

Investigation of submicron particles as emulsion stabilizers

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Porous microspheres of silica or hybrid composition play an important role in numerous applications. One of them is as microscaffolds, which have specific chemicals grafted, immobilized or stored, for a targeted effect either by contact or by controlled release. These microscaffolds are possible to be prepared by microemulsion techniques combined with the sol-gel method. The stability of the emulsions is a key factor for those microscaffolds quality.

The first stage of this work regarded the optimization of the porous microspheres synthesis procedure. Several studies were performed, evaluating the effect on the resulting microspheres of the surfactant concentration, the emulsification speed, and the mechanical stirring speed. The critical parameters were then chosen taking into account the particle morphology and the size distribution.

The second stage of this work regarded the synthesis of silica submicron particles, developed as emulsion stabilizing agents, their hydrophobization treatment using hexadecyltrimethoxysilane to make them more suitable for water-in-oil emulsions and their comparison with commercially available particles.

The submicron particles were tested as emulsion stabilizing agents, at different concentrations, and their effect was compared with that of typical surfactants, namely SPAN 80, currently used in the synthesis of the microspheres, and Pluronic P123, on a water-in-oil emulsion using decahydronaphthalene as oil phase. The emulsion stability was evaluated by visual and microscopy observation, and the emulsion volume fraction was assessed along the time, as well as the evolution of the emulsion droplets size and their distribution. Small silica particles of 200 nm in diameter with a hydrophobization surface treatment at a concentration in the range of ca. 2 to 5 wt% (relative to the organic phase) were the ones exhibiting better performance as emulsion (W/O) stabilizers.

Key-words: Pickering emulsions, emulsion stability testing, silica particle synthesis, hydrophobic treatment.

1. Introduction**1.1. Emulsion stability studies**

Most emulsions' instability mechanisms depend on the tendency for droplets coalescence, so that a method to study the emulsion stability could be the assessment of the droplet size and distribution along the time. The stability increases with smaller and more homogenous dispersed droplets, so it is possible to study the stability by changing parameters such as stirring speed, stirring time and observing the droplet size and distribution over a certain time period. For example, a change in stirring speed can lead to a different size of droplets and alter the visual aspect of the emulsion in a way that can be seen to the naked eye. By using a microscope, it is also possible to see the droplets inside the emulsion and determine their size distribution.

1.2. Pickering emulsions

Since Pickering [1] back in 1907, emulsions that utilize solid particles instead of a surfactant, called Pickering emulsions, have been studied.

The main advantages of using solid particles instead of a surfactant are the environment sustainability benefits, reduced possibility of coalescence and the fact that solid particles can be made of a specific material or can be functionalized, in order to be tailored for specific applications.

1.3. Silica hybrid porous microspheres by sol-gel

The silica hybrid porous microspheres are possible to be synthesized by using the sol-gel process combined with emulsion techniques. The "sol" is a colloidal suspension that leads to the formation of a "gel". The process undergoes four steps; 1) alkoxysilane precursor hydrolysis, where alkoxy groups (OR) are replaced with hydroxyl (OH) groups, forming silanols Si-OH; 2) silanol condensation, where the Si-OH group from the first step will lead to the formation of Si-O-Si siloxane bonds, with the release of alcohol or water as byproducts. As time advances the number of siloxane bonds increases and more individual molecules aggregate in the colloidal solution "sol" to start forming a network; 3) gelation and aging, where clusters formed in the first and second step, collide, starting to form links and combine into a single cluster. As the clusters combine, the stiffness of the gel increases until the last link is formed; 4) drying, where water, alcohol or other volatile components that were present are removed. [2-5]

1.4. Silica submicron particles by modified Stöber process

As developed by Stöber, back in 1968 [6] the silica submicron particles production technique will be based on the sol-gel process by using an alcoholic solution with ammonia as catalyst. By changing the ratios of the components in the mixture, the size of the particles can be controlled, in the range of 50 nm to 1 µm diameters. The process can be done in either one step or two steps, one step, if the condensation step occurs before the end of the hydrolysis, or two steps, if the condensation step occurs after the hydrolysis. The two steps advantage is the more control over the process as the hydrolysis and condensation steps are separated. The main advantage when comparing with the conventional sol-gel process, is the smaller dimension of the particles and the more control over the synthesis process.

