 or 4 Bentonite
Phase B	Emollient	20
Phase C	Preservative	1

2.1.1. Bentonite Emulsions formulation – liquid oil phase

Dispersion: The particles were first dispersed in the water phase with an Ultrasonic Processor (Fisher Scientific FB-705) during 300 s at 80% amplitude – between 25000 and 30000 J.

Emulsification – simple Pickering emulsion: the phase B and the phase C were added to the phase A for 30 s under vigorous stirring (11,000 rpm) using a rotor-stator digital Ultra-Turrax (IKA, Freiburg, Germany) equipped with the dispersing head S25N-25 F. Then, the emulsification was continued for 90s at 80% amplitude – between 13000 and 14000 J - to form an emulsion with the Ultrasonic Processor used previously.

Finally, the mixture was put under stirring (Turbotest, radial flow turbine of 55 mm diameter, VMI Rayneri) at 500 rpm for 15 min. After that, the emulsion was degassed at low pressure and split into two samples, stored at 50°C and ambient temperature for stability monitoring.

2.1.2. TiO2 Emulsions formulation – liquid oil phase

Dispersion: The procedure is the same as for the preparation of the Bentonite dispersion.

Emulsification: The phase B and the phase C were added to the phase A under stirring (11,000 rpm) using a rotor-stator - Ultra-Turrax (IKA, Freiburg, Germany) equipped with the dispersing head S25N-25 F. Then, the emulsification was prolonged for 1min 30s with the UltraTurrax (11,000rpm). Finally, the mixture was put under stirring (Turbotest, radial flow turbine of 55 mm diameter, VMI Rayneri) at 500 rpm for 15 min. After that, the emulsion was degassed at low pressure and split into two samples, stored at 50°C and ambient temperature for stability monitoring.

2.2. Addition of components for the complexified formula

The complexification process and formula are the same for both particles.

- *pH adjustment*: The pH of the formula was adjusted with NaOH at 1g/L drop by drop under stirring until the pH value reached 5.5 before stirring with the Turbotest.
- *Glycerin*: Glycerin was added in the aqueous phase at the same time as the particles (phase A).
- *Xanthan gum*: Xanthan Gum was added under stirring after the emulsification step just after the addition of the phase C and before homogenization with the Turbotest.
- *Glycerin and Xanthan gum*: Xanthan gum was grabbed in glycerin and the mixture was added under stirring after the emulsification step after the addition of the phase C and before homogenization with the Turbotest.

2.3. pH measurement

The pH was measured with a pH meter HACH SensION+ PH3 calibrated before each session of measures.

2.4. Optical microscopy

Two optical microscopes were used to observe the microstructure of the emulsions:

- LEICA - DMC 2900 microscope equipped with a digital camera at a magnification of x100 under the bright field. LAS V4.9 software was used to analyze the micrographs.
- NIKON – Eclipse Ni-U microscope equipped with a digital camera at a magnification of x100 and the software Nikon; Y-TV55 was used to analyze micrographs.

Each emulsion was diluted at 50% with ultrapure water before measurement.

2.5. Droplet size analyses

SALD-7500, a laser diffraction particle size analyzer from Shimadzu Co., Ltd, Japan was used to measure the droplet size. The technique used is static light scattering with a laser (405nm). Emulsions were diluted with ultrapure water to reach an optimum absorption parameter of 0.2.

To determine the size of the objects in the medium, the Mie theory was used with a refractive index of 1.40-0.02i for the Bentonite particle and 3.35-0.05i for the TiO_2 particles. The size distribution was acquired in volume and number representations. The volume representation focuses on the large size objects, whereas the number representation focuses on the small but is more present in the medium objects.

2.6. Rheology measurements

Flow curves: Rheological tests were realized with a rheometer (HR1, TA instruments) at 20°C and were triplicated with a solvent trap to avoid sample drying. A resting time of two minutes was applied after the loading of the sample to limit the shear stress generated by the device. Continuous shear flow from 0.001 to 1200 s^{-1} (logarithmic scale) tests were carried out for 300s with a 40mm aluminum parallel-plate and with a fixed gap of 100µm.

Viscoelastic properties: The viscoelastic properties (linear viscoelastic region) were measured by a rheometer (HR1, TA instruments) at 20°C using dynamic measurements and were triplicated with a solvent trap to avoid sample drying. Oscillatory strain sweep tests were performed at a frequency of 1Hz at increasing strain ranging from 0.1% to 100% (logarithmic scale) using a 40 mm parallel-plate aluminum device (40 mm diameter, 100 µm gap). The collected parameters were: the storage modulus (G') in the linear region of the deformation; The loss modulus (G'') in the linear region of the deformation; Tan δ (=G"/G') in the linear region of the deformation; The deformation rate (%), which determines the end of the linear viscoelastic region[12], corresponding to the rate at which G' lost 10% of its value when compared with its value in the linear region.

