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Sol-Gel Microencapsulation Based on Pickering Emulsion

Fabien Salaün, Chloé Butstraen and Eric Devaux

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Abstract

Microencapsulation has been proved to be an efficient technic to entrap and protect active substance in variety fields of application. This process implies two consecutive stages, that is, the emulsion stage, which can be described as a limiting step since it determines the diameter and size distribution of the microcapsules and need to remain stable long enough to allow the membrane to form in the second one. Pickering emulsions are used to improve the stability of the emulsions and to limit the exudation of the active ingredient during membrane formation. The first part of this chapter deals with the description of the Pickering emulsion stabilized with solid particles. The second part focuses on the use of this kind of emulsion in a microencapsulation process, and the last part concerns a study of the influence of the nanosilica particles on microparticle formation obtained from a sol-gel process.

Keywords: Pickering emulsion, silica nanoparticles, sol-gel, microencapsulation, flame retardant

1. Introduction

Pickering emulsions are defined as the dispersion of one liquid into another, with which it is immiscible and stabilized by solid particles. These solid particles adsorb at the interface between the two phases. They exist in nature with, for example, fat crystals in butter or casein particles in milk [1]. Their anchoring at this interface is almost irreversible and the inhibition of coalescence is very effective. Ramsden has shown that emulsions or bubbles can be permanently stabilized by means of fine solid or highly viscous particles placed at the interface of two liquids [2]. Pickering's work published in 1907 describes these phenomena more fully

and shows that these particles, having a greater affinity with the aqueous phase than with the oily phase, are alternatives, often more advantageous than surfactants to obtain easily very stable O/W emulsions [3]. After many years, Pickering emulsions have been studied again since the 2000s and are of increasing interest to researchers. According to Scopus, 17 publications containing the terms "Pickering emulsion" in the title, keywords or abstract were published in 2005, 100 in 2011 and 220 in 2014.

There are various nature and shape of the particles used, such as spherical, cubic, in the form of rods, silica, titanium, melamine-formaldehyde, polystyrene, clays, spores or bacteria. The most common are nano spherical silica particles. Their size must be adapted to the desired emulsion, because an emulsion with droplets of at least a few micrometers is obtained from particles of 1–100 nm and an emulsion with drops of the order of a millimeter with particles of about 100 nm [4]. However, as in the case of surfactants, to allow them to be anchored at the interface, they must be partially wetted by each of the two phases. In general, the particles used are hydrophobic (such as carbon black) or hydrophilic (such as silica). If they are too hydrophilic or hydrophobic, they do not sufficiently stabilize the emulsion, the drops obtained are large (>100 μm) and unstable toward coalescence [5]. A grafting of molecules giving them their affinity with the water-oil interfaces is therefore carried out [6–12]. This is the case, for example, with pyrogenic, hydrophilic silica particles. Pure, 100% of their groups are hydrophilic Si-OH silanols, so they are unable to stabilize the interface except with certain oils. The grafting of hydrocarbon chains, such as dimethyl silyl, reduces their affinity with the aqueous phase, the most hydrophobic ones containing 14% silanols [4, 5].

By adjusting the grafting rate, it is possible to obtain particles of varying wettability. Since the distribution of hydrophilic and hydrophobic groups on the surface of particles is relatively homogeneous, they are not considered to be amphiphilic, unlike surfactants, although they have surface action (except for Janus particles, which have a hydrophilic and hydrophobic part, they have surface activity and are amphiphilic) [5]. The wettability of some particles may vary with pH, and reactive emulsions can be obtained [13–15]. They can also be "modified" by adsorption of surfactants to their surface [16]. Emulsions can also be stabilized with microgels, liquid crystals, spores or bacteria [17–19]. Finally, as with surfactants, it is possible to use a mixture of hydrophilic particles of different types and sizes to stabilize an emulsion [20]. Depending on the ratio between the hydrophilic and hydrophobic groups of their surfaces or their affinity with each of the two phases, emulsions obtained can be direct (O/W), inverse (W/O) or multiple [21–24].

Pickering emulsions are extremely stable. They are of interest for food, pharmaceutical and cosmetic formulations as well as for their coupling with an encapsulation process [25–27]. They also provide good stability for multiple emulsions that are very difficult to stabilize with surfactants that diffuse in the system and can destabilize the system, unlike solid particles. In addition, the use of these nanoparticles can also participate in the formulation of sunscreen creams. Indeed, they help protect against ultraviolet radiation by limiting the use of surfactants [28].