1.5. Hydrophobic treatment

A hydrophobic treatment was done in order to turn the hydrophilic particles into hydrophobic and therefore more suitable for the W/O emulsions employed in the stability tests. Hexadecyltrimethoxysilane (HDTMS) was used, due to its long hydrocarbon chain, that gives the particles the required hydrophobicity character. [6–9]

2. Experimental part

2.1. Materials

TEOS and GPTMS were supplied by Dow Corning, Hydrochloric acid 37% was supplied by Carlo-Erba, ammonia solution 25% was supplied by Merck, SPAN 80 was supplied by Merck, Pluronic P123 was supplied by Sigma-Aldrich, decahydronaphthalene was supplied by Merck, absolute ethanol was supplied by Fisher Scientific, n-hexane was supplied by Merck, KCl was supplied by Merck and the commercial silica particles were supplied by UBE EXSYMO CO., LTD.

2.2. Silica hybrid porous microspheres synthesis

The method used to make the sol-gel porous microspheres was based on a previous study [6] consisting of four steps:

1) Pre-hydrolysis of the silanes, by mixing TEOS, GPTMS and an aqueous solution of HCl 0.05 M, in the proportion 1:1:0.75 (w/w), then stirring for one hour, in a closed cup, using a magnetic stirrer, at room temperature. 10 minutes before the end, 300 µl of HCl at 37% was added. 2) An emulsion was done by mixing decahydronaphthalene and SPAN 80, in the proportion 100:6 (w/w) and stirred at 18000 rpm 13 minutes before the end of the pre-hydrolysis. After 3 minutes 45g of water were added while stirring for more 10 minutes. 3)

The emulsion was then placed inside a reactor in a heating mantle, just keeping the temperature at ca 25 °C. After, the emulsion was stirred at 600 rpm and the pre-hydrolyzed solution was added to the reactor dropwise, using the following temperature profile, 1 hour at room temperature, 1 hour and half at 65°C, 10 minutes at 70°C, 15 minutes at 75°C, 1 hour at 80°C, 1 hour at 85°C and 30 minutes at 90°C. 4) The reaction product was then filtered under vacuum, using n-hexane as a solvent. The solids were dried at 45 °C overnight.

2.3. Silica submicron particles

The process to make the submicron silica particles is based as indicated in [7]. 1) a solution (I) was prepared with 0.0238g of KCl, 9.45g of ethanol, 1.648g of TEOS and 4 ml of an aqueous solution of ammonia (25%), 2) a solution (II) with 26.12g of ethanol and 4.12g of TEOS. 3) the solution I was placed in a reactor at 35°C and mechanical stirring of 240 rpm and after 1 hour, 6 ml of the solution II was added every hour to the reactor while waiting another hour after the complete addition. 4) Finally, the mixture was centrifuged at 7000 rpm, washed with ethanol and centrifuged again for two times, then it was dried at 45°C for 24 hours.

2.4. Hydrophobic treatment

The method used for hydrophobic treatment was the following: 50 ml of distilled water was acidified to pH 3 using HCl at 37%. Then 0,562 ml of HDTMS was added to the acidic aqueous solution and stirred at 300 rpm for 1 hour at 50 °C. After 1 hour, a certain amount of particles was placed in the mixture and stirred for 30 minutes at 300 rpm and 50°C. After 30 minutes the mixture was centrifuged at 5000 rpm for 5 minutes. The remaining solid was dried at 60°C.

2.5. Particle characterization

For particle characterization it was used scanning electron microscopy, using the JEOL JSM-70001F Field Emission Scanning Electron Microscope and Fourier transformed infrared spectroscopy using a PerkinElmer, Spectrum Two, FTIR spectrometer equipped with a Pike Technologies Miracle® ATR accessory at 4 cm⁻¹ resolution and 4 scans of data accumulation.

2.6. Stability studies involving surfactants

The surfactant stability tests were done by mixing decahydronaphthalene together with the surfactant, at variable concentrations (2g, 4g, 6g and 8g for SPAN 80 and 2g, 4g, 6g, 8g, 10g and 12g for Pluronic P123). It was mixed and stirred at 18000 rpm during 3 minutes by using an IKA Ultra Turrax T-18. After 3 minutes, water was added and the mixture was stirred for more 10 minutes. After 10 minutes, the emulsion was placed in a test tube.