2.7. Contact angle measurements on particles pellets

Formation of Pellets: The powder was dried for 12 hours in an oven at 100°C and 50 mg were compressed under 5 tones by a FRITSCH pellet press.

Contact angle measurements: the device used was a portative goniometer Scangaule PGX+ equipped with a camera and a mirror to visualize the liquid droplet deposited on the surface, in association with a the PocketGogniometer® 4.3.0.6 software. A syringe (0.77 mm in diameter) was used to depose the droplets on the surface of the pellet and its volume was increased by the addition of five successive drops (advanced contact angle) of a volume between 2-6µL each (approximative total volume 10µL). Pictures were taken after each liquid addition and the advanced contact angle was determined on the identified triple point (intersection of the liquid, solid, and air phases). Advancing contact angles were measured at least in five replications for all liquids.

The solvents used for the surface free energy measurements were ultrapure water, formamide, and diiodomethane. The oils used for the wettability were caprylic capric triglycerides, olive oil, and phytosqualane.

Surface energy calculations: To determine the surface energy, the Van Oss model was used to solve the Young equation with 3 the known composites of the 3 reference solvents.

2.8. Surface characterization

FT-IR measurements were recorded in absorbance mode over the 4000-650 cm^{-1} region at a resolution of 8 cm^{-1}, with 4 accumulated scans, using a Perkin Elmer Frontier FT-IR spectrometer (PerkinElmer, Villebon sur Yvette, FRANCE) with ATR mode (Diamond/Zinc Selenide crystal). Spectrum analysis was performed on the Spectrum program Version: 10.4.00.0190. In this measurement mode, the measures were realized on the extreme surface chemistry.

2.9. Extraction method

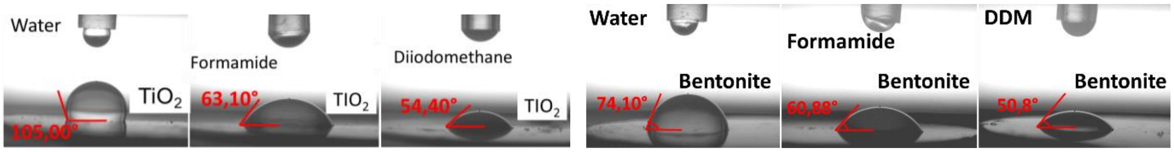
The extraction technique consists in eliminating sequentially the two phases and their constituents.

Results and discussion

1. Usual impacting factors for Pickering emulsion stability and properties

1.1. Surface free energy of the particles

The surface energy of the particle was determined based on the calculation from the contact angle acquisition (Figure 1).



a) TiO_2 – 3 reference solvents contact angle measurements

b) Bentonite – 3 reference solvents contact angle measurements

Figure 1: a) TiO_2 and b) Bentonite contact angle formed with water, formamide, and diiodomethane, the 3 reference solvents for the measure of the surface energy

Using the contact angle measured for each reference liquid on dried pristine TiO_2 pellets and thanks to the components of the reference liquids, the Van Oss equation can be solved to determine the surface free energy and its components for dried pristine TiO_2 (Table 3).

Table 3: Components of the surface energy of TiO_2 and Bentonite particles

	Components ($mJ.m^{-2}$) - TiO_2	***Components ($mJ.m^{-2}$) - Bentonite***
γ^{LW}	33,3	29,1
γ^{-}	1,2	12,5
γ^{+}	1,2	0,4
γ^{S}	**35,7**	**33,8**

The pristine TiO_2 particles essentially have a non-polar behavior and, minor basic and acidic monopolar contributions (the γ^{+} and γ^{-} are low and of equal intensity). These non-null polar components may influence their capacity to interact with the interfaces in the emulsion.

The pristine bentonite particle also has a non-polar behavior, minor acidic contribution, and a non-negligible basic contribution superior to the acidic contribution. The non-modified bentonite particle has non-polar and basic behavior. These characteristics may influence their capacity to interact with the interfaces in the emulsion.

1.2. Physico-chemical properties of oils

The viscosities of the 3 different oils have been calculated with a rheometer (flow curves) and are indicated in Table 4.