2. Stability of Pickering emulsions

2.1. Particle wetting and contact angle measurement

In order to adsorb at the interface, the particles must be partially wetted by each of the two phases. This wetting is characterized by the contact angle measured on the aqueous side between the interface and the tangent to the particle at the point of contact between the three elements (if the gravitational forces are negligible in relation to the capillary forces, which are generally the case for nanoparticles). The angle of contact depends on the interfacial energies between the solid and the two phases and is given by Young's law (Eq. (1)).

$$\cos\theta = \frac{\gamma_{solid/oil} - \gamma_{solid/water}}{\gamma_{water/oil}} \tag{1}$$

When the contact angle is less than 90°, the particles are known as hydrophilic, and when it is greater than 90°, they are called hydrophobic [21, 29, 30]. To facilitate the choice of particles used, a parallel can be made with the hydrophilic lipophilic balance theory, the angles below 90° correspond to an HLB between 9 and 15 and the angles above 90° correspond to an HLB between 3 and 7 [4]. In addition, as in the case of surfactants, Pickering emulsions generally follow the Bandcroft law, according to which the continuous phase is that for which the particle has the most affinity [31]. This is the case for silica particles, when 65% of their surface groups are silanols, the particles are mainly hydrophilic, their affinity is greater for the aqueous phase and the favored emulsion is direct. Several models describe this phenomenon. The most commonly accepted method is based on the spontaneous curvature dependence of the interface on the particle contact angle. In addition, in this case, the particles inhibit more effectively the coalescence and Ostwald ripening, their sterically hindered being greater. There are also amphiphilic particles, whose distribution of hydrophilic and hydrophobic groups are not homogeneous but separated into two distinct regions, one hydrophilic and the other hydrophobic. They are produced by chemically modifying part of the particle to change its wettability. These particles are called Janus particles and are three times more effective at a 90° contact angle than conventional particles and maintain interfacial activity even at 0 and 180° contact angles [32].

Since the particles used in Pickering emulsions are generally nanometric, it is difficult to measure their contact angle. In the literature, several studies present methods of measuring particle contact angle at the interface. However, they can only be used for particles with a diameter higher than 20 μm and are subject to uncertainties or require special equipment. It is also possible to use the data available in the literature to select a particle type. The type of the particle-stabilized emulsion depends mainly on this contact angle. Other parameters such as particle size and shape, the phase into which the particles are introduced, their concentration, the volume fraction of the dispersed phase, the polarity of the oil, the viscosity of each of the two phases, the presence of additives such as electrolytes, surfactants or flocculating agents and the method of operation also influence the direction of the emulsion obtained. Indeed, it is better to introduce particles into the external phase to promote the formation and stability

of the emulsion [5, 33, 34]. This phenomenon is related to the difference in hydrophobia of particles wetted by water or oil. In fact, the feed angles (from oil to water) are larger than the feed angles (from water to oil) at the interface. The particles therefore have a more hydrophobic behavior when introduced into the oil and preferentially induce the E/H type and they are more hydrophilic when placed in the aqueous phase enhancing H/E emulsions [35]. As with surfactants, the type of oil, and in particular its polarity and the volume ratio between the two phases influence the type of emulsion obtained with the same particle [33, 36].

2.2. Anchoring particles at the interface and energy aspects

Once the particle is placed at the interface, the stability of the emulsion depends on its anchoring. The more force required to remove the particle from the interface, the more stable the emulsion is. For small particles (less than a few micrometers in diameter), gravity can be considered negligible. Clint and Taylor defined the particle-water contact area as $2\pi r^2(1-\cos^2\theta)$ and the flat area of water surface missing $\pi r^2 \sin^2\theta = \pi r^2(1-\cos^2\theta)$, where R is the radius of the particle [37]. By replacing the air with the oily phase, the free energy needed to remove the particle from the interface is defined by Eq. (2).

$$E \;=\; 2\pi r^2 (1 + \cos\theta)(\gamma_{solid/oil} - \gamma_{solid/water}) + \pi r^2 (1 - \cos\theta)\, \gamma_{water/oil} \tag{2}$$

Young's equation (Eq. (1)) allows simplification to obtain Eq. (3).

$$E \;=\; \pi r^2 \, \gamma_{water/oil} \,(1 + \cos\theta)^2 \tag{3}$$

Binks completed these results by defining the energy needed to remove the particle from the interface in Eq. (4) with the negative sign corresponding to the particle removal from the interface to the aqueous phase and the positive sign to the oily phase [5].

$$E \;=\; \pi r^2 \, \gamma_{water/oil} \,(1 \pm \cos\theta)^2 \tag{4}$$

According to this equation, the particle is strongly anchored at the interface for =90° and the extraction force decreases rapidly on each side of the interface to become weak between 0 and 20° and between 160 and 180° for a pyrogenic silica particle at the water/toluene interface. Moreover, this energy is much lower for tiny particles (r=2 nm) than for "big" ones (r = 8 nm) for which it reaches 1000 × kT at 90° (kT representing the thermal energy expressed as a function of Boltzman constant k and temperature T), the adhesion can then be considered irreversible. The adhesion energy is strongly dependent on size and varies according to the square radius. Thus the very small particles, having a size comparable to that of surfactants (<0.5 nm), are very easily removed from the interface, they are therefore not good emulsion stabilizers [5]. However, the particle size must be submicronic to obtain a satisfactory emulsion. The adhesion energy also depends on particle size and contact angle. The interfacial tension between the two phases has little influence on these results. The anchoring at the interface of particles with a diameter of about 10 nm with a contact angle of between 20 and 180° is therefore almost irreversible, which gives these emulsions an infinite stability.

