Silica particles with grafted UV-filter for the stabilization of pickering emulsions

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Abstract: Pickering emulsions have been prepared using silica particles grafted with UV-filter as stabilizers. Such formulation contains all the ingredients of a sun protection product: organic UV-filter, inorganic particles as anti-UV screen and oil. Grafting the UV-filter is expected to prevent deep penetration of potentially harmful organic molecules inside the skin. *p*-methoxycinnamate has been immobilized onto to the surface of fumed silica particles. The UV-filter molecule was attached to silica by means of a short (C2) or a long (C10) alkyl spacer to study their effect on grafting degree. Better water dispersion was obtained for the two materials. The water dispersion particles remained stable for 40 days. The hydrophobically-modified silica, with different grafting degrees and linkers, were used for the formulation of o/w Pickering emulsions with various oils of cosmetic relevance: silicone oils of different viscosities and octylbenzoate. The stability and drop size distributions in the different emulsions are evaluated. Stable emulsions were obtained with oil contents in the range 10% to 60%. UV-absorbing ability was retained after immobilization of UV-filter molecules onto silica particles in all emulsion.

Key words: Pickering emulsions, UV-filter, modified silica, sunscreen formulation..

Résumé: Des émulsions de Pickering ont été préparées en utilisant des particules de silice modifiées par des filtres UV. Une telle formulation contient tous les ingrédients nécessaires pour la protection solaire: filtre organique anti-UV, des particules inorganiques jouant le rôle d'un stabilisant et de l'huile. Le greffage du filtre UV à la surface de la silice a été réalisé pour empêcher la pénétration profonde de molécules organiques, potentiellement nuisibles, à l'intérieur de la peau et à atteindre la circulation sanguine. Dans ce travail, le p-méthoxycinnamate (agissant comme filtre solaire) a été immobilisé sur la surface de la silice fumée (A200). La molécule de filtre UV a été immobilisée à la surface de la silice par l'intermédiaire de chaines hydrocarbonées à deux ou à dix carbones (C2 ou C10) afin d'étudier l'effet de la longueur de chaîne de l'agent de couplage sur le taux de greffage. Les particules dispersées dans l'eau sont stables pendant 40 jours. La silice hydrophobe préparée a été utilisée pour la préparation de formulation à base d'émulsions de Pickering huile dans l'eau. Ces émulsions sont préparées par plusieurs types d'huiles utilisées en cosmétique: des huiles de silicone de différentes viscosités et le benzoate d'octyle. . Les résultats de mesures de spectres UV montrent la capacité d'absorption de rayonnements UV du filtre est conservée après immobilisation sur silice.

Mots clés : émulsion de Pickering, filtre UV, silice modifiée, formulation de filtre solaire.

INTRODUCTION

Sunscreen formulations contain two types of protection agents: organic UV-filters that are aromatic molecules that absorb UV light and inorganic sunscreen agents that scatter light. A sunscreen formulation is a combination of several active ingredients: UV_A and UV_B filters together with particles made of either titanium dioxide or zinc oxide as inorganic sunscreen [1]. Such materials are spread on skin and should stay there as long as possible. The fast elimination taking place by washing off, rubbing, and desquamation

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of corneocytes from the skin surface is prevented when such UV-blockers penetrate the skin to some extent. Deep penetration is disastrous however because the surface protection action is lost and the organic UV-filters may be harmful. It is well-documented that inorganic sunscreen agents penetrate the horny layer of skin to moderate depth and do not significantly reach the viable skin layers (viable epidermis and dermis) [2-5]. Attachment of the organic UV-filter molecules to inorganic particles is a way to prevent their deep penetration inside skin. Pickering emulsions are stabilized by solid particle in place of the classical emulsifier [6]. Hydrophobically modified inorganic particles are known as efficient stabilizers of Pickering emulsions [7]. Hydrophobically modified silica is widely used for that purpose [8], although bare silica (hydrophilic) also stabilizes Pickering emulsions in some instances [9]. Therefore, there is a need for new systems able to reduce the use of surfactants that cause adverse effects. Among others, silica (or silica gel) offers a number of advantages. It is non toxic and shows acceptable in vivo biocompatibity. The grafting of the sunscreen directly onto the surface of silica particles used as emulsifier allows avoiding the use of surfactant and to maintain the sunscreen agent at the surface of the skin after its application and reduce its penetration in the deep layers of the skin. However, the grafting of the sunscreen agent should not alter its essential UV-filter property. Before grafting to the surface of silica, the sunscreen molecule needs to be modified by introduction of grafting groups.