Table 4: Dynamic viscosity of the 3 oils used (OO, CCT, and PS) measured at 25°C

Oil	**Dynamic Viscosity (mPa.s) - 25°C**
CCT	16.3 ± 0.3
PS	22.8 ± 0.3
OO	42.9 ± 0.6

High-viscosity oils favor the formation of emulsions with large droplet sizes since the viscosity influences the anchoring of the particle at the interface[13]. Olive oil has the highest viscosity, it should form the emulsions with the largest droplet size, contrary to CCT which should form the emulsions with the finest droplet size.

1.3. Oil Polarity

The oil polarity is then estimated by the measurement of the interfacial tension versus water. Results of the 3 oils can be found in Table 5.

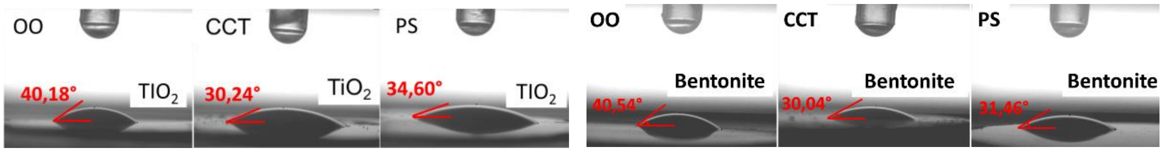
<u>Table 5</u>: Interfacial tension (vs water) of the 3 oils used (OO, CCT, and PS) measured at 20°C

Oil	**Interfacial tension (*vs* water) mN.m^{-1} at 20°C**
OO	18 ± 0,34
CCT	25,8 ± 0,08
PS	54,01 ± 0,51

High interfacial tension of oil against water means that there are more repulsive interactions between the two liquids, explaining why the interface between water and this type of oil is more complicated to stabilize[7]. Phytosqualane is the most non-polar oil with the highest interfacial tension against water, it should form emulsions that are less stable over time and with a large droplet size distribution.

1.4. Oil wettability with the particles

Finally, the wettability of the oils on particles pellets was measured and the results are illustrated in Figure 2.



a) TiO_2 – Wettability measurements for OO, CCT and PS

b) Bentonite – Wettability measurements for OO, CCT and PS

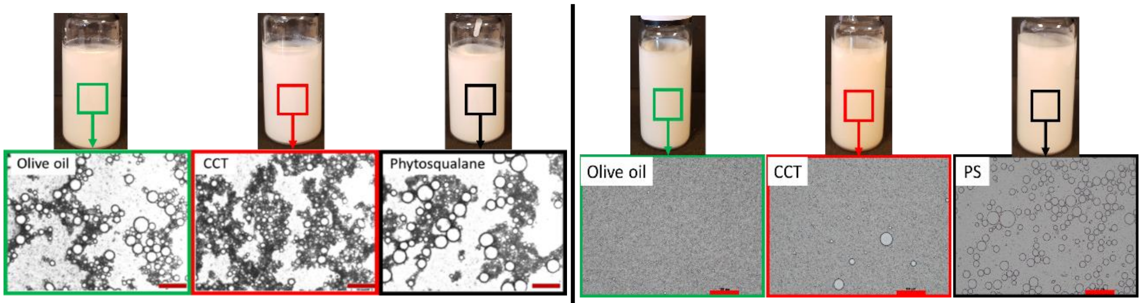
<u>Figure 2</u>: Wettability of a) TiO2 and b) Bentonite particles measured for OO, CCT, and PS

Each oil has a good wettability with the particles. The wettability is higher when the contact angle is low; thus, the particle can fix at the interface with higher energy, and the emulsion should be more stable over time[14]. As we can see for the TiO_2, the emulsions with the CCT should be more stable. For the bentonite particle CCT and PS exhibit similarly low contact angle, implying a better stabilization of the interfaces.

2. <u>Impact of stability factors on the emulsion properties</u>

All the formed emulsions were stable and homogenous at ambient temperature and 50°C for more than 1 month.

The impact of oil viscosity and polarity and the wettability of the oils by the particles were studied through the microstructure and the droplet size of the formed emulsions. The results are shown in the followed illustrations (Figure 3).



a) TiO_2 emulsions – Microstructure and macroscopic aspect of the emulsions formed with **OO, CCT and PS** (scale bar 50µm)

b) Bentonite emulsions – Microstructure and macroscopic aspect of the emulsions formed with **OO, CCT and PS** (scale bare 100µm)

<u>Figure 3</u>: Microstructure and macroscopic aspect *of the simple emulsion formed with* ***a) TiO_2*** *and* ***b) Bentonite*** *particles with OO, CCT, and PS –* ***magnification x200***

The oil viscosity, polarity and wettability do not influence the microstructure or the stability of the emulsion stabilized by the TiO_2 particles. In the case of the bentonite particles, the oil polarity had a significant impact on the microstructure and the droplet size. Phytosqualane is the less polar oil, the microstructure observation showed an aggregated droplet network, and the droplet size was larger than with the two other oils. The viscosity did not have the predicted impact, the olive oil had the finest droplet size distribution. Similarly, the wettability of the particles by the oil had no influence.