The structural particle arrangement at the interface of the Pickering emulsions varies. Various configurations can be observed, that is, (a) the hexagonal configuration forming a monolayer completely overlapping the interface, (b) the two-dimensional gel structure, (c) the dense aggregates which slightly overlapping the surface and (d) the hexagonal structure forming a two-layer or multilayer covering the interface. The recovery rate does not depend on the quantity of particles introduced, but may be partial even if it is sufficient [38]. Midmore has shown that covering at least 29% of the droplet surface is required to stabilize the emulsion [39]. The type of structure obtained and the stability of the emulsion depend on the competition between repulsion and attraction forces between the particles, linked to van der Waals forces, electrostatic and capillary interactions. Unlike surfactants, particles adsorbed at the interface do not necessarily decrease the interfacial tension between the two phases [40, 41]. The stabilization of the emulsion is attributed, in the case of fully coated particles, to the presence of a mechanical barrier (static repulsion) between the two interfaces hindering the coalescence and Ostwald ripening. Electrostatic repulsion phenomena can also occur [4, 42].

In the case of droplets with an incomplete overlap, several phenomena are observed. In the first case, the emulsion is not stable as it stands and the drops coalesce until they are completely covered which leads to an increase in droplet size and a decrease in the interface area [43–45]. The size of the emulsion droplets depends directly on the amount of particles introduced (and therefore likely to cover the interface). The size distribution of the drops obtained in this way is narrow. Chevalier and Bolzinger described three regimes depending on the quantity of particles introduced [4]. In the first regime, there are too few and the stabilization of the emulsion fails. In the second, they are all anchored at the interface and the size is proportional to the quantity introduced. In the latter, size is controlled by agitation parameters and the excess particles remain agglomerated in the continuous phase leading to an increase in the viscosity of the medium. In this case, since the final size is no longer the result of the limited coalescence but of the shearing of the drops, the size distribution is much wider. In general, in order to obtain an emulsion containing 20% oily phase with a size between 10 and 100 μm, 1–6% in weight of partially hydrophobic silica particles must be dispersed in water [46].

In the second case of incomplete overlap, the emulsions are stable despite the not completely covered interface. The phenomena involved are not well understood but are based on the interactions between particles. This stabilization can be explained by two main hypotheses. These can form a dense structure that allows bridging between the drops and avoids contact between the interfaces. This hypothesis is in accordance with the observations of Destribats et al. who noted that particles preferentially place themselves at the zones of junctions between droplets and attributes these phenomena to electrostatic interactions [47]. It is also possible that particles may move at the interface and that their movements are sufficiently significant to allow redistribution [13, 48]. It is usual for particles to occur in solution and at the interface as aggregates, contributing to steric hindered between the drops and without affecting the stabilization of the interface. As for surfactants, it is possible to use a mixture of particles with different contact angles to stabilize the emulsions. In this case, it is also possible to induce phase inversion by adding hydrophilic particles in a W/O emulsion or hydrophobic particles in an O/W emulsion or by modifying the volume ratio between phases [5].

3. Pickering emulsions and encapsulation

The studies of Velev and his team in 1996 and 1997, showing the potential of Pickering emulsions for microencapsulation and the development of advanced materials in general, were one of the reasons for the renewed interest of the scientific community in Pickering emulsions in the 1990s [49–51]. Thereafter, Weitz, Bon and their collaborators in the 2000s prepared capsules from Pickering emulsions with controlled size, permeability and mechanical properties [52–55].

Pickering emulsions are already a way to encapsulate the core [52]. However, it is necessary to reinforce this protective layer to obtain mechanically resistant capsules. Several methods can be used. A chemical crosslinking agent can be used to bind particles together [46, 56–60]. It is also possible to use thermofusible nanoparticles that soften above their glass transition temperature to form a polymer film around the droplet [53, 61, 62]. Pickering emulsions can also be combined with traditional encapsulation processes.

The processes used are mainly physicochemical and chemical. Layer-by-layer processes (with pairs of alginate, chitosan and whey polymers, e.g. methoxylated pectins) over stabilized emulsions with silica nanospheres or clays (laponite) make it possible to obtain controlled porosity capsules depending on the number of layers and the affinity between the electrolytes used in the synthesis conditions for controlled release applications, in particular in the medical field [63, 64]. Several studies also deal with coacervation, particularly on the inner side, to form a polymeric film solidifying the Pickering emulsion [14, 65]. Many studies employ chemical encapsulation processes. Thus, styrene or methyl methacrylate mixed with an initiator can also be polymerized on the outer or inner face of a Pickering W/O or O/W emulsion, respectively [66, 67]. One of the main applications is thermal energy storage with the use of phase change materials (PCMs). In this case, the stabilizing particles can have several functions. They inhibit radical reactions in the aqueous phase [68]. The initiators of Atom Transfer Radical Polymerization (ATRP) can be located by grafting on nanoparticles [69]. They can also be used as a nucleation point for polymerization, as in the case of the emulsion of a styrene and AIBN (azobisisobutryonitrile, a primer) mixture in water stabilized by silica nanoparticles functionalized with methacryloxypropyltrimethoxy silane (MPTMS). The presence of MPTMS double bonds C=C allows copolymerization with styrene during radical polymerization. In situ melamine formalin (MF) polymerization processes are also described in the literature. Thus, the use of organo-modified silica nanoparticles increases the encapsulation efficiency of PCM by improving emulsion stability and providing a precipitation site for MF membrane formation [70]. The use of certain particles such as hydroxyapatite, a mineral species of the phosphates family, coupled with Artemisia argyi, a Chinese medicinal plant, allows the preparation of microcapsules having antimicrobial properties [71]. Furthermore, Pickering emulsions can also be coupled with sol-gel processes [72]. For example, a Pickering W/O emulsion stabilized with poly(methyl methacrylate) nanoparticles (PMMA) encapsulates hydrophilic substances (live organisms, drugs, enzymes, and bacteria) and protects them from both precursor and catalyst. The emulsion droplets are functionalized with an amphiphilic catalyst to direct the sol-gel reaction from TEOS. The amount of precursors added allows the porosity of the membrane to be adjusted [73]. A Pickering W/O emulsion stabilized by silica nanoparticles, mostly hydrophobic after hexadecylsilane grafting, followed by continuous phase sol-gel gelling, produces