2.7. Stability studies involving submicron particles

The particles stability tests were done in a similar way to that of the surfactants before described. Submicron particles were added to one of the phases, according to a selected particle concentration, (0.2%, 2% and 5.3% wt% of organic phase) and sonicated for 10 minutes using a VWR ultrasonic bath. After 10 minutes, the other phase was added and the mixture was emulsified at 18000 rpm for 10 minutes by using an IKA Ultra Turrax T-18. The resulting emulsion was placed in a test tube. All surfactant and particles samples were placed side by side and observed at regular periods of time, by naked eye and using an optical microscope. During the observations, a photo of the emulsion inside the test tubes was taken using a Fujifilm FinePix S5700 with autofocus.

3. Results and discussion

3.1. Synthesis of silica hybrid porous microspheres

The different microspheres syntheses carried out in this work had the goal of (a) optimizing the synthesis parameters, (b) reducing the size and agglomeration of the microspheres, and (c) reproducibility studies. The reference parameters (SD23) were 9800 and 600 rpm as the emulsification speed and mechanical stirring speed and 6 g of SPAN 80. (Figure 1)

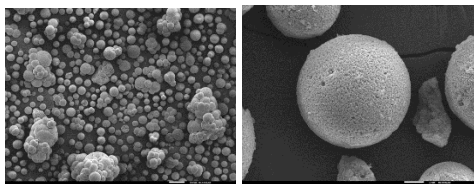


Figure 1 - SEM photomicrographs of SD23 (scale bar =100 μm at image of the left and 10 μm at the image of the right)

When the speed was increased from 600 to 800 rpm, SD24, the corresponding SEM photomicrograph showed that the microspheres tend to break which suggests that the stirring at 800 rpm was too much. (Figure 2)

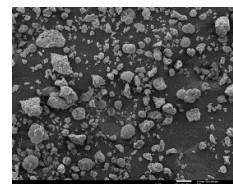


Figure 2 - SEM photomicrograph of SD24 (scale bar =100 μm)

On the other hand, the increase of the emulsification stirring speed was tested in order to lead to a decrease in the droplets size and hopefully to a more stable emulsion. Indeed, the increase in the emulsification stirring speed from 9600 rpm to 13000 rpm (SD25), and then to 18000 rpm (SD26) was found to result in a lower agglomeration of the microspheres, as can be observed in the SEM photomicrograph of SD26. (Figure 3)

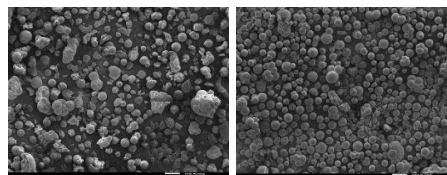


Figure 3 - SEM photomicrographs of SD25 (left) and SD26 (right) (at the same magnification (scale bar = 100 μm))

Based on the above results, less agglomeration and less fragmentation for SD26, the conditions employed for SD26 were those selected to proceed with the studies.

In what regards the amount of surfactant employed in the syntheses, the increase in quantity from 6 to 8 g (wt% of organic phase) of SPAN 80 (SD27) was found to not improve the morphology of the particles. Indeed, the resulting particles (Figure 4) were very similar to the ones obtained with 6 g (SD26), but some of the microspheres show fragmentation, therefore there were no gains in increasing the concentration, so the quantity of SPAN 80 was maintained.

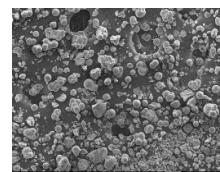


Figure 4 - SEM photomicrograph of SD27 (scale bar = 100 μm)

When the synthesis was repeated under the same conditions of SD26 there was fragmentation of some

microspheres, which did not occur anymore in a second attempt. In this latter one, it was visible that the microspheres were very similar (Figure 5, right) to the ones obtained before (SD26) shown in Figure 6. So, the process could be reproduced

From the above described studies, it was concluded that the processing conditions employed in SD26 were the ones that result in the best microspheres quality, namely 18000 rpm as stirring speed in the emulsification step, 600 rpm as mechanical stirring speed inside the reactor and 6 g (w/w% of organic phase) of SPAN 80.