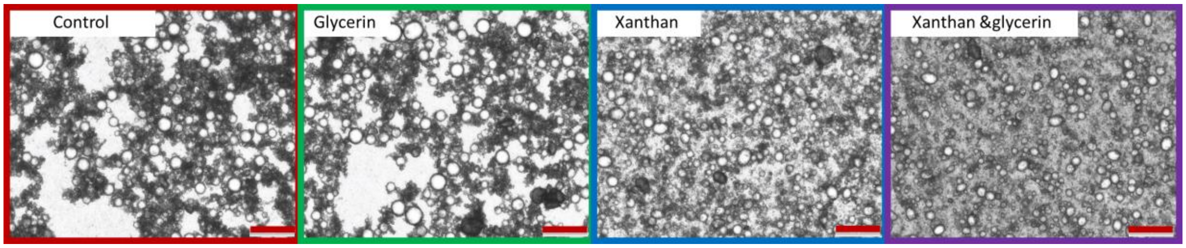
These results are linked to the surface proprieties of the particles:

- TiO_2 particle is hydrophobic but with a non-null polar contribution. This particularity masks the effect of the oil viscosity and permits to obtain very stable complex and simple systems.
- Bentonite particle is relatively hydrophobic (contact angle with water around 74°) with a basic contribution. This particularity permits obtaining very stable, complex and simple systems but makes the particle sensitive to the oil polarity contrary to TiO_2 particles. The capacity of stabilization of the particles is reduced with non-polar oil like phytosqualane.

3. <u>Addition of classical cosmetic components – Glycerin and Xanthan gum</u>

All the formed emulsions were stable and homogenous at ambient temperature and 50°C for more than 1 month. The impact of the addition of the other components was also studied through the microstructure and the droplet size determination of the formed emulsions. The results are shown in the followed illustrations (Figure 4).

a) Influence of the added component on the microstructure of TiO_2 emulsions (scale bar = 50µm)



b) Influence of the added component on the microstructure of Bentonite emulsions (scale bar = 100µm)

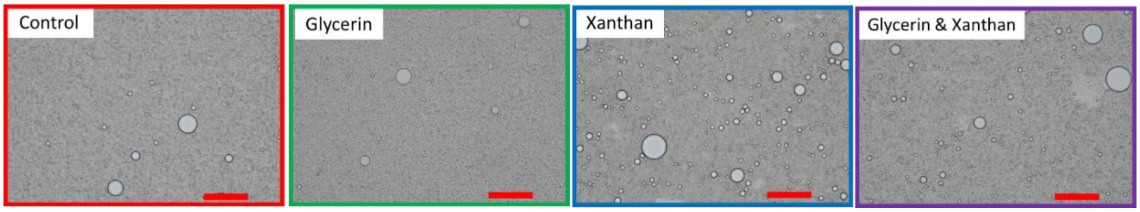


Figure 4: Influence of the added component on the microstructure of the a) TiO_2 and b) Bentonite emulsions, magnification x200

For both particles, glycerin had no impact, whereas xanthan had two opposite effect. In the case of the TiO_2 particles, xanthan gum decreased the droplet size and reduced the aggregation phenomenon. The addition of xanthan changes the microstructure: the size distribution is finer and the droplets appear more deformed and not spherical. For the bentonite particles, the addition of texturizing agents increased the droplet size but had no impact on the emulsion microstructure.

According to the literature, an increase in viscosity can have two influences: increase or decrease the stability. The increased stability can be explained by the increase in viscosity, thus preventing the dispersed oil droplets from meeting and thus coalescing[13]. This seems to be the case for emulsions stabilized by TiO_2 particles, the droplets are smaller and no oil phase appears on the top of the emulsion even after 3 months. In this case, xanthan was added afterward, the emulsion was already formed. Therefore, the texturizer only played the role of emulsion stabilizer. The size of the drops being smaller than for the control formulas, allows us to make the following hypothesis: the microscopic observations being realized at 48h, the size of the drops evolves between the day of formulation and the day of observation, but the texturizer prevents this evolution by increasing the viscosity of the medium.