The aim of this work is to immobilize the sunscreen molecule at the surface of silica by simple modification and use of alkoxysilane as coupling agent and to prepare emulsions from these materials and to study their characteristics and stability over time and also to ensure the maintenance of its UV-blocking effect.

Hence, the present paper reports the immobilization of organic UV-filters on silica inorganic particles and the formulation of Pickering emulsions using such hydrophobically modified particles. Methoxycinnamoyl ester grafted to silica mimics the widely used UV_B-filter.

1. Materials and methods

1.1. Materials

Prop-2-enol, 10-undecylen-1-ol, triethoxysilane (TES), and trans-methoxycinnamic acid (4-phenylpropenoic acid) (MCA) were purchased from Sigma-Aldrich. Fumed silica Cab-O-Sil with an average size of primary particles is 12 nm and a specific area of 200 m^2g^{-1} was obtained from Cabot Corporation (Tuscold, ILL). Emulsifiers Silicone oil DC®200 5, 10 and 20cSt were from Dow Corning and octyl benzoate were supplied from Stéarinerie Dubois.

1.2. Synthesis

1.2.1. Synthesis of silylated esters

Triethoxysilyl-3-propyl methoxycinnamate (SiAMC) and triethoxysilyl-3-undecyl methoxy-cinnamate (SiUMC) were synthesized in two steps by esterification of methoxycinnamic acid (MCA) by allyl alcohol (1) or undecenylic alcohol (2) to provide an ester a terminal vinyl function (E_1 or E_2), followed by hydrosilylation of the vinyl group by triethoxysilane (TES). The synthesis and characterization of these derivatives were reported in previous work [10].

1.2.2. Grafting of silylated esters onto silica surface

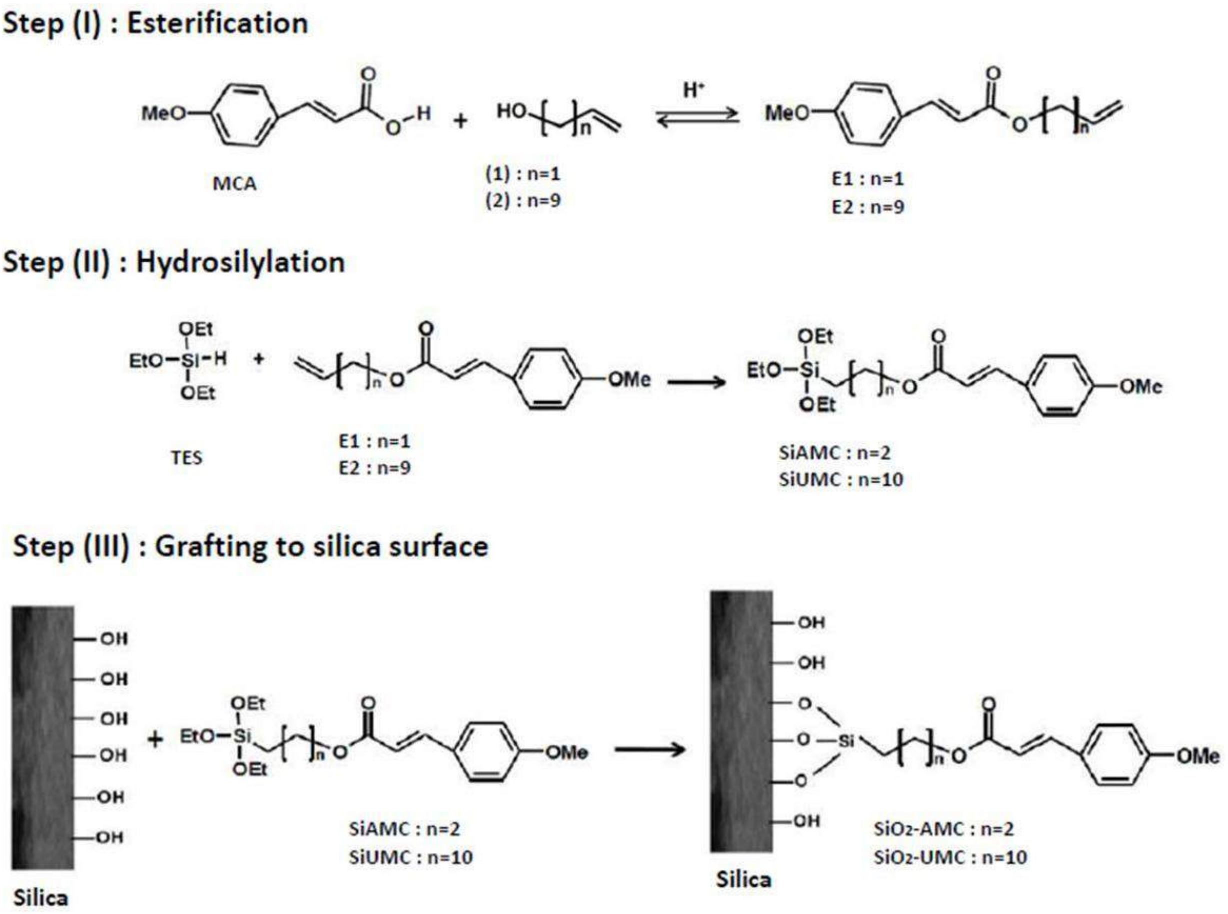
The surface modification of the fumed silica was carried out by grafting the silylated esters through condensation reaction between ethoxysilane groups and surface silica silanol groups [10-11-12] (Scheme 1). The grafting of the silylated esters (Sil-MCA) and (Sil-UMC) onto silica surface yielded (SiO_2-MCA) and (SiO_2-UMC) respectively. The graft density of the silylated esters on the silica surface was determined by elemental analysis and thermogravimetric analysis.