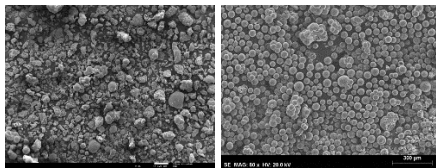


Figure 5 - SEM photomicrographs of SD29 and of SD32 (at the same magnification, scale bar = 100 μm at the imaged of left and 300 μm at the image of the right)

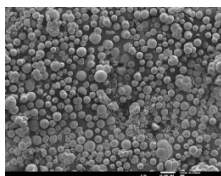


Figure 6 - SEM photomicrograph of SD26 (scale bar = 100 μm)

FTIR-ATR was employed to characterize the obtained microspheres in terms of chemical structure. Figure 7 Shows the FTIR spectrum achieved for the reference sample SD23, and it was found to be very similar to the remaining samples prepared by varying the processing conditions, i.e. there is a remaining glycidyloxy organic functionality (derived from GPTMS) in the siloxane network. (Figure 7)

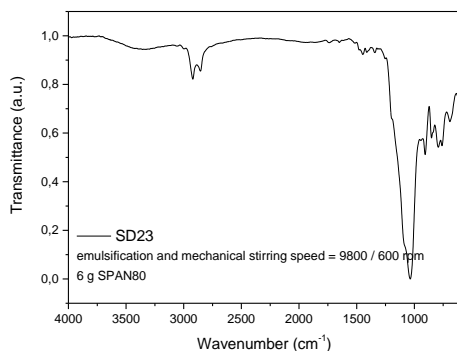


Figure 7 - FTIR spectrum of reference sample

3.2. Synthesis of silica submicron particles by a modified Stöber method

Repeating several times the synthesis (based on the Stöber method) previously explained in the Experimental section, it was possible to conclude that such synthesis protocol is not straightforward in what regards reproducibility. The particles were similar, but with a varied size distribution and agglomeration in each synthesis. Figure 8 left, shows the particles obtained in synthesis SD28, where a particle size in the range of 0.1 – 1.6 μm is observed, while particles obtained using exactly the same protocol, synthesis SD36, exhibit a very homogeneous particle size distribution, with particles of ca. 0.3 μm . (Figure 8, right)

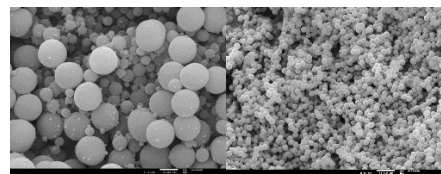


Figure 8 - SEM photomicrographs of SD28 (image on the left) and SD36 (image on the right) for the same magnification. (scale bar = 1 μm)

The reduction on the concentration of KCl to 92% (SD48) and to 84% (SD46) of its original amount did not result in a visible benefit, in what regards the aggregation issue, when compared with the original KCl concentration (SD44).

The SD36 particles showed the best result, i.e. the particles size was smaller, size distribution was homogeneous and there was no apparent agglomeration visible. By that reason they were chosen to proceed in this work, i.e. for the emulsion stabilization studies. (Figure 9)

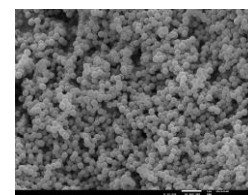


Figure 9 - SEM photomicrograph of SD36. (scale bar = 1 μm)

The FTIR spectrum (Figure 10) is very similar to the one obtained for the porous microspheres, which is expectable since both are made of silica, however the submicron particles obtained in SD28 do not exhibit any presence of epoxy groups (peaks at 3050, 1250, 900 and 850 cm^{-1}), as expected, since in this synthesis only TEOS was used as Si precursor.

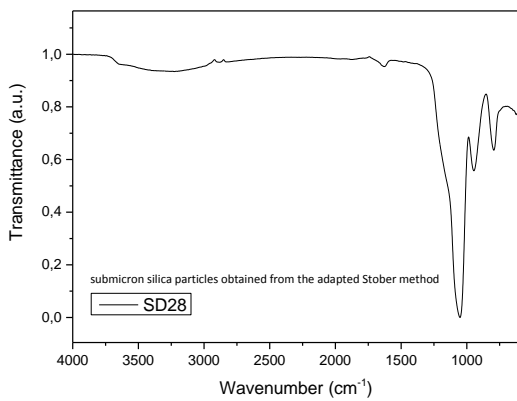


Figure 10 - FTIR spectrum of SD28 particles

3.3. Hydrophobic treatment

The particles used for the hydrophobization treatment, carried out with HDTMS were SD36 and N2N, and the samples obtained were referred as SD36H and N2NH respectively, throughout this work. Figure 11 and Figure 12 show a comparison of the non-treated and treated particles. A big similarity among those prepared in this work (SD36) and those commercially achieved (N2N) can be depicted.