The decrease in stability is due to the kinetics of emulsification and the need for more energy to fix the particle at the interface[13]. In a viscous medium, the energy to move the particles is more important, if the viscosity is too important the droplets coalesce before the placement of the particles at the interface. This is the case for the bentonite particle emulsions which show a larger droplet size distribution. The viscosity modifies the kinetics of emulsification and the energy to move the particle at the interface may not be enough. In this case, the previous hypothesis is not valid.

These differences are due to the differences in surface composition, the modifications and grafting of the TiO_2 particles influence the energy and the rate of the fixation at the interface of the particles. Such differences could also be explained by the difference in viscosity of the formed emulsions, to confirm this hypothesis more investigations on the viscosity are required.

4. Influence of the addition of the other components on the particle properties

The influence of the addition of the other components was studied using IR analysis of the particle's surface. The results for the pristine and extracted TiO_2 particles are presented in the following IR spectra (Figure 5).

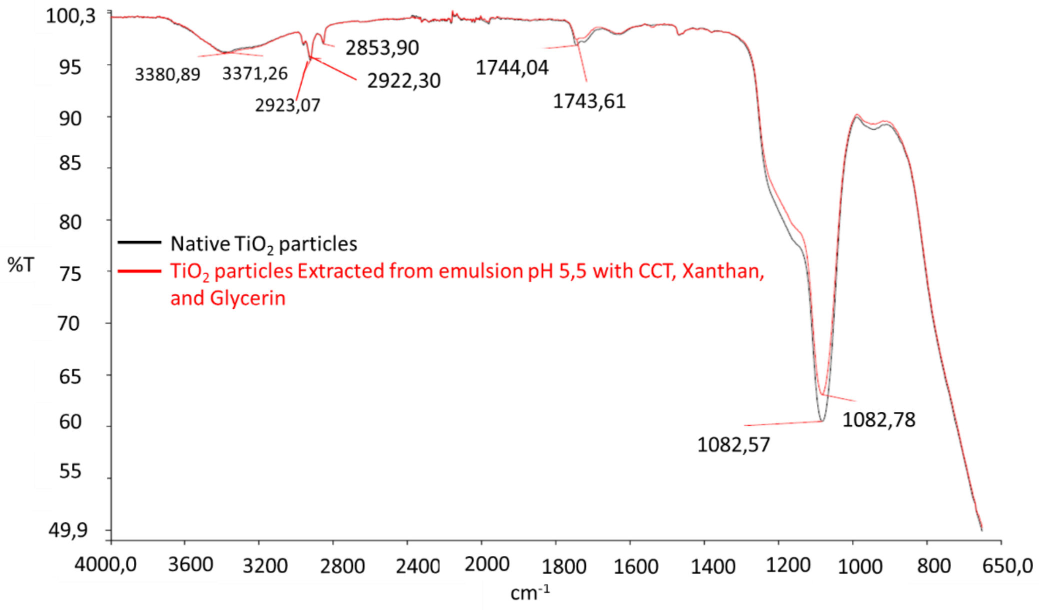


Figure 5: IR-Spectra of the a) pristine and b) extracted particles of TiO_2

The most common method of extraction of particles dispersed in a classical emulsion is ultracentrifugation. The objective is to break the structure of the emulsion and detach emulsifying molecules from the interface. However, the attachment of particles to the interface is irreversible in the case of Pickering emulsions.

The extraction method did not significantly modify the surface of the particle. Moreover, the addition of glycerin and xanthan did not influence the surface chemistry of the TiO_2 particles. This is an indication of the stability of the particle after its introduction into a formula. Thus, the particle is a good alternative to the usual surfactant. This hypothesis needs to be supported by environmental and toxicologic measurements.

Conclusion

The selected particles were successfully able to stabilize simple and complex systems. The surface proprieties of the particles influenced the microstructure of the emulsions and the droplet size. Glycerin had no impact, whereas xanthan gum decreased the droplet size and limited the aggregation phenomenon in the case of the TiO_2 particles, and increased the droplet size in the case of bentonite particles. Such differences could be due to the differences in surface proprieties of the particles or to the viscosity of the formed emulsions.

A successful extraction method was developed and did not modify the particle surface. Moreover, the other components, xanthan gum, and glycerin had no impact on the surface chemistry of the selected particles.

A more challenging component such as perfume (known for its positioning at the interface) and cosmetic actives (susceptible to reacting with the particles) will be investigated in the future. Another interesting point will aim at understanding the real environmental and toxicological impacts of these formulations and particles from the process.

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Conflict of Interest Statement. NONE.

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