1.3. Preparation of dispersion silica

Dispersions of silica powders at 1% (w/w) in water were prepared as following. Silica powder was first wet in the aqueous phase by mixing with an Ultra-Turrax disperser and thereafter dispersed using an ultrasound disperser Sonics Vibracell 75042 equipped with a 3 mm shaft at 500 W during 3 min. Those dispersions were used for preparation of Pickering emulsion. Granulometric analyses were carried out by means of dynamic light scattering using a Malvern NanoZS instrument. The 1% silica dispersions were diluted so as to meet the concentration range requirement of dynamic light scattering where the count rate of the instrument is around 200 kHz.

1.4. Preparation of Pickering emulsions

The type of emulsion (w/o or o/w) depends on wettability properties of particles [13]. Oil-wet particles tend to stabilize w/o emulsions and



Scheme 1: Grafting of UV filter onto silica surface.

water-wet particles tend to stabilize o/w emulsions. For this reason, the silica was first dispersed in water using an ultrasound disperser. The oil and aqueous dispersion were mixed together with an UltraTurrax ® device (Germany) at 22,000 rpm during 2 min (cold process) and an o/w emulsion was obtained.

1.5. Particle size measurements

The size of silica particles dispersed in water was measured by small angle light scattering using a MasterSizer® 2000 (Malvern). The refractive indexes of the dispersed and dispersing phase were 1.46 for silica particles 1.332 for water, 1.40 for silicone oil, 1.491 for octyl benzoate. The viscosity of used silicon oil was 5, 10 and 20cSt. Optical microscopy pictures of the emulsions were taken with a Leica® DM LM (Germany) optical microscope equipped with a video camera. A drop of the aqueous suspension was observed in transmission mode between glass slide and cover slip at magnifications of the objective ranging from ×10 to ×100. Emulsion droplet size measurements were determined using the image analysis software AnalySIS®. Pickering emulsions granulometry was also performed by small angle light scattering (MasterSizer® 2000, Malvern, UK). The refractive indices used in the Mie optical model were: 1.46 for silica particles, 1.332 for water, 1.40 for silicone oil and 1.491 for octyl benzoate.

RESULTS AND DISCUSSION

1. Grafting of modified UV filter onto silica surface

Grafting the silylated methoxycinnamate to silica afforded a solid powder that will be used for the manufacture of Pickering emulsion. Silica grafted with AMC and UMC are referred to as SiO_2-AMC and SiO_2-UMC in the following. The characterization of these materials was developed in a previous study [10]. The surface coverage of the produced samples was calculated from the carbon content assuming that ethoxy groups had totally reacted during the grafting reaction to silica [14-15]. Elemental analysis of carbon gave 6.66 %

for SiO_2-AMC and 4.46 % for SiO_2-UMC, which corresponded to 1.8 µmol.m^{-2} and 0.9 µmol.m^{-2} coverage respectively. This indicates that partial of the immobilized silanol groups have contributed to the attachment of UV-filter moieties. Grafting density remained moderate compared to the density of Si-OH of bare that contain 4.5 hydroxyl groups per nm^2 according to the technical information from the manufacturer and checked by TGA. The results (Table 1) revealed a larger grafting degree of the short ester chains, although the same silanol content are used in both cases. This result can be related to steric hindrance effects. Thermal analysis of SiO_2-AMC and SiO_2-UMC samples showed mass losses of the order of 8.80% and 5.60% respectively. The total mass loss of SiO_2-AMC was larger than that recorded for SiO_2-UMC. This result was expected since it was related to the grafting degree in the corresponding sample determined with elemental analysis. The amounts of organic moieties bound to the silica surface, estimated from the corresponding mass losses were 2.02 and 0.88 µmol/m^2 for SiO_2-AMC and SiO_2-UMC samples respectively (Table 1).