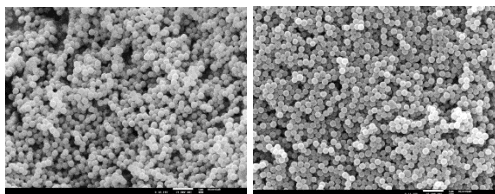


Figure 11 - SEM photomicrographs of SD36 and SD36H (scale bar = 1 μm)

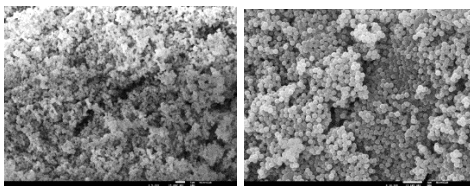


Figure 12 - SEM photomicrographs of N2N and N2NH (scale bar = 1 μm)

When comparing the FTIR spectra of the SD36 and N2N particles before the treatment (black) and after (red) (Figure 13 and Figure 14) the treatment, it is possible to see some peaks in common with the HDTMS, which do not appear in the spectrum of the particles before the treatment. Those peaks are at ca. 2920 cm^{-1} , 2850 cm^{-1} and 1450 cm^{-1} , which are relative to C-H stretching modes and C-CH₂ bonds. These could indicate the presence of HDTMS, since it is the only compound with

hydrocarbons in the siloxane network. Figure 14 indicates not only the presence of the HDTMS, but also that the treatment with HDTMS was more effective on the surface of the particles N2N than in SD36 particles. Both particles, SD36H and N2NH, were employed in the emulsion stability studies.

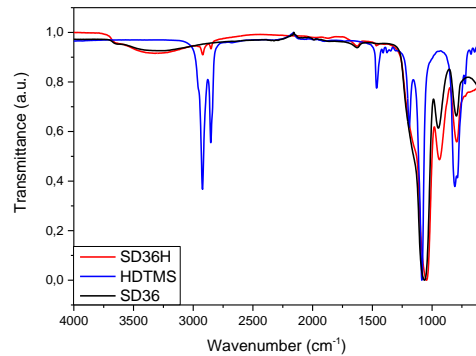


Figure 13 - FTIR spectra of the SD36 particles before and after the hydrophobic treatment

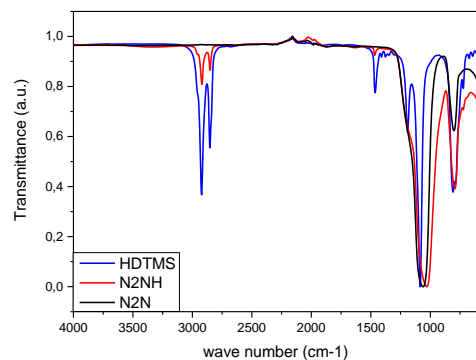


Figure 14 - FTIR spectra of the N2N particles before and after the hydrophobic treatment

3.4. Effect of the surfactant

3.4.1. Study of SPAN 80

The surfactant typically employed in the synthesis of the porous hybrid microspheres of this work is SPAN 80, added to the oil phase, so that the emulsion stability tests started by assessing the effect of such surfactant. After preparation of the W/O emulsion, at 18000 rpm during 13 minutes, the obtained emulsion was placed in a test tube and it was left to rest during several days. Observation of the emulsions and photographs were taken from time to time. The increase in the concentration of SPAN 80 led to an increase of the emulsion stability, as less oil phase got released to the top of the test tube, over the same time period. Figure 15 shows the evolution of the emulsions. The emulsion volume fraction that remains in the test tube over time

was compared. (Figure 16) It was concluded that 6 g of SPAN 80 was the optimum amount for this system. It corresponds to the slowest and least intense emulsion destabilization process, within the timeframe studied, which also corroborates the optical microscopy emulsion observation results before described.