a controlled porosity foam [1]. The W/O/W emulsion is stabilized by hydrophobic silica for the first W/O emulsion and then hydrophilic silica functionalized with cetyltrimethylammonium (CTAB, a cationic surfactant) for the second H/E emulsion. The interface is then mineralized via a sol-gel process, the nucleation is directed to the interface by CTAB. It also solubilizes TEOS, which does not require prehydrolysis. The oily phase is wax, with a high rate of expansion at around 37°C, allowing thermal controlled release of the internal aqueous phase [24].

4. Sol-gel microencapsulation

These last years, sol-gel microencapsulation approach has gained increasing interest to develop specific applications with high added values. The silicone membranes allow the physical and chemical protection of various types of active ingredient such as dyestuffs [74], drugs [75], enzymes or bacteria [76], flame retardants [77], etc. The polysiloxane membranes possess adequate mechanical properties [78], and chemically and thermally stable due to their amorphous structure [79]. In addition, they are compatible with most medical or pharmaceutical formulations, biocompatible, non-toxic, and have been approved as an inactive ingredient in pharmacopeia by the Food and Drug Administration.

During the encapsulation of active ingredients by sol-gel, it is necessary to control the formulation and the experimental conditions to obtain materials with the desired properties. The first step is to select the appropriate precursor(s). The chemical properties of the precursor(s) and active ingredient(s), as well as the environmental conditions are the main parameters to take in account for the selection of the possible solvent and catalyst. Furthermore, appropriate surfactant(s) should be used. Silica microcapsules can be obtained from organosilane monomer, mainly tetraethoxysilane (TEOS) as silica precursor, or mixtures in mild conditions either by a one step process or by a multi-stage process. The shell formation mechanism is relatively complex and depends mainly on the pH adjustment during the various synthesis steps. For a starting system from an oil in water emulsion, a major key of this process is the self assembly of silica precursor on the organic droplets under elaborate conditions, which required for a reasonably rapid hydrolysis reaction to eventually form the silica shell. In syntheses of silica nanoparticles or microcapsules by sol-gel route, gelation is not observed. Indeed, when the size of the particles are sufficiently important, electrostatic repulsions stabilize them and prevent the condensation of particles between them without hindering the condensation of monomers in solution onto their surface [80]. It is generally carried out in diluted aqueous medium. Kortesuo et al. also showed that an increase in the amount of water, exudation and encapsulated allow to decrease the release of the core substance despite particle agglomeration and therefore the formation of clusters [81].

Considering a hydrophobic active substance, the first step is the realization of the oil in water emulsion, with the use of surfactants. Ionic surfactants such as CTAB or sodium dodecyl sulfate (SDS) provide a small pore size (2–4 nm), while non-ionic surfactants such as Tween® (polysorbates) induce the formation of bigger pores (approximately 10 nm) and a thinner membrane [79]. Thus, according to the design of the microcapsules, the release behavior of the active substance can be well controlled. However, according to Ciriminna et al., the

"impermeable" encapsulation of lipophilic products by a silica shell resulting from a sol-gel process is complex [82]. Indeed, complex emulsion processes (O/W/O) using a high amount of surfactants and/or high shearing rate have been developed to obtain tiny droplets (0.1–3 μm) to allow the formation of homogeneous particles and avoid migration of the active ingredient.

One of the first approaches to encapsulating lipophilic active ingredients has been developed by Magdassi et al [83]. It is based on the mixture of active and alkoxysilane emulsified in a solution of water and surfactants. The catalyst (acid or base) is added at the end of the emulsion to allow the capsules to formation by polycondensation at the interface with the aqueous phase. As many hydrophobic substances are solubilized, at least partially in TEOS, MTES or MTMS, many processes are based on the mixing of the active ingredient with the precursor (s) that then constitutes the dispersed organic phase. However, in this type of process, the hydrolysis of the precursors is more difficult and the capsule remains loaded with precursors that do not participate in the formation of the membrane.An alternative is the use of Pickering emulsions, which have been studied by Detribats et al. for the encapsulation of waxes to be released under thermal stress [84]. They have the advantage of allowing control of capsule size and act as a nucleating agent when the capsules are synthesized (they have been previously functionalized with a cationic surfactant, CTAB). Moreover, they are stable for several months and limit the exudation of the active ingredient. Barbe et al. have shown that for pH less than 2, although the structure formed is rather open, it condenses during drying and gives a dry microporous structure with pore sizes of about 1 nm [85]. When the pH increases, the network has a superior mechanical strength and higher rigidity due to crosslinking, drying leads to cracks formation and increases pores size. At pH 7, they range from 2 to 20 nm and at pH 11, the average size is 9 nm. Moreover, the diffusion of the active ingredient is not carried out or only slightly through the micropores, the increase in pH leads to an increase in the release rates of the active ingredient.