Hydrophobicity of the dry silica particles varies by grafting degree of UV-filter. It is known that very stable emulsions, of both the oil-in-water (o/w) and the water-in-oil (w/o) type depend on particle hydrophobicity. Thus, if particles usually termed hydrophilic are held at the interface and stabilize o/w emulsions, whereas if particles termed hydrophobic are still held at the interface but stabilize w/o emulsions. Such partial grafting is in the range of commercially available hydrophobically modified silica often used for the preparation of Pickering emulsions. As example the silica HDK® H30 from Wacker Chemie is grafted with dimethylsilyl groups up to 50% coverage [8].

Table 1: Elemental analysis of prepared silica.

Sample	Carbon content (%)	Surface coverage (µmol/m^2)	
		E.A.	TGA
SiO_2-AMC	6.66	1.8	2.02
SiO_2-UMC	4.46	0.9	0.88

2. Dispersion in water

Dispersion of the grafted silica in water by an ultrasonic disperser allowed the disruption of most agglomerates. Because the grafted organic UV-filters make the silica surface more hydrophobic, dispersion in water was difficult and required several sonications. The final particle size measured by dynamic light scattering just after preparation, was 140 nm for both types of silica (Figure 1). This diameter is close to that reached upon dispersion of the fumed silica Aerosil 200 powder used as starting material for UV-filter grafting. The diameters are also consistent with those obtained with commercial hydrophobized silica particles manufactured from pyrolysed silica. The stability of modified SiO_2-AMC and SiO_2-UMC silica particles dispersions in water was performed through measurements of particle size by dynamic light scattering over a period of 56

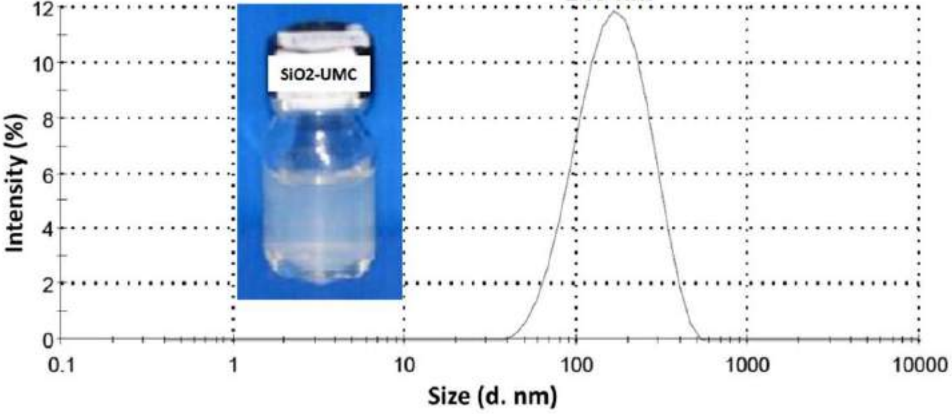


Figure 1: Dynamic light scattering of dispersion measurement of 1% SiO_2-UMC silica and photo of sample.

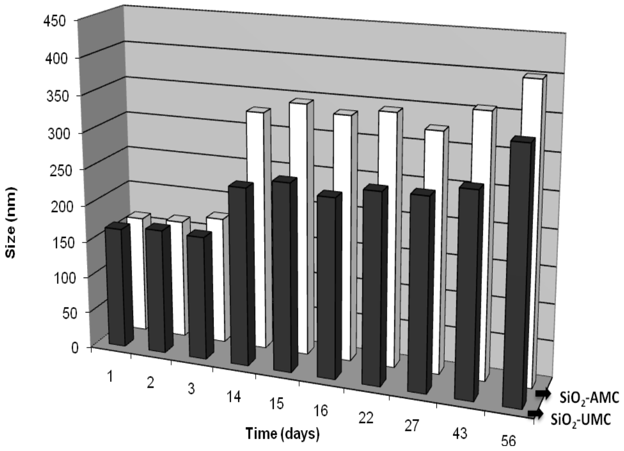


Figure 2: Stability study of water dispersed particles SiO_2-AMC and SiO_2-UMC.

days (Figure 2). The two samples exhibit similar behavior. The measured particle size remains constant (140 nm) up to two weeks, and starts to increase after this delay. Hence, stock solution of silica dispersions in water can be conserved and reused without further treatment up to two weeks.