Figure 15 - Evolution of the emulsion using 6g of SPAN 80, from 0 hours to 8 days

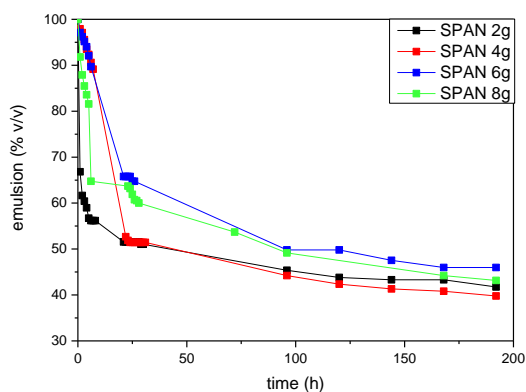


Figure 16 - Plot of the evolution of the emulsion with SPAN 80, i.e. percentage of emulsion remaining along the time, for 2, 4, 6 and 8 g of SPAN 80 added to decalin, the dispersing phase of the emulsion.

3.4.2. Study of Pluronic P123

Pluronic P123 is another type of surfactant that was studied in this thesis. For all Pluronic P123 concentrations tested in this work, the emulsion destabilization phenomenon was based on emulsion sedimentation, as well, together with a very well resolved oil phase liberated to the top of the test tubes. This phenomenon started to occur at a relatively short time and the emulsions did not suffer noticeable change after 3 days. Moreover, the increase in concentration of Pluronic P123 is found to reduce the release of the oil phase over the same time period, as it happened in the study with SPAN 80. When observing the emulsion part from the test tubes, through optical microscopy, non-uniformly distributed drops were found even for 0 hours, except for 10 and 12 g of Pluronic P123, where a uniform drops size distribution was exhibited for 0 hours and 2 weeks

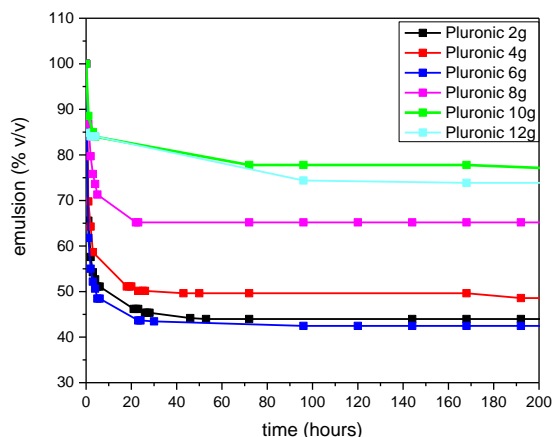


Figure 17 - Plot of the evolution of the emulsion with Pluronic P123.

When comparing the plot results from Figure 17, one can conclude that 10 g of Pluronic P123 (followed by 12 g) is the optimal surfactant amount, which results in less separation and, therefore, in a more stable emulsion.

When comparing both surfactants, at optimum contents, one can conclude that Pluronic P123, at 10g, results in less separation than SPAN 80, at 6 g. Therefore, 10 g of Pluronic P123 might be used as a promising stabilizer for the emulsion employed in the synthesis of the porous microspheres of this work.

3.5. Effect of the particles

Table 1 compiles the results of all the stability studies realized. Since the emulsion in study is water-in-oil type, hydrophobic particles would in theory be more adequate for this type of emulsion and, therefore, lead to smaller droplets and to a better droplets distribution than hydrophilic particles. In fact, in comparison, the SD36H ones provided a more stable emulsion than SD36, despite the tendency for emulsion sedimentation observed. It was observed that SD36H promote similar results as those in the presence of surfactants.

Using N2N particles at 2%, there were no apparent changes in the visual aspect of the emulsion until 3 hours, when it was possible to see coalescence, as the water phase was visible at the bottom and, after four days, it was possible to see sedimentation as the oil phase appeared at the top, with the emulsion remaining in the middle.

The same particles N2N, but after a hydrophobization treatment, were also tested in terms of their effect in the emulsion stability, at 0.2, 2 and 5.3%. This former concentration (0.2%) was not enough to give a proper emulsion. Droplets were too large, forming, as observed in Figure 18 a white blueish phase, while there was since $t=0$ a dark blue phase composed by the colored water phase at the bottom. With the time, ca. 1 day, the poor emulsion sedimented, with the oil phase migrating to the top of the test tube.