To obtain encapsulation with few or no exudation of the active ingredient, it is also required to incorporate a sufficient amount of silanes. Zhang et al. obtain a reduced release for a ratio of active mass to silane 50/50 [86]. Similarly, according to Aster et al., incorporating 5–20 mol% (preferably 8–15%) of alkyl groups in the structure results in slightly porous capsules containing hydrophobic products, the affinity between the silica shell and the active ingredient is increased by the presence of lipophilic alkyl groups. For an amount less than 2%, the capsules are porous and for a amount more than 25%, capsule formation is made difficult and requires the use of specific emulsifiers and catalysts. In addition, Sullivan et al. showed that to some extent, the addition of organo-modified silanes, dimethyldiethoxyysilane in the study, increases the thickness of the membrane and results in a decrease of the release [87]. Microcapsules prepared in basic pH are formed from silica nanoparticles that clump together to form the membrane [88]. The porosity of the membrane is therefore important and the tightness limited. On the contrary, a synthesis in an acidic medium promotes the formation of microcapsules that reduce exudation of the active substance. The recommended pH is generally between 2 and 3 [86]. Indeed, they synthesized spherical microcapsules with a well-defined, low-porous membrane at a pH of 2.89. The synthesis has a duration of 48 h at 35°C [89]. When they pre-hydrolyzed the silane, it was reduced to 24 h and the decrease of the pH to 2.45 further limited the exudation of the active ingredient. To minimize these duration of the synthesis to 4/5 h, it is possible to carry out a double catalysis.

5. Microencapsulation for flame retardant via sol-gel route

Sol-gel process was used to entrap a liposoluble flame retardant compound, that is, bisphenol A bis(diphenyl phosphate) (BDP) from Devan chemicals (Belgium). In a microencapsulation process, the first step is the emulsion step, which can be described as a limiting one since it determines the mean diameter and size distribution of obtained microparticles. The emulsion need to be remained stable during the formation of the shell from the condensation of the reactive species, used as monomers. The originality of this work is the use of nanosilica particles to promote the formation of a Pickering emulsion. In our previous attempts, we have observed that the use of a non-ionic surfactant such as Tween® 20 during the process leads to a decrease of the thermal stability of the microcapsules, and it was difficult to obtain the desired size range, that is, from 10 to 100 μm, to use these microcapsules for a specific textile application.

In this study, nanosilica particles, Aerosil R816 (Safic Alcan, France), have been used to realize the first process step. Thus, emulsion has been prepared with 10 wt.% of BDP in a aqueous solution containing 0.5, 1 and 3 wt.% of Aerosil R816 previously dispersed in 100 ml of water. The agitator used is mobile with four inclined blades rotating at 1000 rpm for 30 min. The emulsion obtained is sufficiently stable, if its droplets have an average diameter of about 30 μm. The preparation of microcapsules as depicted in **Figure 1**, was realized with the addition of 0.5 of CTAB (Sigma Aldrich, France) after the formation of the emulsion, and 100 ml of 10 wt.% of tetraethoxysilane (TEOS, Sigma Aldrich, France), hydrolyzed at pH 2.8 in a formic acid solution was added dropwise in the solution. The mixture is kept under stirring during 1 day at 45°C to promote silane condensation. Thereafter, sodium hydroxide solution (10 wt.%) is added up to pH 6 to form a thick shell around the droplet. After, a maturing step for 1 h, the particles are washed and filtered to be dried at 50°C during 24 h. CTAB was used to initiate migration of hydrolysed silanol molecules to the droplet surface.

5.1. Shear rate step

The shear rate step was monitored by optical microscopy (Axioskos Zeiss equipped with a camera, IVC 800 12S) every 5 min for 1 h to follow the emulsion size distribution (**Figure 2**). At the beginning of the emulsion, most droplets have an average diameter between 100 and 500 μm, and few droplets are smaller than 100 μm. A decrease in droplet diameter is observed during the first 25 min. Indeed, after 5 min of shearing, the largest droplets have a size of about 500 μm, to reach 300 μm after 20 min. After half an hour, their diameters decrease to 200 μm. In addition, small droplets (mean diameter less than 100 μm) begin to form after about 20 min. Between 30 min and 1 h, the size distribution does not change. The balance between shear and coalescence is therefore reached after 30 min of agitation for the quantity of nanoparticles used and the droplet size is satisfactory (mainly between 10 and 100 μm).