It was also noticed that the size of the dispersed SiO_2-UMC particles remained smaller than that of SiO_2-AMC along the whole observed period. The size of water dispersion of unmodified silica was of 162 nm, which is in the same range of that obtained with the material after modification. Thus the modification of silica has not affected the size of water dispersions. The diameter of the elementary particles of bare silica was 12 nm; but those elementary particles are irreversibly aggregated by sintering during their synthesis, so that the smallest diameter of the unbreakable aggregates in a well-dispersed suspension is much larger than the diameter of the elementary particles [16].

3. Preparation of Pickering emulsions

Pickering emulsions were prepared in two steps. Grafted silica were first wetted and dispersed in water, and then the emulsification of oil was carried out using Ultra-Turrax disperser. Various emulsions were prepared with increasing proportion of oil (from 10 to 90%) at constant silica amount (1% in the aqueous phase). Oils of

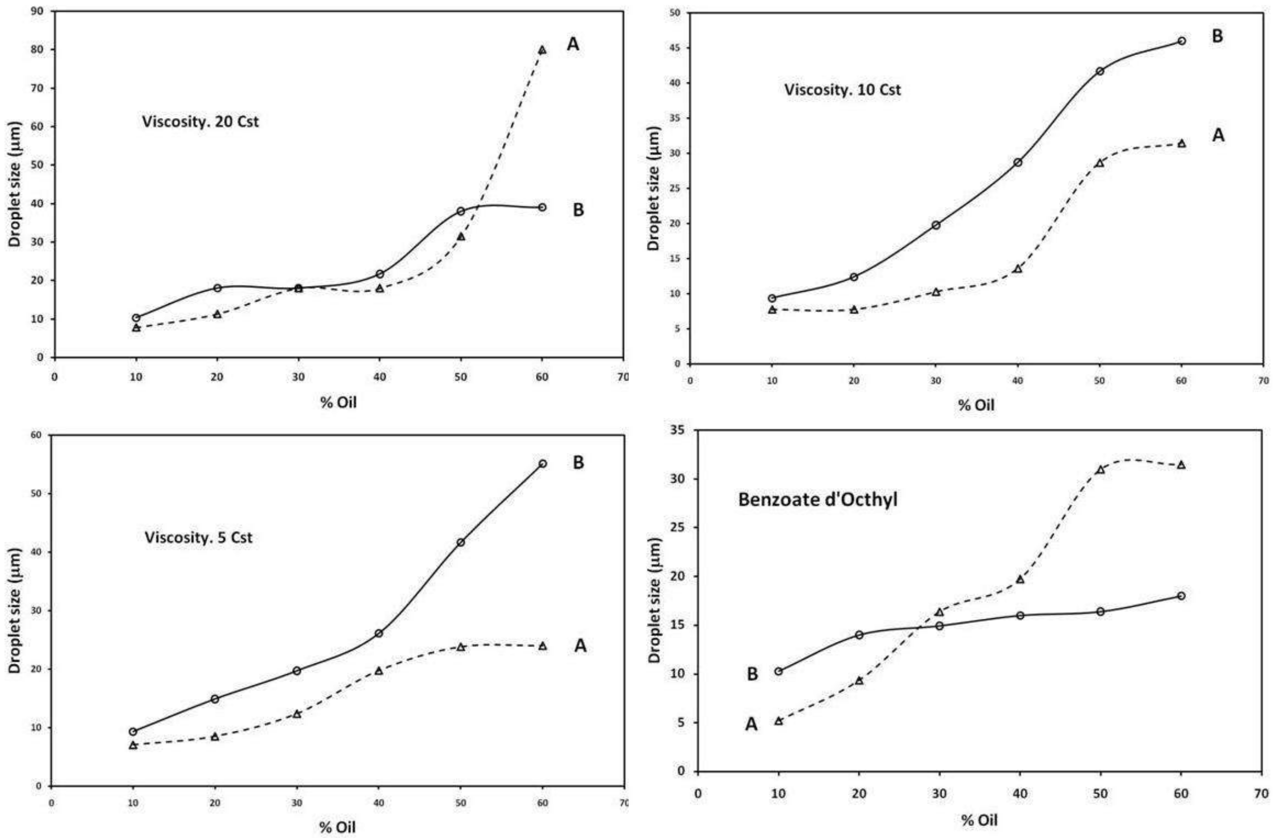


Figure 3: Diameter of emulsion droplets as a function of oil contents and silica types: (A). SiO_2-AMC and (B). SiO_2-UMC.