So, it is concluded that when using 0.2% of N2NH particles no emulsification was achieved. Some of the water droplets remained in the oil phase and sediment over time.

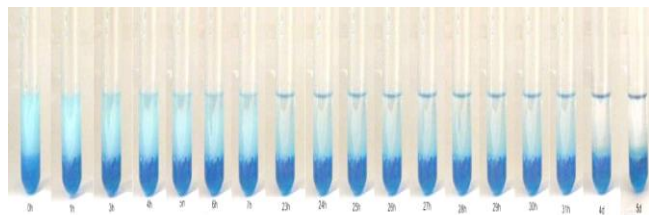


Figure 18 - Evolution of the emulsion using 0.2% of N2NH particles from 0 hours to 5 days

When the concentration was increased to 2% the emulsification was already possible. Sedimentation occurred as a (well resolved) oil phase got released to the top, but no apparent changes were detected after that, as the emulsion remained stable for the 5 days. This is a similar result to that obtained when using adequate surfactants to this type of emulsion.

When the concentration of N2NH particles was increased to 5.3% once again the sedimentation occurred and no apparent changes were detected after that, as the emulsion remained stable for the 5 days. Very similar results to the ones obtained with 2% of N2NH were achieved, except in the optical micrography that shows an emulsion not so stabilized after 5 days, as in the case of 2% of N2NH. It could be concluded that 0.2% the particles were insufficient to cover the droplets as no emulsion was formed, however at 2% and 5.3% there were more available particles and therefore could cover the surface of the droplets and prevent their coalescence.

By the plot results (Figure 19) the most suitable particle system to use would be the N2NH particles at 2%, since they result in a good compromise between speed of destabilization in the first couple of hours and stability over longer periods of time. They are slightly better than N2NH at 5.3%, in what regards these points.

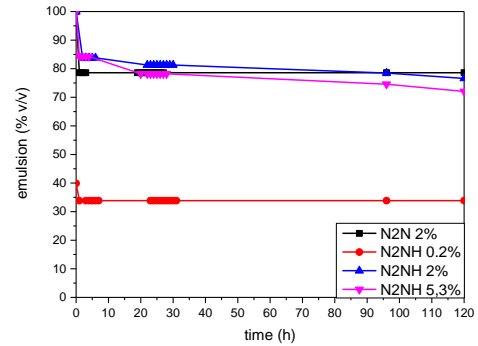


Figure 19 - Plot with the evolution of emulsion with N2N and N2NH particles

Comparing with the first set of particles, SD36 and SD36H, N2NH particles were the ones which presented the best performance in what regards the emulsion stabilization of the synthesis of the porous microspheres. This goes in accordance with the discussion that hydrophobic and smaller particles are more suitable to stabilize W/O emulsions. Table 2 shows a compilation of the above described results.

3.6. New synthesis

The tests with emulsions using 10 g (w/w% organic phase) of Pluronic gave less phase separation instead of using 6 g (w/w% organic phase) of SPAN. Therefore a new synthesis was proposed to evaluate the effect on the microspheres, SD50, using the same sol-gel process method as described before with the exception of replacing SPAN with 10 g (w/w% organic phase) of Pluronic. The particles obtained were characterized by SEM. The results showed that the particles agglomerate, so another synthesis, SD52, was done by reducing the quantity of Pluronic to 8g. (Figure 20)

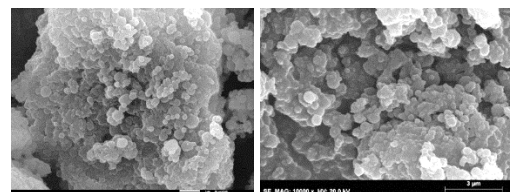






Figure 20 - SEM photomicrographs of SD50 (10g Pluronic P123) and SD52 (8g Pluronic P123)

(scale bar = 1 μ m)

Table 1 - Summary and comparison of the emulsion stability study results

Realized studies	Emulsion schematic ^(a)	Time span of the study	Emulsion %v/v along the time of study
SPAN 80		2 weeks	
		2 weeks	
		2 weeks	
		2 weeks	
Pluronic P123		2 weeks	
		2 weeks	
		2 weeks	
		2 weeks	
		4 weeks	
SD36		4 weeks	
		4 weeks	
SD36H		4 weeks	
N2N		5 days	
N2NH		5 days	
		5 days	
N3N1		4 weeks	<p>Poor emulsion or no emulsion</p>
		2 weeks	