5.2. Stability of the Pickering emulsions

Figure 3 shows the optical micrographs obtained by optical microscopy of emulsions made with 10 g of dispersed phase sheared for 30 min with 3.1 and 0.5 wt.% of silica nanoparticles.
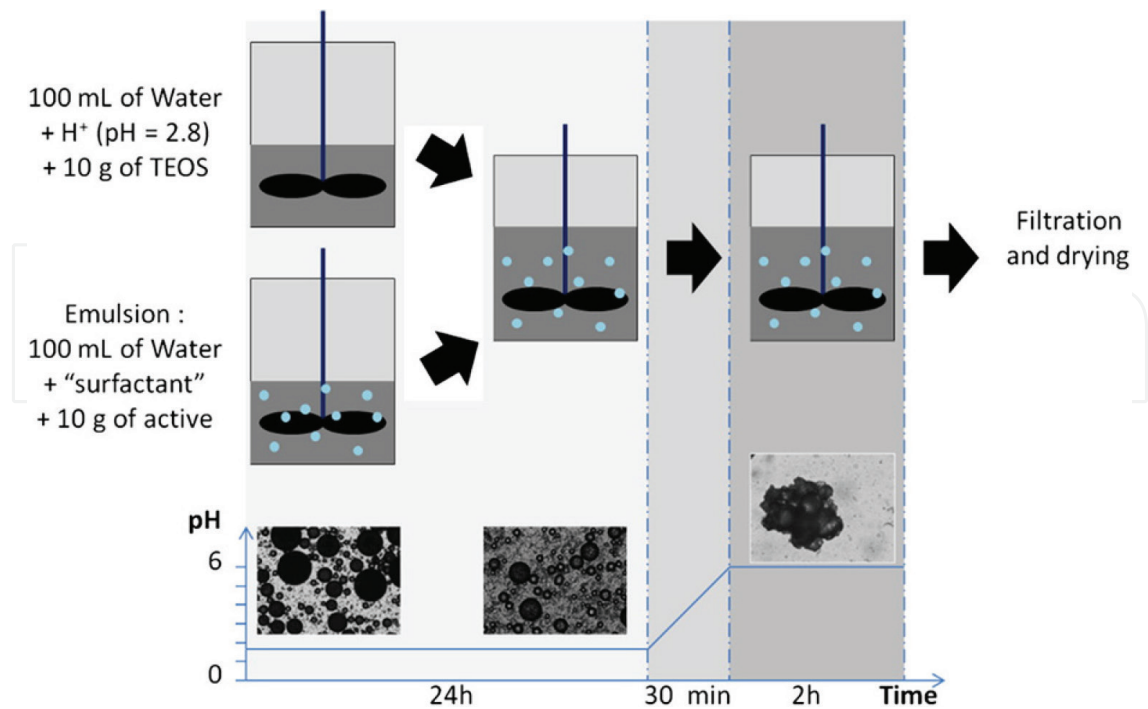
Figure 1. Schematic representation and optical microscopy at the various step of the sol-gel encapsulation. Reprinted from Ref [90] with permission from Elsevier.
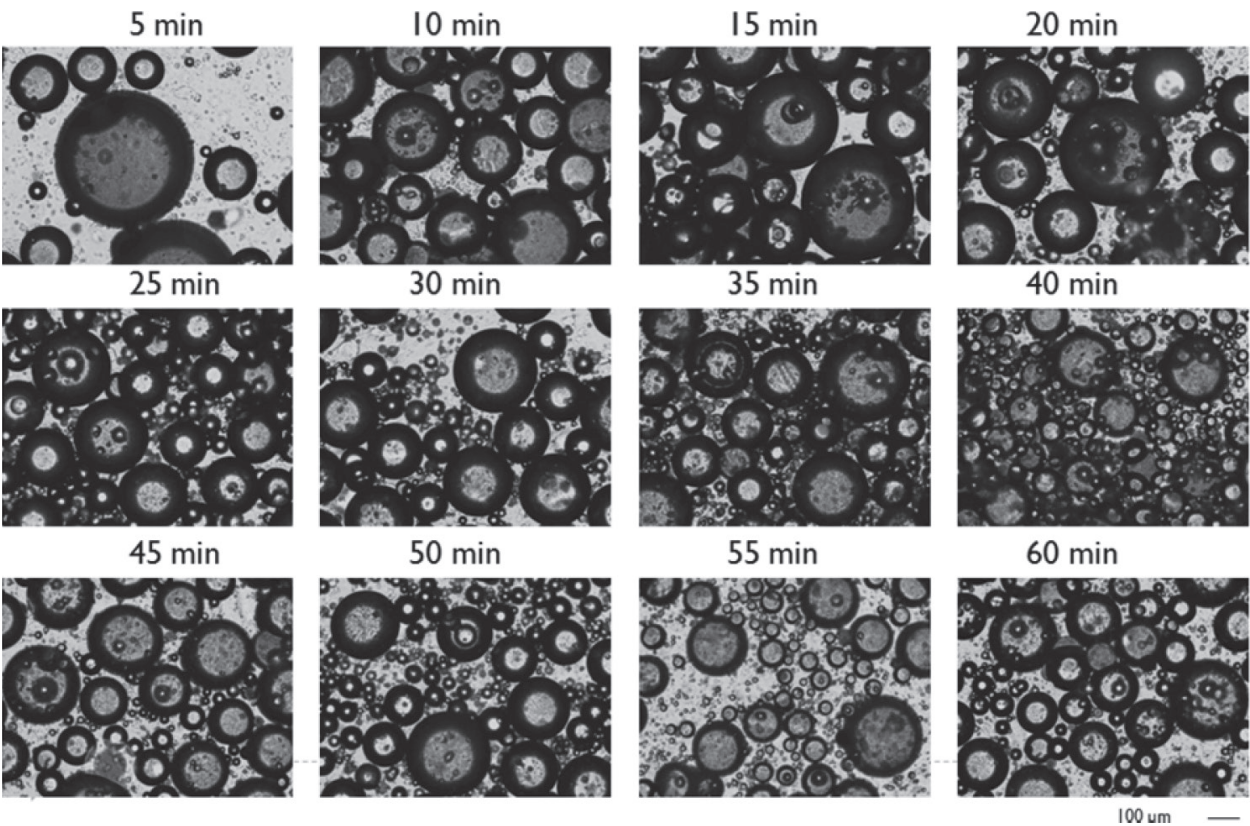