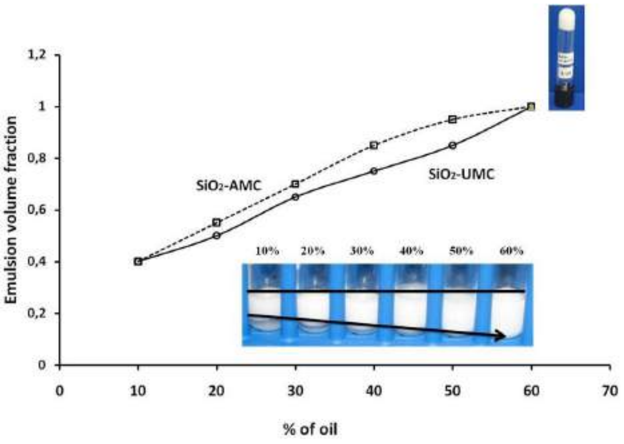


Figure 4: Emulsions volume fraction of silicone oil (10Cst) stabilized by 1% SiO_2-AMC and SiO_2-UMC for increasing amounts of oil (10%, 20%, 30%, 40%, 50% and 60%).

different viscosity were used for the preparation of emulsions in order to study their influence on the particle size. For this purpose, three silicon oil with different viscosities (5, 10 and 20 cst) and octyl benzoate were used.

In all cases, a slight increase of droplet size was observed with the increase of oil percentage. A little difference in size was observed between the two systems (SiO_2AMC and SiO_2UMC) for the different oils except that for silicon oil with 20Cst viscosity which shows close the same sizes for two systems with only one perceptible difference at 60% oil content (figure 3 and 4).

In all cases, successful o/w emulsions were obtained for oil contents below 60%: the whole oil content was incorporated in oil droplets and there was no oil release upon storage. Figure 4 shows the emulsions after a short storage period for different oil used. The creamed emulsion can be distinguished as a white top layer; a clear layer of aqueous phase remains at the bottom. The volume fraction occupied by the creamed emulsion increased as the oil content increased. The full volume was occupied by the emulsion at 60% oil content; there was no creaming for such composition. Therefore, the creamed emulsions contained 60% oil. Above 60% oil content, the full oil was not emulsified. A stable emulsion was obtained however in the bottom layer after a clear top layer made of free oil has formed. The same features were observed for both silica and two different oils (silicone oil and octyl benzoate).

Droplet sizes measured by light scattering ranged between 8 µm and 100 µm. The droplet mean diameter increased as the oil content increased at constant silica content. Indeed, the droplet diameter is related to the volume-to-area ratio by $D = 6V(\text{oil})/A$, where the interfacial area A is constant because the silica concentration is constant in all preparations.

Optical microscopy pictures illustrate the behavior of emulsions that was characterized by light scattering. Figure 6 shows the silicone oil droplets of emulsions stabilized by SiO_2-AMC. Indeed the droplet size increased as the oil content increased. Droplet remained spherical in shape for oil content below 50%. High-internal-phase-ratio emulsions with characteristic polyhedral droplets were obtained at 50% and 60% oil content.