	5.3% ^(b)		4 weeks
N3N3	0.2% ^(b)	no emulsion	4 weeks
	2% ^(b)	no emulsion	2 weeks
	5.3% ^(b)		4 weeks
N6N3	0.2% ^(b)	no emulsion	4 weeks
	2% ^(b)		2 weeks
	5.3% ^(b)		4 weeks

- a) The white color represents the organic phase (O), the light blue the emulsion (E), and the dark blue the water phase (W), PE means poor emulsion, in a flightier blue.
- b) All the percentages are in wt% of the organic phase

A synthesis (SD53) was carried out using the same procedure as indicated before, with the exception of using the particles N2NH at 2wt% (w/w% of the organic phase), instead of SPAN 80. The particles obtained were characterized by SEM. (Figure 21)

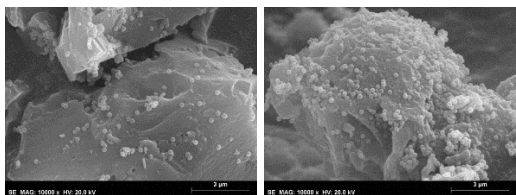


Figure 21 - SEM photomicrographs of SD53 (scale bar = 3 µm)

Even though the previous study showed that the N2NH increase the stability of the emulsions, the synthesis result shows less particles and more agglomeration, due to a probable emulsion destabilization. in comparison to the reference synthesis, using SPAN80. Nevertheless, the particles used in the emulsion showed potential to be used as stabilizer in W/O emulsions and therefore could be used in the porous microsphere synthesis process as a replacement of the surfactant, after a more detailed study.

4. Conclusions

Optimum processing parameters for the synthesis of the porous hybrid microspheres, taking into account the best results in terms of particles agglomeration, particle roundness and

morphology and desired roughness/porosity, were found to be 18000 rpm of stirring speed of emulsification, 600 rpm of mechanical stirring speed in the reactor and 6 g (w/w% of organic phase) of SPAN 80.

In what regards the submicron silica particles, 300 nm particles in size were obtained using a modified Stöber process, nevertheless it was found to be difficult process to reproduce. In spite of all the efforts, during this work it was not possible to optimize the process in order to control the aggregation, which compromised the achievement of a large enough quantity of particles for the emulsion stability studies

The hydrophobization of the submicron silica particles prepared in this work, as well as of similar commercial particles was successfully done, using hexadecyltrimethoxysilane, whose long tail of carbons would impart hydrophobicity to the particles' surface.

The surfactant stability studies showed that the use of Pluronic P123 would prevent more oil separation then when using SPAN 80, and hence a more stable emulsion. When using SPAN 80, even though, there was a larger oil separation, the emulsion showed less coalescence, the droplets were of smaller dimension, and the droplet's size distribution seemed more homogeneous.

The particle stability studies (Pickering emulsions) showed that the hydrophobic modified particles, when used at ca. 2-5 wt% of the organic phase, were able to produce more stable emulsions. The best result was achieved for the commercial particles sample

HIPRESICA FQ N2N of 0.2 μm in diameter, with the hydrophobic treatment (N2NH).

This work will proceed with the validation of these findings, in what concerns full replacement of SPAN 80 by either Pluronic P123 and by hydrophobized N2N particles in real synthesis experiments of the porous hybrid microspheres. A first trial was already done for both Pluronic P123 and N2NH particles, but the obtained particles or were not spherical or exhibited tendency to be agglomerated. More optimization trials will need to be done in a near future. Nevertheless, the behavior of the emulsion when using these particles suggests that they could be used to stabilize an emulsion during the sol-gel synthesis, if a more detailed study is performed so the conditions can be optimized.

5. Future work

Some work aspects were not included in this thesis, especially due to lack of time, which are herein suggested:

- Rheology study of the emulsions
- Study the effect of other parameters (T, pH) on the stability of the emulsions.
- Study the effect of the concentration of Pluronic P123 on the porous microspheres synthesis.
- Optimizing the porous microspheres synthesis parameters while using the hydrophobic particles

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