Figure 2. Optical micrographs of the emulsion with 1 wt.% of Aerosil R816 versus time. Reprinted from Ref [90] with permission from Elsevier.
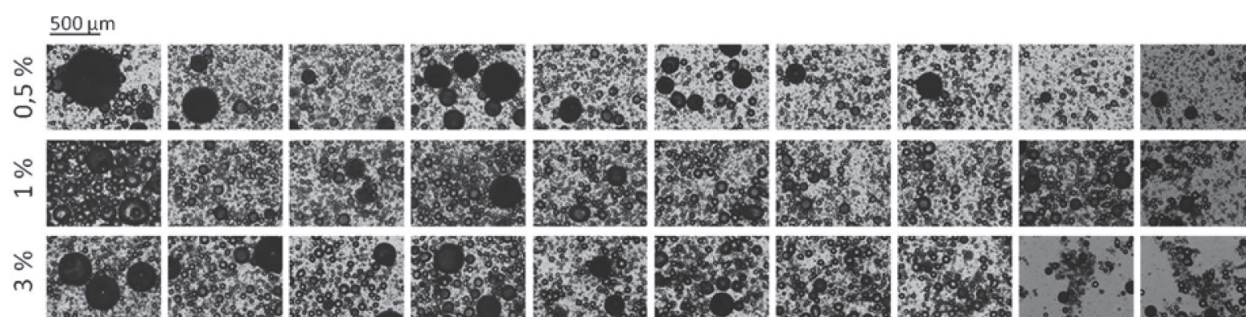
Figure 3. Stability of the emulsion according to the amount of nanoparticles (magnification by 10).

After stopping the stirring, samples were taken at different times between 5 min and 1 week to check the stability of emulsions stabilized with silica nanoparticles. A re-dispersion is achieved by manual agitation. In all cases, droplets of a few micrometers to 500 μm are observed. For both active ingredients, the largest diameters are visible with 0.5 wt.% of nanoparticles. There are few variations in size between 1 and 3 wt.% and the droplets are mostly smaller than 100 μm. For emulsions with 0.5 wt.% nanoparticles, the average diameter is larger and the size distribution is wider. Emulsion size tends to decrease with the quantity of nanoparticles up to a limit size [91].

In each case, the stability is satisfactory, since after 1 week of storage, the phases remain separated with very few rearrangements and size variations. Size does not increase with storage time. Thus, no coalescence or Ostwald ripening is observed after this aging period. No limited coalescence is observed after 5 min. As a result, the droplet coverage by nanoparticles is reached, and size is determined by the efficiency of the agitation process, that is, a limited coalescence occurs in less than 5 min. Considering the study conducted by Chevalier and Bolzinger [4], describing three distinct regimes according to the silica nanoparticle content of oil-in-water emulsions, it can be established that with 0.5 wt.% of particles the second regime is reached, while with 1 and 3 wt.% it is the third one. To avoid thickening of the solution and interactions between silanols and excess particles during shell synthesis, the smaller excess particles are favored.

The "infinite" stability of Pickering emulsions for the system studied in this study has been observed. Despite the creaming and sedimentation, the emulsion stabilized by nanoparticles of silica remains stable for more than a week without the observation of phenomena of irreversible destabilization such as coalescence or Ostwald ripening. Manual agitation is sufficient to disperse the droplets in the medium. The mechanical agitation required during membrane formation is therefore sufficient. Emulsions stabilized using 1 wt.% of nanoparticles and stirred for 30 min are selected for further study. In fact, they allow to obtain droplets with an average diameter of about 3 μm and a size distribution of between 10 and 60 μm.

5.3. Silica shell formation

The silica particles were prepared by sol-gel encapsulation from the previous emulsions. The sol-gel polymerization is carried out in two stages, that is, the hydrolysis of the silica

precursors is followed by their condensation in order to initiate the formation of the Si-O-Si network. Hydrolysis allows the formation of silanol species in presence of water, which are at a later stage involved in the reaction to create a Si-O-Si bridge with the release of a water molecule during the condensation. Even if, hydrolysis can be realized under acidic and basic conditions with a minimum pH value at pH 7 and an exponential increase for low and high pH, low pH increases the hydrolysis rate and inhibits condensation, which is the limiting step in these conditions. And, the basic state favors rapid condensation, which leads to the formation of inhomogeneous shells and aggregates. The result is a small and uniform growth of the capsules, resulting in dense and homogeneous polymeric shells. Therefore, the choice of pH allows to control the size and shape of the particles.