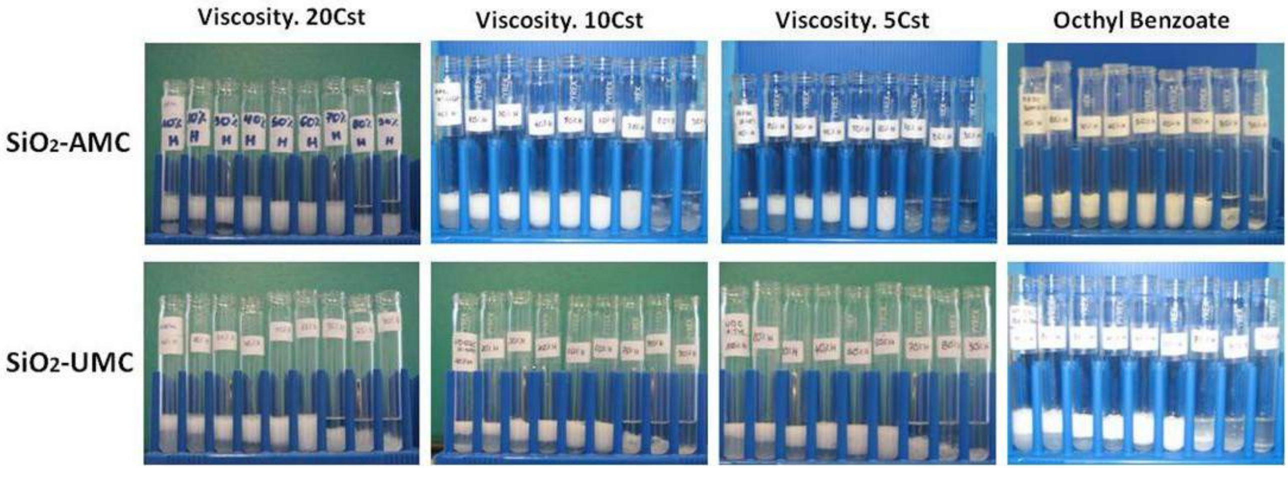


Figure 5: Emulsions of silicone oil and octyl benzoate stabilized by 1% SiO_2-AMC and SiO_2-UMC for increasing amounts of oil (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90%).

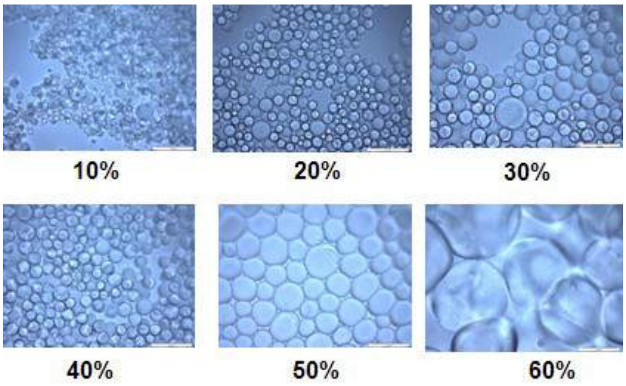


Figure 6: Optical microscopy pictures of o/w emulsions stabilized by SiO_2-AMC solid particles with various amounts of silicone oil (from 10 to 60%) (×50, bar = 50 µm).

Creaming did not cause the loss of stability. Indeed oil droplets of the original size are still present in the creamed emulsion (Figure 7). Creaming took place because of the large size of emulsion droplets. Coalescence was prevented by the silica layer, even when droplets are at close contact in the creamed layer.

The diameter of emulsion droplets stabilized by SiO_2-AMC was constant over 3 months storage, showing the high stability of such emulsion, even at high oil content. The emulsions stabilized by SiO_2-UMC were less stable since the droplet diameter increased upon storage.

4. UV characteristics of Pickering emulsions

The UV spectra present an absorption band at 310 nm that goes with the UV absorption zone of octhylmethoxycinnamate. We notice that even a state of formulation (Pickering emulsion o/w), the particles SiO_2-AMC and SiO_2-UMC do not lose the absorption activity of UV_B radiation.

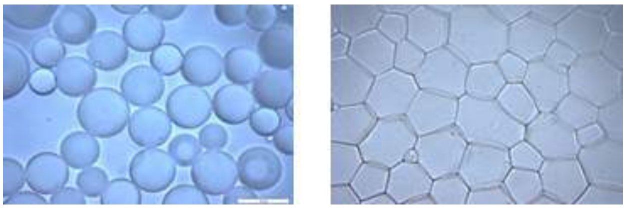


Figure 7: Optical microscopy pictures of o/w emulsions of silicone oil stabilized by SiO_2-UMC solid particles before and after creaming: Left: full emulsion; right: creamed layer (×50, bar = 50 µm).

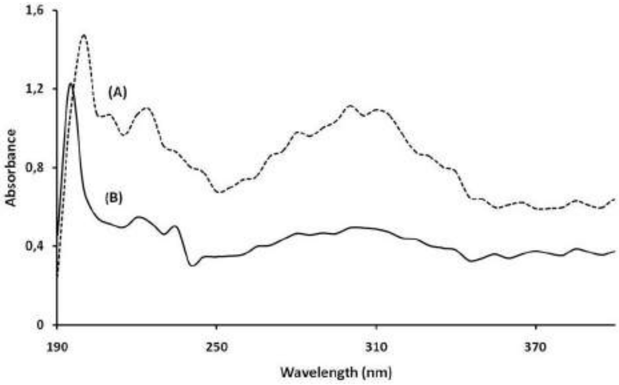


Figure 8: UV spectra: (A) SiO_2-AMC and (B) SiO_2-UMC.