Thus, in this work, the shell polymerization was first performed under acidic conditions for 24 h to promote controlled shell growth before pH neutralization, resulting in rapid condensation and hardening of the shell. In addition, CTAB was added after emulsion completion and prior to the addition of hydrolysed TEOS in the medium to facilitate silanols migration at the droplet interface prior to condensation.

Optical microscopy was also performed during particle synthesis and photographs are presented for each step in **Figure 1**. No significant morphological changes are observed during the first 24 h of shell formation. On the contrary, as expected, pH neutralization leads to rapid shell formation and aggregation of particles in clusters. This aggregation should even be accentuated by the presence of the cationic surfactant.

After, the formation of the shell, microcapsules were hardened, washed, filtered and cried at 50°C during 24 h to obtain a thin powder. The use of water to clean the capsules allows removal of silica species that did not react and also ethanol molecules released during the hydrolysis. The SEM observations of the obtained powder show the formation of aggregates with a mean size from several micrometers up to 500 μm (**Figure 4**). The may be related to interconnected silica capsules, formed by coagulation and/or crosslinking reactions between reactive groupments of the silica shells during the synthesis, and more specially during the increase of the pH in the solution. In fact, the pH modification leads to uncontrolled and
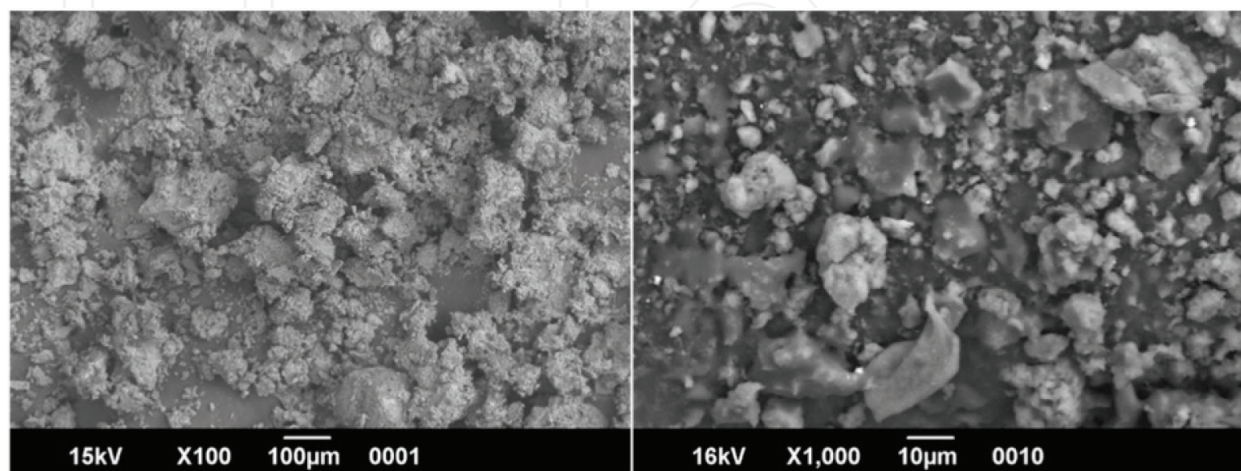

Figure 4. SEM micrographs of microcapsules.

heterogeneous condensation of silanols in the continuous medium. Furthermore during this step, the existence of depolymerization mechanism coupled to a weak formed interface leads to the breakage of particles before the mechanically strong silica layer was formed from TEOS. Thereafter, the formation of tiny droplets was further stabilized by the presence of CTBA molecules in the water. Thus, this particle networking could be even magnified by the huge amount of cationic surfactant used to foster silanols migration toward the interface.

6. Conclusions

Microencapsulated FRs typically consists of core materials, that is, FRs, entrapped in a shell material to form a core-shell structure. According to the required effect, the choice of a particular process is mainly determined by the physico-chemical properties of the FR compounds, and the desired thermo-mechanical properties of the polymeric shell. Thus, it could endow especial properties with the core materials by forming a solid shell. Since the last decade, microencapsulation via sol-gel route has been recognized as a promising method in various application fields to protect active substance. These types of particles are biocompatible with a limited toxicity and have good properties in terms of chemical and thermo-mechanical stabilities. Silica microcapsules can be obtained from organosilane monomer, mainly tetraethoxysilane (TEOS) as silica precursor, or mixtures in mild conditions either by a one step process or by a multi-stage process. The shell formation mechanism is relatively complex and depends mainly on the pH adjustment during the various synthesis steps. It has been shown that the use of Pickering emulsion with nanoparticles provides more highly stable emulsions and can promote silica shell formation. The formation of a template by O/W Pickering emulsion is a delicate interplay between the emulsion stability, oil polarity and sol-gel reaction kinetics. Furthermore, morphology of capsules produced with Pickering emulsion is smooth, dense and aggregated.

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