Sunscreen formulation with both SiO_2-AMC and SiO_2-UMC at 60% silicone oil showed the same characteristic absorption band at $\lambda max=310$ nm as that of modified silica used in the production of Pickering emulsion. The produced emulsion shows the conservation of the absorbance ability of UV_B blocker. The higher absorption observed for the emulsion prepared with SiO_2-AMC compared to that done with SiO_2-UMC, for the same quantity of silica in the preparation, is related to the higher grafting degree of sunscreen for the former.

The ratio of absorbance at 310 nm for two the emulsions (abs/abs=2) is close to that of the grafting density as calculated from elementary analysis 2.26 (table 1).

Droplet size of o/w emulsion depends of two main factors: (i) the proportion of silica dispersed in aqueous phase used for preparation of emulsion. (ii) the weight ratio M(oil)/M(Silica) [13-17]. SiO_2 -AMC was used for the study in different proportions in water dispersion in the range 2 to 10wt.%, and the emulsion was produced from each aqueous silica dispersion by addition of 20 wt.% octhyl benzoate oil. The droplet size was assessed by light scattering amusement. The results (figure 9) show the decrease of particle diameter with the increase of silica content. The addition of silica promotes the formation of smaller size particles resulting in emulsion with higher stability because the extent of stabilized interfacial area is proportional to the amount of stabilizer. The droplets size distribution in Pickering emulsion can be varied by adjusting the proportion of oil content while keeping the concentration of particles constant. Figure 9 presents the evolution of droplet mean diameter for different oil/ silica ratio.

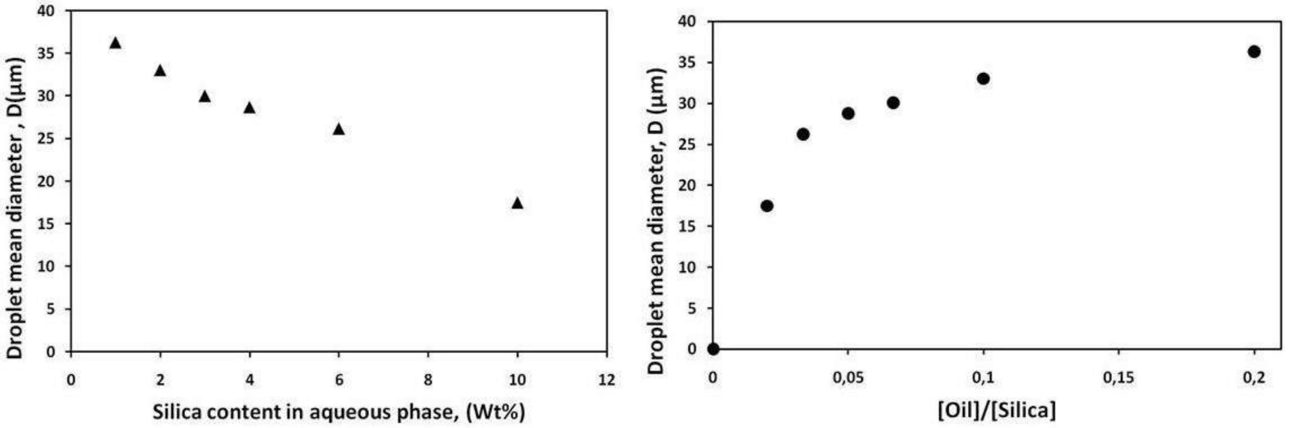


Figure 9: Left: emulsion droplet size as a function of silica ratio (Wt%). Right: emulsion droplet size as a function of M(Oil)/M(SiO_2-AMC) in the aqeous phase.

CONCLUSION

Grafting the silylated methoxycinnamate to silica was done by use of short (C2) or long (C10) alkyl spacer producing SiO_2-AMC or SiO_2-UMC materials respectively. The grafting degree was 1.8 µmol.m^{-2} and 0.9 µmol.m^{-2} for SiO_2-AMC and SiO_2-UMC respectively. Successful o/w emulsions were obtained for oil contents below 60%. Shape and size characteristics have shown that droplets remained spherical in samples with oil content below 50% and their size ranged between 8 µm and 100 µm. The produced emulsion shows the conservation of the absorbance ability of UV$_B$ blocker. The higher absorption observed for the emulsion prepared with SiO_2-AMC compared to that done with SiO_2-UMC, was related to the higher grafting degree of sunscreen for the former. The diameter of emulsion droplets stabilized by SiO_2-AMC was constant until 3 months of storage, showing the high stability of such emulsion, even at high oil content.

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